THE INDUSTRIAL DEVELOPMENT OF TRANSPARENT CONDUCTING COATINGS BY A SOL-GEL ROUTE

By

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Abstract

Transparent conducting coatings are used in a wide range of applications, particularly displays and photovoltaic devices, and demand is anticipated to increase with the rise of plastic electronics. Indium tin oxide, deposited by sputter coating, is widely used. Concerns over the cost and long term availability of indium, together with environmental concerns over production, are driving a search for more efficient deposition methods and alternative materials.

This work represented the early stage development of industrially applicable coatings, hence the work was performed with a supply chain partnership to facilitate commercial uptake. Sol-gel technology was used to facilitate direct printing of patterned layers. Precursors were selected and a processing route developed. Values for glass transition and crystallization temperature were found to be considerably lower than the accepted bulk value. Dip-coated parts yielded indium tin oxide coatings with transparency of 98% and resistivity of $1.5\text{x}10^{-2}\Omega$cm fired in nitrogen and 98% transparency, $3.0\text{x}10^{-2}\Omega$cm resistivity fired in air. A printed coating was produced with 93% transparency and 7.0Ωcm resistivity. It was established that the limitations to conductivity arose from low film thickness and lack of macro-scale connectivity within the layer. Initial work was also conducted in preparing tin oxide and silicon-doped zinc oxide coatings.

For Dad

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Glossary of Terms and Acronyms

This is not a comprehensive list of terms used within the thesis, but describes the more commonly used terms and acronyms found throughout the text, particularly those related to sol-gel processing and chemical synthesis. These are defined in full within the body of the text, but a summary is provided here for ease of reference by the reader.

Aerogel	A gel structure which has aged by reaction at all possible points of contact.
Alcogel	A 'wet' gel in which the remaining space in the container is occupied by liquid.
Alkyl	A ligand constituting an unsubstituted carbon chain, bonded directly from a carbon atom at the end of the chain to the cation.
Alkoxide	An alcohol-derived ligand, bonding to the cation through substitution at the proton.
DAP	1,2-Diaminopropane.
DMAP	3-(Dimethylamino)-1-propylamine.
FOM	Figure of merit. Since transparency α and conductivity σ are dependent on film thickness they can be related by the equation $\sigma/\alpha = -\{R_r \ln T\}^{-1}$ where R_r is the sheet resistance in Ω/square and T is the total visible transmission.
Gel	A network structure which spans its container.
IMS	Industrial methylated spirits. A commercial mixture of ethanol and methanol, supplied 'dry' (water-free).
IPA	Isopropyl alcohol; propan-2-ol in IUPAC notation.
Ligand	In a molecular structure, a group or chain bonded to the metal cation.

PLD	Pulsed laser deposition – a coating deposition technique using laser energy to evaporate material from a target, the plume forming a deposit on a substrate. Has the advantage of being suitable for rapid screening of a wide range of materials.
Sol	A dynamic liquid state, in which an equilibrium exists between precursor, hydrolysed species and condensed molecules.
TEA	Triethanolamine.
TCO	Transparent conducting oxide.
TCC	Transparent conducting coating.
TRL	Technology readiness level. A 1-9 scale denoting maturity of technology from initial concept through to production.
Xerogel	The gelled state after treatment to remove the solvent.
XLD	Xylylenediamine.

CHAPTER 1 – INTRODUCTION

1.1 Project background

This project was carried out under the EngD programme in Engineered Materials for High Performance Applications in Aerospace and Related Technologies in the Department of Metallurgy and Materials at the University of Birmingham as a seconded employee from TWI Ltd. Additional funding was received from the EPSRC. The EngD scheme had recently started in order to provide a route to industrially focussed research with a particular focus on advanced materials. TWI Ltd is an independent research and technology organisation (RTO) with a remit to develop technology in joining, surfacing and related technologies.

Sol-gel is a process for the fabrication of ceramic materials from solution. Its principal advantage is the dramatically reduced processing temperatures compared with conventional high-temperature fusion methods.

Over the preceding decade TWI had been developing its expertise in sol-gel processing, both through its internally funded core research programme and through sponsorship of two PhDs (Han 2006), primarily focussed on the development of silica-based transparent hard-coats, culminating in several patents (Taylor 2000; Taylor 2006).

The overall aim of the present work was to extend TWI's capability in sol-gel coating to expand the range of markets served. The work sought to take TWI's sol-gel expertise in producing silica-based, sol-gel derived coatings and use it to develop other materials, specifically indium tin oxide (ITO) as a transparent electrical conductor, used in devices such as displays, EMF/RF shielding and photovoltaic cells. The work was funded by TWI under its core research programme. Subsequent work was performed as part of a collaborative programme, funded by the DTI under its LINK ISD programme.

1.2 Research need

The development and introduction of new technology is critical to the continued competitiveness of a business. The work presented within this thesis bears this statement in mind throughout.

The particular technology addressed by this EngD relates to the application of coatings by use of the sol-gel technique. Sol-gel processing can be used in a wide variety of applications, of particular interest being those which use a high-cost process to deposit the same material, *e.g.* a vacuum deposition technique such as sputter coating, or a lower cost process which deposits a material with inferior performance characteristics.

Sol-gel materials are ceramic in nature. When used to produce coatings, this makes the process ideal for conferring properties such as hardness and corrosion resistance, with the option to select electronic and magnetic properties. The specific properties required may be obtained by selection of appropriate constituent materials.

Further to compositional considerations, the liquid nature of the coating composition determines suitable coating processes. The removal of liquid, both during the coating process and subsequently during the drying phase, has a significant influence on which processes are applicable to forming a particular coating structure. Finally, the specific parameters of the curing step, either at elevated temperature or using ultraviolet (UV) irradiation, determine factors such as degree of cross-linking (and therefore density and porosity), and potentially crystallinity. There may of course be limitations on the temperature which can be applied, determined by the temperature capability of the substrate or of desirable organic constituents within the coating composition.

In industrial terms, the sol-gel process is relatively new, having only formally been exploited commercially for approximately 35 years (Dislich 1971) and then only in niche applications, for example in the manufacture of high purity glasses for optical fibres and colloidal silica (Grace 2006) and thermal control coatings for architectural glass (Geffcken and Berge 1939). It has the capability to add enhanced functionality and to fabricate hybrid organic-inorganic materials to address emerging markets and its reduced processing temperature requirements may improve the energy efficiency of ceramic deposition. Since the process does not require a vacuum, it is compatible with continuous processing and hence supports flexible manufacturing. In order to expand the range of applications for which sol-gel coating is a preferred solution, further research is required.

An element of fundamental research is needed to improve understanding of the fundamental chemical reactions and their influence on structure/property relationships. In conjunction with this underpinning work, specific research is required for each application to optimise compositional and processing factors.

The work presented within this thesis addresses aspects of both generic understanding and optimisation in respect of specific applications.

1.3 Objectives

The overall technical objective of this project was to develop a capability to deposit a sol-gel derived transparent conducting coating (TCC). The specific objectives were:

- To deposit sol-gel derived ITO coatings on glass and characterise them in terms of transparency, microstructure and electrical resistance.
- To develop an ITO system and compare performance with equivalent commercially available sputtered ITO.
- To develop novel materials for use as TCCs.

1.4 Anticipated benefits

Development of TCCs by a sol-gel route will result in significant savings in respect of processing and materials costs, together with associated environmental benefits.

Characterisation of some of the fundamental properties of the coatings evaluated will enhance understanding of applications to which they are suited, improving the selection process for coatings in future applications.

1.5 Thesis structure

Characterisation through research leads to an understanding of the coating system, and defines whether it meets the need of the customer (Parry 2000). This thesis focuses on the development of sol-gel derived coatings and the characterisation of their properties, important in both their development and ultimately in their industrial application. The work is presented in two sections.

Section A

The first section provides both an industrial and a technological context for the work. The former is summarised in respect of the options currently available for commercial R&D, the latter in respect of materials and processes applied to the project and the alternative options available.

Chapter 2. Innovation is development and introduction of new technology. Commercial R&D is the process of innovation, and therefore essentially defines the context for the research need for this project. In order for a business to compete it is essential to innovate, otherwise competitors will ultimately introduce superior products. The innovation process is therefore discussed, providing the industrial context for this project. Types of innovation are considered, with reference to factors of scale. The options for funding innovation are considered with reference to these factors and a summary assessment of appropriate routes to funding particular developments is made.

Chapter 3. The general methods of sol-gel processing are outlined, including the mechanisms proposed by which the chemical reaction proceeds. Particular emphasis is placed on the production of coatings. The mechanisms of coating formation and curing are examined, together with industrially applied methods for coating deposition. These place in context some of the difficulties experienced in the industrial application of the sol-gel coating process.

Section B

In the second section, the development of TCCs is presented as a case study. In addition to the technical advances described it illustrates a particular approach to commercial R&D, based on the circumstances and requirements of the project.

Chapter 4. The subject of transparent conductors is introduced, in the context of industrial need. The current approach to industrial fabrication of transparent conducting coatings is described and the need for further development defined, including suitable routes to project support, based on the maturity of the technology and the scale of development required. The overall objective of the case study is defined, together with subsidiary objectives, split into two phases of development.

Chapter 5. The current state of the art in transparent conductors is described. They are usually doped semiconductors, for example tin-doped indium oxide (ITO) or antimony-doped tin oxide (ATO), prepared as thin films on glass or plastic by sputter coating. Options are discussed with respect to material types; physical and electronic properties and deposition methods.

Chapter 6. The first phase of development of transparent conductors via a sol-gel route is presented in detail. This includes process details, precursor selection and analytical methods and the resulting performance.

Chapter 7. The second phase of development is introduced in terms of overall project structure. The work was carried out with funding from the DTI, in collaboration with other partners who, collectively, formed a supply chain for the material. Their roles in the project are explained in the context of the work performed.

Chapter 8. The approach adopted to development of ITO in the second phase of development is presented in detail. This includes process details, precursor selection and analytical methods, with particular reference to the structure-property relationships between precursor and coating material. The work described also includes coating deposition and thermal treatment.

Chapter 9. The development of alternatives to ITO is described, as a complete process from material selection, reduction to practice using rapid screening and the steps taken to transfer this approach to a sol-gel route.

Chapter 10. Approaches to development of a printable material are described, together with the materials development necessary to implement them. This work particularly focuses on routes to controlling the rate and extent of structural evolution.

Chapter 11. The findings of the work are discussed in the context of their scientific understanding developed and their technical and commercial significance.

Chapter 12. Conclusions are presented, together with recommendations for further work, in order to suggest the direction for further development of materials in order to better meet industrial need.

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CHAPTER 2 - APPROACHES TO COMMERCIAL RESEARCH AND DEVELOPMENT

2.1 The nature of innovation

The defining feature of commercial R&D is innovation. Innovation is distinct from invention. The latter pertains to an original thought or idea which only becomes innovation once it has been successfully introduced for commercial benefits (DTI 2003).

The concept of innovation as a key feature in industry is not new. By the mid-nineteenth century Karl Marx and Friedrich Engels recognised that “the Bourgeoisie cannot exist without constantly revolutionizing the instruments of production. Conservation of the old modes of production in unaltered form was, on the contrary, the first condition of existence for all earlier industrial classes. The bourgeoisie, during its rule of scarce one hundred years has created more massive and more colossal productive forces than have all preceding generations together” (Marx and Engels 1848).

2.2 The need for industrial research

“Virtually all of the economic growth that has occurred since the eighteenth century is ultimately attributable to innovation... under capitalism, innovative activity... becomes mandatory, a life-and-death matter for the firm and *innovation has replaced price* as the name of the game in a number of important industries” (Baumol 2002).

Innovation is essential to the continued existence of a business. Without innovation, it is inevitable that eventually competitors will either introduce new, superior products which better address market need, rendering the original product obsolete, or will find a more cost effective way to manufacture the existing product, rendering the original route non-viable. In either case, innovation is required to counter this threat and is therefore essential for any business operating in a competitive and global marketplace. In the USA, new products less than five years old account for 52% of sales and 46% of profit (Cooper and Kleinschmidt 1993).

2.3 The innovation process

The traditional starting point for innovation is considered to lie between pure and applied research but this is overly simplistic; a more realistic situation may be represented by considering research in terms of market readiness. This is represented in figure 2.1.

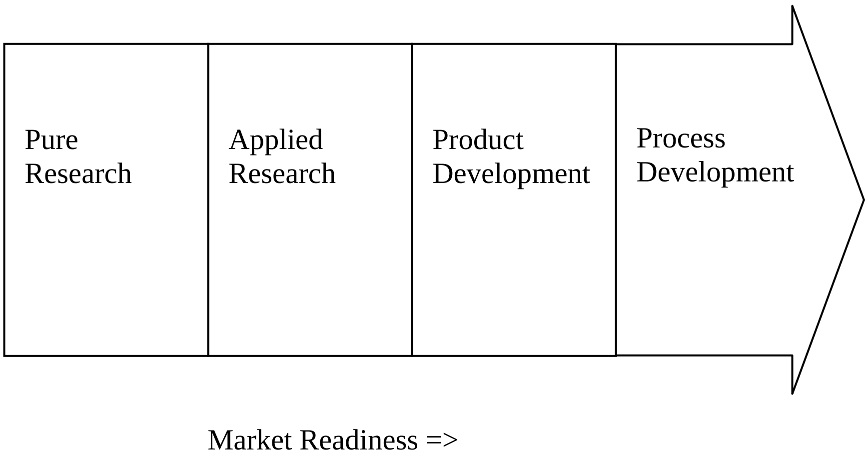

Fig.2.1. The research progression from invention to innovation.

Figure 2.1 illustrates that the progression from research to development is actually a continuum, corresponding to increased market readiness, or alternatively decreasing time to market. Whilst the exact point on the continuum which may be considered the start of innovation is open to debate, a reasonable definition may be obtained by regarding research as industrial if it pertains to a tangible product, and therefore most closely corresponds to applied research.

The concept of progression from research to development is developed further in the use of technology readiness levels (TRLs). TRLs are a systematic measurement system that supports assessments of the maturity of a particular technology and the consistent comparison of maturity between different types of technology (Mankins 1995). Used originally by NASA and latterly more generally adopted (Technology Strategy Board 2008), the TRL approach may be used to provide a summary view of the technology maturation process. Technology readiness may be divided into nine levels, incorporating basic research into new technologies; focussed technology development; development and demonstration for specific applications; development to first fabrication and finally system launch and operation. The nine levels may be summarised as follows:

TRL1	Basic principles observed and reported.
TRL2	Technology concept and/or application formulated.
TRL3	Analytical and experimental critical function and/or characteristic proof-of-concept.
TRL4	Component and/or breadboard validation in laboratory environment.
TRL5	Component and/or breadboard validation in relevant environment.
TRL6	System/subsystem model or prototype demonstration in a relevant environment.
TRL7	System prototype demonstration in operating environment.
TRL8	Actual system completed and qualified through test and demonstration.
TRL9	Actual system proven through successful service.

TRLs may be used to describe the process of industrial research in the introduction of new products.

It is, however, erroneous to regard innovation solely as a factor in new products; innovation may occur at any stage in the lifetime of a product, as illustrated in figure 2.2.

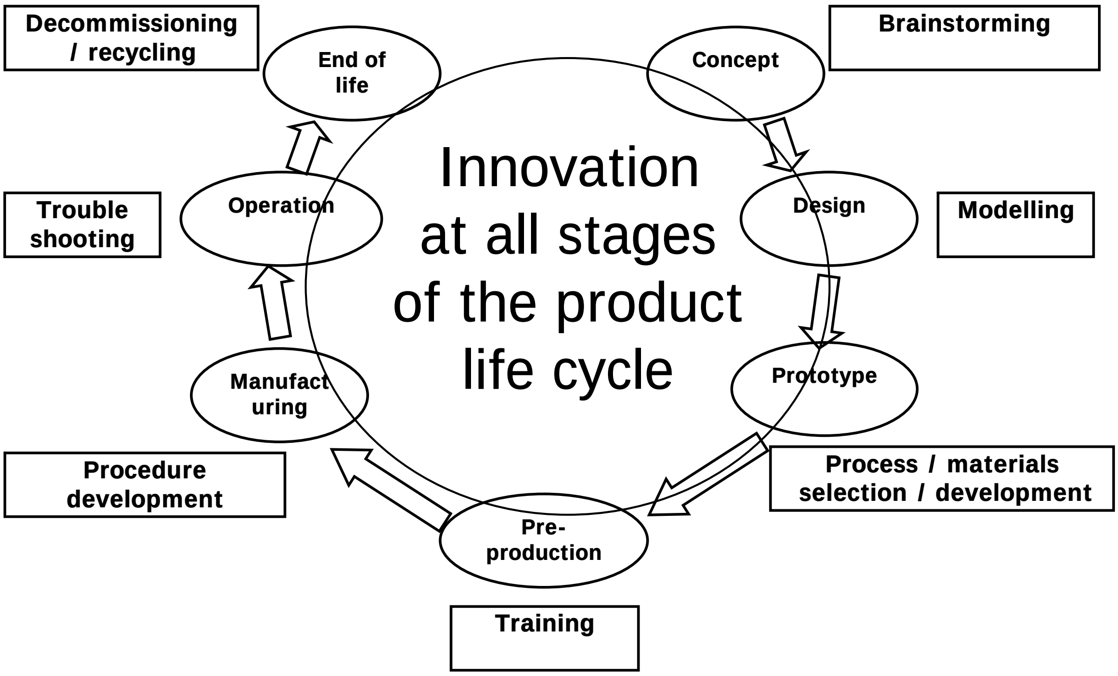

Fig.2.2. Illustration of opportunities for innovation throughout a product lifecycle (TWI 2006).

In this context, technology maturity can be separated into three progressive stages, followed by decline, as shown in the product life cycle in figure 2.3.

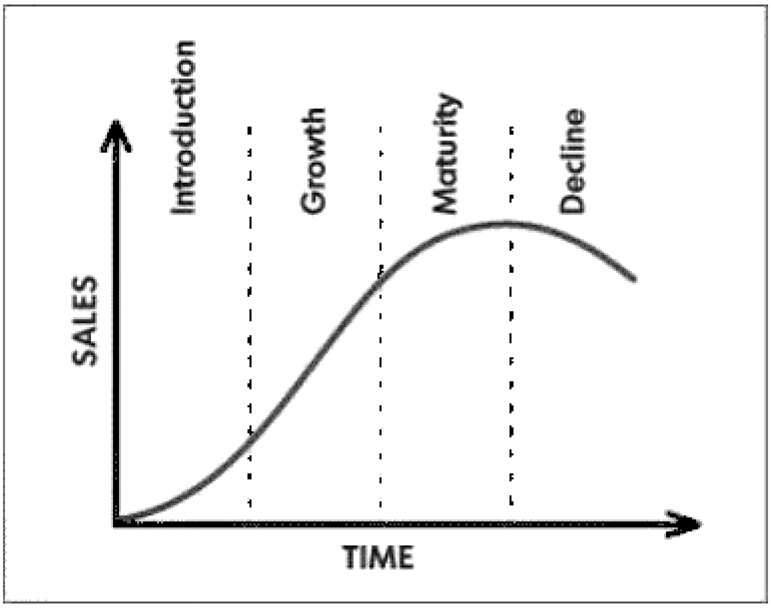

Fig.2.3. Product life cycle after Levitt (Levitt 1965).

1. Immature technology. In an industrial context, this has not achieved production volume and usually constitutes research. Work under this classification spans the range from initial concept through to proof of concept at the laboratory scale. This stage may include both pure and applied research and corresponds to TRLs up to and including TRL 4.
2. Intermediate technology. Based on existing technology, this may be iterative development, making incremental advances to a known process; or technology transfer, taking a known process from one sector and developing the changes necessary to transfer it to a different sector. This corresponds to product development, incorporating TRLs 5 to 9.
3. Mature technology. Having been accepted industrially within a given sector and constituting the established method, whilst it is accepted on a day-to-day basis, R&D may continue in a process of ongoing product development, leading to next generation products updated to incorporate new technologies. This extends the mature phase of the product lifecycle shown in figure 2.3, extending profitable production. R&D backup may also still be required when the production process fails, for troubleshooting and failure investigation. Additionally, in an industrial context, process success is measured against delivery, using metrics such as yield and lifetime. This stage corresponds to process development and is beyond the timeframe of TRLs in product maturity. Understanding of process variables therefore tends to be empirical rather than theoretical and process improvement can sometimes be gained by employing an R&D facility in providing the latter approach.

In order for an application to be commercially successful, rather than merely possible, it must significantly improve on a current product or process, or create an entirely new commodity (Livage 1998). Many technology fields in the early stages of investigation follow the ‘hype cycle’ (Fenn 2009), illustrated in figure 2.4.

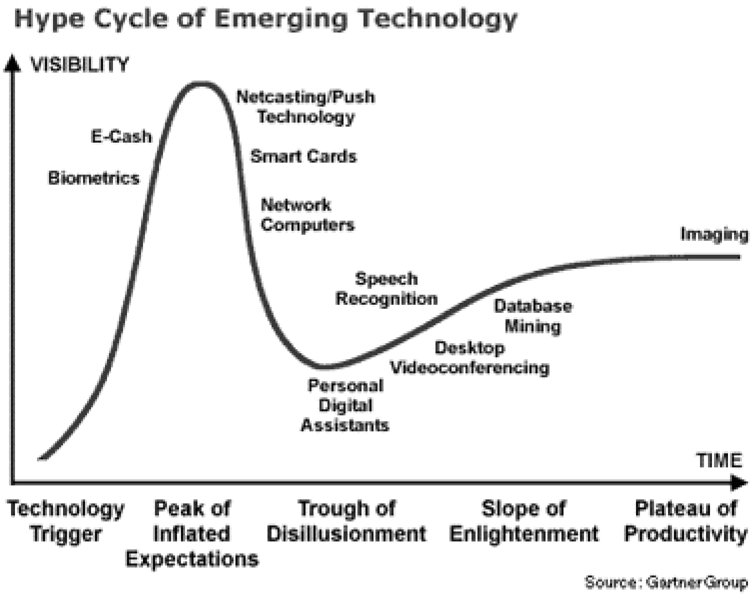

Fig.2.4. Gartner’s hype cycle (Fenn 2009).

The cycle illustrates visibility/interest in a technology against time and consists of a series of phases. Following an initiation trigger, the peak of visibility is achieved in a ‘Peak of Inflated Expectation’. This stage is followed by a backlash when expectations are not met, the ‘Trough of Disillusionment’, evidenced by the substantial reduction in industrial and applied research funding when the promised results are not delivered. There follows a resurgence of interest (Slope of Enlightenment) which recognises the realistic benefits which the technology offers, followed finally by a stable phase of general market acceptance, the ‘Plateau of Productivity’.

2.3.1 The conflict of interest between theoretical understanding and practical application

A significant factor in considering innovation is that, since it is defined by commercial introduction, the level of understanding required is in theory no greater than that needed to facilitate that introduction. Any additional development of theoretical understanding may, from the industrial perspective, be regarded as drawing on resources without a commercial return. This trade-off between understanding and practical application is illustrated in figure 2.5.

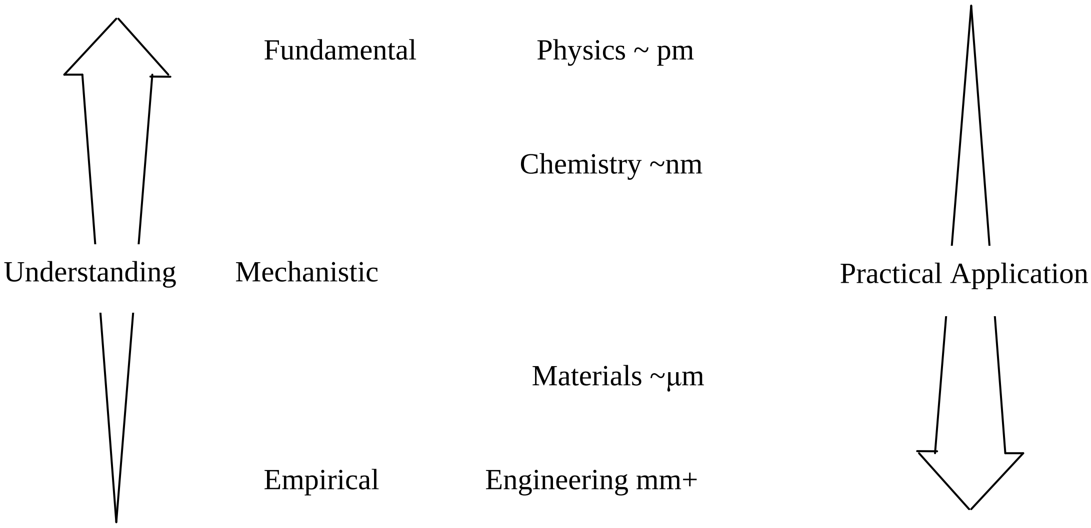

Fig.2.5. The trade-off between understanding and practical application.

It is instructive to observe that the level of understanding may also be correlated with length scale, corresponding to different disciplines in science and engineering. Industrial requirements are generally founded on engineering, requiring an empirical solution at the macro scale (with the exception of failure investigation where mechanistic understanding is generally required). In order for an R&D provider to deliver effectively to industrial requirements at least a mechanistic understanding is required. Recognition of this requirement for a greater level of understanding is a substantial factor in the separation of R&D from manufacturing functions. A fundamental understanding is intellectually satisfying, and forms the basis of academic work, but may well not be required for industrial use. This may generate a conflict of interest between an academic approach, which is focussed substantially in the area of invention, and an industrial approach focussed on innovation.

A recent trend however has been towards developing an increased understanding in an industrial context. This approach has been used to meet several different objectives, including satisfying health and safety requirements, enabling continued production, and to extend the capability of existing processes and materials through formal optimisation processes such as designed experiments. For example, the application of Taguchi methods is now standard practice at Ford’s engine plant in Dagenham (American Supplier Institute INC 1988). The same approach is increasingly leading to the development of a higher level of understanding alongside the practical application of new materials and processes in order to maximise performance.

2.3.2 The scale of innovation

The effects of innovation steps span a tremendous range. The smallest effect is felt in incremental innovation which is a cumulative process. It manifests itself as a process of continuous improvement, where each individual step may be so small that it is not observed (Freeman and Perez 1988). As a strategy, it has the advantage of building on known strengths and thus minimises risk. It is, however, vulnerable to major market trends, since it is not able to respond rapidly enough to remain competitive. The features of incremental innovation make it a favoured strategy for larger, more established companies which tend to be more risk aware and since it minimises financial risk. It is an appropriate strategy for stable markets where a substantial history of development has reduced the likelihood of a major market shift. It is also a common approach in safety-critical applications, since it minimises the risk of an undesirable outcome.

Radical or disruptive innovation occurs when an event facilitates the introduction of an alternative, preferable approach to an existing technology (Freeman and Perez 1988), for example the introduction of the jet engine or the float glass process. Radical innovation is therefore less frequent than incremental innovation. It requires the introduction of fundamentally new technology and therefore has a higher cost of entry for existing companies with capital invested in existing technology than for new entrants without existing technology, which will become redundant. It therefore presents an opportunity for redistribution of market share, based on time to adoption of the new ‘dominant design’.

Radical innovation is generally the product of significant R&D effort, during which substantial investment is made in developing different approaches before the successful route is established Uncertainty exists over when a successful development will be made. The reward is in being the first entrant and hence best able to establish market share. The acceptance of a given product is uncertain, the classic example being the failure of the technically superior Betamax over the more rapidly adopted VHS system for video tape recording. Market demand is unpredictable and dependent on a broad range of techno-economic factors. As such, it is a higher risk, higher cost strategy.

Radical innovation is therefore used by companies which wish to enter new sectors, or in large companies which choose to make a substantial investment to improve the overall probability of success, ensuring their long-term viability by protecting against vulnerability to major market trends. Radical innovation is substantially increased in emerging sectors, since the probability of any given approach having been previously tried is reduced.

Changes in the techno-economic paradigm are the most substantial form of innovation (Freeman and Perez 1988). Examples include the development of powered flight, or the internet. These are analogous to Kuhn’s scientific paradigm shifts (Kuhn 1962). Schumpeter first considered their significance in respect of innovation, under the title ‘change in pre-analytic vision’ (Daly and Farley 2003). Whilst such events are impossible to forecast, it is predictable that a series of radical innovations follows rapidly in their wake, since as described above, they present opportunities to evaluate a whole series of known technologies in a new context. Rapid identification of, and response to new techno-economic paradigms is therefore the key to their successful exploitation.

Whilst it remains true that innovations may arise at any point in the life-cycle of a product, it is also inevitable that mature technologies present fewer opportunities. The need for R&D is a direct consequence of the shortcomings of the *status quo*. In order to justify the cost of investment and simply to overcome inertia, these must be significant. Thus, while development may be made during the course of continuous improvement, it is less likely that a step change will occur, since more of the options are likely to have been explored in the course of earlier development work and the solution is less likely to be a found in the application of previous work in a new context. However, where opportunities do exist, they tend to be easier to pursue. Mature technology is more frequently associated with established companies, who generally have a stable revenue stream. They are, therefore, more likely to be able to fund the necessary level of research, however if they have established practices the level of inertia may prevent the work from being carried out.

Conversely, R&D opportunities are far more frequent in emerging technologies. Unfortunately, these are also the fields where research budgets are already heavily stretched, particularly in small, start-up companies which frequently have to attract private venture finance.

The companies with the greatest number of options for R&D tend to be both established and forward-looking, hence seeking introduce change. Such companies may already be in full commercial operation, with known problems which have been accepted into the culture with procedures to minimise their impact. Advances in technology may facilitate the resolution of such problems, allowing more efficient operation in an incremental fashion. Alternatively, they may be seeking to introduce a radical innovation in their product which requires new materials or processes. The same technology development may constitute both a radical innovation and an incremental improvement for different parties within a supply chain, as illustrated in the case study presented in Part B.

As is apparent from the above discussion, the timing of a response to major change is critical to a company’s continued success. In order to effect such a response, awareness of market trends and drivers is essential, together with a facility to predict future trends. Approaches to technology forecasting are discussed below.

2.4 Techniques for technology forecasting

2.4.1 Why forecast?

Within every business decision, some estimate of the future is implicitly made. This may be a conscious exercise within the decision making process. Alternatively it may be made unconsciously as an implicit part of the decision which carries risks that:

a) Technological feasibility automatically leads to a development process without assessment of its desirability.
b) Current market demand is followed blindly.
c) Product lines are pushed to their extreme without consideration of a suitable transition point for radical change.
d) Demand is created artificially in response to scientific or technological developments (technology push), or to maintain skills and capabilities.

A planned approach to technology forecasting can overcome some of the above issues and allow assumptions to be stated, tested and amended as more data becomes available. One approach to forecasting is the development of a technology roadmap.

2.4.2 Technology roadmapping

Successful innovation must meet a need, either within the industry or from the market. An effective method for determining the timing of innovation is technology roadmapping, a process which is driven by needs rather than solutions. The main advantage of technology roadmapping is that it provides forecasting information to make better investment decisions by identifying critical technologies and technology gaps (Garcia and Bray 1997).

In order for roadmapping to be successful it is critical to work to clear objectives and carry out the exercise with input from the right people, ideally spanning the development chain from research through to production.

2.4.3 Approaches to technology roadmapping

Different approaches to roadmapping may be used, depending on the objective to be achieved; the most common being the product roadmap (Phaal, Farrukh et al. 2001).

2.4.3.1 Extrapolative

An extrapolative roadmap is formed by plotting previous developments in a product and projecting future trends by extrapolation. It therefore assumes a continuation of existing technology. Extrapolation is a traditional approach to roadmapping, being derived from scientific or engineering principles. Its principal limitation is that it fails to allow for radical change. Development in other fields may undermine the assumptions on which it is based. An extrapolative approach therefore provides a reasonable short-term estimate but has very limited capability for longer term projection.

2.4.3.2 Morphological

A morphological approach is based on the assumption that a total set of requirements must be met in order for a product to exist. It was originally developed by Zwicky and applied to the development of jet aircraft (Coyle 2003). By presenting the production process as a matrix containing each individual step and assessing the options for each, the approach used in any specific step can be altered whilst retaining complete functionality. Zwicky’s example is shown in figure 2.6.

Self contained – carries all chemicals necessary for activation and operation	No motion	No thrust augmentation	Gaseous state	**Continuous operation**	Propellants are self-igniting
If air propelled, carries only fuel and uses atmospheric oxygen	**Translatory motion**	**Internal thrust augmentation**	**Liquid state**	Intermittent (pulsating) operation	**Artificial ignition is necessary**
If propelled through or over water, uses water as propellant reacting with an on-board water-reactive chemical	Rotary motion	External thrust augmentation	Solid state		
If propelled through or over the earth, may use earth as propellant reacting with on-board earth-reactive chemical					

Fig.2.6. Zwicky’s morphology of jet engines (Coyle 2003).

By analysis of the weakest process steps, the approach can be used to identify breakthrough opportunities within an existing product. The text in bold in figure 2.6 indicates Zwicky’s solution for an ‘aerojet’. It is, however, not suited to identifying future products.

2.4.3.3 Normative

A normative approach begins with a statement of need and then seeks to identify a route to achieving it. It therefore avoids the weakness of extrapolative approaches which limit future developments to those which can be foreseen through incremental change. If the number of opportunities is greater than the number which can be pursued then a normative approach provides a route to selection.

A normative approach is only meaningful if constrained. Constraints may be applied through consensus as to the validity of the need and its desirability. The scope must be constrained such that events impact on one another, otherwise a practical route to achieving the need cannot be identified.

A further constraint which may be applied is that of timescale. A Delphi approach may be used, based on consensus. The Delphi approach assesses the view of a number of individuals as to their personal opinion as to the timescale over which a particular development can be achieved or will be required. If the group is sufficiently large and knowledgeable then a reasonable assessment may be achieved from the median value.

2.4.4 Strategic planning roadmaps

The normative approach with a Delphi approach to timescale assessment has been widely adopted in strategic planning roadmaps (Phaal, Farrukh et al. 2001) , a schematic illustration of which is shown in figure 2.7.

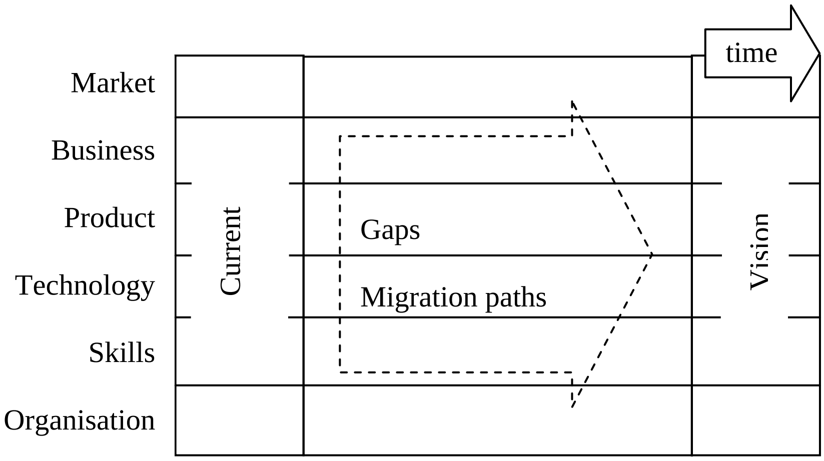

Fig.2.7. The strategic technology roadmapping process (Phaal, Farrukh et al. 2001).

Strategic technology roadmapping is constrained to a particular field of technology and initiated from industry and market trends related to the field. These are external drivers such as energy efficiency, reduced manufacturing costs *etc*. The internal products required to address these drivers are then identified. The roadmap is completed by establishing the necessary links (shown as arrows), from initiation of capability to delivery of a product to address market trends. By considering the *x*-axis as a timeframe, the necessary actions and their timing may be identified.

Technology roadmapping is particularly useful when the investment decision is complicated by lack of clarity with regard to selection of alternatives, timeframe of the requirement or when the development of multiple technologies needs to be coordinated (Garcia and Bray 1997). It should be noted that, in addition to the technological capability, necessary resources are considered at the bottom of a roadmap. Routes to obtaining such resources are discussed below.

A further factor is that different aspects of a development, either product or technology, may be performed by different providers. The objective of the roadmap is to establish that the technology exists in a suitably accessible form, not necessarily that it is wholly owned or developed in-house. It is therefore reasonable for both industry and research providers to perform roadmapping exercises, since the research provider needs to identify trends early enough to carry out preliminary research in order to be capable of addressing the needs of industry when they arise. Consequently, the roadmap for a technology provider is likely to include a greater number of long-term developments than that of a manufacturer, in anticipation of the future market trends which industry may wish to address.

In developing a roadmap, it is highly probable that more trends will be identified than can be addressed with the resources available. The challenge is to ensure that the technology provider’s roadmap correlates with the roadmaps of the end users it wishes to serve. Prioritisation is therefore required. A useful mechanism for assessing priorities is to use a ‘SWOT’ analysis. This is a two stage process, the first identifying Strengths, Weaknesses, Opportunities and Threats associated with a particular business and the second using them to determine which of the opportunities identified from the roadmapping exercise best address these needs.

Strengths and weaknesses are the capabilities of the business. These are internal factors, including:

- Research and Development
- Marketing
- Management information system
- Management team
- Operations
- Finance
- Marketing
- Human resources

Opportunities and threats are the possibilities arising in the environment. These are external factors including environmental factors:

- Social
- Technological
- Economic
- Environmental
- Political
- Values

and the ‘5 forces of industry’:

- Threat of new entrants
- Power of suppliers
- Power of buyers
- Threat of substitutes
- Intensity of competition

The relevant factors for the business under consideration are identified and tabulated under each of the four SWOT headings.

The second stage of the process is the development of an action plan. The structure used for this is shown in figure 2.8.

	Opportunities	**Threats**
Strengths	Exploit in short term	Market aggressively
Weaknesses	Develop capability	Avoid

Fig.2.8. The development of an action plan from SWOT analysis.

The matrix shown in figure 2.8 indicates the appropriate type of action associated with each combination of internal and external factors. In respect of trends, the strengths/opportunities sector provides the short term priority, where exposure should be maximised. The strengths/threats sector provides the second priority, depending on the level of competitiveness required. The greatest long-term benefits are to be derived in the weaknesses/opportunities sector, since these areas have the greatest potential for future growth, while the weaknesses/threats sector should be avoided.

In use, the line items identified in the first stage of the SWOT analysis are ranked in order of priority. The higher ranked items in each category are then transferred to the appropriate box in the matrix and an action plan developed in line with the appropriate action type. The entire process is illustrated in figure 2.9.

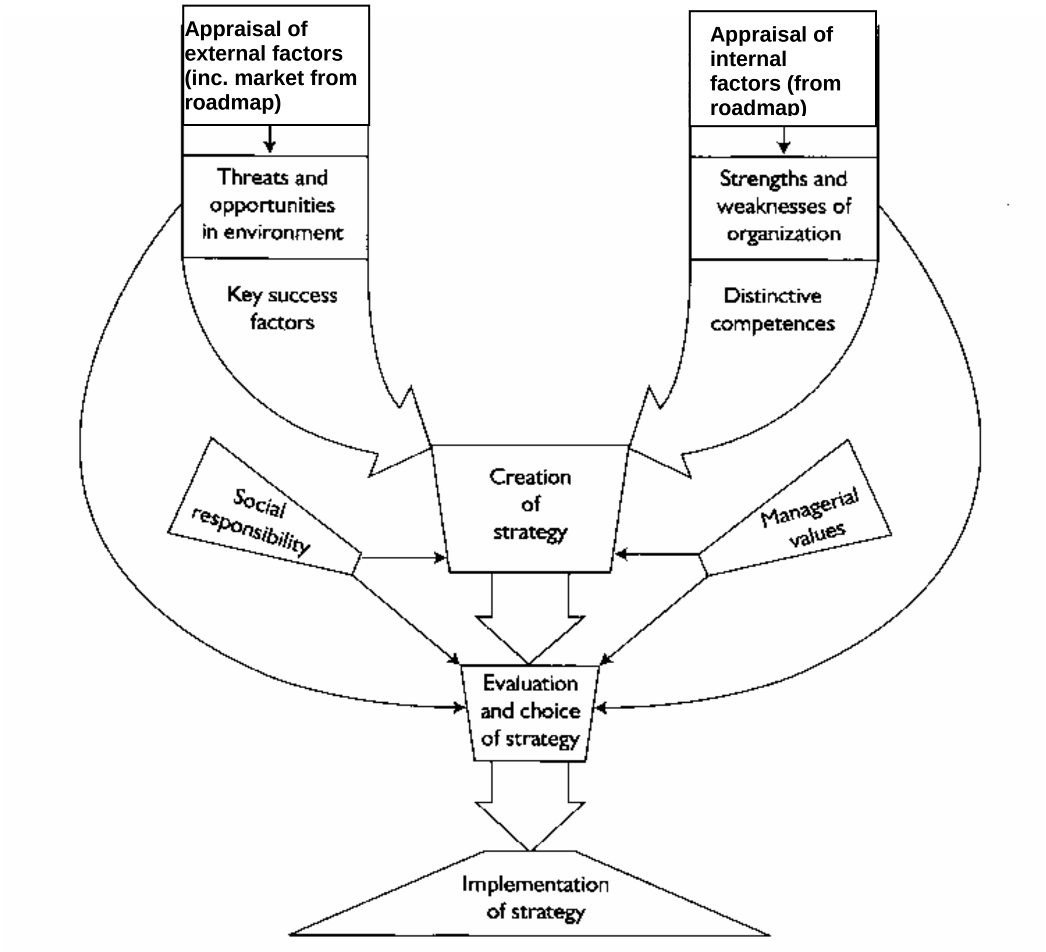

Fig.2.9. The development of a strategic plan from a SWOT analysis.

2.5 Resources, project types and funding mechanisms

2.5.1 Selection criteria

Research work is typically structured into projects with defined objectives and a timeframe. Within this general structure, there are many criteria which need to be considered in respect of how a particular piece of work should be carried out. These include:

The maturity of the technology (TRL)

The scale of the problem to be addressed (cost/timeframe)

The value of the work to the IP owner once completed

The commercial sensitivity of the results

The parameters listed above are heavily interlinked, however the options for a given project can generally be determined by reference to the first two parameters. Since investment is required to carry out any work it is necessary to consider available funding mechanisms.

2.6 Resources: The provision of industrial R&D

Provision for R&D may be made in a variety of ways. Companies may either operate internal research projects. However, for the reasons discussed above, a substantial number of industrial R&D projects involve the participation of a third body who acts as a research provider. The options for the provision of R&D are discussed below.

2.6.1 Internal R&D

Direct research within companies is carried out in a range of different ways. Some larger companies still retain the model of a dedicated research centre with a long-term research strategy. However, increasingly the trend in larger companies is towards carrying out only shorter term developments, such as process improvements, directly in-house, whilst future technology is either acquired through purchase of IP or funded indirectly under contract.

The trend for small, venture-capital (VC) funded start-up companies which are heavily IP based continues subject to the immediate financial climate. This trend, starting in the early 1990s, was based on an increasing tendency for universities (or their staff) to exploit commercially viable IP by forming spin-out companies (Cambridge Enterprise 2008). These companies aim to be VC backed, with a model of a large up-front cash injection to fund development towards a future product. A substantial proportion of such companies are expected to fail (Moore 2002), however those which survive can generate exceptionally high returns. For such companies the entire focus is R&D, however they tend to be human resource limited, being inherently small and therefore lacking in breadth of expertise. The total time from investment to return is critical, since expenditure of the initial investment can ultimately prevent further progress. External support can accelerate progress in areas which are key to eventual success but not core to the company’s own IP.

2.6.2 External R&D

External research providers in the UK are to be found within institutes of higher education (predominantly universities), in research and technology organisations (RTOs) and via consultancies.

2.6.2.1 Universities

Universities form a traditional seat of R&D. Drawing funding for research (predominantly from the EPSRC in the context of this thesis) which funds both pure and applied research at institutes of higher education. Current practice is a bias towards basic science in applied projects (EPSRC 2008), with funding being made available to leverage participation in collaborative projects (Technology Strategy Board 2008). Universities may also perform directed research, either in collaboration with other partners or directly for companies.

The principal limitation of most universities is the relatively rigid timeframe under which research can be carried out. This arises from the prioritisation of training activities; availability of staff falling in line with the academic year. Resourcing a project generally requires a dedicated individual and it is difficult to reallocate staff from existing work. Therefore, it is usually necessary to fit within the structure of a student project or postdoctoral placement. These relatively rigid mechanisms place discrete boundaries on the type of project which can easily be performed, although some universities have developed more flexible structures where their level of industrial income is significant.

Universities do, however, being dedicated to research and having access to capital equipment grants, tend to have the latest state-of-the-art equipment, although generally on a relatively small scale compared with industrial processing. They tend to be an excellent fit to developing detailed understanding of the fundamentals of a process due to their extensive facilities for characterisation.

2.6.2.2 Research and technology organisations

This EngD was based in a research and technology organisation (RTO), hence this mechanism for the provision of industrial R&D is discussed in detail.

RTOs were originally established in the 1940s to bridge the gap between the then esoteric technology generated in university departments and the direct needs of industry in their particular sector, which are as diverse as casting, paints and cocoa research (AIRTO 2008). A number of the original RTOs have ceased to exist, while new organisations with wholly commercial origins have come into existence (TTP 2010).

RTOs now provide industry with engineering solutions through:

- information
- advice and technology transfer
- consultancy and project support
- contract R&D
- training and qualification
- personal membership

RTOs operate under either private ownership or a membership model. The latter ensures independence and generates income by subscription. The fee pays to support access to information which is provided free at point of use and is supports internal investment in immature technology to remain at the forefront. By canvassing its members, an RTO can ensure that investment is directed towards developing the appropriate capabilities to be ready to address future market trends on the roadmap.

Projects may be conducted for individual member companies on a confidential basis and include both R&D and consultancy work. The pressures of publication do not apply to RTOs as they would to Universities, simplifying the issue of confidentiality. Since RTO activity is wholly based on research projects, they can develop expertise in management of complex project types such as group sponsored and collaborative projects which involve participation in medium- and long-term R&D and Technology Transfer with other organisations. In this respect, RTOs continue to fulfil the original role of interfacing between academia and industry. RTOs typically have active links with UK and overseas universities in collaborative research activities and in utilising Engineering Doctorate or PhD students, as appropriate, to progress fundamental aspects of key technologies.

One area where balance is constantly required is that, in order to maintain staff who can respond rapidly to clients' needs, an RTO must operate with surplus capacity which requires funding. Ongoing innovation is an approach to reducing this challenge, since the resulting licence income may be reinvested in the business to fund new ideas and exploratory projects. In the case of TWI, an RTO in the field of joining and surfacing technology, associated income arising from the innovation portfolio, including new Members and contract work, is at least five times the licence income (TWI 2006).

The operational model for a membership based RTO is illustrated in figure 2.10.

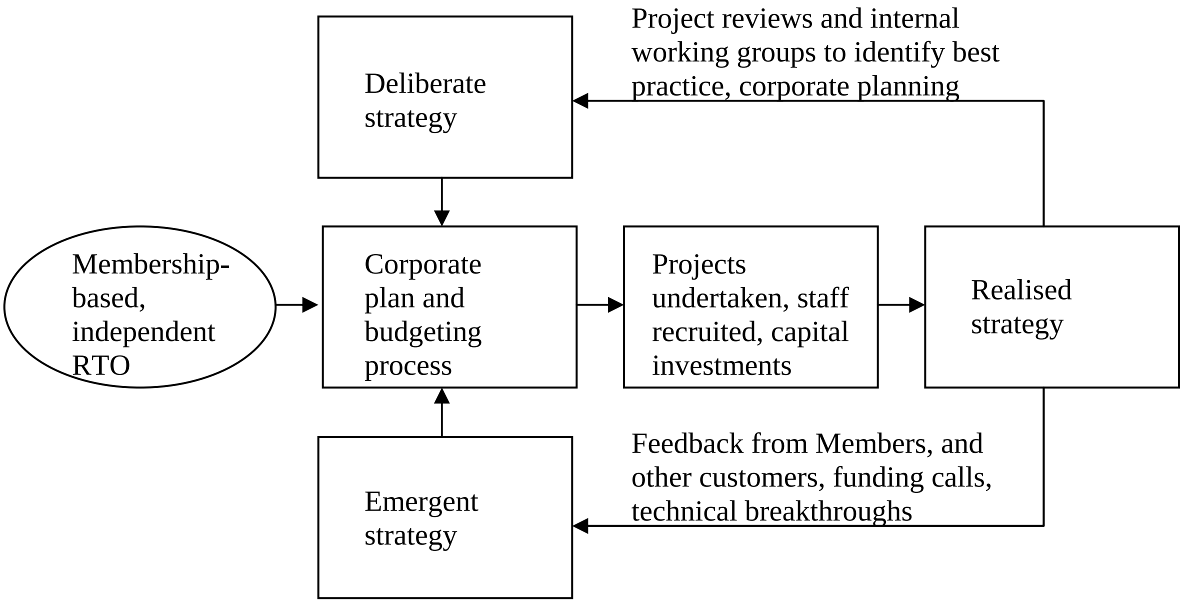

Fig.2.10. The operational model for a membership based RTO (Routley 2007).

The model indicates the requirement for an RTO to incorporate both planned strategy from internal development and emergent strategy, developed directly in response to its members.

2.6.2.3 Consultancy

At this stage, consultancy should be briefly discussed. Consultancy may be provided either through individual consultants, or through larger companies (Cambridge Consultants 2008). Consultancy can go some way to overcoming the limitations of internal R&D since it resolves the issue of internal expertise. It does, however, not generally provide access to equipment and is unlikely to provide direct developmental facilities. The individual consultant is, therefore, most successful when used to address short-term issues with known solutions, rather than where an R&D solution is required. The larger consultancy organisations are keen to take responsibility for new product development, however they tend to make use of technology providers such as Universities or RTOs for access to facilities. The distinction between consultants and RTOs could be defined as one of focus, the former being product focussed and the latter technology focussed.

2.6.3 Funding mechanisms for R&D

Whilst the majority of pure academic research in the UK is directly funded by the engineering and physical sciences research council (EPSRC), routes available for funding commercial R&D are considerably more diverse. If the work is not to be directly funded from the organisation's own internal budget then various other sources can support the work, each with its own specific requirements and inherent complications. The principal classifications are summarised below:

2.6.3.1 Internal funding

Directly funding development in-house gives the greatest degree of control. IP is automatically contained, hence no short-term decision needs to be taken over how the arising IP should be pursued. This is particularly significant if it may be exploited as patentable technology, a trade-secret or retained as know-how. This funding route is, however, limited by the resources available to the organisation in question, both in terms of materials and equipment, and in terms of staff availability and skills. The latter can be more significant than many smaller organisations initially realise. The cost of hiring staff with specialist knowledge may be preclusive and the rate of progress made by staff without the appropriate expertise is at best reduced during the training phase, particularly since it is likely that they will be required to train themselves from the literature. A conflict of interest arises between short term income generating activity and longer term development work, which further complicates this mechanism for research. It is, however, a satisfactory mechanism for many larger organisations which can retain a specialist research facility to support ongoing development in their field. This acts as a bespoke source of expertise and assists competitiveness, both through the direct relevance of its activities and also by preventing access to the expertise by competitors. In these circumstances, internal development would be a preferred route, since it utilises existing resources in the most efficient manner possible.

2.6.3.2 Direct external funding

When the level of work required exceeds the resources available to an organisation, either in terms of equipment, knowledge or staff, but sufficient budget is available, an alternative route is to contract the work to an R&D provider. A provider with suitable equipment and know-how can frequently deliver the work more rapidly than if carried out in-house. Suitable activities to fund in this fashion may be very diverse in scope, ranging from simple consultancy, such as providing information about an unfamiliar process (I've just taken up brazing and my joints all fail - tell me how to do it properly) to novel solutions to complex problems which may take many years to solve.

The work is subject to a contract which, if correctly drafted, ensures that a suitable arrangement is made in respect of secrecy and IP ownership. The relationship may be likened to that with a solicitor or lawyer, in that a professional service is provided, based on the time required. In this respect it differs significantly from an engineering construction contract, where the contract is based on delivery of a tangible product. The contract should make allowance for the possibility that the work may demonstrate conclusively that a particular product or process cannot be achieved. This reflects the risk element of R&D, risk (and reward) typically remaining with the purchaser rather than the provider. Since R&D purchase may be made due to limited internal capacity, it is reasonable to assume unfamiliarity with this distinction and it is therefore imperative that the purchaser is aware of risk before work commences.

2.6.3.3 Group funding

Where a programme of work is attractive to several companies but not subject to sensitivity regarding IP, it can be cost-effective for these companies to collectively sponsor a project. This reduces individual cost and risk, whilst improving leverage on funding.

Project management challenges arise when

a) The technology is critical to the business of competitors who are potential sponsors of the project. The desire to gain competitive advantage promotes secrecy which hinders project success. The level of secrecy varies by industry sector and the implications of the technology involved. Thus the oil and gas sector will openly discuss their requirements for next generation pipeline materials, as they are critical to safe operation, while the materials supply sector tends to be secretive about similar technical issues that impact on competitive advantage (Woollin 2009). The former is therefore more suited to development through group sponsored projects.

b) Although the generic problem is common, the detailed requirements differ between potential sponsors. This complicates the project management, since the direction should remain sufficiently generic that it benefits all sponsors equally.

A consequence of the above challenges is that a more rigid contractual framework is generally required for group sponsored projects than single sponsored projects, since balance must be maintained between sponsors in the scope of the work.

2.6.3.4 Collaborative funding

In contrast to group funded projects, described above, the collaborative project is a mechanism of partnership between organisations, rather than a group funding the research provider. In circumstances where a group of companies can collaborate (with or without a dedicated research provider) in a development, public funding may be made available. The objective in providing the funding is to facilitate development which would not otherwise occur; consequently the type of project which will attract funding is inevitably either higher risk or involves organisations which would not otherwise be able to commit the research budget required. The funding available may be significant, frequently in the order of £500,000 per partner (EU 2008) with funding rate proportionate to the risk, higher risk projects securing 50-

75% funding. Collaborative projects therefore go some way to providing a route for smaller, less established companies operating in immature fields to facilitate research.

In the UK, funding tends to be made available either at local level by the regional development agencies (RDAs) or devolved administrations (DAs), at national level by the government through the Technology Strategy Board (TSB) (Technology Strategy Board 2008) and through various national bodies such as the Carbon Trust (Carbon Trust 2008) with interests in developing technology in specific themes, or through the European Commission under Framework programmes (EU 2008). In each case, specific rules apply. The funding schemes may either be themed, calling for projects in a specific field, as in the EU ‘Co-operation’ and TSB calls (European Commission CORDIS 2008; Technology Strategy Board 2008) or open to applications in any field where the project structure conforms to the aims of the call as in the EU ‘Research for the Benefit of SMEs’ call (European Commission CORDIS 2007). Since the objective in making funds available is to promote industrial growth and economic benefit, collaborative projects inevitably require a route to ensure commercial uptake. As a consequence, this can be a viable route to developing higher risk, longer term technology which to succeed will require integration across a supply chain which is frequently formed from the project partnership. The vertically integrated project structure ensures that the partners, who have greatest access to the data, are non-competitive in the field and are, ideally, mutually beneficial.

Since the funding body bears a substantial proportion of the risk and will not directly generate any return in the event of project success, the express secondary objective in funding projects is to foster links between industries, outside the direct scope of the project, enhancing overall competitiveness. In this respect, participation in collaborative projects may be beneficial to the companies concerned.

2.7 Selection criteria for an approach to R&D

Commercial R&D is a service industry, the output of which is knowledge. The R&D process consists of a series of discrete stages. Starting from the definition of needs to address the appropriate trends, a series of objectives can be determined. The scope of work required can then be established and by consideration of the factors described above, an appropriate project type, R&D provider and funding mechanism can be determined.

In operation, a commercial R&D project (much like an academic project) combines collation of existing knowledge and making incremental development. Given the added complications of ensuring an appropriate IP position and satisfactory delivery against contract, a commercial R&D project requires particularly strong project management. This factor is recognised by external funding bodies, as shown within the guidelines for funding for particular calls (European Commission CORDIS 2009) which typically allocate between 5 and 10% of project budget directly to this activity. These factors form part of the selection criteria for the R&D provider, particularly in larger, more complicated projects.

The two parameters of technology readiness and scale of the development can be used to form a matrix from which a suitable funding mechanism can be selected. The suitability of the mechanism then depends on the acceptability of the compromise required relative to the other parameters. Thus the matrix shown in Table 2.1 can be produced.

		Technology Readiness		
		Immature	Intermediate	Mature
Size of Project (£)	<10k	Individual/Internal		Internal/Individual
	10-50k	Internal/Collaborative		Internal/Individual
	50-100k	Collaborative		Internal/Individual
	>100k	Collaborative	Collaborative	-

Table 2.1. Options for project funding type, based on project size and technology readiness.

Within this thesis, the technology investigated was at the immature stage. The two phases of the case study presented were £50-100k and >£100k respectively. The first was internally funded by TWI while the second was carried out with collaborative funding. Further details of the selection of each approach are provided within Chapter 4.

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CHAPTER 3 - SOL-GEL PROCESSING

3.1 Introduction

The sol-gel process is a chemical method for making inorganic glasses from solution. The process uses precursors in the form of a solution or dispersion, which undergo a series of chemical reactions to form first a liquid sol and subsequently a solid gel. The gel is then dried and cured to a glassy inorganic material at relatively low temperature, typically below 500°C and in some cases at room temperature. This is in contrast to the traditional high temperature fusion routes used for synthesizing of glasses and ceramics where sintering temperatures are a high percentage (<75%) of the melting point, i.e. typically over 1500°C. The material may be crystallized with additional energy input.

Sol-gel materials typically have high levels of homogeneity and purity. The majority of materials prepared by sol-gel processing are oxides, but the process may also be used to prepare nitrides and carbides (Milonjič, Čerovič et al. 1998). Organic-inorganic hybrid materials may also be prepared, since the low processing temperature does not scission the bonds within the organic component. For a comprehensive description of all aspects of sol-gel processing, the reader is referred to “Sol-Gel Science” by Brinker and Scherer (Brinker and Scherer 1990).

3.1.1 Polymeric vs. colloidal routes

Sol-gel processing divides into two branches, distinguished by the type of precursor selected. The colloidal route employs particulate precursors, whilst the polymeric route employs metal alkoxides (Brinker and Scherer 1990; Taylor and Fernie 1998).

Colloidal precursors are discrete, primary colloidal particles, predominantly oxides and usually spherical, with a diameter of between 1 nm and 1 μm. The particles can be precipitated from solution or produced in the vapour phase, as for example with fumed silica. The particles are of high purity, usually above 98%. The particles are dispersed in a liquid carrier, typically water and coalesce to form a gel. The process is shown schematically in figure 3.1.

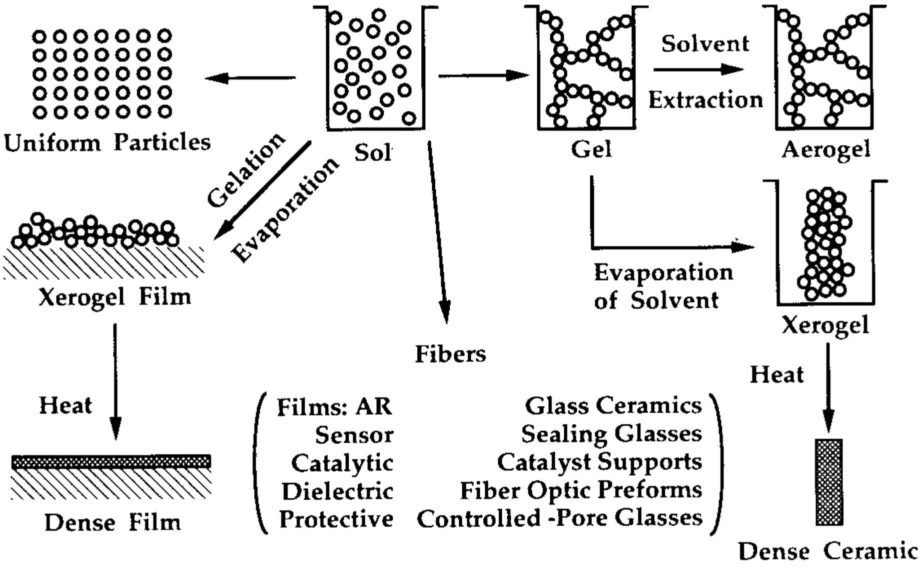

Fig.3.1. The colloidal sol-gel process (Brinker and Scherer 1990).

The dispersion or coalescence behaviour of the particles is dependent on their surface charge. To achieve dispersion it is necessary to generate repulsion between the particles, via an electrostatic charge. The repulsive charge on the surface of the particles then inhibits subsequent reaction. The surface charge must therefore be neutral for gellation to occur.

Surface charge is controlled by pH. The equivalence point of the particles is termed the point of zero charge (PZC) and is material specific, the particle acting as a Lewis acid or base. The PZC values for a range of common oxides are listed in table 3.1.

Oxide	**PZC**
SiO_2	2.5
SnO_2	4.5
TiO_2	6.0
Cr_2O_3	8.4
Fe_2O_3	8.6
Al_2O_3	9.0
MgO	12.0

Table 3.1. pH value of the point of zero charge for various oxides (Balfe and Martinez 1986; Flory 1991).

In practice, colloidal sol-gel processing is achieved by dispersing the powder in water which, being amphiprotic, stabilizes the charge on the surface with either protons or hydroxide ions, as can be seen from inspection of table 3.1, dispersing the particles. The precursor is then activated by the addition of either an acid or a base as required, adjusting the pH to achieve the necessary PZC. At this point, a collision between the colloidal particles can result in reaction and consequent coalescence. As further free particles collide and react they form a network which ultimately spans the container. At this point, the network is described as a gel. Further reaction can then occur between adjacent particles via the process of Ostwald ripening. In this process the smaller particles are dissolved and re-precipitated on the surface of the larger particles, driven by an overall decrease in energy through the reduction of surface area to volume ratio (Brinker and Scherer 1990). Subsequent solvent removal and curing steps result in a solid, glassy material.

Polymeric sol-gel processing uses liquid or dissolved precursors rather than colloidal particles. These are typically metal alkoxide compounds with the chemical formula $M(OR)_n$ where M is metal ion, O is oxygen, R is an organic group and n is the valency of the metal. Particles are therefore molecular, in the region of 0.5nm. The precursors are usually prepared by chemical reaction, often from simple metal salts such as halides or nitrates. Since the salts may be highly purified, a slightly higher purity may be achieved than with the colloidal approach.

The precursor is diluted/dissolved in an appropriate organic solvent, frequently an alcohol. Water is then introduced to initiate hydrolysis and condensation reactions. Process conditions are altered to shift the equilibrium of the reaction towards network growth and hence gellation, achieved either by varying pH or increasing concentration. Since condensation occurs at a molecular level, adding blocks to the ends of chains, the structure may be regarded as polymeric (Brinker and Scherer 1985; Scherer 1988; Brinker and Scherer 1990; Szu, Greenblatt et al. 1990). This may be either linear or branched, depending on process conditions.

Subsequent drying operations result in a fragile aerogel structure with limited cross-linking. This may be further densified by additional energy input, either thermal or radiation (Brinker, Roth et al. 1985).

The individual process steps are discussed in further detail below.

A comparison of colloidal and polymeric sol-gel is shown in table 3.2.

Colloidal	**Polymeric**
High purity	Very high purity
Limited range of precursors	Wide range of precursors
Fewer fabrication variables	Many fabrication variables
Rapid gelation	Slow gelation
Suitable for fabrication of monoliths and powders	Suitable for fabrication of aerogel, coatings and fibres
Able to produce multi-component systems and composites	Able to produce multi-component systems and composites

Table 3.2. Comparison of colloidal and polymeric sol-gel (Taylor and Fernie 1998).

Although there are similarities between the colloidal and polymeric routes, there are also substantial differences which make them suitable for different applications. One of the principal advantages of the colloidal route is its use of water rather than organic solvents. It therefore presents fewer environmental issues and has greater compatibility with recent volatile organic content (VOC) regulations for coating compositions (EU 1999).

The principal physical differences in materials prepared by the polymeric and the colloidal route relate to the distinction in primary particle size. Colloidal particles are two to three orders of magnitude larger than the polymeric precursor; an effect which is amplified during Ostwald ripening of the former, which eliminates the smaller particles. Ostwald ripening enhances mechanical strength but increases porosity due to poor packing density, coincidentally rendering solvent removal more facile. These factors make the colloidal route more suitable for producing monolithic structures and powders (with subsequent melt processing when required to produce fibres). They also, however, result in higher processing temperature or time requirements to form a dense final product. As such, coatings are more readily achieved by a polymeric route.

An additional factor is that of homogeneity. Colloidal materials are homogenous at the particle scale, however polymeric materials may be homogenous at the atomic scale, a factor of particular significance in multi-component systems such as doped semiconductor materials (Sakka and Kamiya 1982).

3.2 Polymeric sol-gel processing steps

The processing steps of a polymeric sol-gel process are illustrated in figure 3.2. The factors associated with each step are discussed in detail below.

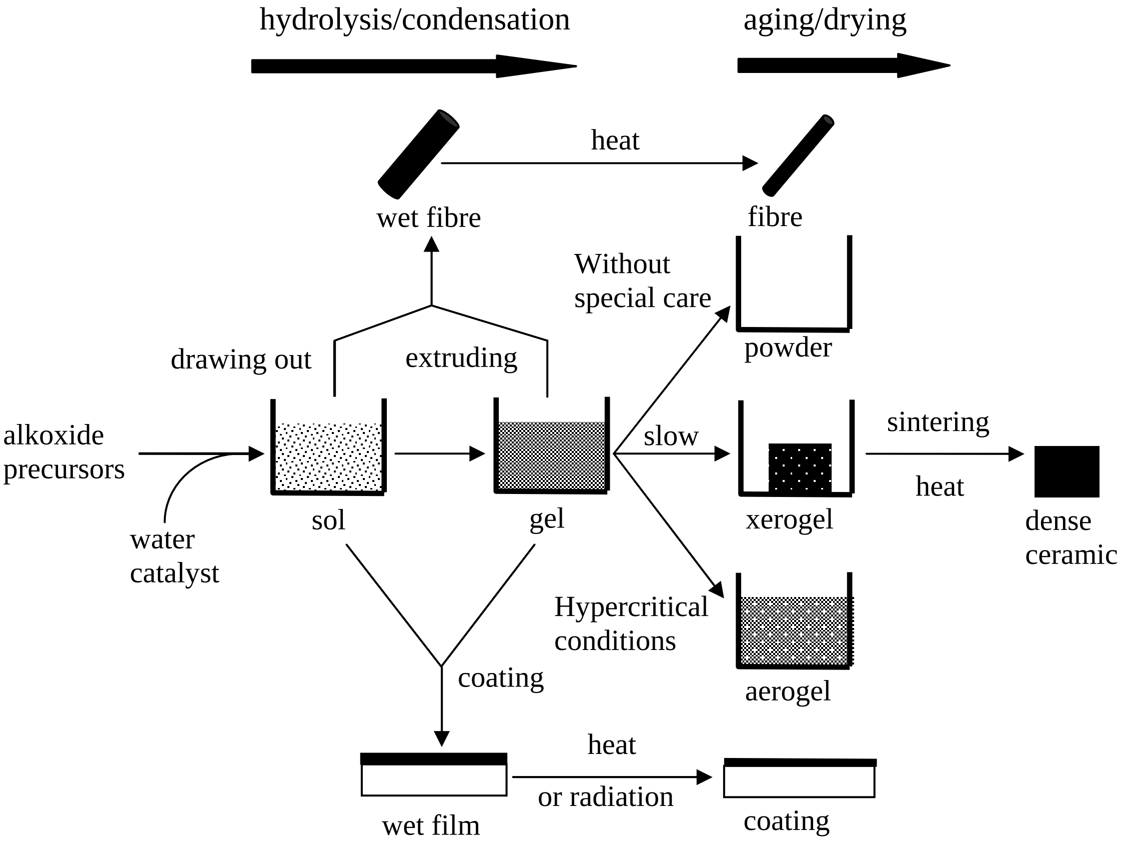

Figure 3.2. Overview of the sol-gel process (Han 2006).

3.2.1 Precursor selection

The overwhelming majority of sol-gel processes concern oxides prepared from metal alkoxide compounds, with the chemical formula $M(OR)_n$ where M is metal ion, O is oxygen, R is an organic group and n is the valency of the metal. The factors which affect processing are the electronegativity and valency of the metal and the nature of the R-group.

Electronegativity determines the polarity of the metal-oxygen bond. The more electropositive the metal, the more polar (*i.e.* ionic in character) the bond. It should be borne in mind that the solution is non-aqueous and hence the precursors are not subject to ionic dissolution. Consequently, increasing polarity within the bond increases reaction rate within the sol.

The valency of the metal ion determines the number of formal bonds which can be formed within a glassy structure. In crystalline structures, the co-ordination of any given cation and anion pair is partial within the lattice structure. In glasses, the lack of ordered structure results in domination of local bonds. Consequently, the valency corresponds directly to the co-ordination number of the cation. As such, monovalent cations can only form dimers, divalent cations can form linear or bent chains and trivalent or higher cations can form branched structures.

This factor is significant in respect of compositional selection, since whilst a range of glassy oxides may be formed by sol-gel processing which are not possible by thermal processing, for example glassy titanium dioxide (Hydrogen Solar Ltd 2007), single cation compositions are not possible for mono- or divalent cations, since there is no bonding mechanism by which to form a three dimensional network (gel). In compositions containing multiple cation types, additions of lower valency cations may be made to a higher valency cation structure, resulting in network modification in similar fashion to the formation of conventional glasses such as soda-lime float glass (Pfaender 1995). The lower valency ions form non-branching links (divalent) or end nodes (monovalent) within the network, but a considerable addition may be made without reducing the average valency below two, the critical factor for network formation.

Processing is affected by the size and shape of the R group. A small, compact ligand reduces steric hinderance to reaction with a consequent increase in reaction rate. The smaller group also decreases facility for charge delocalisation, increasing the polarity of the M-O bond, resulting in decreased reactivity with larger or equivalent ligands. This can be seen from a comparison of reaction rates between orthosilicates with increasing sized ligands. The principal work in this field was performed by Chen *et al* (Chen, Tsuchiya et al. 1986) who showed a marked increase in hydrolysis rate with decreasing size of alkyl group, summarized in table 3.3.

$Si(OR)_4$	$k\times10^{-2}(l\ mol^{-1}s^{-1}[H^+]^{-1})$
$Si(OCH_3)_4$	19.0
$Si(OC_2H_5)_4$	5.1
$Si(OC_3H_9)_4$	1.9
$Si(OC_6H_{13})_4$	0.83

Table 3.3. Hydrolysis rate constants for a range of orthosilicates with increasing ligand size (Aelion, Loebel et al. 1950; Chen, Tsuchiya et al. 1986; Brinker 1988).

Since the dispersion solvent is conventionally an alcohol it may undergo ligand exchange with the precursor. Exchange is an equilibrium reaction but is energetically driven towards the smaller ligand. Consequently, the dispersing alcohol should be the same as or larger than the corresponding alkyl group. An alternative is to use an aprotic solvent, but from an industrial perspective this has undesirable implications in increasing VOC content.

3.2.2 Hydrolysis and condensation

Conversion of the dispersed precursor into the solid gel is dependent on a series of chemical reactions with water. The initial reaction is hydrolysis, which is a substitution reaction at the metal ion, exchanging the -OR group for -OH. Subsequent reactions condense the -OH group, either with an unreacted -OR group, forming an alcohol, or with another OH group, forming water. The result is an M-O-M bond. The reactions are shown schematically in equations 3.1 to 3.3.

$$\equiv \mathrm{M{-}OR} + \mathrm{H_2O} \underset{\leftarrow \ \text{esterification}}{\overset{\text{hydrolysis} \ \rightarrow}{\rightleftharpoons}} \equiv \mathrm{M{-}OH} + \mathrm{ROH} \tag{3.1}$$

$$\equiv \mathrm{M{-}OR} + \mathrm{HO{-}M} \equiv \underset{\leftarrow \ \text{alcoholysis}}{\overset{\text{alcohol producing condensation} \ \rightarrow}{\rightleftharpoons}} \equiv \mathrm{M{-}O{-}M} \equiv + \mathrm{ROH} \tag{3.2}$$

$$\equiv \mathrm{M{-}OH} + \mathrm{HO{-}M} \equiv \underset{\leftarrow \ \text{hydrolysis}}{\overset{\text{water producing condensation} \ \rightarrow}{\rightleftharpoons}} \equiv \mathrm{M{-}O{-}M} \equiv + \mathrm{H_2O} \tag{3.3}$$

There are several parameters which affect the rate and direction of hydrolysis and condensation reactions, including the activity of the metal alkoxide, the nature of the solvent, pH of the solution, temperature and water/alkoxide ratio. Catalysts (acid or base) are also an important factor as these may be used to accelerate the reaction sequence. These parameters are discussed below.

It can be seen from the above reaction sequence that the production of a M-O-M bond consumes a single water molecule. Water consumption may be direct, if the reaction proceeds via condensation of an alcohol, formed from an alkoxide ligand and a hydroxyl group. Alternatively, a water molecule may be formed from the condensation of two hydroxyls. In this case, two water molecules are consumed initially in hydrolysis reactions, however one molecule is subsequently liberated through the condensation step; a net consumption of a single molecule. Water is therefore required for the reaction to proceed and hence both the total quantity available and its concentration have an influence on the reaction sequence and consequently on the properties of the gel.

Since each combined hydrolysis and condensation reaction consumes a single water molecule, the total quantity of water required for hydrolysis to proceed to completion is approximately half-stoichiometric with respect to the number of alkoxide ligands present. This disregards the effect of end-groups, which are presumed to be a relatively small proportion of the total if condensed polymeric structures are relatively large. Larger quantities of water, up to fully stoichiometric with respect to the alkoxide ligands, allow a greater proportion of ligands to hydrolyse simultaneously, increasing the potential for chain branching. Smaller quantities of water, below half-stoichiometric, prevent full hydrolysis from occurring, although a network structure may still be formed, particularly since it is energetically favourable for hydrolysis to occur on unreacted species, rather than consuming remaining alkoxide ligands on cations already incorporated within the network.

If the water concentration is low, water availability becomes the rate limiting factor as hydrolysis becomes the rate limiting step. Water availability may also be restricted since alkoxides are frequently immiscible with water and a mutual solvent such as a small chain alcohol is usually used. In some systems it is possible to initiate reaction directly between the alkoxide and water. This results in formation of an alcohol in the hydrolysis reaction, as shown in equation 3.2 above, which homogenises the initially phase-separated system. This reaction sequence has the drawback of rate acceleration during reaction, as the extent of mixing increases.

Water concentration may be used to advantage in controlling reaction of highly reactive precursors and particularly when two different cations with different reaction rates are to be processed into a homogenous glass.

Since the above reactions are equilibria, in order to promote the forward reaction to effective completion it is necessary to shift the equilibrium position substantially towards condensation. This is most effectively achieved by either acid or base catalysis of the reaction.

An acid catalyst may be used to accelerate reaction since the proton is attracted to the oxygen in the alkoxide bond and reaction occurs via electrophilic attack. Conversely, a base may be used to promote nucleophilic attack via the metal centre (Gunner, Jones et al. 2006). The two mechanisms of catalysis produce different structures during growth of the polymeric chain.

Since acid catalysed reactions proceed via electrophilic attack, the probability of hydrolysis of a given cation decreases proportionally to the number of alkoxide ligands. The resultant network structure is therefore more likely to be linear, with few branches, strongly resembling an organic polymer. Low water concentration also favours formation of linear rather than branched structures, since the probability of hydrolysis occurring with a less-reacted species is greater than with a more-reacted species.

By contrast, since a base-catalysed reaction proceeds via nucleophilic attack, the probability of reaction at a given nucleus remains largely unaltered as hydrolysis proceeds. Reaction at a reacted site is in fact slightly favourable, since the –OH ligand has a more negative charge than the alkoxide ligand, hence the metal cation is slightly more positively charged and therefore more readily attacked. The resulting structure is therefore highly branched and the solubility of small M-O-M-chains under basic conditions favours the production of a smaller number of larger, spherical particles. In this respect, base catalysis results in a sol structure which closely resembles that formed via a colloidal route, however colloidal suspensions contain a broad range of particle sizes whereas the base-catalysed alkoxide route results in a much narrower particle size distribution. The process was developed and patented for silica particle formation by Stober (Stober 1972).

3.2.3 Structural evolution

The sol, as described above, only has structure within the condensed groups. These groups have no interrelationship and hence the sol is a dispersion or suspension with liquid characteristics. The transition to a material with solid characteristics occurs at gellation.

The gel point is defined as that at which an interconnected network is formed (Taylor and Fernie 1998). Since the sol is in equilibrium, it is necessary to alter process conditions to destabilise the system and allow reaction to proceed. Gellation is controlled by the same factors as hydrolysis and condensation, *i.e.* the concentration of water, pH, solvent concentration, temperature and the alkoxide structure. In addition, since the forward rate of reaction may be relatively slow, the total volume may be relevant to the overall gellation time. In a coating process, gellation is commonly effected via solvent evaporation from the wet film.

At the point of gellation, the sol becomes an alcogel (wet gel). Chemically, the alcogel is similar to the sol, containing both the solvent and the connected gel phase, the transition being in morphology. The alcogel is the solid phase, being an inherently porous three-dimensional network, bonded via metal oxide bonds. The original solvent fills the pores within the gelled network. The alcogel transition is illustrated in figure 3.3.

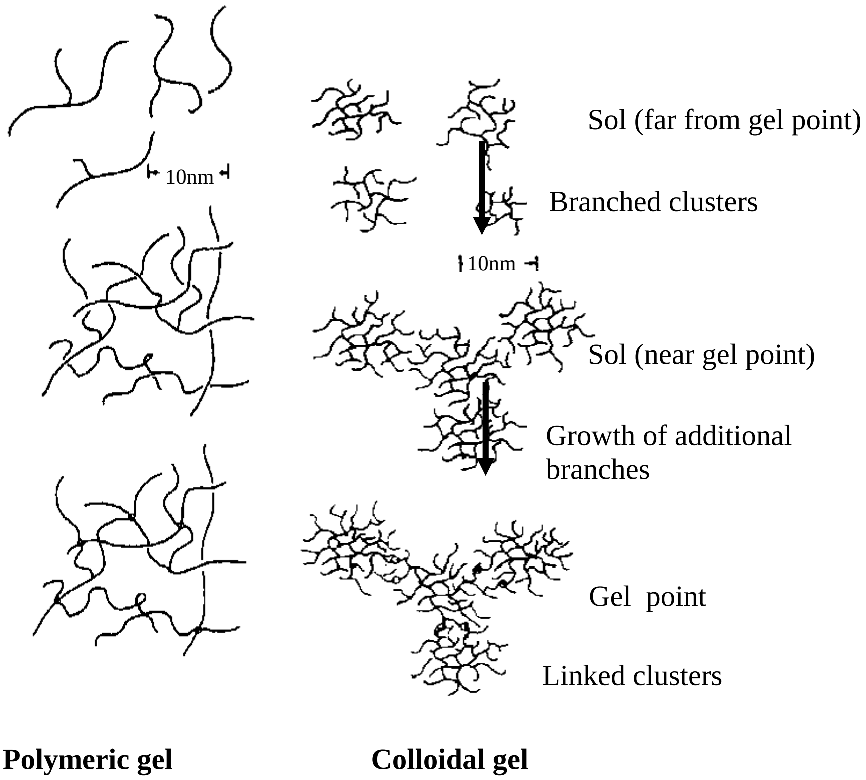

Fig.3.3. Gel formation in polymeric and colloidal sols (Han 2006).

Alcogel formation is not an end point of reaction sequence; the gelled structure is dynamic. Although the transition from liquid to solid results in constraint, the bonds within the structure are initially single points of interaction and allow considerable flexibility. Since the initial hydrolysis and condensation reactions are incomplete, condensation may continue after gelation has occurred (Balfe and Martinez 1986), the process being termed aging. Ongoing reaction increases cross-link density and reduces the pore volume, shrinking and densifying the network. In both colloidal and polymeric gels, the reaction proceeds to a steady state where steric considerations prevent further reaction, at which point the structure is termed an aerogel.

For practical materials, the next step in processing is the removal of solvent from the pores. This forms a xerogel (xero from the greek for dry). Solvent removal may be effected through evaporation in an ambient environment or under supercritical drying conditions (above the critical temperature and critical pressure). The removal of solvent leads to pore collapse and consequent shrinkage; a xerogel may reduce in volume by ~90% relative to the alcogel, depending on the extent of prior aging. This high degree of dimensional change results in large capillary stresses and hence the xerogel often cracks during drying.

The extent of structural evolution within the gel is dependent on the rate of evolution and the time between gellation and drying. In a practical coating process, it is likely that no significant gel aging occurs, the gel progressing rapidly from alcogel to xerogel. The lower density of the un-aged xerogel results in greater shrinkage and therefore a greater likelihood of cracking, however the greater potential for subsequent condensation reactions increases the ability of the system to ‘heal’ cracks in subsequent curing steps.

In order to achieve curing, it is necessary to provide additional energy. This facilitates cross-linking and further densification in the solid state. In a polymeric system, the alkoxide bond frequently absorbs ultraviolet (UV) electromagnetic radiation and polymerisation may be achieved via this mechanism. Alternatively, heat may be used in either polymeric or colloidal systems. This is directly equivalent to sintering of bulk ceramics, but the smaller scale of the particles decreases the energy input (and hence temperature) significantly. For comparison, sintering of bulk quartz glass requires temperatures in excess of 1200°C (Yong-Taeg, Fujino et al. 2002) whilst colloidal sol-gel derived systems may be sintered at 500-600°C (Brinker, Roth et al. 1985) and in polymeric xerogels this may be reduced to below 200°C (Brinker, Roth et al. 1985).

The distinction between colloidal and polymeric gels is the smaller particles present in the latter. Decreasing particle size results in a higher surface area to volume ratio and consequent higher energy, thus less energy input is required. In a practical coating process, this has implications for process selection. Higher process temperatures increase energy costs and the complexity of the equipment required, which must be offset against the lower cost of the precursor materials and solvents. The principal technical consideration in coating formation is the compatibility of the substrate with the processing conditions. A colloidal coating process would be compatible with a ceramic or glass substrate and with the majority of metals, however for coating metals with lower temperature capability (e.g. aluminium and brass) or plastic substrates a polymeric process is required.

The cured state is dependent on both oxide composition and temperature/energy input delivered. Irrespective of composition, the initial state of the xerogel is glassy, having no long range order. In the extreme, the composition may be melted and hence form a material which corresponds to the bulk state. If the energy input is, as commonly used, insufficient to melt the coating, reaction will proceed to a greater or lesser extent and the final coating is likely to contain some elements of residual structure, in the form of porosity or organic groups. The glassy state of the material does however facilitate flow above a glass transition point, T_g and this may be suppressed relative to the bulk T_g to a considerable extent (Dislich 1971)**.** This may allow xerogel films to 'heal' more effectively than relying on chemical reaction alone. The composition of the oxide determines its stability as a glass. Many silica structures are stable glasses, however the majority of other oxides are not. If enough energy is provided then the crystallization temperature T_c is exceeded and the structure crystallizes, *i.e.* develops long range order. As with T_g, it has been observed that T_c may be considerably depressed relative to the bulk value for an equivalent oxide system (Dislich 1971)**.** Crystallization represents the ultimate state achievable within sol-gel processing.

3.3 Products and applications

3.3.1 History

Sol-gel processes occur naturally in the formation of precipitated minerals, mostly silicates, including agate and opal (Frischat, Heide et al. 2001) and the petrification of wood by the impregnation of silica (Iler 1979). The first known use of sol-gel coating dates to 5600BC with the use of lime plaster as flooring in huts on the banks of the Danube (Srejović 1972). Lime is colloidal calcium hydroxide, prepared from burned calcium carbonate and used as a gel. This process was well known to the Romans and first documented in the 1st century BC (Rowland and Noble Howe 1999).

The term sol-gel was first used by Ebelman (Ebelman 1844), who observed the gellation of a tetraethyl silicate solution exposed to the atmosphere for a period of a few weeks. He then noted that further exposure resulted in separation of a solid phase from a residual liquid, the solid being transparent and hard enough to scratch glass. A limited amount of further work developed the discovery (Freidel and Ladenburg 1867; Konrad, Bachle et al. 1929) including the identification of the hydrolysis and condensation mechanisms (Konrad, Bachle et al. 1929) but it was not until 1939 that the first industrial application was identified, with the patenting of a sol-gel dip coating process for depositing metal oxides on glass (Geffcken and Berge 1939). Further academic work was performed through the 1950s (Aelion, Loebel et al. 1950; Mehrotra 1953) but the first work with the specific objective of developing sol-gel processing to exploit its material properties was not published until 1969 by Roy (Roy 1969) and 1971 by Dislich (Dislich 1971). Roy, working on behalf of Owens-Illinois developed high purity glasses for sputter targets, which were discontinued in 1970 because of cost (Thomas 1988). Dislich developed a processing route for high purity borosilicate glasses which had significance for the burgeoning optical fibre industry – more conventional routes leaving an excessive concentration of iron impurities. This work led to the first real commercial application of sol-gel processing.

Dislich ultimately collated his work in 1988, providing summary information covering fabrication of a number of products developed by Schott, including anti-reflective coatings for automotive use, solar reflecting coatings (IROX), contrast enhancing filters, anti-reflective coatings and transparent conductors (Dislich 1988).

The publication of papers in the field is illustrated in figure 3.4. and shows the continuing rise in academic interest in the field since its inception in the early 1970s.

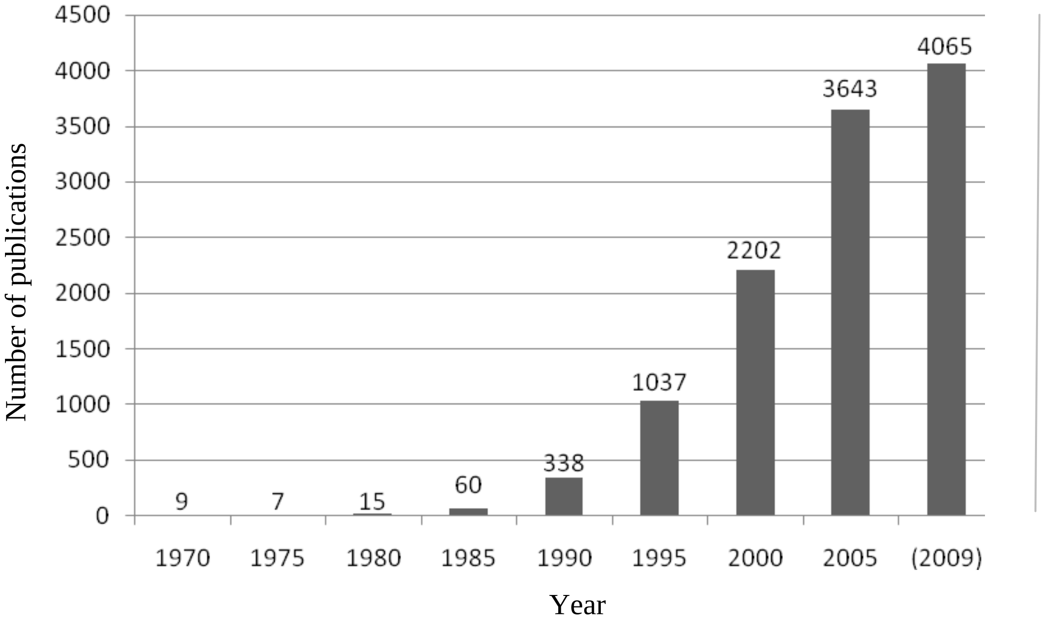

Fig.3.4 Representative illustration of the rise in academic interest in the field of sol-gel processing, based on the number of published papers in the field indexed by Web of Science (Thomson Reuters, 2009).

As with many technology fields in the early stages of investigation, sol-gel processing follows the Gartner ‘hype cycle’. Whilst figure 3.4 shows ongoing academic interest, the ‘Peak of Inflated Expectation’, for sol-gel processing with commercial objectives occurred in the 1980s, coincident with the general rise in interest in advanced ceramics. This can be seen from the substantial number of commercially focussed developments undertaken by companies such as Schott within this period. The ‘Trough of Disillusionment’ spanned approximately a decade from 1995, during which research remained predominantly academic, with the discontinuation of a substantial number of the commercial products. More recently however, there has been a resurgence of interest (Slope of Enlightenment), taking advantage of the unique series of properties which may be delivered by sol-gel processing. This can be seen in the UK from the number of collaborative projects funded by the DTI in the field. Being application focussed, projects do not always make reference to the technical approach adopted but since 2000, 15 publicly funded projects can be identified which incorporate sol-gel technology (Badheka, Johnson et al. 2002; Kirwan 2003; Research Assessment Exercise 2003; Hawkins and Bowen 2005; DTI 2006; Gunner, Jones et al. 2006; One North East 2007; CORDIS 2008; Manchester University 2008; Manchester University 2008; Sharp 2008) and a further 10 projects can be identified, funded by the European Union Framework programme (CORDIS). These projects span a very wide range of applications, from the development of cadmium replacements in high temperature pigments and opto-electronic materials (Hawkins and Bowen 2005) to the development of coatings for Extended Life Microtooling by Advanced Coatings (ELMACT) (Manchester University). Successful outcome from these projects would in ‘hype cycle’ terms be a stable phase of general market acceptance, the ‘Plateau of Productivity’.

3.3.2 Product forms

It is possible to use the sol-gel process to fabricate a wide variety of forms, including nanoscale spherically shaped powders (Stober), thin film coatings and monoliths, ranging from fully dense to extremely porous aerogel materials (3-150mgcm^{-3}). These materials may then be further processed, using conventional processes such as sintering or melt-processing, to produce solid structures or drawn fibres. The process has a number of advantages over conventional processing techniques, summarised in table 3.4.

Advantages	**Disadvantages**
Better homogeneity from raw materials	High cost of raw materials
Better purity from raw materials	Large shrinkage during processing
New non-crystalline solids may be prepared outside the range of normal glass formation.	Residual fine pores
New crystalline phases may be prepared from non-crystalline solids	Residual hydroxyls
Better glass products from the gel form	Residual organic structures/carbon
Lower temperature of preparation: a. Saving energy. b. Avoiding reaction with container walls, improving purity. c. Avoiding phase separation. d. Avoiding crystallization. e. Facilitating deposition on low melting point substrates. f. Minimising evaporation losses. g. Minimising air pollution.	Health hazards of organic solutions
	Long processing times

Table 3.4. Some advantages and disadvantages of the sol-gel method over conventional melting for glass (Mackenzie 1984).

3.3.3 Monolithic materials

The disadvantages outlined above are particularly limiting for fabrication of monolithic materials, due to the high stresses generated from shrinkage during drying. To prevent cracking, extremely long drying times (years) or supercritical conditions are required. This limits applications to those where no other method can be identified, since it is highly unlikely that a sol-gel route would be commercially preferable. The extremely low density of aerogel materials can be applied in fabrication of ultra-lightweight structures with very low thermal conductivity. Their very low mechanical strength has found application in the capture of small meteors in space (Brownlee, Horz et al. 1994). Alternatively, the aerogel can be filled and sintered, one application being the manufacture of Cherenkov detectors for use in high energy physics (Cantin, Casse et al. 1974). One major use of sol-gel based impregnation is the Starfire route to fabrication of silicon carbide from carbosilanes (MacDonald 2002). Here, the principal advantage is the greatly reduced processing temperature which is compatible with the use of carbon as a coating on fibres in the fabrication of SiC-SiC composites.

3.3.4 Powders

Powders are the conventional form from which most ceramics and glasses are fabricated. Using sol-gel methods to produce powders avoids the need to accommodate drying stresses and the powders may then be handled using conventional methods. The principal advantages of using sol-gel derived powders are usually the purity and the size and uniformity of grains. The small particle size facilitates considerable reduction in sintering temperatures, due to enhanced reactivity.

Sol-gel derived alumina powders are made using the Stöber process for use as abrasives. The process was patented by Norton (Cottringer, van de Merwe et al. 1986) and is currently used by Universal Abrasives, a division of Saint Gobain. The process is also used to manufacture zirconia powder for application as a thermal barrier coating by thermal spraying (Joshi, Srivastava et al. 1992). Aerosil alumina is used as a filler for improving the performance of plastics, being added to high performance and liquid silicone rubbers, for example Viton as used for high temperature seals (Eddy, Badesha et al. 2000) and to improve abrasion resistance in biomedical applications such as dental implants (Strang 1986).

Colloidal silica, prepared using the Ludox process, patented by the North American Aluminium Association in 1959 (Grace 2008) finds a wide range of applications, including an additive to printing inks, where it provides a matt finish and stops ink from adjacent sheets from bonding to one another, and as treatment of paper to minimise ink penetration. Sol-gel reactions are also used to graft functional silanes in products including shampoos, toothpaste and adhesives.

The powder form may also undergo subsequent conventional processing. The advantage of high purity may be used in the manufacture of fibre-optic cables - conventionally processed glasses containing too much iron. In this process, the gel is dried in a chlorine rich atmosphere to eliminate silanols and the powder is melted, the fibres being pulled via spinnerets.

Where complete removal of organic and silanol phases is not critical, drying or sintering may also be applied, depending on the end product required. Ethyl silicate and high silica tetraethylorthosilicate (TES 40) are used as the binder for high performance zinc and aluminium-rich primers. (Drinberg, Gurevich et al. 1960)**.** Whilst true sol-gel coatings are considered below, the majority of conventional hardcoats make use of sol-gel processing, the most commonly used variants being effectively sol-gel derived colloidal silica in a siloxane matrix, for example AS4000 and AS4700 made by DuPont.

3.3.5 The Application of sol-gel processing to coatings

Probably the most attractive application of sol-gel processing is in production of coatings, since most of the disadvantages listed in table 3.4 above do not apply; the volume of material consumed being small and, if the coating is thin (<1µm), stress may be accommodated by shrinkage in the z direction (Strawbridge and James 1986; Mahner, Datchary et al. 2005). The maximum thickness which can be prepared is dependent on the substrate and coating combination. In subsequent steps, a facile pathway through the coating thickness facilitates elimination of residual contaminants.

As referred to above, the earliest commercial application identified for sol-gel processing was in a coating (Geffcken and Berge 1939). This was patented by Glasswerke Schott, who continued to develop sol-gel technology for various coating products, including the first large scale application in IROX® glass. This material consisted of a palladium/titania coating, applied to architectural glass for thermal control; the palladium and titania providing absorption and reflection respectively at the desired wavelengths. IROX® glass achieved considerable commercial success, its highest profile application being the European Patent Office. It was replaced commercially by PVD coatings such as Pilkington K glass when large scale, in-line magnetron sputter coating became sufficiently developed. The high cost of the precursors for the sol-gel process meant that, despite the relatively low coating process cost, the sputter coating process became more cost-effective.

Sol-gel coatings are also used commercially for anti-reflective coatings, typically for application to the front glass panel of solar thermal panels. These may be silica-based, incorporating high levels of porosity to achieve a bulk refractive index halfway between glass and air to enhance light capture (Becker, Dauwalter et al. 2006). The process was developed by Schott Glasswerke and is now applied by Centro Solar. Alternatively alternating layers of high and low refractive index may be used, at varying thicknesses, optimized to varying wavelength. Brinker *et. al*. achieved success with a multi-layered structure of titania/silica prepared by spinodal decomposition of a mixed sol (Brinker and Scherer 1990). This showed an increase in performance of 44% compared with uncoated cells and this coating method continues to find applications (Yoldas and O'Keeffe 1979)**.**

A very similar approach is applied to the Lexus wing mirror. Here, the property of interest is the capability of the anatase phase of titania to facilitate photocatalytic decomposition of organic material, making the wing mirror self-cleaning.

A silazane (Si-N) coating, branded Tutoprom, is used as an anti-graffiti coating on German railways.

As described above, many sol-gel derived particles are applied to coatings such as AS4000, applied as a hardcoat to visors and spectacle lenses. Where a thick coating is required, TES40 or colloidal silica may be mixed with ceramic particles as a binder. At the opposite end of the scale, sol-gel processing has been applied by Owens Illinois to the deposition of doped silicates on wafers (Thomas and Tillman 1983). Various dopants have been used, including arsenic, antimony, boron and phosphorus for semiconductor devices.

The principal problem associated with deposition of sol-gel coatings is that the large residual stresses in the final material often cause cracking. This becomes particularly apparent when the film thickness exceeds 0.5µm, although film thicknesses up to 1µm have been reported (Le Luyer, Lou et al. 2001). The ability of a coating to survive curing is strongly dependent on substrate properties, particularly mismatch in the coefficients of thermal expansion.

Where the application does not require highly inorganic properties, for example in protective applications, low curing temperatures may be used to advantage. By deliberately incorporating an organic component in the composition an inorganic-organic hybrid material may be formed. This may be achieved by using precursors which incorporate an element of organometallic bonding, the organic group providing a residual side-chain within the network. This can act to provide steric hindrance and a bonding mechanism to organic species. The coating therefore attains a lower total cross-link density and with the addition of organic resins may take the form of interpenetrating organic and inorganic networks, as identified in materials such as Vitresyn (Taylor 2000). In both cases, the coating acquires increased toughness, at the cost of a slight loss in overall ceramic character (e.g. reduced hardness, scratch resistance and barrier properties).

3.3.6 Coating adhesion mechanisms

The dominant mechanism for adhesion between sol-gel derived coatings and the substrate is via chemical bonding. Consideration is required, however in defining coating formulations which are compatible with the preferred substrate type.

With inorganic (metallic or ceramic) substrates, a bond may be formed between hydrolysed species in the sol and the surface, analogous to the hydrolysis/condensation sequence discussed above. This results in a bond structure consisting of an atom originating from the substrate, bonded via a bridging oxygen to an atom originating from the coating, shown schematically in figure 3.5 (a). The bridging oxygen may arise either from a surface hydroxyl, or from within the coating composition, however in either case the resulting coating is analogous to a native oxide surface.

With organic substrates an alternative bonding mechanism is required. Where a hybrid coating material is used, a functional group may be incorporated in the structure via an organometallic bond in some or all of the alkoxide precursors. This bond may react with corresponding functional groups on the substrate, shown schematically in fig. 3.5 (b) (Hull and Clyne 1996). This mechanism may be applied to, for example, acrylates, methacrylates and epoxy (glycidoxy) species. Alternatively, Chou et. al. reported the use of oxygen plasma etching to improve the adhesion of inorganic sol-gel coatings to polymeric substrates (Chou and Cao 2003). The mechanism postulated is the formation of hydroxyl groups on the polymer surface by the plasma, resulting in a similar bonding mechanism to that which applies to inorganic substrates, but with a resultant alkoxide bond.

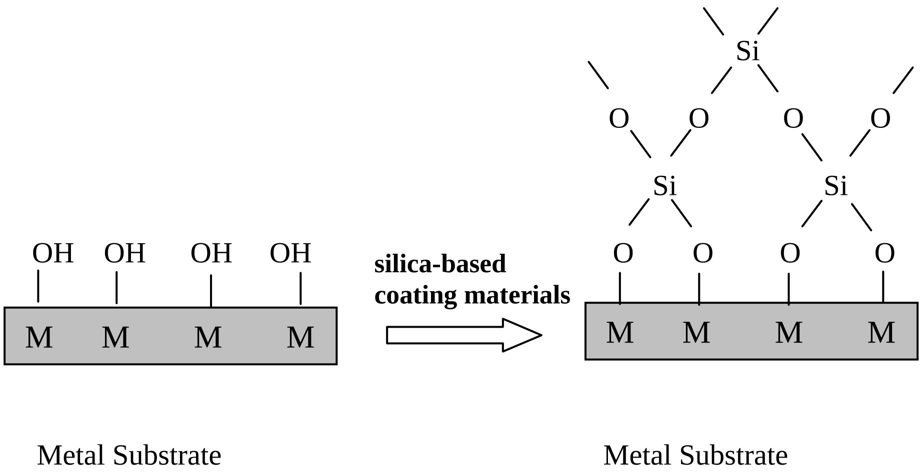

Fig.3.5(a) Adhesion of silica coating to metal substrate (Han 2006).

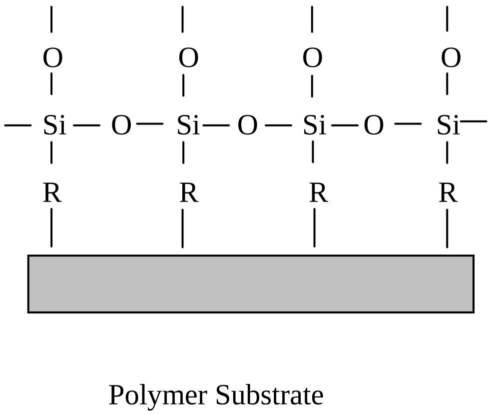

Fig.3.5(b) Adhesion of silica coating with functional group to polymer substrate (Hull and Clyne 1996).

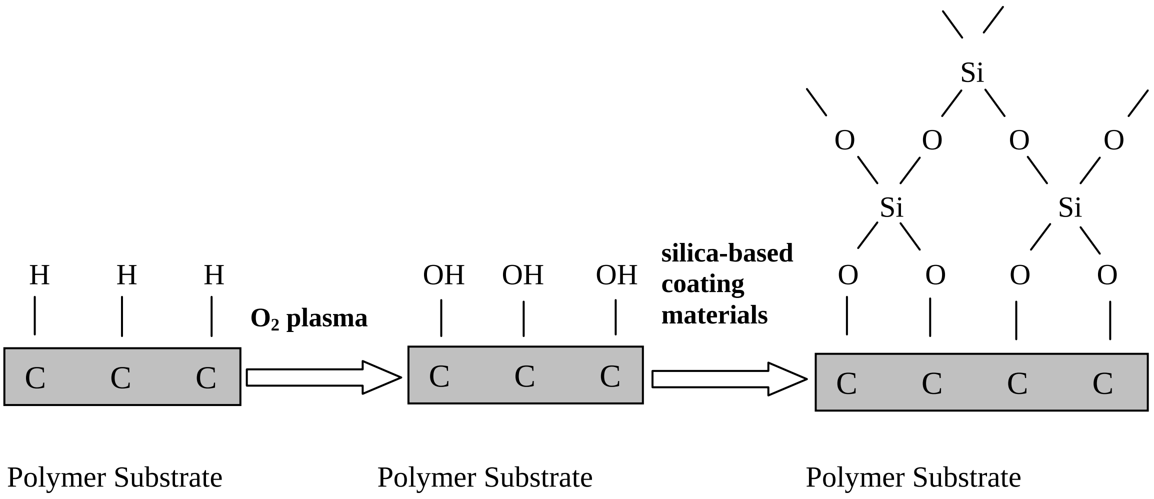

Fig.3.5(c) Adhesion of silica coating to polymer substrate etched with O_2 plasma (Chou and Cao 2003).

Fig.3.5. Schematic diagrams of silica-based hybrid coating material on different substrates deposited by various methods.

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CHAPTER 4 – INTRODUCTION TO CASE STUDY

4.1 Introduction

The overall aim of this work was to establish the potential for using a sol-gel approach to the production of transparent conducting coatings (TCCs), which are used to give additional functionality to transparent substrates. They are commonly found in applications as diverse as anodes for flat panel displays and photovoltaic devices; high performance resistive heaters and electromagnetic shielding. Coincidentally, their optical properties make them suitable for solar control glazing for buildings.

Transparent conducting oxides (TCOs) are typically wide band gap semiconducting materials and are often doped to improve electrical properties. Tin-doped indium oxide (ITO) is preferred for many applications, however there are alternatives such as cadmium stannate, cadmium telluride, antimony doped tin oxide (ATO) and fluorine doped tin oxide (FTO). The relative merits of these materials are discussed in Chapter 5.

For practical reasons such as cost and inherent transparency, TCOs are not used as monolithic materials but are applied as coatings - TCCs. The properties of a TCC are strongly dependent on the preparation method. Commercial manufacture is currently limited to CVD for low grade, bulk coatings and sputter coating for high specification materials.

The limitations of sputter coating have resulted in solution based methods for fabricating TCCs receiving considerable interest (Maruyama and Kojima 1988; Phillips CFT 2001; Puetz and Aegerter 2008). Solution processing can be carried out at atmospheric pressure and is suited to in-line processing. A liquid phase coating process, such as sol-gel, also offers the major potential advantage of using printing to directly write the required pattern. Direct writing is an additive process, hence offers a significant process simplification (and cost reduction). It also offers the potential for reel-to-reel coating.

Sol-gel materials for TCCs are commercially available but do not reach the requisite performance targets for display use. As discussed in Chapter 3, there are two different forms of sol-gel processing, based on colloidal particles and the alkoxide route. The materials currently available are colloidal which, relatively speaking, give large particle sizes and poor homogeneity. Use of an alkoxide route gives a higher density starting film, reducing sintering temperature and improving homogeneity. This method was adopted within the project.

Transparent conducting materials are discussed in detail in Chapter 5, including consideration of the options for materials and their properties, together with fabrication routes.

4.2 Industrial need

4.2.1 Applications and their corresponding performance requirements

TCCs have three primary fields of application, namely displays, photovoltaics and glazing in architectural and automotive applications. They are widely used in several industrial sectors and development of higher specification or lower cost materials would be of particular value to the electronics, automotive, aerospace and construction sectors.

The performance achievable from a given TCC is limited both by the intrinsic properties of the material and by the production method. Each application has a wide range of requirements, both technical, including transparency, spectral response, conductivity and surface finish, and commercial, including cost of materials, deposition and patterning. In each application, the prioritisation of these requirements determines material selection. Similarly, improvement in properties of a given material expands the range of applications for which it is suited.

4.2.1.1 Displays

Displays are most commonly considered in the sense of dedicated display equipment, such as computer monitors and televisions, however they are frequently integrated into other equipment, for example in car dashboards, aircraft cockpits and white goods. An introductory summary is provided of the various types of display currently available at the market or near market stage, together with their characteristics and suitable applications.

4.2.1.1.1 Phosphor emission displays

Several common display types are based on the excitation of phosphors. The phosphor may be selected with an appropriate band gap to emit a specific colour, using a combination of red, green and blue phosphors to produce a colour display. In many phosphorescent display architectures, the phosphor is deposited on the front glass panel and is excited using a high energy source such as an electron beam or plasma, generated within a vacuum gap in the device architecture.

The cathode ray tube (CRT) is the most familiar vacuum type display and has formed the basis of the standard television set since its invention in 1926 (Baird 1931). The CRT uses a hot cathode to produce a beam of electrons which is accelerated through a charged grid and directed using electromagnets to scan across and array of phosphor dots on the front panel. It is cheap, simple and reliable, but the maximum angle through which the beam can be deflected is 110° (Klöppel, Trube et al. 2000) so is relatively bulky.

The vacuum fluorescence display (VFD) operates on the same principle as the CRT but uses individual cathodes for each pixel. The acceleration voltages are low compared to CRT and hence the lower energy electrons require different phosphors. The Field Emission Display (FED) has a similar structure to a VFD but uses an array of cold cathodes, each shaped to a fine tip, to generate high energy electrons by application of a high potential difference between the cathodes and the metal grid placed above them. Each pixel in a FED or VFD may therefore be individually addressed and compared with a CRD the display is thin and flat.

Plasma display panels (PDPs) use excitation of a rare gas which emits in the UV to excite phosphor pixels on the front panel. PDPs have good viewing angle and are replacing the CRT for large sizes, since they are only 75-100mm thick. They are however much more expensive.

In all the above display types the internal volume requires a high level of hermeticity and the display is usually constructed in glass, making it heavy.

The CRT was until 2008 the world’s leading display in terms of market share, being used for the majority of televisions and computer monitors (Globalsearch 2008). Its limitations mean that other display types, most of which are thin film displays, are rapidly gaining market share.

4.2.1.1.2 Thin film displays

In contrast to the displays described above, thin film displays do not require an internal vacuum gap in their structure for the transmission of radiation. This significantly reduces thickness, weight and the requirement for hermeticity, although the device materials are often oxygen and moisture sensitive so a seal may still be needed. The most common substrate material is consequently glass, although it would be desirable to use transparent plastics to reduce weight and cost and offer greater opportunities for design.

The device consists of a layered structure, at its simplest comprising an electro-active material placed between two electrodes which serve as anode and cathode, at least one of which is necessarily transparent in order to view the display. In order to show data, the display is divided into a number of pixels, formed by etch patterning.

Displays may be driven either by individual addressing of pixels or by multiplexing an array. Independent addressing provides the most control over the display, with the fastest switching time, however it requires a driver for each pixel whereas multiplexing reduces the number of drivers to the sum of the rows and columns. A typical multiplexed structure is a matrix of rows and columns where each individual pixel is addressed by its row and column location, the display being scanned row by row in similar fashion to a CRT.

At its simplest, the rows and columns form anodes and cathodes, each intersection forming a pixel. Switching ‘on’ a pixel is achieved by applying a d.c. bias to the cathode and grounding the corresponding anode. Once the bias is removed, the pixel reverts to its initial state. This display architecture, known as a passive matrix, has limitations, since it provides leakage pathways via pixels adjacent to that being addressed, which are then slightly activated, resulting in ‘ghost’ images. The switching rate is also dependent on the response time of the display element.

The alternative is to use an active matrix, which incorporates thin film transistors, the pixel being charged from a source line and separately switched from a gate line. A capacitor is used to ‘actively’ maintain the state of the pixel until it is next addressed. The active matrix therefore allows shorter switching time and much more rapid refresh rates, whilst eliminating ‘ghosting’. It does however require more complex wiring using multiple layer fabrication including dielectrics and thin wires between pixels; each of these has implications for TCC performance.

Several types of thin film display are significant to current and emerging markets. Liquid crystal displays (LCDs), light emitting diodes (LEDs) and thin film electroluminescent (TFEL) displays are of particular interest.

An LCD consists of two sheets of polarising material, usually aligned perpendicular to one another, with a liquid crystal solution between them. The internal surfaces of the polarising material form electrodes. At rest, the liquid crystal is aligned helically with the surface features on the polarising filters, allowing light to pass through the display. When a potential difference is applied across the liquid it causes the crystals to straighten and the light does not pass through the second filter, the pixel appearing black.

LCDs are not emissive, so to create a bright display the crystals are backlit, the crystal acting as a shutter. To create a colour display, filters are placed between the backlight and the crystal. Both electrodes must be transparent for the backlighting to pass through the entire display structure.

LCDs are driven either passively (PMLCD) or actively (AMLCD). This is significant since LCD switching speed is generally poor, hence scanning a large passive matrix display line by line as is too slow for acceptable image quality. Active matrices are much more expensive to produce.

AMLCDs are suitable for colour displays up to 40” diagonal, as used on television screens. They are lightweight and thin, but suffer from loss of efficiency due to the backlight and poor viewing angle since the light is polarised on passing through the filters.

Light emitting diodes (LEDs) are semiconductors which emit light when an electrical current is passed through them. The semiconductor can be inorganic or organic (OLED), the latter having either a small molecule or polymeric (PLED or light emitting polymer – LEP) structure.

In its simplest form a single LED is used as an indicator light, found on computer monitors, fridges etc. Multi-pixel displays are constructed by depositing and patterning an anode, emitter and cathode layer in sequence. In order to emit light, one of the electrodes is transparent. This is typically the anode, since the charge injection of this layer is better matched to the emitter. Like LCDs, LEDs are thin and lightweight. They can be driven as passive matrices but unlike LCDs cannot be driven as active matrices, since they draw too much current to be sustained by a thin film capacitor. High quality displays therefore require individual pixel drivers. They are more efficient than a backlit LCD and also have a much better viewing angle.

PMLCDs are switching devices so carry essentially no current. Resistivity is therefore secondary and the key drivers are optical transparency and cost per area, including a patterning process. Since transparency is increased with decreasing film thickness, films are produced with a thickness below 100nm, giving transparency in excess of 95%. The minimum limit on film thickness becomes that at which the tracks remain continuous on patterning. The liquid crystal layer is relatively thick, in the order of microns, so surface finish of the TCC is not significant.

AMLCDs may have similar requirements, although if the capacitor and source or gate line are constructed from the TCC film then electrical performance becomes more significant, requiring properties similar to an LED display

LED displays are current carrying and resistivity is therefore the limiting factor. For the anode layer of a typical passive matrix device, a sheet resistance of 15Ω/square is required. This can be achieved with a film thickness of 150nm, giving an optical transparency of approximately 90% transmittance. The emissive layer is thin, in the order of hundreds of nanometers, hence surface properties become significant, as do contaminants within the TCC, which may diffuse into the emissive layer and reach a significant concentration, reducing emission.

The most common electrode type for thin film displays is sputtered ITO, which combines patterning properties with reasonable surface, however OLEDs are immature as a technology and future development of specific electrode materials is anticipated. The multi-layer oxide/metal/oxide type electrode has been specifically developed in order to increase conductivity in OLEDs.

Thin Film Electroluminescent (TFEL) devices are equivalent in structure to an LED, being solid state thin film structures. In contrast to LEDs, the emissive layer is a phosphor and application of an AC voltage across the structure emits high energy photons. TFEL is the longest established thin film emissive display, having been initially developed by Sharp in 1974 (Krasnov 2003). Since then, the technology has been used for ultra-thin, rugged, high reliability displays in military and medical applications. Further development has been limited by availability of suitable phosphors and the limited efficiency of front face emission due to lateral light transmission within the film.

One of the major enabling technologies required for the next generation of displays is an improved TCC, forming a key need on the UK’s strategic technology roadmap (House of Commons 2009).

4.2.1.2 Photovoltaic devices

Amorphous silicon photovoltaic devices are deposited on transparent conducting electrodes whilst thin film photovoltaic devices are, in effect, LEDs operating in reverse and hence have similar intrinsic requirements to LEDs in display applications.

In either device architecture, the impinging sunlight has to pass through one of the electrodes to reach the active layer, so refractive index plays a significant role. Optical quality is less critical, since visual defects do not significantly affect power density across a unit unless they represent a significant fraction of the total area. For volume markets, cost is the primary driver. Consequently, although ITO shows the best performance it is generally replaced by lower cost options, such as cadmium stannate, although environmental concerns over cadmium are driving the search for a replacement. In amorphous silicon devices, the silicon layer is deposited under a hydrogen plasma, which requires that the TCC be resistant to reduction.

4.2.1.3 Glazing

The spectral response characteristics of TCCs are exploited in the construction sector for glazing. Generally, TCCs absorb light in the ultraviolet region of the spectrum and transmit in the visible, up to a plasma edge in the infrared where a sharp transition to reflection occurs. The solar infra-red electromagnetic radiation is then reflected back to the atmosphere and does not heat up the interior of the building or vehicle, without significant loss of transmission of the visible spectrum.

The position of the plasma edge can be tuned during manufacture to produce the coating best suited to a climate. In a hot climate it is desirable to reduce air conditioning costs so a wavelength of 0.7microns is ideal to reflect the solar near-infra-red wavelengths responsible for heating (approximately 0.7 to 2μm (Gordon 2000)). Silver and ITO have optimum wavelengths but are high cost materials and a lower cost material would represent a significant advance.

An identical function is found in ‘heat mirrors’ or dichroic filters. These are used to prevent heat loss from broad spectrum incandescent lamps and in lamps used for curing photosensitive coatings and inks to prevent the infra-red from being transmitted to the substrate and causing damage.

In a cold climate it is desirable to transmit all of the solar radiation into a building, so the plasma wavelength is adjusted to be above 2μm.

Any oxide TCC can be tuned to increase its plasma edge wavelength by reducing dopant concentration, since the plasma edge is dependent on average spacing of the dopant centres, as discussed in Chapter 5.

A related application is in UV shielding for glazing, particularly in buildings such as museums where fragile works of art are to be protected from degradation. Anti fading glass is commonly available as a framing option for pictures. The ideal material is undoped zinc oxide, which has a sharp absorption transition below 400nm while transmitting the whole visible spectrum. Unfortunately, on doping, zinc oxide undergoes an absorption shift into the UV and no longer absorbs near UV light. Some electrochromic devices, such as mirrors and displays, are subject to UV degradation and hence a TCC which combined high conductivity with UV screening would be advantageous.

Tin oxide has also been applied as an anti-vandal protective coating on glazing, since it resists etching by hydrofluoric acid, which has previously been used to cause damage to glass surfaces.

The principal driver is cost per unit area with no patterning requirement. Spectral response across the UV, visible and infrared range and good surface finish on a macro scale are essential. In EMI/RFI shielding applications a low level of conductivity is required, with sheet resistance in the region of 1×10^6 Ω/square (Gordon 2000).

4.2.1.4 Other applications

The electrical properties of TCCs are used in transparent heaters to remove ice and condensation from mirrors and vehicle and aircraft windscreens. They are also required on LCD screens for operation at low temperatures, as the crystal switching rate is temperature dependent. Continuous TCC films are used for Electromagnetic Interference and Radio Frequency Interference (EMI/RFI) shielding and as anti-static coatings.

Being current carrying, resistive heaters require a lower sheet resistance, approximately 50-80 Ω/square. Requirements for transparency and patterning are dependent on application. For ruggedised displays the heater lies over the display area so reduced transparency results in reduced efficiency for the device. Currently, US regulations require transparency in automotive glass to exceed 70% (U.S. Department of Transportation) so high transparency is required in the TCC layer.

TCCs also find applications in a number of niche markets, including touch panels (Kukureka 2005), gas sensors and wear resistant coatings.

4.2.2 Market estimation

The world market for LCDs (the largest display market using ITO) in 2007 was over 3M units, with a value of $68 billion in sales (Globalsearch 2008). Although the industry has since suffered a slow down, analysts fully expect growth rates of between 10 and 50%, depending on the market segment. Mobile phone production reached 1200M units production per annum in 2008 (Llamas 2009), representing a display area of approximately 1.5Mm^2. Manufacturers have invested in larger area substrate handling facilities, the overall manufactured price per unit area reducing by a factor of approximately two every two generations. This puts pressure on material and process costs as these become the limiting factors. Cost reduction therefore represents a significant advantage.

OLED and LEP are high value, niche products, in which the UK has a considerable market share. When it is considered that such displays are frequently integrated in other equipment, ranging from car dashboards to stereos and white goods to mobile phones, the market displays in everyday use in the UK may be estimated to exceed 250M.

An estimate of the world market for anodes can be determined from sputter target consumption which according to the Business Communications Company in November 1999 was 190,000kg in the advanced display market alone, projected to 350,000kg in 2004 (Robert Moran Semiconductor Manufacturing 2000). The same source calculated the world market for sputtered films in displays at 8.7Mm^2 in 1999, rising to 21Mm^2 by 2004. This data is now ten years old, but since the manufactured volume of devices has exceeded predictions, it is reasonable to presume that this represents a conservative estimate.

The aerospace market for heated displays is known to be worth approximately £1million per annum in the UK alone, with global figures of approximately £10million. The automotive industry consumes 10M tons of glass per annum globally (Fry Consultants 2006).

Glazing applications are the largest market for flat glass, consuming 65% of the total annual production (Fry Consultants 2006). Relatively small volumes are used in heated windscreens and mirrors. Profit margins are also lowest in this sector, hence material and process costs must be minimised and greater use is made of non-vacuum deposition techniques, including CVD and sol-gel, in order to produce anti-reflective coatings.

Climate control is currently the largest segment of the glazing market, European consumption of low emissivity glass being in excess of 60Mm^2 per annum (Glassonweb 2004). This market is growing rapidly in response to increasing desire for energy efficiency, since glazing within a building represents the greatest source of energy loss per unit area (EU 2006; TNO Built Environment and Geosciences 2007)

4.2.3 Drivers for improved performance

Whilst it is clear that the technological advance offered by successful development of a sol-gel route to TCCs is significant, in order to establish its validity as a commercial proposition, assessment is required as to whether it offers sufficient improvement over current processes.

The performance achievable from a given TCC is limited both by the intrinsic properties of the material and by the production method. Applications have a wide range of drivers, both physical, including transparency, spectral response, conductivity and surface finish, and commercial, including cost of materials, deposition and patterning. The substrate material is most commonly glass, although transparent plastics would be desirable from weight, design and cost perspectives. In each application the prioritisation of these drivers determines material selection. Similarly, improvement in properties of a given material expands the range of applications for which it is suited.

The TCC market is strongly cost driven. Indium is an inherently expensive element. Its principal uses are as a metal in electronics and as ITO in displays. Consumption is relatively stable at approximately 300 tons per annum, in line with supply. However, increasing demand for displays projects an increase in demand, to exceed 850 tons per annum. Although approximately 60% of ITO sputter targets can be recycled, a breakthrough in thin film solar cell performance would lead to demand outstripping supply (Jansseune 2004).

DC sputter coating dominates the current generation of commercial high performance TCCs. It produces a continuous film on the substrate which requires post patterning.

The patterning process is a series of coating and removal steps. These are dependent on good alignment and process control (particularly times and concentrations) to ensure satisfactory etching. Under-etching leaves electrical contact (shorts) between regions, whilst over-etching reduces pixel definition and may cause breaks in fine line regions, resulting in open circuit tracks. Thorough inspection is therefore required, which is challenging due to the low contrast between coated and uncoated regions. The patterning process therefore requires a high level of process control, making it costly and time-consuming.

Etching is also a subtractive process and a typical device has only 40% active area, wasting 60% of the ITO film. The pre-recession price for indium peaked at $750/kg vs. tin at $26/kg on the Rotterdam market (MetalPrices 2009), hence reducing indium wastage has significant potential for cost savings.

One of the major limitations to increased commercial development of large area PV and display devices is the high cost associated with batch production of sputter coated components, a problem which would be overcome by successful introduction of a solution based process.

CVD methods are also used, particularly in the depositing large area FTO coatings for glazing applications but the material is difficult to etch, so is not used in patterned anodes. Direct writing of patterns would obviate the need for etching.

Sol-gel materials for TCCs are commercially available, including FTO and ATO developed for EMF shielding applications (Keeling and Walker 2004; Keeling and Walker 2007). Compared with ITO, these currently have insufficient conductivity for use as display anodes. Currently, there are no commercial suppliers of polymeric sol-based coatings, although a significant amount of academic research has been carried out which was used as the baseline for this project.

4.2.3.1 Summary of requirements

Each of the above applications has particular requirements in respect of transparency and conductivity. These are summarised in table 4.1.

Application	**Transparency (%)**	**Sheet resistance (Ω/square)**	**Figure of Merit**
Solar control glazing	70	-	-
Anti-graffiti coating	70	-	-
UV shielding	70	-	-
Dichroic filter	70	-	-
EMF/RFI shielding	70	$1x10^3$	$2.8x10^{-3}$
LCD electrode	90	$1x10^3$	$9.4\ x10^{-3}$
Touch panel	90	$1x10^3$	$9.4\ x10^{-3}$
Static dissipation	90	$1x10^3$	$9.4\ x10^{-3}$
EL display	90	200	$4.7x10^{-2}$
Resistive heater	70	80	$3.5x10^{-2}$
PV electrode	90	30	0.31
LED electrode	90	15	0.63
Commercial ITO	90	13	0.73

Table 4.1 Transparency and conductivity requirements for a range of example applications for TCCs.

The sheet resistance requirement for applications may be presented in a form similar to a Boston Square, with respect to market volume and likely cost. These, together with a Boston Square for volume vs. cost are shown in figure 4.1 below.

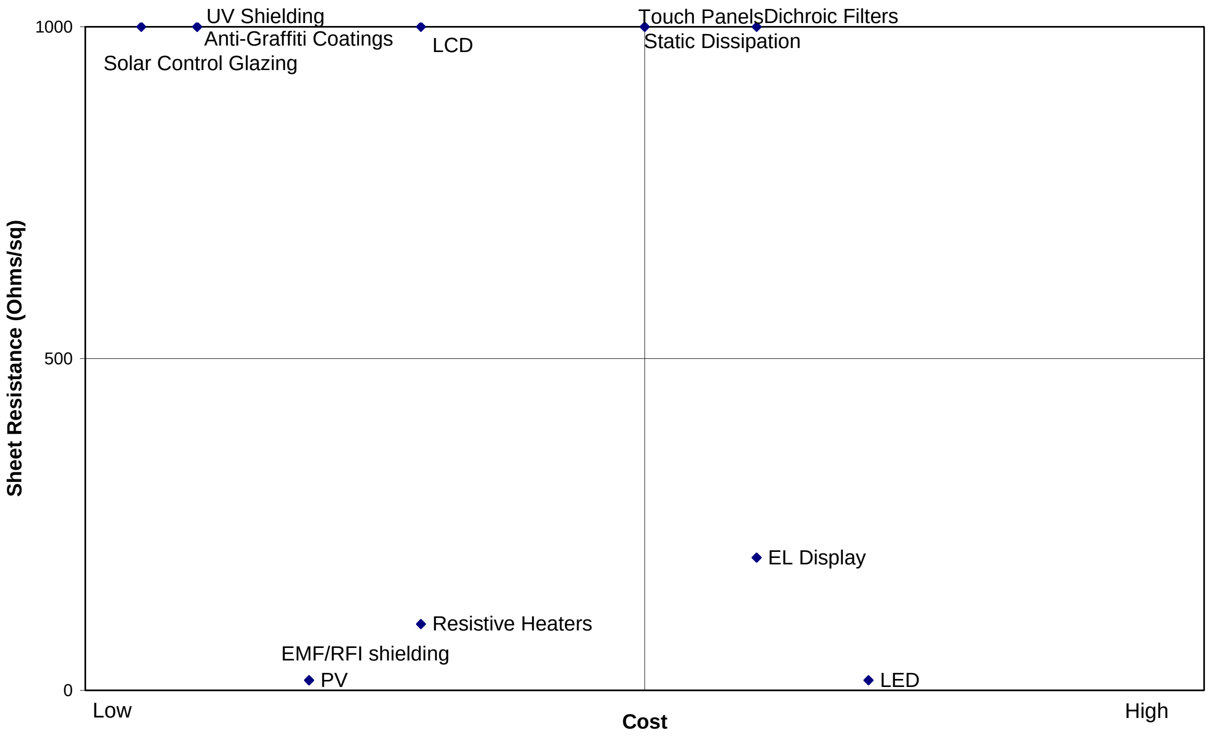

Fig.4.1 (a) Boston Square representation of cost vs. sheet resistance requirements for TCC applications.

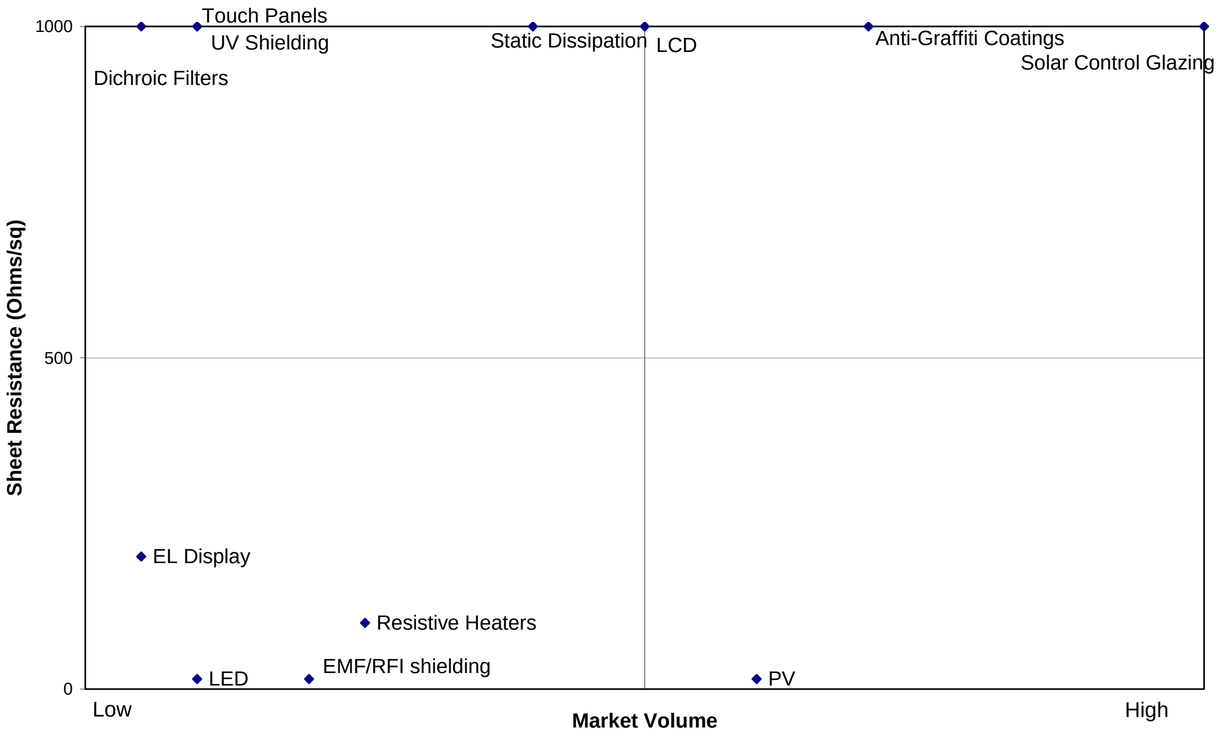

Fig.4.1 (b) Boston Square representation of market volume vs. sheet resistance requirements for TCC applications.

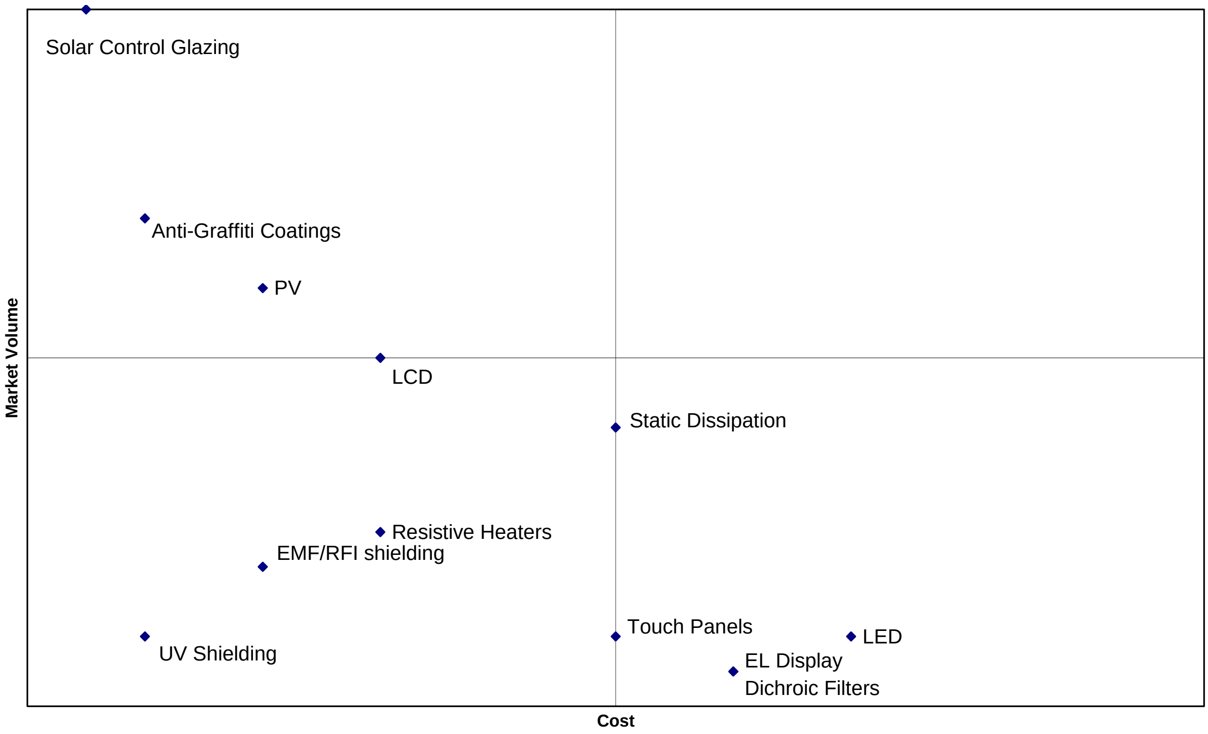

Fig.4.1 (c) Boston Square representation of cost vs. market volume for TCC applications.

Fig.4.1. Boston squares indicating the market needs for TCC performance.

The Boston squares indicate the market needs for TCC performance, with reference to market attractiveness (figure 4.1(c) shows market attractiveness alone). Consideration of performance requirements indicates that a coating with even moderate conductivity could meet the needs of some markets. The cost of the process then indicates whether high value markets such as touch panels, static dissipation on electronic equipment and dichroic filters could be addressed, or whether a product would better meet the needs of high volume markets such as anti-graffiti coatings, LCD anodes or solar control glazing. With increasing performance, more markets become accessible, increasing commercial value within the product. A route with performance equivalent to sputter coated ITO would address the needs identified within figure 4.1(c) based on cost alone.

4.3 Consideration of objectives, TRL and appropriate project type

The purpose of this project was to demonstrate the capability of fabricating a transparent conducting coating via a solution synthesis (sol-gel) route. The coating composition selected for initial study was ITO, since this was identified as the best fit to market need and a range of fabrication procedures has been reported (Furusaki, Kodaira et al. 1986; Mattox 1991; Scalvi, Messias et al. 1998).

It was apparent from the literature that work in the field was restricted primarily to limited academic research, with a single collaborative research project reported (Phillips CFT 2001); a second having subsequently been reported (Puetz and Aegerter 2008). The starting TRL may therefore be assessed as 2, from the definition discussed in Chapter 2, since basic principles had been observed and reported (TRL1) and the programme and a technology concept and/or application formulated (TRL2) (Mankins 1995). The work was at an early, concept stage in the project lifecycle (TWI 2006) and hence carried a relatively high risk and consequently the greatest potential for reward. A low TRL indicated a phased approach to research, through a series of tasks to reduce developmental risk. It was identified that the initial proof-of-concept could be conducted via a relatively modest programme. As identified in Chapter 2, an appropriate route for funding small-scale, early stage work is internal funding, which was undertaken within TWI since the necessary capability was available.

4.3.1 Task 1 – TWI internally-funded feasibility study

The initial task was performed to establish the feasibility of transferring academic results to an industrial setting. The objective of the initial work, agreed with the Research Board at TWI, was to deposit sol-gel derived ITO coatings on to glass and characterise them in terms of microstructure and electrical resistance.

The work successfully demonstrated that an ITO film could be deposited by sol-gel coating onto glass. With reference to TRLs, this task moved the TRL from 2 to 3, since characteristic proof of concept was demonstrated, displaying analytical and experimental critical function (Mankins 1995).

4.3.2 Task 2 – Collaborative development programme

Following a satisfactory outcome, the scale of the challenge and its potential return, combined with the high risk factor inherent in a low TRL, indicated that the concept was appropriate for development in collaboration with appropriate partners, with additional public funding. Investment at an early stage in the development process offered potential rewards for all partners, as discussed below. In order to progress the development further, the next task needed to address coating process, thickness and sintering conditions.

4.3.2.1 Project scope and objectives

The second phase of the work sought to address the above needs by taking an additive approach to producing patterned layers. Materials were to be sol-gel based and deposited from solution. Specific precursors for both ITO and novel alternative TCCs needed to be developed, processed by a sol-gel route and formulated into an ink suitable for deposition by printing. Screen printing was selected since it can accommodate a wide range of ink viscosities and patterning can vary from a simple, plain region to a complex series of tracks. This allows patterned electrodes to be directly written (an additive approach) rather than etched from a continuous film (a subtractive approach), with consequent cost and waste savings.

Within the scope of the project, test plaques were to be dip and spin coated and then an ink developed for screen printing. Performance was to be characterised and compared with commercially available material. The programme sought to develop ITO with a system performance equivalent to commercially available sputtered ITO. It also sought to develop an indium-free system, targetting a performance 60% of the ITO value. The project had the following specific objectives:

i) Supply of baseline ITO precursors
ii) ITO with optical transparency >90% at 400nm and electrical resistivity <50Ω/square.
iii) Supply of improved ITO precursors
iv) Printed ITO with comparable performance to (ii).
v) Supply of alternative Indium free TCC precursors
vi) Indium-free material with optical transparency >90% at <85Ω/square.
vii) Supply of improved Indium free precursors
viii) Printed indium-free material with comparable performance to (vi)
ix) Deliver unpatterned and patterned demonstrators.

4.3.2.2 Project structure needed to achieve the objectives

To deliver the above scope of work required technical expertise in a wide range of disciplines, including synthetic chemistry, sol-gel processing, ink formulation and printing. In order to support this development, access was required to state-of-the-art analytical facilities and current research capability in the development of transparent conducting materials. This range of skills would not fall within the scope of a single organisation, requiring collaboration between industrial and academic partners. Since the range of technical expertise would, if the project delivered a material with commercial value, lead ultimately to a natural supply chain there was commercial value to manufacturing companies in participating within the project.

With reference to Chapter 2, a project which requires the input of a number of companies, each of whom can derive long term benefit from participation, is most appropriately undertaken with collaborative funding. At the time of the research, the UK government made suitable funds available via the Department for Trade and Industry (DTI), via competitive calls. Equivalent funding is now provided via the Technology Strategy Board (TSB). Such funding calls are themed according to subject areas which are strategically important to UK industry, due to either an existing or emerging presence. The concept for this proposal aligned with the LINK Information Storage and Displays (ISD) programme.

The UK is a leading developer of next generation displays through innovative companies such as CDT (OLED), MicroVue (liquid crystal on silicon), MED (LEP on silicon) and PFE (FED) and ongoing development of ruggedised displays at GE Aviation. All of these ultimately require a TCC. Sustaining this competitive advantage needs support in the peripheral technologies, such as anode materials.

Such a process would also provide spin-off benefits to manufacturers of photovoltaic cells and glazing, since the production cost is likely to be reduced. Since, in this case, considerable benefit would accrue to the UK, funding from the UK government was a suitable route.

The proposal team brought together a supply chain across UK industry, backed by world class academic expertise to generate an alternative product stream in the UK, to gain market leading fabrication and commercial advantages in high added value products. The partnership contained a materials developer (Epichem), ink formulator (Gwent Electronic Materials) and screen printing company (DEK), together with an end user (MCE Newmarket). Sol-gel development was performed by TWI, with underpinning materials research, deposition and characterisation by Oxford University and the University of Birmingham.

The project offered to benefit the whole supply chain through increased demand and profitability. The scope was designed to enhance partner competitiveness through enhancements in material quality and performance amongst other factors, in the global marketplace. Subsequent development time and costs would be reduced through the application of processing experience, procedures and performance evaluation built up in the project. Within UK manufacturing as a whole, the results of this proposal were designed to accelerate the uptake of printed TCCs, reducing waste and cost, helping UK companies to establish a world-wide position in offering high performance, quality components to high added value markets.

Public funding added value by enabling the project team to access high investment technology and undertake the research work outlined at an acceptable risk level. The work would otherwise struggle to be cost effective and receive internal funding, if undertaken outside of the collaborative framework by one partner alone. In this sense the LINK programme funding brought together the proposal team to common advantage, with the goal of addressing the development of a printed TCC at a pre-competitive level.

The dynamics of this market are such that the development of a TCC which is printable (and In-free) would be taken up rapidly. The dynamics of the electronics industry are well known and the partnership was well placed to exploit this developing market through a combination of manufacturing and licensing of IP.

This project sought to develop a technological solution to existing problems with anodes and a UK-based supply chain to deliver it.

4.3.2.3 Partners - inputs and outputs

The project consortium comprised a series of UK Small to Medium Size Enterprises (SMEs) spanning the optoelectronic supply chain. Publicly funded projects are part-funded, in this case at 50% of project value. Consequently, having taken account of higher funding rates required to cover the costs of the three research providers (TWI, Oxford University and The University of Birmingham) the prevailing funding rate for the industrial partners was in the region of 35%. For all partners (with the exception of the Universities, which were fully funded) the balance of costs was met by in-kind contribution, in the form of effort. Consequently, each partner anticipated long-term benefits from participation in the project. The role of each partner in the project and their expected return from participation are discussed below.

4.3.2.3.1 Epichem Ltd

Epichem was founded in 1983 to supply high purity specialty chemicals and gases to the semiconductor industry. The company has become the global leader in this area with facilities in each major market region (Europe including the UK, US, Japan, Far East). This market has always been customer driven, therefore concentration of resources, timely response to evolving needs and focused investment are of paramount importance.

Product development has been vigorously pursued to allow the reproducible isolation of high purity material, particularly with low metal impurities. This has been achieved through in-house effort in combination with extensive involvement in collaboration with leading academic and industry groups. Both synthesis routes and analytical methods have been identified and optimised to afford products recognised as the highest purity worldwide. The second objective in product development has been to maintain this high product quality when scaling up processes in a safe manner.

Epichem sought to grow a precursor sales business for transparent conductors of the order of £3million per annum turnover (Rushworth 2002).

4.3.2.3.2 Gwent Electronic Materials

Gwent Electronic Materials (GEM) Ltd. was founded in 1988 to manufacture materials for the electronics and associated industries. Products are manufactured directly for individual customers and are tailored to suit specific processes. GEM Ltd. has grown to become a major supplier of paste and ink to industry with current production capability in the region of 100,000 to 200,000kg per year. This is coupled with an extensive range of testing and analysis equipment to ensure that products meet the highest standards.

GEM Ltd’s product range includes conductive and dielectric inks for all forms of substrates, passive or active components; dielectric pastes for all forms of substrates, passive or active components, serving the industrial, automotive and sensors sectors. GEM are currently developing a new range of Low Fire Materials which have reduced the firing temperature from the normal 400 to 450°C range to 150 to 350°C. This new revolutionary type of system means that it is now additionally possible to fire onto polymeric rather than ceramic materials.

It is the policy of GEM Ltd. to ensure that they remain leaders in the provision of new materials for their sector of industry. Transparent conductive inks are a natural fit to their product range and they sought to become distributors to industry.

4.3.2.3.3 DEK International

DEK International is the world's leading provider of advanced Pre-Placement manufacturing solutions for the electronics circuit board assembly and semiconductor industries. The Company was founded in 1969 and almost immediately specialised in providing printing equipment, materials and technology to the then newly emerging microelectronics industry. DEK is now the world’s leading supplier of volume production screen printing equipment with 650 people world-wide and turning over $100,000,000 US in 2002.

DEK has also adapted printing technologies for use in the wafer-fabrication industry. DEK supply precision screen printing solutions in many fields including general electronic, medical, automotive and aerospace applications

Supply of printing equipment and the deposition of TCC inks represented a potential new market. As a direct result of participation in this programme, DEK sought to generate sales of 2000 printer units (Hobby 2003).

4.3.2.3.4 MCE

Micro Circuit Engineering (MCE) was part of Smiths Aerospace and is a leading supplier of high reliability electronics for aerospace, military, transport, telecommunications, computer, medical and industrial applications. Many thousands of device types have been designed and manufactured for a wide range of customers for over 20 years.

MCE supports a wide range of electronic circuit technologies to provide a complete solution to the design and manufacture of electronic components. As part of MCE’s strategy for growth, MCE is actively developing capabilities for the manufacture of ruggedised displays, where ITO coatings are an integral part of the display assembly and of the heating elements.

For MCE, the development of unpatterned, solution based TCCs is estimated to have a medium term value of £40k p.a. For patterned, solution based TCCs an order of magnitude saving is expected on substrate cost (from a current processed cost of $30/14” sheets to $3/14” sheets and a scalability to Generation 6 dimensions of 1.2m square). MCE sought to exploit this potential market, through the supply of patterned, solution based TCCs for a range of applications in various industrial sectors. It is estimated that this potential market would have a value to MCE in the region of £200k p.a (Riches 2003).

4.3.2.3.5 TWI

TWI was the lead partner and project co-ordinator. TWI brought considerable background expertise in sol-gel processing, together with a long history of technology transfer, realised both directly to business and also through the management of collaborative projects. The primary technical role of TWI was to further develop the sol-gel route already partially established to yield ITO, and to identify synthesis routes to the alternatives highlighted by the academic partners.

4.3.2.3.6 Oxford University

The Chemistry department brought relevant background expertise in the synthesis and development of functional materials for industrial applications. Previous work has included the use of cationic and anionic substitution and exchange to alter the electronic and structural properties of materials and the development of new synthetic methods for functional materials.

Oxford University undertook the materials modelling activity for alternatives to ITO, and fabricated prototype materials via microwave synthesis (Edwards, Porch et al. 2004).

4.3.2.3.7 The University of Birmingham

The University of Birmingham has a long history of conducting interdisciplinary research into functional materials with expertise in superconducting and magnetic materials systems, metal-insulator transitions, microstructure-property relationships and synthesis and processing of advanced materials.

The development of a wide range of thin film deposition and evaluation facilities placed Birmingham in a strong position to play a significant part in the project. This work includes a new PLD processing procedure for thin film materials whereby thin film materials may be oxidised after deposition. This method allows deposition of amorphous precursor films, which are then treated outside of the ablation chamber with the metallic cation of choice to produce crystalline, c-axis oriented films.

Birmingham undertook to prepare prototype coatings via PLD. They also provided characterisation of the ITO alternatives and the developmental sol-gel derived materials (ITO and alternatives) (Abell 2002).

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CHAPTER 5 - TRANSPARENT CONDUCTING MATERIALS

5.1 Overview

There is no such thing as a perfectly transparent conductor. In real materials the intensity of impinging electromagnetic radiation is attenuated and hence they transmit under 100% of light. They also have resistive losses, hence are less than 100% electrically conducting. A material is defined as a transparent conductor if it transmits more than 70% of light in the visible region of the spectrum and has electrical conductivity greater than $10^3\Omega$cm. In practical applications, transparent conductors are deposited as thin films on a substrate, forming a transparent conducting coating (TCC) since there are no electrically conducting materials which are sufficiently transparent to be used in monolithic form.

The first report of a TCC was in 1907, when Badeker (Badeker 1907) observed that oxidation of a thin cadmium metal film resulted in transparency whilst retaining conductivity. Since then a wide range of other materials has been examined, including thin metal films, binary oxides and nitrides and doped oxides (Saif, Memarian et al. 2000). The most intensively studied and industrially applicable coating types are doped oxides. Materials of commercial interest include tin oxide doped with antimony (ATO) or fluorine (FTO) and indium oxide doped with tin (ITO). These, together with alternative materials, are considered fully below.

Selection of TCCs is highly dependent on application, since they have many parameters which can be tuned. There are regions of the electromagnetic spectrum over which TCCs are transparent, reflecting and absorbing; they have varying work functions and different types of charge carriers (electrons or holes). In making a device incorporating TCCs, synthesis temperature, thermal stability, resistance to plasmas and ease of etching may be important. The end user may have other requirements, such as chemical durability, smoothness, hardness, flexibility, cost and toxicity.

TCCs have found a wide range of applications in fields as diverse as displays, heaters and solar glazing. The challenge in real applications is to find an appropriate compromise between the above properties.

5.2 Basic materials physics

The mechanism of conductivity in metallic thin films is conventional metallic conductivity, derived from the delocalisation of electrons across the lattice. Transparency is achieved by using extremely thin layers, lying below the skin depth in the region of 20nm. In order to avoid oxidation, such films are typically prepared from relatively noble metals. Since the electron configuration which makes them oxidation resistant also makes them very soft, the films are fragile; this is significantly limiting to their application.

The majority of practical TCCs (and by definition all TCOs) are therefore semiconductors. The starting point for these materials is a transparent oxide, doped to generate a wide band gap semiconductor with a relatively high concentration of free electrons in the conduction band, resulting in the desired electrical properties.

5.2.1 Conductivity

Whilst there are many ceramic materials which are transparent in the visible region of the spectrum (Dislich and Hussmann 1981), very few of them have the appropriate band structure to obtain electrical conductivity through doping. Following the electron-gas model for conduction, the electrical conductivity of a material, σ is given by:

$$\sigma = ne\mu \qquad (5.1)$$

n = density of free electrons; e = charge of electron; μ = electron mobility

where

$$\mu = e\tau / m^* \qquad (5.2)$$

τ = electron resistivity relaxation time; m^* = free electron effective mass

Thus conductivity may be expressed as

$$\sigma = ne^2\tau / m^* \qquad (5.3)$$

According to Mott's model (Mott 1961), the temperature dependence of conductivity differs between metals and semiconductors.

For metals:
σ (T→0) $\neq 0$ (electrons are free)

For semiconductors:
σ (T →0) = 0 (electrons are localized)

The behaviour of a material as a metal or semiconductor is dependent on the carrier concentration (density of free electrons) and has a critical threshold, n_c. This is illustrated in figure 5.1.

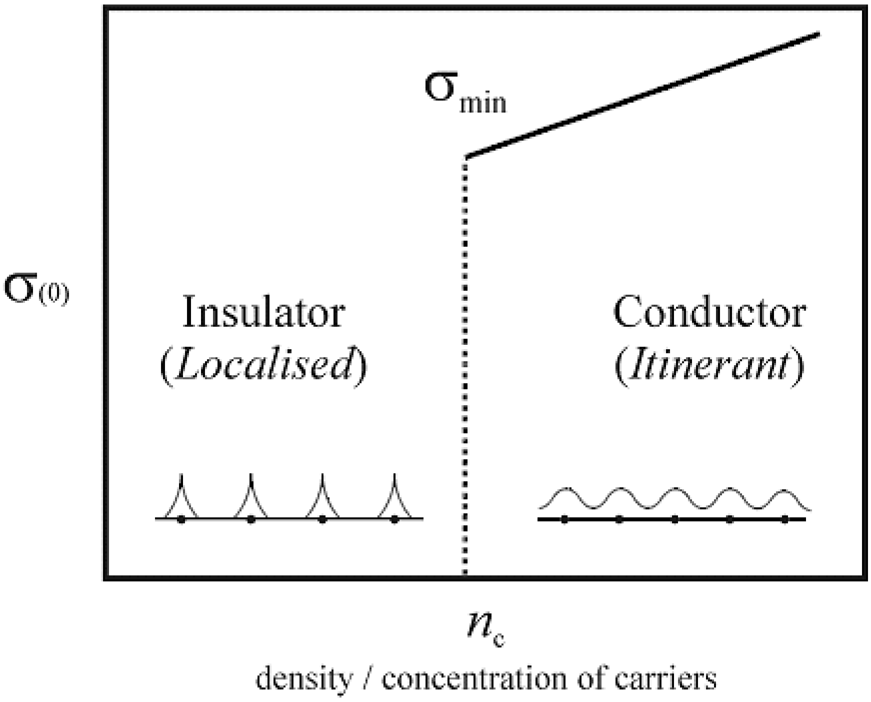

Fig.5.1 The Conductor-Nonconductor Transition at T = 0K (Mott 1961)

The Mott criterion for conductivity (Mott 1990) is expressed as:

$$n_c^{1/3}\, a_H = 0.26 \pm 0.05 \qquad (5.4)$$

where a_H is the Bohr radius.

For a doped semiconductor, the transition can be expressed in terms of average carrier separation, d_c, as shown in figure 5.2.

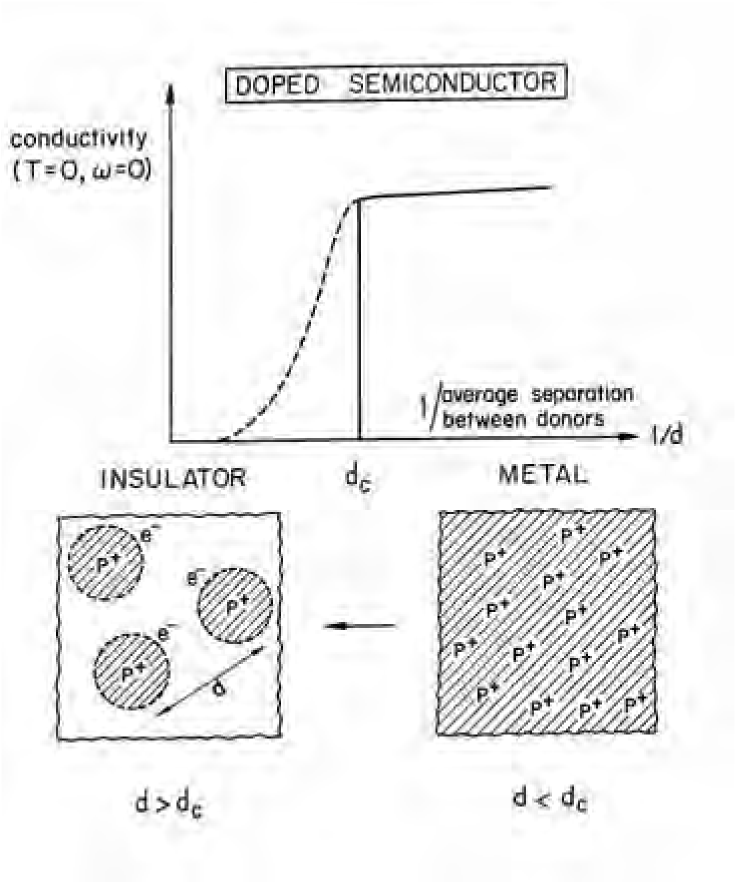

Fig.5.2 The transition between insulating and metallic behaviour in semiconductors, expressed as a function of separation between dopant carriers (Mott 1961).

Here, the Mott criterion term n_c is approximately $2.5a_H$ (Mott 1990).

Conductivity is also dependent on coating thickness, generally remaining constant above a threshold value of 100nm. Below this value, decreasing thickness produces a corresponding increase in inherent resistivity (Maruyama and Kojima 1988). This is due to:

- Increased grain boundary scattering.
- Increased relative importance of surface roughness.
- An increase in the number and importance of voids and defects present in the coating, reducing connectivity.

Conductivity is also a function of dopant concentration, since dopant ions disrupt the lattice, decreasing charge carrier mobility. There is consequently a threshold dopant concentration, above which a material becomes insulating. To maximise conductivity the dopant concentration must be optimised.

5.2.2 Transparency

A defining feature of TCCs is high transmission of electromagnetic radiation in the visible spectrum (~300-700nm). When light impinges on a surface it may be absorbed, refracted, reflected or transmitted. Evidently, the objective in a transparent material is to maximise the latter by minimising the three mechanisms for attenuation of transmission. In practice, refraction has little effect on transmission, since the TCC is very thin so dispersion and scattering are minimal. Its principal influence is therefore in increasing reflective losses of non-normally incident light (which is considered as a reflective loss). Mechanisms for absorption and reflection are considered in turn.

Absorption is a function of available energy transitions within the lattice at wavelengths lying in the visible part of the electromagnetic spectrum. When a photon impinges on the surface, it is absorbed if an energy transition within the molecule can be excited by the photon; available transitions being defined by the band gap. The band gap is the energy transition between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The threshold value of the band gap, E_G, is 3.75eV: above this value the energy of transition falls outside the visible range and the material therefore does not absorb in the visible spectrum. The band gap therefore defines the high energy, short wavelength boundary for optical transparency.

Reflection at a surface is dependent on the surface morphology, its refractive index and whether the material exhibits metallic or non-metallic behaviour at the incident wavelength.

Surface morphology influences reflection, since increased roughness provides an increased likelihood of an angle of incidence above the critical threshold (within multiple reflections) however it is not generally desirable to increase surface roughness as it increases light diffusion and has negative effects on device performance.

Refractive index is a fundamental property, being proportional to the permittivity of the material. Refractive index is defined relative to that of a vacuum, at 1. Soda-lime glass has a refractive index of approximately 1.5 and most metal oxides have refractive indices between 1.5 and 2.0. A law of mixtures applies, so lower refractive indices may be achieved by incorporation of porosity (Becker, Dauwalter et al. 2006). However, this is detrimental to conductivity. The refractive index of non-metallic materials contains only a real term, however that of metals is complex.

In non-metallic materials, the relative differences between the refractive indices of two materials result in refraction, i.e. directional change, of the incident radiation. When the light is incident normal to the surface it continues undeflected, however when the light is not normal to the surface it is deflected further from normal as it passes into a material with higher refractive index and closer to normal when passing into a material with lower refractive index. The angles of reflection and refraction are determined from Snell's law:

$$n_i \sin\theta_i = n_t \sin\theta_t \qquad (5.5)$$

Where n_i = refractive index of the impinging medium; θ_i = incident angle; n_t = refractive index of the transmission medium; θ_t = transmitted angle

This is illustrated in figure 5.3.

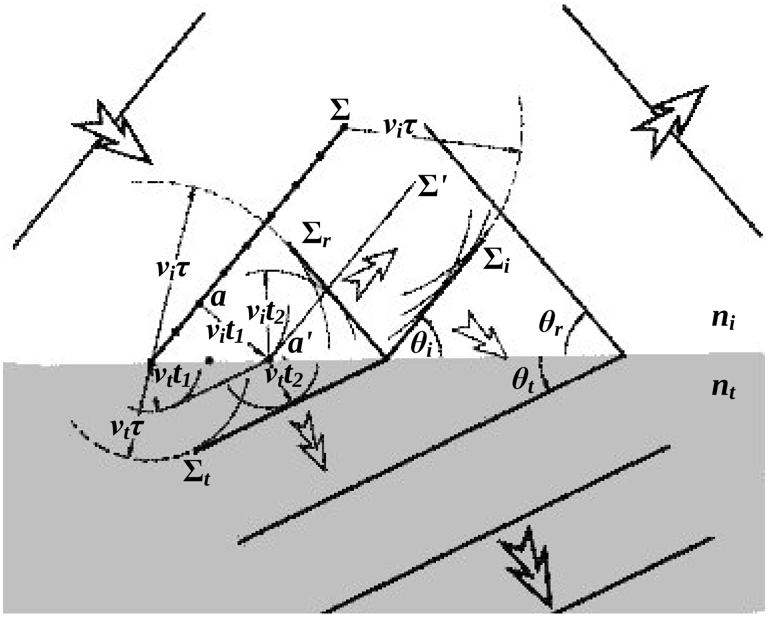

Fig.5.3 Schematic representation of the principle of reflection and refraction at a surface due to difference in refractive index according to Huygens' principle, illustrating Snell's law (Hecht and Zajac 1974). An incident wavelet Σ is shown progressing during time t_1 to Σ'. Using the speed in the initial (v_i) and transmitted (v_t) media, the wavelet can be followed from its original incident point and from point a to a', and subsequently from each point in time t_2, to construct reflected (Σ_r) and transmitted (Σ_t) wavelets. $\tau = t_1 + t_2$.

When passing from a material with higher refractive index to one with a lower refractive index the angle of incidence has a critical threshold, θ_{crit}, above which complete reflection results defined by:

$$\theta_{crit} = \arcsin(n_i / n_t) \qquad (5.6)$$

The proportions of light reflected and transmitted are governed by the reflection (R) and transmission (T) coefficients derived from the Fresnel equations. Separate equations are derived for the parallel and perpendicular coefficients:

$$R_{\|} = \left[\frac{n_i \cos\theta_i - n_t \cos\theta_t}{n_i \cos\theta_i + n_t \cos\theta_t}\right]^2 \qquad (5.7)$$

and

$$R_{\perp} = \left[\frac{n_i \cos\theta_t - n_t \cos\theta_i}{n_i \cos\theta_t + n_t \cos\theta_i}\right]^2 \qquad (5.8)$$

and

$$T = 1 - R \qquad (5.9)$$

The proportion of light reflected and transmitted in the transition from air to soda-lime glass is illustrated in figure 5.4.

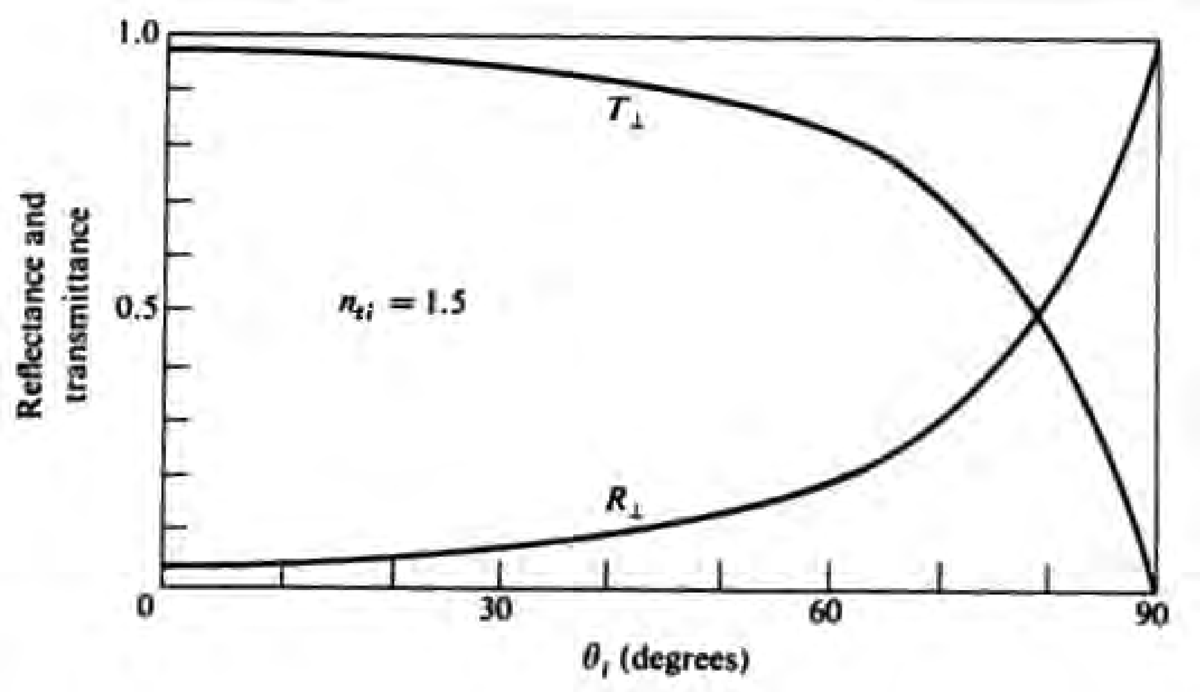

Fig.5.4 Relative proportions of light reflected and transmitted in the transition from air to soda-lime glass ($n_t/n_i = 1.5$) with varying incident angle (Hecht and Zajac 1974).

From inspection of figure 5.4 and consideration of equations 5.7 and 5.8, it is apparent that even when light is incident normal to the surface ($\theta_i = \theta_t = 0$; $\cos\theta = 1$), a proportion is reflected, according to:

$$R = \left[\frac{n_i - n_t}{n_i + n_t}\right]^2 \tag{5.10}$$

This reflection relates to the permittivity of a material. In transitions from glass to air, 4% of incident light is reflected, whilst for an oxide with a higher refractive index, e.g. for bulk ITO with a refractive index of 1.96, 11% of incident light is reflected (note, real losses for TCCs are reduced due to low film thickness).

In a material which is transparent in the visible region of the electromagnetic spectrum, the upper wavelength (ω) of transparency is bounded by the plasma edge, defined from:

$$\omega^2 = ne^2 / \varepsilon_0 m^* \qquad (5.11)$$

m^* = free electron effective mass, n = density of free electrons, e = electronic charge, ε_0 = permittivity of free space

Above the plasma edge an electron gas response is experienced, i.e. metallic reflection is observed. In metallic materials, as noted above, the refractive index, and hence permittivity (ε_c) is complex:

$$\varepsilon_c = \varepsilon\left(1 + i\frac{\sigma}{\omega\varepsilon}\right) \qquad (5.12)$$

Thus the propagation constant (k_c):

$$k_c = \omega\sqrt{\mu\varepsilon_c} \qquad (5.13)$$

(where μ is the permeability of the material) separates into real and imaginary components:

$$k_c = \alpha + i\beta \qquad (5.14)$$

For a metal, the imaginary component dominates and substitution of (5.12) into (5.11) gives:

$$\beta \approx \sqrt{\frac{\mu\omega\sigma}{2}} \tag{5.15}$$

The amplitude of the transmitted radiation is attenuated as a function of the imaginary term. Penetration of electromagnetic radiation is defined by the skin depth, being the distance (δ) over which the amplitude is attenuated to e^{-1} of its original amplitude and is therefore:

$$\delta = \frac{1}{\beta} = \sqrt{\frac{2}{\mu\omega\sigma}} \tag{5.16}$$

The derivation of skin depth is given in full by Griffiths (Griffiths 1999).

Thus the skin depth for a typical metal is extremely small, in the order of 1-20nm within the visible region of the spectrum. For semiconductors with a fixed number of carriers, an increase in the mobility of free carriers increases the skin depth and hence results in an increase in film transparency.

5.2.3 Performance characteristics for transparency vs. conductivity

From the above definitions for transparency and conductivity, the region over which materials can exhibit both properties can be defined.

From the Mott criterion for conductivity, given in equation 5.4:

$n_{\min}$ can be determined as (n_c)

$n_{\min} \sim 1 \times 10^{19}\ cm^{-3}$

The upper boundary for carrier concentration is determined by the plasma frequency (5.11):

$$\omega^2 = ne^2 / \varepsilon_0 m*$$

Since ω is proportional to √n, $n_{\max}$ can be determined as:

$n_{\max} \sim 2 \times 10^{21}\ cm^{-3}$

Therefore, for conductivity, the Mott criterion requires a minimum carrier density of $1\text{x}10^{19}\text{cm}^{-3}$, while the plasma edge defines an upper boundary to carrier density of $2\text{x}10^{21}\text{cm}^{-3}$, above which the material becomes optically reflecting.

Transparency α and conductivity σ are inversely related, dependent on thickness. The most effective measure of performance is therefore quantitative figure of merit (FOM) as first postulated by Gordon (Mliki and Bennaceur 1993) by the equation:

$$\sigma/\alpha = -\{R_r \ln T\}^{-1} \tag{5.17}$$

where R_r is the sheet resistance in Ω/square and T is the total visible transmission.

This metric suggests that absolute performance is independent of film thickness. In practice, this is not strictly true, since conductivity is increased with increasing crystal grain size, which requires a thicker film, hence the relative performance of thicker films is improved. Conductivity is also a function of dopant concentration, since dopant ions disrupt the lattice, decreasing charge carrier mobility. Therefore, to maximise conductivity, the dopant concentration must be optimised.

A dopant would ideally be a high valency cation, in order to maximise electronic effect while minimising the concentration.

5.3 Transparent conducting materials

Transparent conductors can be made from ultra-thin metal films, semi-conducting metal oxide films or a multi-layer composite structure with metal sandwiched between semiconductors. More recently, attempts have been made to develop organic films based on polyethylene-dioxythiophene/polystyrene-sulphonate (PEDOT/PSS) (Kirchmeyer and Reuter 2005), carbon nanotubes (Glatkowski 2003) and graphene (Tung, Chen et al. 2009) but to date, these do not show sufficient performance to be viable.

Metallic transparent conductors are prepared from ultra-thin films of gold, silver, copper or platinum (Saif, Memarian et al. 2000). In order to obtain sufficient transparency the films are below 20nm thick. They are easy to prepare, using PVD methods, but are intrinsically high cost materials and are soft, thin and easily damaged which limits their practical application.

An alternative to pure metallic films is a sandwich structure in which the metal layer is deposited between two layers of TCO. The multilayer structure is used to combine the high conductivity of a metal with the durability of a semiconductor. Typical combinations include $SnO_2/Ag/SnO_2$ and ITO/Ag/ITO (Chakaroun, Lucas et al. 2009), however these films have limited chemical stability, since the metal layer reacts rapidly on exposure to the atmosphere. This requires that devices are prepared under conditions which prevent oxidation and are then hermetically sealed, restricting their use.

Pure binary metallic oxides are not conducting in their fully stoichiometric form, for example both SnO_2 and SnO are insulators. In order to obtain conductivity the lattice must be disrupted. This can be achieved by changing the stoichiometry, for example introducing oxygen vacancies, e.g. SnO_{n+1} where $0<n<1$. Binary oxides of In, Sn, Zn and Cd show good transparency and conductivity, depending on the deposition method, and resulting defect concentration. In practice, whilst creating oxygen deficiencies is relatively simple and good conductivity can be achieved, such oxides tend to be rather unstable and prone to either oxidation or reduction.

Consequently, most practical oxide based TCCs are prepared by adding a dopant in order to distort either the cation or anion lattice. Typical cation doped materials are tin oxide doped with antimony (ATO), indium oxide with tin (ITO). Zinc oxide doped with aluminium (AZO) has also been investigated and shown to have comparable properties to ITO. The material was made commercially available under the brand 'Azoy' (van Osten, Rix et al. 2003), however performance was found to deteriorate rapidly. A typical anion dopant system is fluorine doped tin oxide (FTO). Doping levels are typically up to 5at%. Higher concentrations result in a decrease in conductivity, due to a high concentration of ion impurity scattering centres, reducing carrier mobility.

5.3.1 ITO

ITO is considered as a representative example material, being the most commonly used TCC due to its combination of high electrical conductivity and optical transparency, together with good adhesion, mechanical resistance and chemical stability. The latter is a balance between high stability which enhances device performance but with sufficient solubility to facilitate patterning by etching.

A thin In_2O_3 film is an insulator under everyday conditions, however when tin (Sn) is substituted at the indium lattice points this acts as an n-type dopant and the film becomes conductive. There is an upper limit for this substitution, normally considered as 9 ±3at%. Above this value, both ionisable and non-ionisable structural defects are formed, reducing conductivity.

The highest conductivity values have been achieved with additions of between 4 and 6at% tin (Manifacier, Szepessy et al. 1979).

In_2O_3 crystallizes in the cubic bixbyite structure or C-type rare-earth sesquioxide structure (Odaka, Iwata et al. 1997). The unit cell contains 80 sites, of which 32 are occupied by indium ions and 48 occupied by oxygen ions; the structure is illustrated in figure 5.5(a). The cell consists of two non-equivalent InO_6 structural units (Binczycka, Uhrmacher et al. 2005) illustrated in figure 5.5(b).

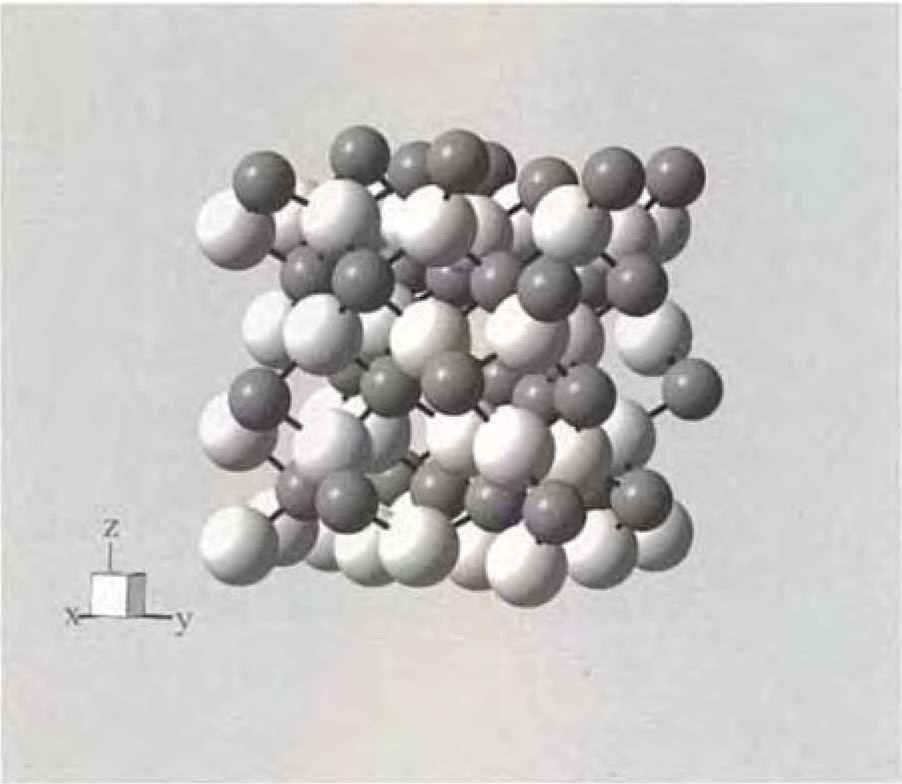

Fig.5.5(a) Space model of the bixbyite unit cell, showing 32 indium (light) and 48 oxygen (dark) atoms (Odaka, Iwata et al. 1997).

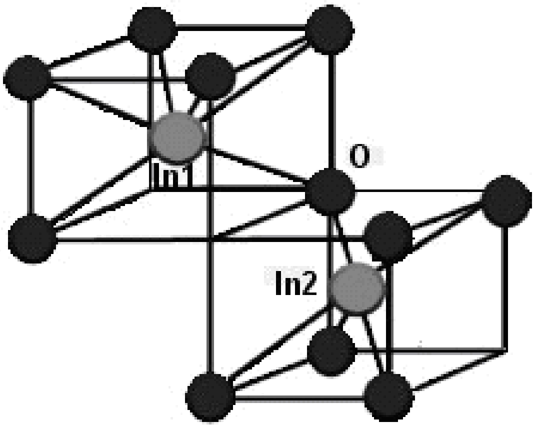

Fig.5.5(b) The two non-equivalent InO_6 structural units (Binczycka, Uhrmacher et al. 2005).

The lattice structure may be regarded either as two non-equivalent distorted octahedra, or in simple cubic unit cell notation as two body centred cubic cells with two vacant anion sites in each structural unit (Fuchs and Bechstedt 2008), denoted "B" and "D" according to international notation. The B sites lie approximately at the corners of the cube, across a body diagonal while the D sites are at diagonally opposite corners of a face. This is illustrated in figure 5.6.

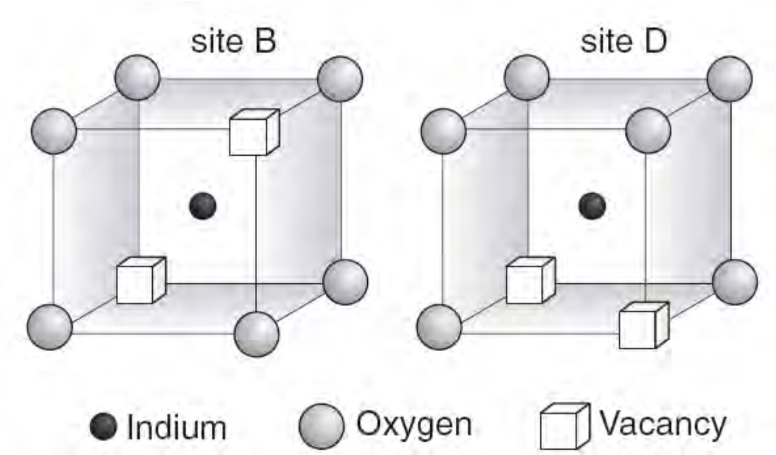

Fig.5.6 Vacant sites within the In_2O_3 lattice (Binczycka, Uhrmacher et al. 2005).

The lattice parameter of undoped In_2O_3 is 10.117 Å. Doping the structure with tin increases the lattice parameter, up to a plateau value above 6% of 10.125Å (Tian 2005), shown in figure 5.7.

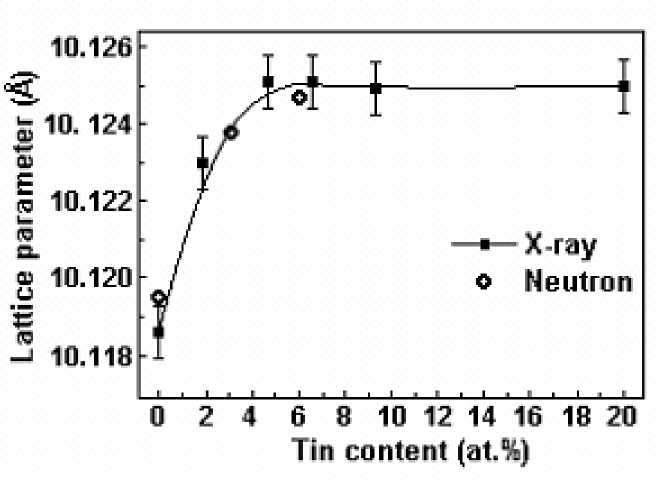

Fig.5.7 Change in ITO lattice parameter with the atomic percentage of tin content (Tian 2005).

The tin dopant is incorporated as Sn^{4+} into the In_2O_3 lattice, substituting for the indium atom. Such a substitution is possible because the ionic radius of tin is smaller than that of indium. The valence difference between In^{3+} and Sn^{4+} results in the donation of a free electron to the lattice, forming a valence state close to the empty conduction band, i.e. an n-type semiconductor, as illustrated in figure 5.8.

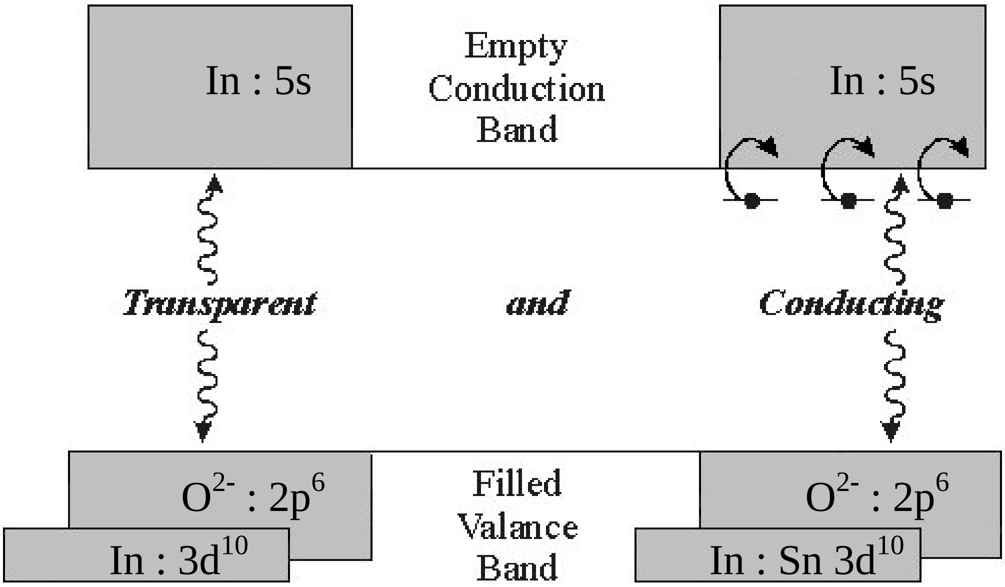

Fig.5.8 Schematic model for the band structure of a transparent semiconductor (illustrated by ITO) after Fan and Goodenough (Fan and Goodenough 1977).

5.4 Materials selection

Although the combined properties of transparency and conductivity are defining for TCCs, in practical devices a number of other factors may require consideration. Ongoing research is currently focussed on enhancing properties, particularly optical and electrical performance. A particular areas of development is in new materials such as Nb doped TiO_2 (Furubayashi, Hitosugi et al. 2005) which shows considerable promise, resistivity of $2x10^{-4}\Omega cm$ having been reported at 97% transparency, although currently the need for high substrate temperature during deposition is limiting for commercial application. Another direction under consideration is the characterisation of ITO prepared by different process routes, in order to understand the process-structure-property relationship, leading towards deposition of materials with enhanced performance on plastic substrates (Wakeham, Thwaites et al. 2009). This latter trend marks a move away from attempts to develop organic TCCs.

5.4.1 Optical and electrical performance

As described above, the properties of transparency and conductivity may be discussed in terms of a FOM value. By this measure, the best performing materials are fluorine doped zinc oxide (FZO) and cadmium stannate, with AZO, ITO and FTO showing approximately half the performance. Typical FZO films are deposited with a sheet resistance of 5Ω/square at 97% transparency, compared with ITO at 6Ω/square with a transparency of 96%. The FOM for common materials are summarised in table 5.1.

TCCs do not have particularly high conductivity, hence in order to carry sufficient current to drive pixels in active matrix devices to a suitable brightness an additional metal layer is often used in the non-emissive regions. This may be a sputter-coated film of Cr/Al/Cr (Chakaroun, Lucas et al. 2009).

For use as an electrode, the work function of a TCC becomes significant since good matching of the energy levels of the electrode and the adjacent layer enhances device efficiency. Injection of electrons and holes require low and high work functions respectively (Gordon 2000). Available work functions range from 4.2eV for fluorinated zinc oxide (FZO) to 6.0eV for platinum, ITO lying at 4.8eV (Gordon 2000). Surface treatments can be used to alter the work function, but expanding the range would lead to more efficient devices.

Material	**Resistivity (ųΩ-cm)**	**Electron Concentration (cm^{-3})**	**Work Function (eV)**	**Figure of Merit (Ω^{-1})**	**Plasma Wavelength (μm)**
Ag	1.6				0.4
Cd_2SnO_4	130	$5x10^{20}$		7	1.3
In_20_3:F	$4.4x10^{-4}$	10^{20}		80% trans	
In_2O_3:Sn	100	$>10^{20}$	4.8	4	1.0
SnO_2:F	200	$4x10^{20}$	4.9	3	1.6
Sn0:Sb	$8.4x10^{-4}$	10^{20}		0.4	
TiN	80				0.7
ZnO	5x10-4	$7x10^{19}$	4.5		
ZnO:Al	150			5	1.3
ZnO:F	400	$2x10^{20}$	4.2	7	2.0

Table 5.1 Electrical and optical properties for some common TCCs (Gordon 2000; Saif, Memarian et al. 2000)

5.4.2 Chemical Properties

The chemical stability of TCCs is also significant to device fabrication and is very varied, ranging from zinc oxide which is highly soluble in dilute acids or bases through to tin oxide which is notoriously difficult to etch. Whilst the latter is ideal for unpatterned applications, where a pattern must be formed it is necessary to compromise some level of chemical stability in order to process the substrate. For wet processing, ITO is etched by HCl + HNO_3, conc. HBr or $FeCl_3$. TCCs may also be removed by laser ablation or reduced by hydrogen plasmas (Brain, Lewis et al. 2000). Chemical stability is summarised in table 5.2.

Material	**Oxidizing Acids**	**Reducing Acids**	**Strong Bases**	**Hydrogen Plasma**	**Etchant**
Ag	Soluble	Stable	Stable		Dilute acid
TiN	Stable	Stable	Stable	Stable	H_2O_2 + NH_3
TiO_2	Stable	Stable	Stable	Stable	-
In_2O_3:Sn	Soluble	Soluble	-	-	HC1 + HNO_3/ $FeCl_3$/conc. HBr
Cd_2SnO_4	-	Soluble	-	-	-
ZnO:Al	Soluble	Soluble	Soluble	Stable	Dilute acid/Ammonium chloride
SnO_2:F	Stable	Soluble	Stable	Reduced	Zn + HCl/$CrCl_2$
ZnO:F	Soluble	Soluble	Soluble	Stable	Dilute acid/Ammonium chloride

Table 5.2 Chemical stability of common TCCs (Weast 1986).

In contrast to patterning, where a degree of chemical instability is required, for subsequent aspects of device fabrication a level of stability may be required. For example, in tempering architectural glass it must be taken above its annealing point, in the region of 650°C for soda-lime glass (Rawson 1991) which may affect the properties of a TCC via recrystallization and grain growth. This has a greater effect on, for example, ITO than on cadmium stannate. In the manufacture of amorphous silicon cells on TCCs the silicon is deposited from a hydrogen plasma which can reduce the TCC. By reference to an Ellingham diagram it can be seen that zinc oxide is particularly stable with respect to reduction and consequently may be preferred for this application (Wanka, Lotter et al. 1994).

Most TCC components are regarded as non toxic, although some of the precursor compounds are toxic to varying degrees. The two notable exceptions are zinc which is an essential element and cadmium which is highly toxic and banned in some regions, despite its good electrical and optical performance.

5.4.3 Physical properties

For some applications, particularly where thin overlayers are part of the device structure, it is necessary to keep the TCC film as thin and smooth as possible. In order to maintain transparency, coating thickness is typically between 100 and 250nm. In terms of resistivity for a given film thickness the best performance is achieved with a metal film such as silver, but as previously discussed such films are too fragile for practical devices. Ranking by hardness using Moh’s scale, on which diamond is 10, gives tin oxide at 6.5, ITO at 5 and silver below 3. For reference a typical glass substrate is approximately 6. Hardness values are summarised in table 5.3.

Material	**Moh’s Hardness**
TiN	9
SnO_2	6.5
Soda-lime Glass	6
In_2O_3	~5
ZnO	4
Ag	Low

Table 5.3 Hardness of TCCs (Gordon 2000).

Polycrystalline films generally have a rough surface. Crystal growth in sputter coated ITO is in the form of laminar platelets, producing an inherent surface roughness which can be minimised to 3.5nm Ra with appropriate process control. Additionally, the sputtering process produces insulating nodules on the target surface. These are periodically sputtered off, resulting in spikes in the coating surface with a height in the order of microns.

For most applications a rough surface is undesirable, since image clarity is reduced and where the coating is used for surface protection, metals scrape on the surface, leaving a thin film known as metal marking. In order to achieve a smoother surface the film must usually be polished which adds to cost. The surface roughness of a TCC is significant if a subsequent layer is to be applied, particularly in thin film display applications.

5.4.4 Cost

Cost can also become a major issue, especially in ‘low tech’ applications. Indium is particularly expensive and since it is obtained as a by-product from other metal ores the supply cannot be readily increased. The pre-recession price for indium peaked at \$750/kg vs. tin at \$26/kg on the Rotterdam market (MetalPrices 2009). Silver is also expensive; by contrast zinc is extremely low cost.

5.5 Fabrication

The deposition process used to manufacture a TCC plays a major role in its microstructure and hence its conductivity and optical properties. To obtain high performance from a TCC requires a well-defined coating composition and structure, dependent on very close process control in fabrication. Process-structure-property relationships were comprehensively reviewed by Tahar *et al* in 1998 (Tahar, Ban et al. 1998) and by Gordon in 2000 (Gordon 2000).

A wide range of techniques has been used to make research and commercial grade TCCs. These include evaporation, sputtering, PLD, CVD, and solution chemical methods. Initially, spray pyrolysis was the predominant technique, developed by Mochel at Corning in 1947 (Gordon 1996) who developed a manufacturing route for ATO. ITO was prepared by Mochel in 1951 (Gordon 1996), again using spray pyrolysis. Spray pyrolysis has now been effectively superseded by alternative processes on grounds of cost and film quality. Today, commercial manufacture of TCCs is split between low grade coatings, predominantly tin oxide, deposited by CVD to produce low cost, large area coatings and Physical Vapour Deposition (PVD) for high specification materials. Current manufacturing methods for various TCCs are summarised in table 5.4. Being a vacuum method, sputter coating has limitations, hence solution based methods for fabricating TCCs have received considerable interest over recent years.

Material	**Production Method**
Ag	Evaporation
Cd_2SnO_4	RF Sputtering
In_20_3:F	CVD
In_2O_3:Sn	DC Magnetron Sputtering
SnO_2:F	CVD
Sn0:Sb	CVD/DC Magnetron Sputtering
TiN	RF Magnetron Sputtering
ZnO	RF Magnetron Sputtering
ZnO:Al	DC Magnetron Sputtering

Table 5.4 Summary of production methods in current use for common TCC materials (Bee 2000; Kester 2000; Saif, Memarian et al. 2000)

Many fabrication techniques produce an amorphous or only partially crystalline coating. To maximise the electrical properties requires a fully crystalline network, produced by a heat treatment above the glass transition temperature. For ITO the glass transition temperature is reported as 450-470°C, the crystallisation temperature being 518°C (Gallagher, Scanlan et al. 1993). Heat treatments above this temperature exhibit a time-temperature relationship in terms of the degree of crystallisation and consequently as the degree crystallinity increases, resistivity falls (Gallagher, Scanlan et al. 1993).

For device fabrication, properties such as synthesis temperature become significant. Thus ITO may be deposited and crystallized at relatively low temperatures, whilst cadmium stannate requires relatively high temperatures. The former can therefore be deposited onto plastic substrates (with a compromise in conductivity) whilst the latter cannot. Reduction of deposition temperature of any TCC without compromising properties would therefore expand its applicability.

5.5.1 CVD

CVD does not require a vacuum and can give a high deposition rate. A pyrolitic CVD process is used to produce high volume tin oxide coatings on glass for architectural applications. A ribbon of float glass is drawn under coaters immediately after pouring and a tin precursor is deposited, typically tin tetrachloride, dimethyltin dichloride or monobutyltin trichloride. The precursor is oxidized by the residual heat in the glass, achieving a minimum resistivity of $1.2\times10^{-3}\Omega$.cm at 550nm thickness (van Mol, Alcott et al. 2005). Introduction of a small percentage of fluorine may be used to form FTO. Coating is very rapid; up to 12m/minute can be coated to a thickness of several microns on a ribbon 3.25m wide (Bee 2000) . This results in a material with 77% direct transmission (83% including indirect transmission) and sheet resistance of 9-15Ω/square (Bee 2000) but is difficult to etch, so is not used in patterned anodes. Quality of film is moderate and surface finish is of the order of 0.5µm which is insufficient for some applications (Bee 2000). Low surface roughness has been achieved experimentally by using a monobutyltin trichloride precursor (van Mol, Alcott et al. 2005).

ITO can be deposited at temperatures around 400-600ºC (Kane, Schweizer et al. 1975; Maki, Komiya et al. 2003), which can soften some grades of glass substrate. Substrate temperature has been reduced to 350 ºC using acetylacetonate precursors (Ryabova, Salun et al. 1982; Maruyama and Fukui 1991) however there is still a high level of residual stress between the film and the substrate which can result in delamination.

The principal limitations of CVD are the high cost of precursors which cannot generally be recycled and the temperature required for coating deposition. Techniques requiring high temperature sintering are undesirable, since such a process is incompatible with amorphous silicon or plastic.

Structured Materials Inc have developed a patented MOCVD apparatus which is capable of putting down uniform oxide films of infinitely variable composition (Tompa 2001). Raw material cost renders this prohibitive as a manufacturing process but its ability to rapidly generate a series of samples attracts interest as a screening technique.

5.5.2 PVD

The simplest PVD technique is thermal evaporation but this is generally restricted to metals since the source must melt or sublime. The technique is carried out under high vacuum ($<10^{-6}$mbar) since this produces high vapour pressures immediately above the melting point. Deposition rate is controllable between 0.1 and 1nm/second, hence precise film thicknesses can be obtained but only thin films are viable. Evaporation is suitable for depositing films of silver, platinum and magnesium.

Sputtering is comparatively fast and high density, high conductivity films can be deposited, both of metals and semiconductors. Sputter coating of TCCs was initially developed by Holland and Siddall in 1955 (Hutson 1961) and is preferred on grounds of film quality. Power sources are either radio frequency (RF) or DC, the latter being used on large commercial deposition systems. The highest performance achieved by sputter coating is resistivity of $1.5 \times 10^{-4}\Omega$cm (McMeeking 2000).

Sputter coating is the standard commercial method for producing optical grade films on areas up to 2x3m (Kester 2000). Current state-of-the-art material is illustrated in figure 5.9. Target utilisation is typically only 30%, with a maximum of 47%. There is also a tendency for nodules of insulating material to build up on the target which then deposit on the film forming spikes. Sputtered films end therefore tend to be very smooth (approximately 4nm Ra) across the bulk of the surface, with intermittent spikes several microns high.

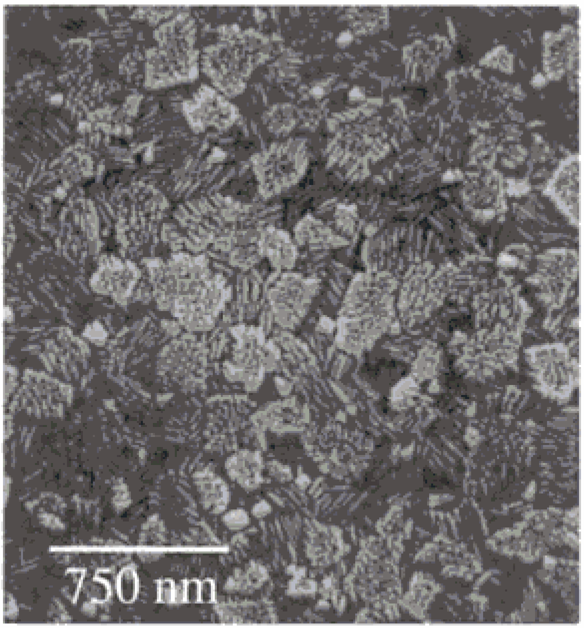

Fig.5.9 High quality crystalline ITO deposited by DC magnetron sputtering at 350°C, resistivity of $1.1 \times 10^{-4}\Omega$cm and transmissivity >90%, showing characteristic 'rice field' structure (Paine, Hyo-Young et al. 2005).

Current state-of-the-art material is deposited by companies such as Applied Films Corp (Applied Films Corporation 2008) whose previous work includes a project to develop smoother ITO using RF overlay on DC sputtering (Klöppel, Trube et al. 2000). The high energy of the impinging particles facilitates initiation of a crystalline phase at a substrate temperature of 150°C, with significant enhancement at 200°C (Olsson 2005).

Areas of recent development include the development of rotating cathode systems to increase target utilisation (Jansen 2000) and the development by Plasmaquest of a remote plasma generating system for high-rate reactive sputtering from metal alloy targets (Calnan 2007). This approach has recently led to accelerated deposition rates of up to 70nm/min at a reduced substrate temperature, making the process suitable for deposition on polymer substrates such as PET and PEN, where a resistivity of $3.8\text{x}10^{-4}\Omega\text{cm}$ and transmissivity of 90% has been achieved (Wakeham, Thwaites et al. 2009). The use of reactive sputtering also overcomes the problem of nodule formation, while the remote plasma generation approach increases target utilisation to 90%.

5.5.3 Solution coating

TCCs prepared from solution have been the subject of considerable interest for nearly 30 years (Arfsten, Kaufmann et al. 1984). This is due to the potential benefits they offer over sputter coated films. Solution processing can be carried out at atmospheric pressure and is suited to in-line processing. It also offers the potential for reel-to-reel coating and direct printing of patterned structures. Solution routes include both thermal decomposition of soluble salts and sol-gel processing to facilitate direct deposition of the oxide. The latter offers greater potential for deposition of atomically homogenous material without requiring ultra-high temperature diffusion treatment.

As detailed in Chapter 3 there are two different forms of sol-gel chemistry, based on colloidal particles and polymeric chains. The materials currently commercially available are colloidal which, relatively speaking, give large particle sizes and poor homogeneity. These do not reach the requisite performance targets for display use (Keeling and Walker 2004; Keeling and Walker 2007). Use of a polymeric route gives a higher density starting film, hence reduces sintering temperature and improves homogeneity.

The desirability of using a solution route to producing TCCs has led to many attempts to develop one. An early attempt, by Arfsten *et. al.* (Arfsten, Kaufmann et al. 1984) was based on that of Dislich and Hussman who prepared coatings of individual metal oxides (including tin and indium), and used alkoxide precursors (Dislich and Hussmann 1981). Dislich collaborated with Arfsten and specified cadmium acetylacetonate and tin *tert*-butoxide as precursors in the formation of cadmium stannate (Arfsten, Kaufmann et al. 1984). Arfsten *et. al.* also disclosed further details of fabrication routes in their patent of 1983 (Arfsten, Kaufmann et al. 1983), using treatment of the indium isopropoxide and tin *tert*-butoxide with acetylacetonate and firing dip coated films in a reducing atmosphere. The performance claimed was comparable with that of commercial sputter coated ITO, but this has not been successfully replicated by subsequent workers.

Work by Furusaki *et.al.* took an approach of direct thermal decomposition (without prior hydrolysis) rather than a sol-gel approach. The best results were achieved using indium 2-ethylhexanoate mixed with tin 2-ethylhexanoate. Good transmittance (>90%) was achieved, but with resistivity restricted to $6x10^{-3}\Omega$cm after firing at 550°C (Furusaki, Kodaira et al. 1986). They achieved improved performance by an order of magnitude to $6x10^{-4}\Omega$cm when using sulphate precursors to precipitate a colloidal suspension which was fired at 500°C in vacuum (Furusaki and Kodaira 1991). Xu *et. al.* used the same precursors but by increasing the firing temperature to 800°C were able to improve resistivity to $2x10^{-3}\Omega$cm (Xu, Shaikh et al. 1987)

Thermal decomposition was also adopted by Gallagher and Ring, in this case of acetylacetonates (Gallagher and Ring 1991) resulting in improvement in resistivity to 1.016x10^{-3}Ωcm using a firing sequence at 500°C including a reducing atmosphere. The lowest resistivity ITO films deposited from thermal decomposition were reported by Maruyama and Kojima, who reported of 2.36x10^{-5}Ωcm from decomposition of acetylacetonates at 600°C under a nitrogen atmosphere (Maruyama and Kojima 1988).

Mattox reports a true sol-gel process, based on indium and tin isopropoxides (Mattox 1991). Takahashi *et. al.* found improved performance from acetates, by the addition of ethanolamine. Using this method they were able to achieve 3.3x10^{-4}Ωcm after vacuum baking at 600°C. Without vacuum baking however, performance was limited to 2.5x10^{-3}Ωcm (Takahashi, Hayashi et al. 1992).

Other routes adopted include the oxidation of chlorides (Burgard, Goebbert et al. 1998; Scalvi, Messias et al. 1998) and the use of tin *tert*-butoxide with antimony ethoxide in the formation of ATO, the latter achieving 2.3x10^{-3}Ωcm. The use of inorganic precursors is fundamentally limiting to coating performance. The sol preparation route inherently leaves chloride ions present in the coating, thus limiting the maximum conductivity of this sol route. In order to improve conductivity, higher purity precursors are required.

The lowest resistivity values of ITO films deposited by the dip coating process are 1.7x10^{-5}Ωcm (Seki, Sawada et al. 2001) and 3.1x10^{-5}Ωcm (Bel Hadj Tahar, Ban et al. 1998).

Routes for the solution fabrication of TCCs are summarised in table 5.5, together with the performance achieved.

Material	**Precursor(s)**	**Resistivity (Ωcm)**	**Reference**
ITO	Indium isopropoxide Tin *tert*-butoxide	$5.8\text{x}10^{-4}$	(Arfsten, Kaufmann et al. 1983)
$CdSnO_4$	Cadmium acetlyacetonate Tin *tert*-butoxide (decomposition)	-	(Arfsten, Kaufmann et al. 1984)
ITO	Indium 2-ethylhexanoate Tin 2-ethylhexanoate (decomposition)	$6\text{x}10^{-3}$	(Furusaki, Kodaira et al. 1986)
ITO	Indium acetylacetonate Tin chloro-acetylacetonate (decomposition)	$1.01\text{x}10^{-3}$	(Gallagher and Ring 1991)
ITO	Indium 2-ethylhexanoate Tin 2-ethylhexanoate (decomposition)	$2.15\text{x}10^{-3}$	(Xu, Shaikh et al. 1987)
ITO	Indium isopropoxide Tin isopropoxide	$9\text{x}10^{-3}$	(Mattox 1991)
ITO	Indium acetylacetonate Tin chloro-acetylacetonate (decomposition)	$2.36\text{x}10^{-5}$	(Maruyama and Kojima 1988)
ITO	Indium sulphate Tin sulphate (colloidal precipitation)	$6\text{x}10^{-4}$	(Furusaki and Kodaira 1991)
ATO	Tin chloride Antimony chloride	$2.5\text{x}10^{-2}$	(Burgard, Goebbert et al. 1998)
ATO	Tin *tert*-butoxide Antimony ethoxide	$2.3\text{x}10^{-3}$	(Guglielmi, Menegazzo et al. 1998)
ITO	Indium isopropoxide Tin isopropoxide	25Ohms/sq	(Qiang Wei, Haixing Zheng et al. 2000)

Table 5.5 Summary of solution routes to TCCs and the performance achieved.

More recently reported work has concentrated on the production of sols from the inorganic salts, particularly the indium and tin nitrates and chlorides, dissolved in acetylacetonate and ethanol respectively (Flores-Mendoza, Castanedo-Perez et al. 2008; Kundu and Biswas 2008; Liu, Yang et al. 2008; Liu, Wu et al. 2009), although Perre *et. al.* adopted an alternative approach, with dissolution in alkaline solution to produce an aqueous route (Perre, McGiveron et al. 2000). It is speculated that these routes have been adopted since alkoxide precursors are not generally available and the work has focussed on characterisation rather than performance; consequently, high purity of precursors has not been critical.

Although a number of different raw materials and solvents have been used, they mainly follow a common methodology. This consists of dispersing the precursors into a solvent and activating a reaction between them. After the solution has been prepared it is deposited onto the substrate. This is followed by a series of heat treatments that:

- Remove volatiles by evaporation or combustion.
- Densify the coating.
- Crystallise the coating.
- Chemically reduce the coating (i.e. removal of oxygen).

These heat treatments may be combined into a single step. (Tahar, Ban et al. 1998). The spread of properties appears to be influenced more by the post-deposition heat treatment than by the starting materials. It is generally observable that lower resistivity is achieved when firing in a reducing or inert atmosphere than firing in air. This is attributable to the formation of oxygen vacancies in the lattice, equivalent to anion doping. These vacancies have been observed to have limited stability, resulting in rapid decay in performance compared with the reported figure.

5.5.3.1 Direct writing

A limited amount of previous work has considered the potential for direct writing. Wei *et. al.* were able to deposit a continuous film of ITO which could then photo-patterned in-situ via modification of isopropoxide ligands with photoactive groups such as phthalates, benzoates and ethylhexanoates (Qiang Wei, Haixing Zheng et al. 2000). Tao *et. al.* took an alternative route to curing, using a CO_2 laser (Tao, Fsaifes et al. 2009). Although their objective was to produce minimum areas of material for characterisation, the approach would be suitable for development of a direct write pattern, with removal of the uncured material.

Bessais *et. al.* attempted to screen print ITO, but the resulting material was found to be segregated indium oxide and tin oxide phases (Bessais, Ezzaouia et al. 1993; Bessais, Mliki et al. 1993). More recent work has sought to produce a porous structure for gas sensing, rather than a transparent conductor (Mbarek, Saadoun et al. 2008).

A route to gravure printing was developed within the EU-funded ROLLED project (FP6-2003-IST-2-004315). This was based on fabrication of fully crystalline ITO nanoparticles, bonded through curing of a silica matrix produced through a sol-gel route (Puetz, Heusing et al. 2005; Puetz and Aegerter 2008). This approach achieved low temperature processing, suitable for deposition on a polymer substrate with a sheet resistance of 1-3kΩ/square.

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CHAPTER 6 - PHASE 1: INITIAL DEVELOPMENT OF A TCC COATING ROUTE

6.1 Introduction

In order to develop a sol-gel coating, two aspects required consideration; the first being the sol (ceramic precursor) composition and the second the coating method. The initial phase of experimental work focussed on development of coating composition and improvements in purity and homogeneity, together with investigation of coating technique and curing regime. Two stages of experimental sol development are described.

In the first stage, initial proof-of-concept work was performed using a sol based on tin chloride and indium nitrate precursors. The sol was deposited by spin coating onto borosilicate glass substrates and subjected to a heat treatment schedule. The coating was then evaluated for crystallinity using X-ray diffraction (XRD).

The use of inorganic precursors is fundamentally limiting to coating performance. The materials are not available in a high purity form and the impurities have a deleterious effect on resistivity. The sol preparation route inherently leaves chloride ions present in the coating, thus limiting the minimum resistivity.

In the second stage, further sol development work concentrated on improving purity and homogeneity. Due to their preparation route, alkoxides are inherently higher purity and a number of alkoxide routes have been described in the literature. The route selected for this work was based on hydrolysis of *tert*-butoxides. Sols were prepared under controlled conditions and deposited by dip coating onto borosilicate glass substrates. Thermal treatment schedules were evaluated in order to optimise sintering. Coatings were evaluated for thickness, using a profilometer to determine thickness change across a step. Contact angle measurements were used to determine change points in coating structure and electrical resistance was measured qualitatively, using a multimeter.

In order to investigate coating conditions a dip-coating rig was constructed. This allowed the coating rate to be controlled by varying the withdrawal rate of the substrate from the sol, using an electric motor drive at a variable rate. Dip coating has the advantage over spin coating of using significantly less sol.

Coatings were produced to investigate withdrawal rate, drying rate, drying angle and curing regime in terms of time, temperature and atmosphere.

6.2 Materials

The substrate used during this programme was 1.1mm thick borosilicate glass, the composition of was qualitatively assessed by EDX analysis and is given in table 6.1.

Element	**Atomic %**
B	12.0
C	3.8
O	58.1
Al	4.4
Si	17.8
As	0.2
Ba	3.7

Table 6.1 Composition of glass substrate assessed by EDX analysis.

The materials used for sol preparation during this investigation are listed below:

Supplied from Sigma-Aldrich Company Ltd:

99.99% Indium(III) nitrate pentahydrate	$In(NO_3)_3.5H_2O$
99.995% Tin(IV) chloride	$SnCl_4$
99% 2,4-Pentanedione	$CH_3COCH_2COCH_3$
99.9% Indium(III) *tert*-butoxide	$[(CH_3)_3CO]_3In$
99.99% Tin(IV) *tert*-butoxide	$[(CH_3)_3CO]_4Sn$
99% 2-Methyl-2-propanol	$(CH_3)_3COH$
90% Industrial Methylated Spirit (IMS)	CH_3CH_2OH

Supplied by Fisher Scientific Ltd:

99% Acetic acid	CH_3CO_2H
99.5% 2-Propanol (IPA)	$(CH_3)_2CHOH$

The reference sample of sputtered ITO was supplied by Applied Films Corporation.

The water used throughout was de-ionised to <10ppm cation concentration.

6.3 Experimental techniques

6.3.1 Sample preparation – first stage

6.3.1.1 Sol preparation

A sol was prepared after the method of Maruyama and Kojima (Maruyama and Kojima 1988) see figure 6.1. Inorganic indium and tin sources were mixed with an organic solvent, 2-4-

pentanedione. A composition of 5at% tin oxide was selected. The indium nitrate salt was dissolved in 2-4-pentanedione, resulting in anion exchange to form the acetylacetonate. The tin salt is insoluble in 2-4-pentanedione and hence was dissolved in IMS. The resulting solution was added to the indium solution where it too reacted with the 2-4-pentanedione to form the acetylacetonate. The two solutions were, by this time, intimately mixed and underwent a degree of co-reaction.

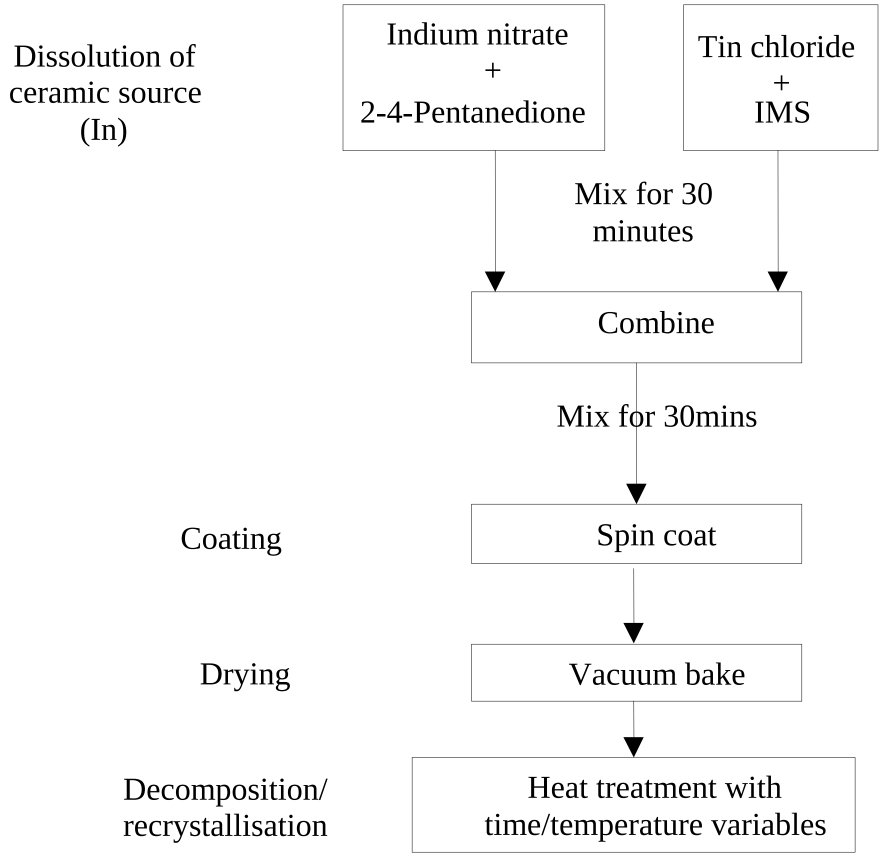


Fig.6.1 Flow diagram showing the manufacture of the inorganic sol-gel coatings.

6.3.1.2 Substrate preparation

The glass was used as supplied in 100mm squares of 1.1mm thickness. Substrates were cleaned prior to coating, using the following procedure:

- Wipe with paper using de-ionised water.
- Five minutes ultrasonic clean in 5% Decon 90 detergent solution in de-ionised water.
- Five minutes immersion in acetone with hand agitation.
- Five minutes immersion in IPA with hand agitation.
- Drip dry.
- Oxygen plasma treatment at 400W for 5mins.

6.3.1.3 Coating procedure

Samples were spin coated using a converted Eppendorf centrifuge. The substrate was fixed to the chuck using double-sided tape, applied to the reverse side. 5ml of solution were then placed on the centre of the substrate, using a spiral pattern to extend the solvent front.

A spin speed of 1000rpm was used. After coating, the substrates were removed from the chuck and transferred to an oven where they were baked at 140°C under vacuum for 16 ±0.5 hours. They were then transferred to an air furnace and fired at 450°C for 16 ±0.5 hours to sinter, followed by further treatment at 550°C for one hour.

6.3.2 Sample preparation – second stage

6.3.2.1 Sol preparation

The initial alkoxide based sol (Sol 1) was prepared using a conventional process for polymeric sols, after the method of Imai et al (Imai, Tominaga et al. 1998), given in figure 6.2. The *tert*-

butoxides were selected on grounds of availability, cost and reaction rate. Sol preparation, consistency and coatability are summarized in table 6.2.

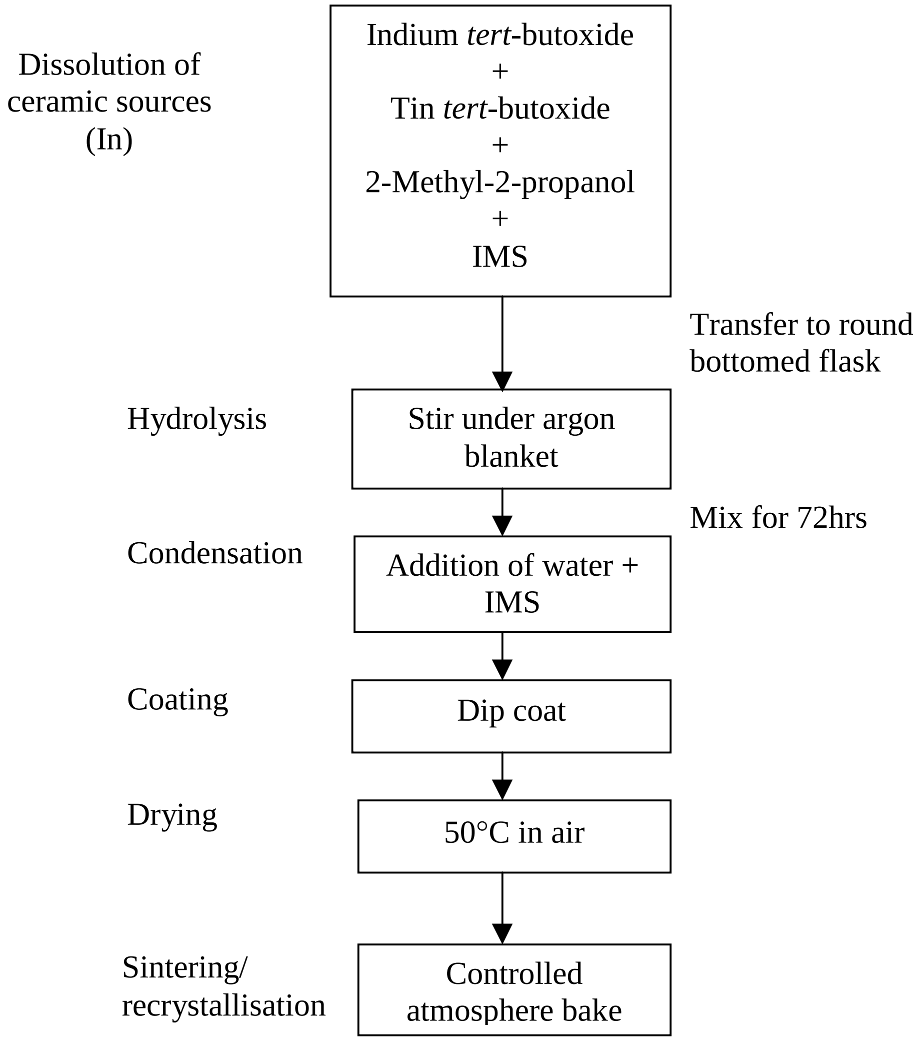


Fig.6.2 Flow diagram showing the manufacture of alkoxide-based sols.

Indium and tin sources were mixed with an alcohol solvent, selected to be isostructural with the alkoxide ligand. A highly controlled amount of water was added to initiate hydrolysis, determined by the volume of IMS added at a constant boiling composition of 5% water. The precursors were mixed in the presence of limited water in order to promote single ligand exchange prior to reaction with an adjacent molecule, promoting linear chain formation rather than three dimensional network growth. Use of dry solvents and an argon blanket restricted water availability throughout the hydrolysis phase.

Additional water was then added to exchange the remaining organic ligands, relying on steric effects to prevent network formation. A gelatinous precipitate formed, indicating that the sol reaction had not gone to completion with the available water. The inhomogeneity of this composition rendered it non-ideal for producing a uniform coating.

The sol was then stored in a sealed container until required for coating.

6.3.2.2 Sol modifications

In order to improve sol homogeneity, a second batch of sol was prepared, as above but with variations in the method of water addition to improve homogeneity. The sol was separated into two batches after initial hydrolysis. The untreated half was allowed to stand, gradually separating into two distinct liquid phases, which were separated. The supernatant liquid was removed, leaving a high viscosity sol (Sol 2).

To the remaining half (Sol 3), addition was made of glacial acetic acid, followed by vigorous shaking. Acetic acid reacts with the alcohol, forming an ester and water. Thus a highly controlled water addition can be made with minimal concentration gradients across the sol, improving homogeneity. This solution was stirred for a further hour to prevent concentration gradients from forming. In practice, a precipitate formed rapidly, indicating inhomogeneity in the sol.

The two sols were then stored in sealed containers until required for coating. Sol fabrication routes for Sols 1-3 are summarised in table 6.2.

Coating	**Preparation route**	**Final hydrolysis step**	**Appearance of sol**	**Coating**	**Comments**
Sol 1	Tert-butoxide hydrolysis under argon	Further addition of water	Segregation of low and high viscosity phases - inhomogeneous	Discontinuous ITO. Too thin and patchy to see by eye	Suitable for development as coating
Sol 2	Tert-butoxide hydrolysis under argon	Atmospheric water adsorption	Separated from supernatant liquid	Continuous, powdery yellow coating. In_2O_3	Further work required to improve homogeneity
Sol 3		Esterification through addition of acetic acid	Segregation of low and high viscosity phases - inhomogeneous	None	Not suitable for further development

Table 6.2 Summary of sol development in phase 1, stage 2.

6.3.2.3 Substrate preparation

In the second stage of the work, substrates were cut down to 25mm square using a diamond scribe. The cleaning procedure was varied to include ultrasonic cleaning, using a range of solvents to remove non-polar, polar and inorganic contaminants:

- 15mins ultrasonic clean in acetone.
- 15mins ultrasonic clean in ethanol.
- 15mins ultrasonic clean in HCl.
- Rinse in de-ionised water.
- Dry with filtered, compressed air.

Where thickness measurements were to be recorded, a strip of ‘flashbreaker’ tape was placed across one side of the substrate in order to leave an uncoated region.

6.3.2.4 Coating procedure

In the second stage, samples were dip coated rather than spin coated in order to minimise loss of sol. Each of the sols was vigorously shaken prior to coating in order to redisperse any agglomerated material.

A simple automated dip coating apparatus was constructed, using a small electric motor to control withdrawal speed between 1 and 47mm/min. Samples were held with tweezers and immersed in the sol, then withdrawn at a rate of approximately 8mm/s, a speed known from previous work to produce a coating thickness of approximately 150nm. The samples were dried in air at 50°C for two minutes and if necessary the tape removed before transfer to a furnace. Sintering was performed in air at temperatures ranging from 300 to 600°C for between 1 and 24 hours, selected to span the sintering, glass transition and crystallisation temperatures in order to evaluate coating evolution. Additional samples were fired at 600°C in nitrogen and vacuum atmospheres.

6.4 Evaluation of coating performance

6.4.1 Crystallinity

Determination of crystalline state and the phases present was performed by X-Ray Diffraction (XRD) using a Philips X-ray diffractometer. A spectrum was collected from the coating surface using K_α radiation with a Cu anode. Samples were scanned over a 2θ range from 10° to 80°. Fitting of spectrum peaks using a Philips PA XRD (v3.2) software database identified crystalline phases.

6.4.2 Thickness

Coating thickness was measured using the step between coated and uncoated regions (where the tape had been applied during coating). Measurements were taken using a Surfcom 130A profilometer. By this method a stylus is placed on the surface of the substrate, the arm being levelled such that a reproducible load is applied. The stylus is then drawn across the surface of the substrate at the selected rate and deviation in surface height is recorded. Profile length was 10mm, approximately 5mm each side of the step, with a scan speed of 0.3mm/s. The tape creates a barrier, causing build-up of coating at its edge, so care was taken to measure from the plateau region. The thickness was calculated as a subtractive distance between lines projected on the 65% peak value either side of the step.

6.4.3 Contact angle

In order to obtain information from fragile coatings, contact angle data can be used as a rapid and quantitative measure of transitions in coating phase and structure with sintering time, temperature and atmosphere. Different surface energies produce a different contact angle with a given solvent, providing a measure of wettability of the surface, hence decreased contact angle corresponds to increased wettability. Change in contact angle is associated with changes in surface state, such as altered surface composition or morphology. A shift in contact angle can therefore be correlated to a transition in coating state such as crystallisation.

Samples were fired in air at temperatures ranging from 300 to 600°C for between 1 and 18 hours and inspected for trend data in contact angle.

Samples were baked in air at 120°C for one hour immediately prior to contact angle measurement in order to ensure a clean, bare surface. They were then allowed to cool and placed in the path of a horizontally mounted optical microscope. A water droplet was placed on the surface, using a Pasteur pipette to maintain constant volume. The sessile drop was photographed and the contact angle with the substrate measured using a protractor. In order to compensate for angular variation, the angle on each side was measured and an average taken.

Contact angles were also recorded for reference samples of uncoated glass and a commercial ITO sample.

6.4.4 Qualitative resistance

Following heat treatment the resistance of each sample was measured using a multimeter. Two-point contact was used across a distance of approximately 5mm and the data compared with values obtained from an ITO reference sample.

6.4.5 Scanning electron microscopy

Scanning electron microscopy (SEM) was performed on coated substrates without sectioning. For insulating materials a gold layer was sputter-coated to prevent charging. For conducting materials, no sputtered film was required. Examination was performed using a CamScan CS44, equipped with a backscattered detector for compositional contrast and facilities for energy dispersive X-ray analysis (EDX).

6.4.6 Atomic force microscopy

Atomic force microscopy (AFM, DI Multimode Nanoscope III) was used to determine surface roughness. The AFM is similar in function to a profilometer, having a small, sharp stylus which is moved across the substrate surface. The stylus is attached to a cantilever which changes in angle with change in vertical position of the tip. A reflected laser can then be used to determine change in tip position optically. The stylus can be accurately placed in the substrate plane such that multiple adjacent passes can be used to build up a ‘map’.

6.5 Results

6.5.1 Initial experiments –inorganic precursors

After vacuum baking, a white coating was observable on the substrate surface. Sintering produced a colour change, the coating becoming yellow, a similar colour to commercial ITO.

The coating did not sinter continuously but became powdery. This meant that coating thickness could not be measured, since the force with which the stylus contacted the substrate was sufficient to scrape the coating off. Further treatment at 550°C for one hour produced no change in crystallinity, as measured by XRD and no change in consistency of the coating.

Since the coating was powdery and therefore discontinuous, no conductivity was measured. XRD analysis showed a partially crystalline ITO diffraction pattern (see figure 6.3).

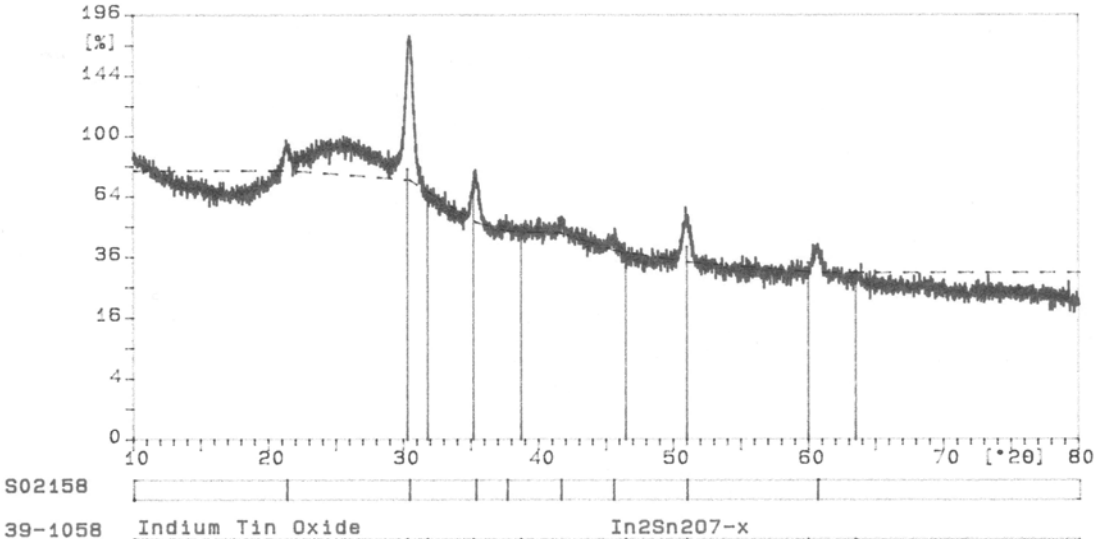


Fig.6.3 XRD pattern for ITO prepared from inorganic precursors after heat treatment at 550°C.

6.5.2 Further development of sols

Sol 1 produced a thin, discontinuous coating. Sol 2 produced a yellow, powdery coating, similar to that produced by the first sol batch. Sol 3 did not produce a coating that was discernible under visual or optical microscope inspection.

The procedure followed was unsuccessful in producing a TCC after significant iterations, with no conductivity observed in any sample. A reference sample of commercial ITO showed a resistance of 18Ω in a similar test procedure.

Coating thickness was measured across the step height. For Sol 1 a coating thickness of 20-60nm was observed. For Sol 2 a coating thickness of 80-100nm was observed. For Sol 3 no coating was observed. The coating surface was rough, consistent with the powdery nature of the sintered product. No definable trend was identified in coating thickness with regard to firing temperature or time.

Reference contact angles for sessile water drops were recorded for the borosilicate glass at 49° and for a commercial ITO sample at 75°. Firing in air, Sol 1 showed a decrease from 59° to 28° with increase in firing temperature from 300-550°C. Sol 2 showed an increase from 37° to 75° on increasing firing temperature from 300-550°C.

Samples produced with Sol 1 and Sol 2 were inspected under SEM. Samples prepared using Sol 1 showed a discontinuous coating, in the form of residual droplets of wetted area. These were microcracked, demonstrating excessive residual stress in the drying stages. EDX analysis demonstrated an ITO composition. Samples prepared using Sol 2 showed a continuously wetted surface but with extensive microcracking. EDX analysis showed an indium oxide composition without tin doping present.

The sol development phase was therefore partially successful, generating a method for producing a high purity sol which deposited as ITO, but not a sufficiently continuous coating to show conductivity.

6.5.3 Further development of coating procedure

It was found that a dipping speed above 10mm/min produced a continuous coating without microcracking of the surface, with a speed of 47mm/min (0.17mm/s) being preferable, cf. 8mm/s for hand withdrawal.

A 6 hour firing cycle resulted in microcracking of the coating. Increasing the firing time to 12 hours minimised cracking, whilst increasing the firing time above 12 hours produced no further change.

EDX analysis showed a tin oxide content of between 2.2 and 3.5at%, compared with 6at% in the commercial sample. Since the input ratio was 5at%, it is reasonable to surmise inhomogeneity in the sol. This is likely to arise from the different rates of hydrolysis of the indium and tin precursors, resulting in some agglomeration of the tin species within the sol. This is supported by the relative instability of the tin chloride compared with the indium nitrate, which has water of crystallisation present in the structure.

Film thickness was measured across a step in the coating using a profilometer. The coating was measured at 70nm for the nitrogen-sintered sample and 115nm for the air-sintered sample, compared with the commercial sample at 170nm.

Surface roughness was measured by Atomic Force Microscopy. R_a values for the surface roughness lie at 6nm for the air sintered sample, 3.5nm for the commercial sample and 2.5nm for the nitrogen sintered sample.

Resistivity was measured by 4-point probe. The commercial sample of ITO showed a resistivity of $2.18 \times 10^{-4}\Omega$cm, the air sintered sample $6.86 \times 10^{-2}\Omega$cm and the nitrogen sintered sample $1.47 \times 10^{-2}\Omega$cm.

Transparency was measured by placing the samples between a red diode laser and a photodetector. A voltage measurement was recorded relative to a borosilicate substrate. It is assumed that the voltage response with intensity is linear. The air sintered sample showed 94% transparency while the nitrogen sintered sample showed 98% transparency. The commercial sample could not be tested since a reference substrate was not available, however the quoted value is 95% transparency.

SEM examination of the nitrogen sintered sample showed the surface to be highly uniform with good surface finish (see figure 6.4). The commercial reference sample showed a continuous, uniform film with a low density of large surface anomalies. High magnification (x8500) revealed a platelet structure to the surface, as shown in figure 6.5.

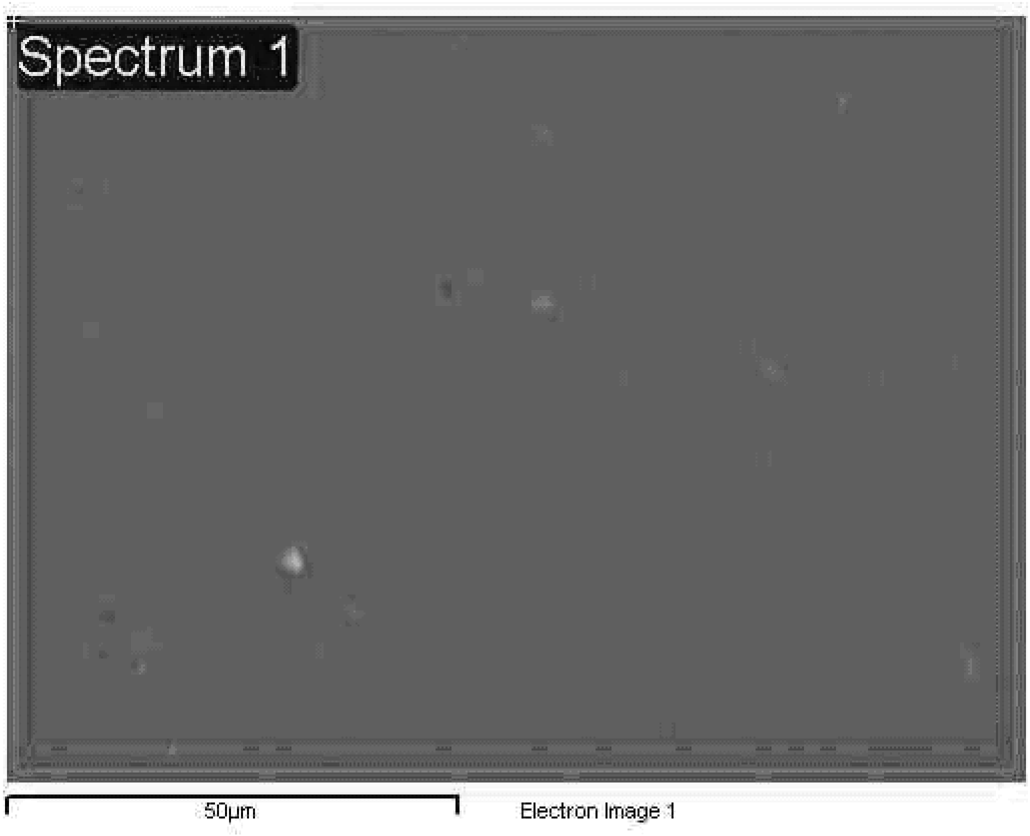


Fig.6.4 ITO prepared by sol-gel coating (scale shows nominal magnification). With the exception of dirt particles the surface is featureless, indicating a smooth, continuous, defect-free coating as required in an ideal coating.

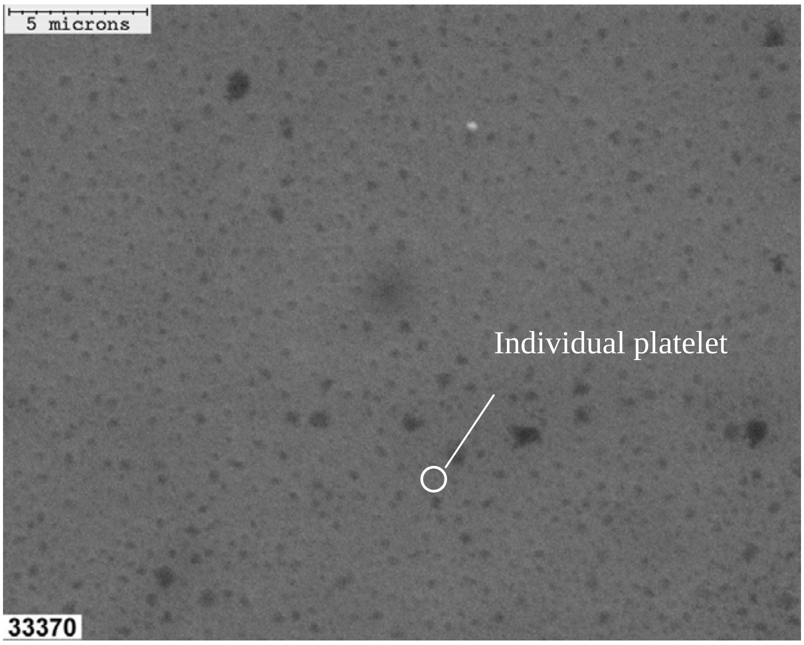


Fig.6.5 SEM micrograph of commercial ITO (scale shows nominal magnification). Dark spots are the centres of individual platelets.

The surface morphology was also examined at higher magnification, comparing commercial sputter coated ITO with the sol-gel derived film, shown in figures 6.6 and 6.7.

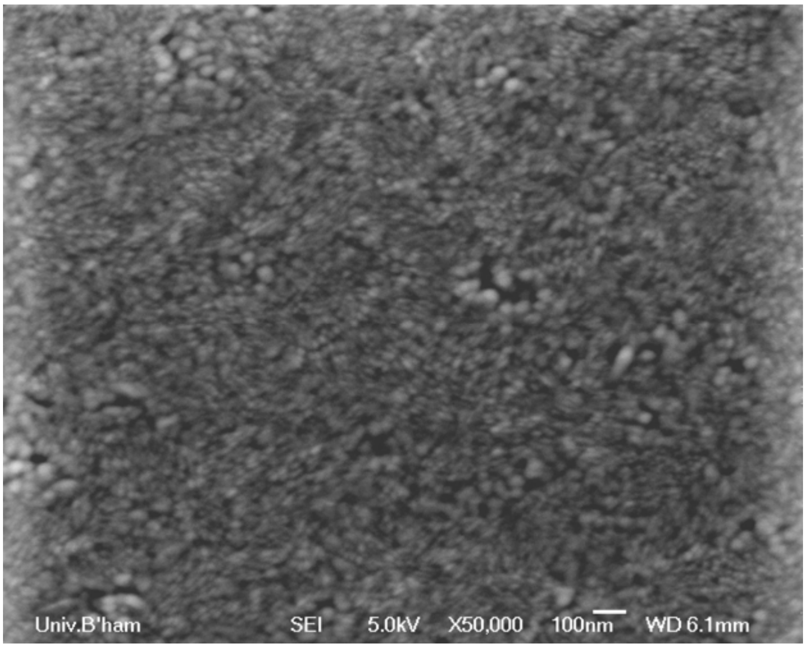


Fig.6.6 SEM secondary electron micrograph of commercial film made by magnetron sputtering, showing grain size.

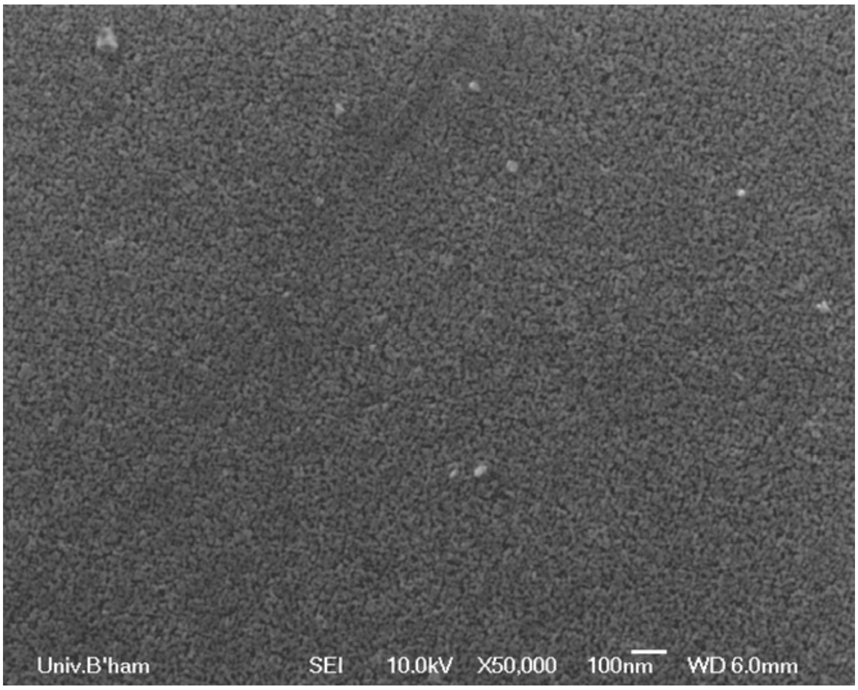


Fig.6.7 SEM secondary electron micrograph of sol-gel derived film, showing grain size.

The surface morphology shows the surface of the sol-gel derived film to be composed predominantly of grains approximately 10nm in diameter, approximately half the size of those in the commercial film.

Coating development work was therefore successful in producing a transparent conductive coating, with the best results obtained at the highest withdrawal rate possible with the equipment available.

6.6 Summary of performance achieved at the end of Phase 1

From the initial study it was apparent that an ITO sol-gel coating could be produced on glass, using inorganic precursors. The coating method did not produce a continuous sintered coating and therefore no conductivity was observed.

Further development produced a sol with high purity, capable of depositing an ITO material. The sol fabrication route did not produce a homogenous sol and the coating was discontinuous but the method showed potential for production of a high quality coating.

Using a dip coating rig a TCC was produced with transparency of 98% and resistivity of $1.5 \times 10^{-2} \Omega$cm. The resistivity measured was approximately two orders of magnitude above the commercial sample. There were a number of possible reasons for this result. The coating thickness was below the threshold required to overcome grain boundary effects, the composition ratio was not ideal and the precursors were known to contain impurities that have an adverse effect on resistivity.

References

Imai, H., A. Tominaga, et al. (1998). "Ultra violet laser induced crystallization of sol-gel derived indium oxide films." Journal of Sol-Gel Science and Technology **13**(1-3): 991-994.

Maruyama, T. and A. Kojima (1988). "Indium-Tin Oxide Thin Films Prepared by Thermal Decomposition of Metallic Complex Salts." Japanese Journal of Applied Physics **27**(10): L1829 - L1831.

CHAPTER 7 - PHASE 2: APPROACH TO FURTHER DEVELOPMENT OF A PRINTABLE TCC

7.1 Project structure

As described in Chapter 5, the second phase of development was conducted in collaboration with partners. The work performed within this EngD included the design and management of the overall work programme. The practical work corresponded to the partnership structure in the form of a supply chain, with materials passing down the chain in successive developmental steps, summarised as follows:

- Material selection
- Preparation of precursors
- Hydrolyis/sol-gel processing
- Ink preparation
- Printing
- Testing & analysis

The approach is described below, in overall summary and in detail for each work package in turn. It should be noted that the work of each partner was conducted primarily ‘in-house’ and a summary provided to the project team via quarterly meetings. This work was necessarily interrelated with the aspects presented in this thesis, but not expressly performed for it, the detail remaining confidential to the partner concerned. Consequently, full detail for the work of other partners is not necessarily given. It is provided in summary to provide a context for the work conducted at TWI and is discussed in subsequent chapters in relation to the results obtained and their implications for the overall project.

7.2 Summary of approach

The approach is summarised below:

Step 1

- Pulsed Laser Deposition (PLD) for rapid material screening
- Characterise films by AFM, 4-point probe and 440nm transmission
- Select material type

Step 2

- Alkoxide-type sol route selected to obtain atomic level homogeneity
- Produce sol precursors with correct rate of reaction
- Match reaction rates for multiple component systems

Step 3

- Produce uniform sol by hydrolysis, using controlled water additions
- Dry to produce homogeneous powder with suitable characteristics

Step 4

- Formulate as Ink
- Requires control of rheology
- Uniform dispersion by milling
- Loading determines film thickness for given screen properties (interrelated)

Step 5

- Test pattern developed
- Print patterned layer

Step 6

- TGA/DSC to determine decomposition temperature and T_g
- High temperature XRD to determine T_c
- Characterize powder properties by SEM and particle size measurement
- Fire in furnace
    - Burn out binder
    - Re-flow glass above T_g
    - Heat above T_c to crystallise

The relationships between these activities are illustrated in figure 7.1.

7.3 Project structure

The work described in steps 1-6 was conducted through a series of work packages (WPs), detailed below. Chapters 8-10 consider the work performed in WPs 1-3 respectively. The work performed in WP 4 supported these work packages and is therefore reported within the appropriate chapter. WPs 5 and 6 were not part of the technical development. Their content is summarised below to illustrate the project structure but they are not then considered further.

An additional work package provided project management. The project was co-ordinated by TWI, which has extensive experience in managing large joint industry projects. The author was appointed as the Project Manager, responsible for all day-to-day management issues and liaison with the DTI via the nominated Project Officer. The project was monitored and controlled through the use of MS Project software tools and critical path analysis.

A Project Steering Committee, comprising a senior representative from each partner organisation and chaired by the Project Manager, was responsible for overall management and issues such as monitoring overall technical progress.

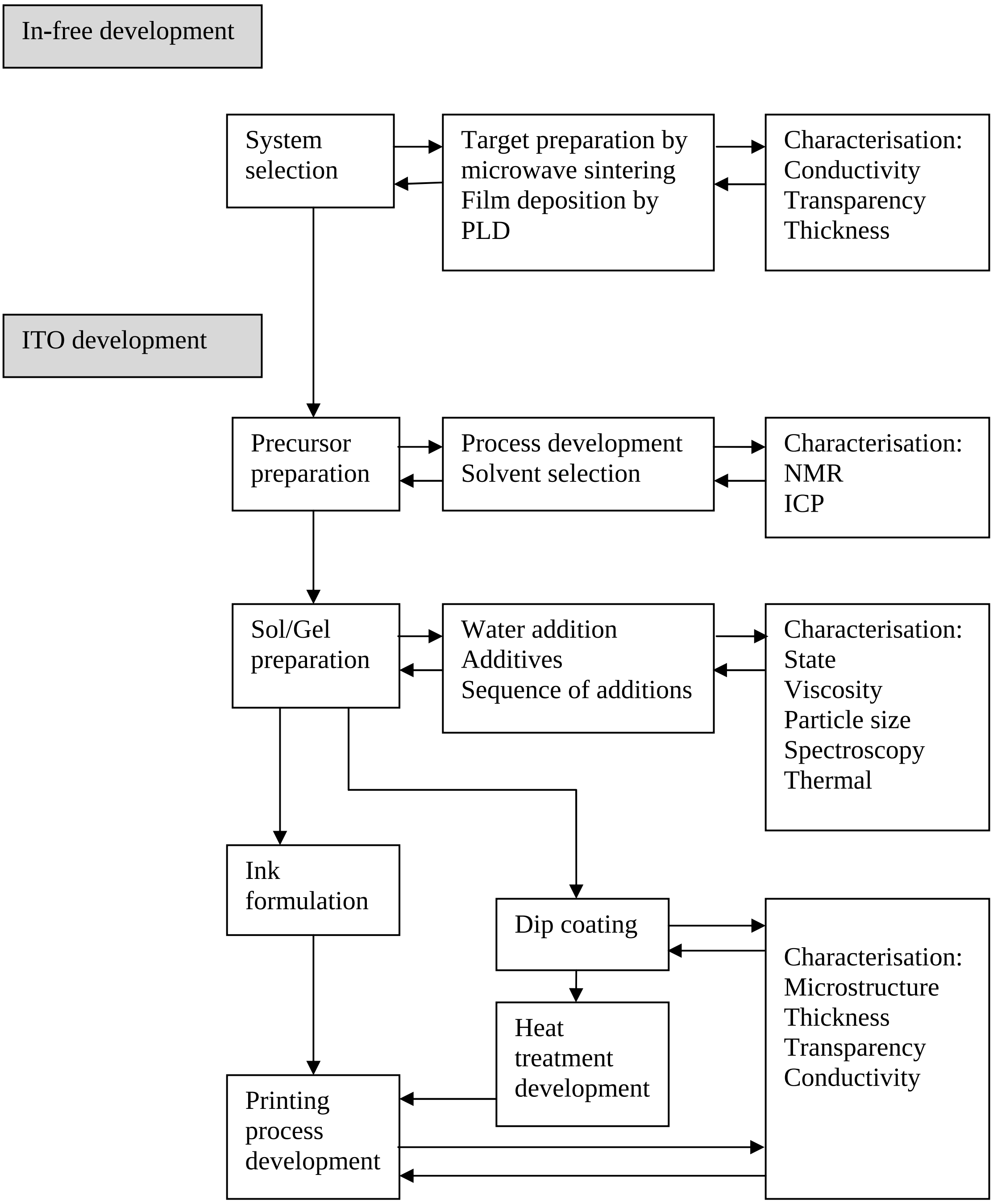


Fig.7.1 Schematic representation of the relationship between activities within the collaborative project.

7.3.1 WP1 - Development of solution derived ITO anode materials

Partners: **TWI**, Epichem, The University of Birmingham

Start: Month 1 Duration: 12 months

This task surveyed potential precursor materials, to select those most suitable for the programme. Precursor materials (indium and tin) took the form of alkoxides, both simple, functional or containing donor ligands. For example, it was known that ethyl hexanoates form suitable precursors for ceria formation (Morlens, Ortega et al. 2003) with the potential to prove analogous for indium and tin. The precursors were converted to a sol in order to form an ITO coating. Dip coated samples were required in order to screen material properties.

Within this project, coating was onto glass substrates, specifically Corning 1737F glass. This grade was selected for two specific properties. Firstly, as a borosilicate glass, this offered the facility for higher processing temperature than a soda-lime glass. Secondly, since surface tin oxide formation from the molten tin bath used in float glass may interact with the dopant tin within ITO, fusion glass was preferred. Corning 1737F is also a standard grade in the display industry and therefore known to be compatible with relevant end markets.

Thin (~150nm) films were deposited, heat treated and fed to WP4 for measurement of physical properties. This iterative loop was followed to optimise the synthesis regime with respect to film properties.

This task also included surface preparation of substrates in order to obtain a suitable surface energy for uniform deposition. Consideration was given to a firing schedule for the deposited film, since an annealing step is required to cross link the sol and form the functional ceramic. The project sought to optimise the time/temperature profile and atmosphere.

Target film properties are specified in the objectives for this project. The technical activities are summarised in table 7.1.

Task	Description of activity	Partners involved
1	Develop an ITO dip coating. Examine the effect of process on electrical, optical and crystallographic characteristics (WP4).	TWI BU
2	Identify optimum curing regime.	TWI/BU
3	Optimise sol-gel precursor route.	Epichem
4	Develop route to printable ITO ink.	TWI

Table 7.1 Technical activity breakdown for work package 1.

7.3.1.1 Deliverables

Dip coated ITO samples	(TWI)
Sol-gel precursors	(Epichem)
100ml ink batch	(TWI)

7.3.2 WP2 –Development of indium-free anode films

Partners: **TWI**, Epichem, Oxford University, Birmingham University

Start: Month 3 Duration: 15 months

Building on knowledge gained in WP1 and WP4, a range of novel transparent conducting materials was assessed. Using a structured approach, the range of families of conducting oxides (including for example tin, antimony, zinc) was reviewed. Physical parameters were considered, including electrical conductivity and optical transmissivity, together with material cost and hazard, both in processing and end use.

The search for new transparent conductors is concentrated in far and post transition metal systems, such as zinc, indium and tin. For example, the non-stoichiometric zinc oxide system, ZnO_{1-x}, is known to be transparent to visible light, but lacks sufficient carrier species for high conductivity. Suitable starting systems were to be investigated, both as a thin film and in bulk, through a series of doping and processing experiments.

The criteria for a material displaying transparent metallic properties are understood (as described in Chapter 5) and may be relatively easily modelled. Through the use of band structure calculations, a prediction was made of materials with the appropriate electronic properties and efforts then made to synthesize these materials.

Materials were prepared as bulk samples by rapid solid state synthesis and assessed for potential as described below in WP4, primarily through conductivity measurement. Films were deposited from promising candidates by PLD and these were assessed for transparency and conductivity.

The most promising candidates were selected to prepare by a sol-gel route and developed following a similar strategy to that adopted for WP1.

Target film properties are specified in the objectives for this project. The technical activities are summarised in table 7.2.

Task	Description of activity	Partners involved
1	Identification of potential indium-free transparent conductive coating (TCC) compositions.	OU
2	Rapid synthesis of bulk materials	OU
3	PLD of promising candidates	BU
4	Develop sol-gel precursors	Epichem
5	Develop sol-gel route	TWI
6	Identify optimum curing regime.	TWI/BU
7	Prepare ink.	TWI
8	Technology transfer of ink fabrication route.	TWI
9	Modelling of TCC properties	OU

Table 7.2 Technical activity breakdown for work package 2.

7.3.2.1 Deliverables

Sol-gel precursors	(Epichem)
Dip coated indium free samples	(TWI)
100ml ink batch	(TWI)
TCC model	(OU)

7.3.3 WP3 – Deposition of anode materials

Partners: **DEK**, TWI, GEM, MCE

Start: Month 3 Duration: 20 months

A platform for screen printing of TCC films from solution was developed. Building on DEK's existing expertise in screen printing, the system was modified to improve coating uniformity and electrical properties. The task considered screen characteristics and machine settings required to achieve 100% pattern reproduction and explore the dimensional limits of pitch and track width. The task also considered screen material requirements in order to maintain high purity deposition and characterise screen life.

A parallel activity was development a suitable ink. This required specification of properties suitable for screen printing, together with limited characterisation of the relationship between ink rheology and film performance. This task also included assessment of ink stability, storage and life. This activity was closely linked with WP4 and partner overlap in both work packages ensured compatibility between the material developed for dip coating and its transfer to a printing ink.

Target film properties are specified in the Aims and Objectives for this project. The technical activities are summarised in table 7.3.

Task	Description of activity	Partners involved
1	Specification of printable ink.	DEK
2	Production of model ink	TWI/GEM
3	Establish minimum reproducible feature size by varying printer settings	DEK
4	Prepare test specimens for end-user partners.	DEK
5	Evaluate printed specimens.	MCE
6	Prepare samples for WP1 and WP2.	DEK

Table 7.3 Technical activity breakdown for work package 3.

7.3.3.1 Deliverables

Ink specification	(DEK)
Ink	(TWI/GEM)
Printed ITO samples	(DEK/TWI)
Printed indium free samples	(DEK/TWI)
Test specification	(MCE)
Printable anode systems demonstrator	(DEK)

7.3.4 WP4 – Evaluation of anode materials

Partners: **The University of Birmingham**, Oxford University, MCE

Start: Month 3 Duration: 18 months

Three discrete levels of assessment were performed.

Initial screening comprised a series of basic tests to select candidate materials based on bulk properties. This primarily applied to the indium free materials produced in WP2. Tests included phase analysis by XRD, chemical composition by SEM-EDX, and comparative conductivity measurement in the bulk state. PLD thin films of selected materials (see WP2) were measured for promising transmissivity/resistivity ratios.

Second level selection was based on dip coated samples on glass. These were examined using Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) to determine morphology and by X-Ray Diffraction (XRD) to determine crystalline phase and crystallite dimensions. Films were evaluated for electrical performance by 4-point probe and for optical transmissivity of film/substrate combinations.

Third level analysis was carried out on printed films in order to assess the effect of the printing process on material performance. Similar methods were applied to those in stage two. Interaction with WP5 produced electrically connected tracks, designed to allow continuity and separation testing for assessment of track geometry limitations.

The results of this work package were fed back into WP1 and WP2 to facilitate iterative improvement. The technical activities are summarised in table 7.4.

Task	**Description of activity**	**Partners involved**
1	Characterisation of commercially sputtered ITO materials	BU
2	Characterisation of dip coated ITO films (WP1)	BU
3	Characterisation of printed ITO anode (WP1)	BU
4	Characterisation of bulk indium free material (WP2)	BU
5	Characterisation of PLD indium free films (WP2)	BU
6	Characterisation of dip coated indium free films (WP2)	BU
7	Characterisation of printed indium free anode (WP2)	BU
8	Electrical testing of connected printed patterns	MCE

Table 7.4 Technical activity breakdown for work package 4.

7.3.4.1 Deliverables

Data set for anode materials: (BU)

- Sputtered ITO
- Dip coated ITO
- Printed ITO
- Dip coated indium free
- Printed indium free

7.3.5 WP5 – Interconnect development

Partners: **MCE**

Start: Month 12 Duration 6 months

To enable rugged device fabrication with novel anodes, it was proposed to assess interconnect requirements, particularly the attachment of busbars, flexible interconnect and direct chip-on-glass architecture. Using samples produced within WP3, trials were proposed to assess the feasibility of making electrical connections to the film materials, using representative solders or adhesives. The electrical, mechanical and optical performance of the materials and connections were to be evaluated in the as-bonded condition and after environmental exposure.

The work was proposed in two stages; the first stage to assess connection to unpatterned 25x50mm films and the second on final parts at 250x200mm.

The proposed technical activities are summarised in table 7.5.

Task	Description of activity	Partners involved
1	Development of interconnect to printed TCC anode.	MCE
2	Development of interconnect to patterned TCC anode.	MCE

Table 7.5 Technical activity breakdown for work package 5.

7.3.5.1 Deliverables

Interconnected, plain ITO devices	(MCE)
Interconnected, plain indium free devices	(MCE)
Interconnected, patterned ITO devices	(MCE)
Interconnected, patterned indium free devices	(MCE)
Interconnect specification	(MCE)

7.3.6 WP6 – Demonstrators

Partners: **TWI**, MCE, DEK

Start: Month 18 Duration: 6 months

It was proposed to use anode materials produced in WP1 and WP2 and interconnect technology defined in WP5 to prepare a heater assembly and interconnected display anodes; the devices to be connected to drivers to show proof of concept and yield working demonstrator models.

The final demonstrator deliverables proposed were an unpatterned, 10.4" diagonal sheet and an interconnected anode pattern as used for a 96x64, 100micron pitch display. The proposed technical activities are summarised in table 7.6.

Task	**Description of activity**	**Partners involved**
1	Prepare device using printed patterned anode (ITO and indium free).	MCE
2	Connect to external driver devices prepared in WP6.	MCE

Table 7.6 Technical activity breakdown for work package 6.

7.3.6.1 Deliverables

Externally connected unpatterned, 10.4" diagonal sheet	(TWI)
Interconnected anode pattern as used for a 96x64, 100micron pitch display	(TWI)

7.3.7 Deliverables and milestones

The specific deliverables proposed for development within the programme are shown in table 7.7.

Deliverable	**Within work package**	**Due date (month)**
The development of a solution based ITO coating	WP1	12
Development of an indium-free alternative to ITO	WP2	15
Screen printable TCO inks.	WP3	12 & 15
A systems demonstrator, consisting of a platform capable of screen printing TCCs.	WP3	18
Development and evaluation of interconnects to the printed/patterned anode.	WP5	18
Characterisation data for printed anode materials and comparison with commercially available TCCs.	WP4	21
Unpatterned 10.4" diagonal demonstrator	WP6	21
Patterned 96x64 anode type demonstrator	WP6	21
Final Report	WP7	30

Table 7.7 Summary of deliverables outputs from each work package within the project.

Each of the deliverables given in table 7.7 is the primary output of a specific work package. The primary milestones within the programme are given in table 7.8.

Work Package	**Milestone**	**Due date (month)**
WP1	Technical transfer of ink route to formulator	10
WP2	Specify ink requirements Establish printed feature sizes	3 7
WP4	Technical transfer of ink route	18
WP5	Interconnect demonstrated to display types	21
WP7	Quarterly review meetings	3,6,9,12,15,18,21, 24,27,30

Table 7.8 Primary milestones within the project.

The relationship between the work packages and their deliverables is illustrated in the GANTT chart shown in figure 7.2.

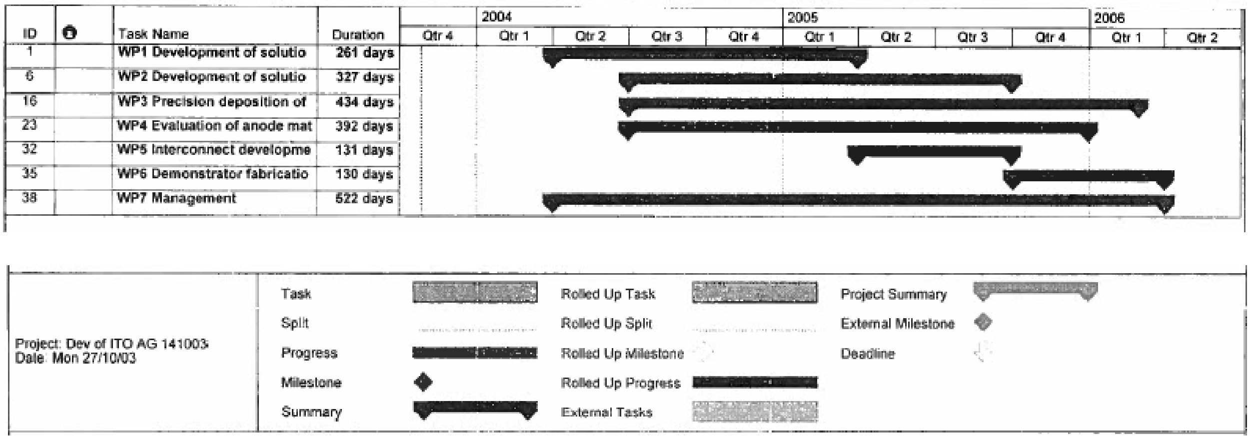


Fig.7.2 GANTT chart showing the timeline and relationships between work packages.

Reference

Morlens, S., L. Ortega, et al. (2003). "Use of cerium ethylhexanoate solutions for preparation of CeO_2 buffer layers by spin coating." Materials Science and Engineering B **104**(3): 185 - 191.

CHAPTER 8 - WP1: DEVELOPMENT OF SOLUTION DERIVED ITO ANODE MATERIALS

8.1 Overview

The precursor materials as made are essentially an inorganic ionic solution. In order to produce an oxide film via a sol-gel route it is necessary to first hydrolyse the precursor in a controlled fashion, resulting in a sol. In this project, the alkoxide sol-gel route was adopted, producing a metastable solvent-borne oxide/hydroxide structure which may be likened to an organic polymer. Further alteration of conditions of concentration or pH cause the sol to gel, forming a network structure.

To prepare an ITO coating, two sets of precursors (one for indium and one for tin) had to be handled simultaneously. In order to achieve good final conductivity it is necessary for the dopant to be uniformly distributed within the matrix. The initial challenge in formulating an ITO sol is that tin and indium precursors with similar ligands have different rates of reaction. The objective in forming a suitable sol is to form In-O-Sn bonds, rather than agglomerate In-O-In and Sn-O-Sn. To this end, the reaction was required to proceed at an approximately uniform rate. Approaches to achieving this result included the selection of different alkoxides for the indium and the tin precursors, the use of precursors with a lower rate of reaction, since the proportionate difference in rate of reaction was then reduced, and the use of low concentrations of water. The range of available reaction rates was first semi-quantitatively assessed in the precursors received from Epichem, providing feedback to facilitate iterative development of subsequent precursor compounds.

Within this work package, potential precursor materials were surveyed and the most suitable were selected. A route was developed for converting precursor materials (indium and tin) to a sol in order to form an ITO coating. Dip coated samples were prepared in order to screen material properties. Films were deposited onto glass plaques and heat treated to characterise physical properties. This iterative loop was repeated in order to optimise the synthesis with respect to film properties.

This work package also considered the supporting activities in producing an optimised film. These included surface preparation of substrates and a firing schedule for the deposited film. Within this project, firing was limited to furnace treatment, which was suitable for the glass substrate. The project sought to optimise the time/temperature profile and atmosphere.

8.2 Preparation of precursors – Epichem

A range of precursors was identified and prepared. Having established that high purity was a requirement for good performance, routes were developed to ensure the removal of inorganic contaminants; hydrocarbons being benign with respect to TCC performance, since they would decompose in subsequent firing. Inductively coupled plasma (ICP) analysis was used to establish purity, with reference to known standards for potential contaminant elements.

8.2.1 First iteration

Following the work undertaken in Phase 1, the initial precursors prepared for benchmarking were the *tert*-butoxides and isopropoxides. Epichem initially prepared co-dissolved solutions of indium and tin *tert*-butoxide and indium and tin isopropoxide. Due to the chemistry involved, only relatively low yields were achieved. The later stage of the project to prepare alternative sources was therefore accelerated.

8.2.2 Second iteration

A second series of materials was produced with different groups. These included dimethyl indium acetylacetonate/dimethyl tin diacetate in toluene/THF, dimethyl indium acetylacetonate/dimethyl tin diacetate in toluene, trimethyl indium tetraglyme adduct/tin *tert*-

butoxide in toluene and dimethyl indium acetylacetonate/tin *tert*-butoxide in toluene. The former two were dispatched to TWI.

ICP analysis showed extremely high purity, the residual contaminants being hydrocarbons.

8.2.3 Third iteration

Following assessment of precursors by TWI it was found that a mixed toluene/THF solvent blend was most suitable for stabilising precursors.

A further series of materials was prepared, comprising indium ethyl hexanoate/tin ethyl hexanoate in toluene/THF and dimethyl indium methoxide/dimethyl tin diacetate in toluene/THF.

As per the second iteration, ICP analysis showed that purity was extremely high, the residual contaminants being hydrocarbons.

The solution identified as most suitable for ink development was indium ethyl hexanoate/tin ethyl hexanoate in toluene/THF. This was successfully scaled to a one litre batch size in a reproducible fashion.

8.3 Sol-gel process development

The range of available reaction rates was first semi-quantitatively determined through assessment of precursors from Epichem, providing feedback to facilitate iterative development of subsequent precursor compounds.

8.3.1 Comparison of precursors

The precursors developed by Epichem and supplied to TWI are summarised in table 8.1.

Material	**RMM**	**Concentration (v/v)**	**Solution stability**
Indium isopropoxide Tin isopropoxide	292.09 354.69	9.5 0.5	No yellowing or precipitation observed after 3months
Indium *tert*-butoxide Tin *tert*-butoxide	333.82 411.15	12 2	Yellowing observed after 3 weeks. No precipitation observed after 3 months
Dimethyl indium acetylacetonate Dimethyl tin diacetate	243.994 266.846	8 1	Precipitation observed within 3 weeks
Dimethyl indium methoxide Dimethyl tin diacetate	175.922 266.846	13 2	Precipitation observed within 3 weeks
Indium ethylhexanoate Tin ethylhexanoate	544.42 691.49	8 1	Yellow. No precipitation observed after 4 months
Trimethyl indium tetraglyme adduct Tin *tert*-butoxide	0 411.15	10 1	Precipitation observed after 1 month, no further testing performed
Dimethyl indium *tert*-butoxide Dimethyl tin diacetate	218 266.85	8 1	Yellow. No precipitation observed after 3 months

Table 8.1 Precursor solutions provided to the project by Epichem.

The ligand structures are shown in figure 8.1.

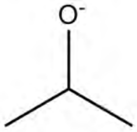
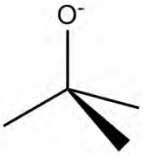
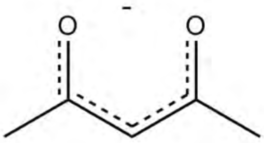
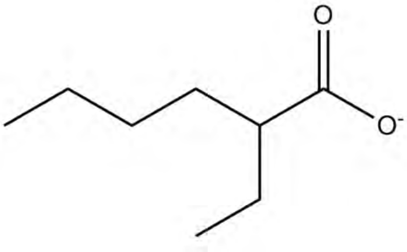
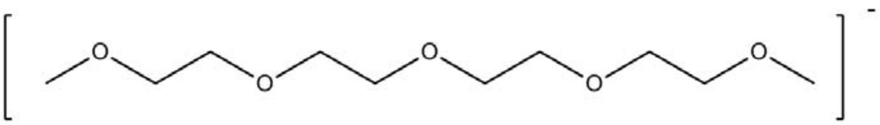
Ligand	Structure
Isopropoxide	
Tert-butoxide	
Acetylacetonate	
Ethylhexanoate	
Tetraglyme	

Fig.8.1. Structure of indium and tin precursor ligands.

To facilitate handling, the quantity of precursor solution processed was 2ml in each case.

8.3.2 Hydrolysis of indium (III) isopropoxide/tin (IV) isopropoxide solutions

The indium/tin isopropoxide solution was observed to hydrolyse rapidly, with some precipitation occurring within a nitrogen atmosphere glove box. Hydrolysis of the alkoxide moieties was initially performed by stoichiometric addition of water. To facilitate the accurate addition of small quantities of water, this was mixed with butanol, selected to ensure that ligand exchange did not preferentially occur between the precursor and the solvent. This was determined by addition of anhydrous butanol (supplied as <0.03% water) to the precursor. It was observed that this solution remained stable for just under three weeks before gellation occurred.

Initial additions were made using a 1:9 (w:w) water:butanol mixture at 1 and 0.5 stoichiometry with respect to precursor ligands and also stoichiometric with respect to metal ions. Further assessment was made at the low concentration level, using a 1:99 (w:w) water:butanol mixture to minimise concentration gradients during addition. Addition was made dropwise whilst continually stirring. The results are summarised in table 8.2.

Water addition	**Gellation time**
Stoichiometric with respect to ligands	Instantaneous
1/2 stoichiometric with respect to ligands	Almost instantaneous
Stoichiometric with respect to metal ions	5mins
Stoichiometric with respect to metal ions – 0.01% solution	5mins

Table 8.2 Effect of water addition on isopropoxide solution.

Gellation proved to be rapid, with addition of 1% water/anhydrous alcohol causing the alkoxide solution to become cloudy, and gellation occurring within a few minutes. Adjusting the water to pH 2 by the addition of hydrochloric acid resulted in instant gellation. Further additions of alcohol aided the dispersion of the gel phase but the solution remained cloudy.

8.3.2.1 The use of 2,4-pentanedione to control hydolysis/condensation

The indium acetylacetonate precursor is used in the majority of recent sol-gel work on ITO. It is commonly formed by refluxing of inorganic indium salts in 2,4-pentanedione (acetylacetone).

2,4-pentanedione is a chelating ligand which is used to control the rate of hydrolysis/condensation, resulting in the formation of stable solutions.

A half-stoichiometric quantity of 2,4-pentanedione (with respect to alkoxide sites) was added directly to the isopropoxide solution. Instant precipitation occurred. This was reversed by the addition of acetic acid (as discussed below), resulting in a clear solution. This solution became cloudy again after approximately 30 minutes.

8.3.3 Hydrolysis of indium (III) *tert*-butoxide/tin (IV) *tert*-butoxide solutions

The *tert*-butoxide precursors were treated in similar fashion to the isopropoxides. Hydrolysis was initially performed with dropwise addition of water:*tert*-butanol at 1:99 (w:w) concentration. Behaviour was similar to that of the isopropoxide solutions, with gellation occurring within 5 minutes even at a stoichiometric concentration with respect to the metal ions. The use of *tert*-butoxides was therefore discontinued, since their behaviour was similar to that of the isopropoxides but the latter were preferred with respect to coating performance.

8.3.4 Hydrolysis of dimethyl indium methoxide/dimethyl tin diacetate solutions

Tin alkoxides are notoriously sensitive to hydrolysis by moisture (even atmospheric moisture), as observed in the case of the isopropoxides assessed above. Consequently, acetates have been used as alternatives (Maruyama and Kojima 1988). The use of the dimethyl indium methoxide/dimethyl tin diacetate solution was explored, again by the addition of water in *tert*-butanol, to improve accuracy.

A stoichiometric amount of water was added (both unadjusted and with pH adjusted to 2) to the solution in a nitrogen glovebox and the vials sealed and removed to a stirrer within the laboratory. Both solutions became slightly cloudy, more so after about 30 minutes, but remained fully liquid after stirring over night for about 20 hours i.e. gellation did not occur even when exposed to additional atmospheric moisture. This occurred due to the build up of a gaseous reaction product at sufficient pressure to force the lids from the vials. From consideration of the reaction sequence, the gas was identified as methane. This gaseous build up occurred over a period of about 1 week, indicating the reaction of the acetate groups to be continuous. After approximately a week, the reaction had proceeded sufficiently to form a precipitated powder. The addition of a half stoichiometric quantity of water did not alter the course of the reaction, neither did stirring the solution under nitrogen in a glove box.

8.3.4.1 The use of 2,4-pentanedione to control hydolysis/condensation

The addition of a half-stoichiometric quantity of 2,4-pentanedione (with respect to ligand sites) did not visibly alter the solution. It still became cloudy immediately on addition of the water. This approach may offer some benefit in increasing ‘pot life’ but the effect was not significant in the few trials undertaken.

The results of hydrolysis of dimethyl indium methoxide/dimethyl tin diacetate solution are shown in table 8.3.

8.3.5 Hydrolysis of dimethyl indium acetylacetonate/dimethyl tin diacetate solution

This solution was observed to show similar behaviour to the isopropoxide solution. Water addition resulted in the formation of cloudy solutions and the effect could be reversed by the addition of acid (as described below). It was notable that the rate of reaction showed dependency on the addition rate. Slower addition resulted in reduced initiation of nuclear sites and hence slower overall precipitation. The results of additions are shown in table 8.3.

8.3.6 Dimethyl indium *tert*-butoxide/dimethyl tin diacetate solution

This solution was observed to show broadly similar behaviour to the dimethyl indium acetylacetonate/dimethyl tin diacetate solution, but with a faster reaction rate. A cloudy precipitate was observed following the addition of the first drop of water:butanol (1:99). At the minimum addition, stoichiometric with respect to tin ligands, added dropwise over 4hrs, gellation occurred within 2 hrs, i.e. before the complete addition was made. The addition of water was therefore discontinued.

The results of additions to the solution are shown in table 8.3.

8.3.7 Indium ethylhexanoate /tin ethylhexanoate solution

Initial trials with addition of stoichiometric water with respect to the ligands resulted in no visible change to the solution in respect of transparency or viscosity, indicating that any hydrolysis events resulted in a stable sol. Since this constituted the maximum water addition of interest, further additions were not made.

Water addition	**Gellation time**
Dimethyl indium methoxide/dimethyl tin diacetate	
2g anhydrous butanol	>6days
Stoichiometric with respect to ligands	>6days, gas evolved
Stoichiometric with respect to ligands + 2 drops 2,4-pentanedione	>6days
Dimethyl indium acetylacetonate/dimethyl tin diacetate	
2g anhydrous butanol	>6days
Stoichiometric with respect to ligands	Instantaneous
0.25 stoichiometric with respect to ligands	10mins via ‘syrup’
Stoichiometric with respect to Sn ligands	3hrs
Stoichiometric with respect to Sn ligands, added dropwise over 4hrs	3days
Dimethyl indium *tert*-butoxide/dimethyl tin diacetate	
2g anhydrous butanol	>6days
Stoichiometric with respect to ligands	Instantaneous
Stoichiometric with respect to Sn ligands, added dropwise over 4hrs	2hrs – addition discontinued

Table 8.3 Effect of water additions on dimethyl indium methoxide/dimethyl tin diacetate and dimethyl indium acetylacetonate/dimethyl tin diacetate solutions.

8.3.8 The effect of pH variation on sol stability

8.3.8.1 Weak acids

Glacial acetic acid and acrylic acid were each added to hydrolysed solutions (stoichiometric with respect to ligands) of both the isopropoxides and dimethyl indium acetylacetonate/dimethyl tin diacetate. In all four combinations, the cloudy, hydrolysed solutions became clear on the dropwise addition of acid (approximately 0.2 ml was sufficient). However, after approximately 30 minutes, the turbidity returned. The solutions were observed to remain in this state for a number of days without gellation occurring.

8.3.8.2 Strong acids

Nitric acid and hydrochloric acid were both added to the hydrolysed solutions (stoichiometric with respect to ligands) of both the isopropoxides and dimethyl indium acetylacetonate/dimethyl tin diacetate. In all four combinations, the addition of a few drops of acid was sufficient to revert to a clear solution, which then remained visibly stable for several weeks. The solutions to which nitric acid was added, although clear, turned a deep yellow colour. It is postulated that nitrate solutions were formed. Addition of hydrochloric acid resulted in visually stable, clear and colourless solutions. In both cases however the solutions did not wet glass slides well, *i.e.* coatings could not be formed.

8.3.8.3 Triethanolamine

The use of ethanolamines (monoethanolamine MEA, diethanolamine, DEA and triethanolamine, TEA) to stabilise indium-based sols has been previously reported (Takahashi, Hayashi et al. 1992). Sols prepared using indium alkoxides are reported to be stabilised by the use of TEA whereas those prepared using indium acetate are stabilised with DEA. A similar study has been undertaken to stabilise zinc-based sols (Kaur, Singh et al. 2004).

8.3.8.3.1 Indium isopropoxide/tin isopropoxide solution

0.467g TEA was added dropwise to 2g of the isopropoxide precursor solution. This addition represented a 1:1 molar alkoxide ligand:TEA ratio as employed successfully in the literature. The solution turned instantly cloudy but became clear after shaking for a few seconds. To this solution, a stoichiometric amount of water (with respect to ligands - 0.056 g), was added dropwise. No precipitation occurred and the solution remained clear. The solution remained clear when water was added in substantial excess (10x stoichiometric) and no visual change occurred.

The amount of TEA added to the isopropoxide solution was varied. 0.23g, 0.12g and 0.046g TEA, corresponding to 0.5, 0.25 and 0.1 stoichiometric amounts (with respect to ligands) respectively was added to the indium/tin isopropoxide solution under nitrogen. All three samples turned instantly cloudy but became clear again after stirring. The time taken to turn clear varied from about 30 seconds to 4 minutes for the samples with high TEA concentration and low TEA concentration respectively. 0.056g water (stoichiometric with respect to ligands) was then added dropwise to each solution, as a 1:9 diluted solution with propan-2-ol. Both solutions with low TEA concentrations became cloudy on addition of the water but the solution with the high concentration of TEA (0.23 g) remained clear. The solution containing 0.12g TEA (0.25 stoichiometric) became clear after several minutes stirring and remained so after stirring overnight. The solution with the low TEA concentration remained cloudy even after stirring overnight.

8.3.8.3.2 Dimethyl indium acetylacetonate/dimethyl tin diacetate solution

0.47g of 9:1 propan-2-ol:water was added to 2g of the mixed dimethyl indium acetylacetonate/dimethyl tin diacetate solution. The solution turned immediately yellow and cloudy. 0.19g TEA was added dropwise. The solution cleared but remained yellow in colour.

8.3.8.3.3 Dimethyl indium methoxide/dimethyl tin diacetate solution

0.1325 g and 0.265 g of TEA (0.25 and 0.5 stoichiometric) was added to two separate samples of 2ml of solution under nitrogen. Both solutions became cloudy and gellation occurred around the inside surface of the glass vial. The extent of cloudiness/gellation was greater for the sample with the higher concentration of TEA. Cloudiness reduced after 5 minutes and a stoichiometric amount of water (in this case 0.032 g) was added to each. Water addition was performed in air and the lids of the sample vials were left loose to allow any gas formed to escape. Bubble formation was clearly visible in the sample with the higher concentration of TEA. The water was not immediately miscible with the solutions and initially there was some visible gellation/precipitation, although clear solutions were generated after stirring for 5 minutes.

Stirring of both samples was continued for 4 hours and a gelatinous precipitate formed at the bottom of the vials. The addition of further propan-2-ol resulted in a reversal of this gellation and a clear solution was formed which remained visually stable for a period of six weeks.

8.3.8.3.4 Indium ethylhexanoate/tin ethylhexanoate solution

0.25g of 9:1 propan-2-ol:water was added to 2g indium ethylhexanoate /tin ethylhexanoate solution. No visible change was observed. 0.07g TEA was added to the solution. No visible change was observed.

8.3.9 Summary of precursor selection

The available precursor options were assessed in order to determine their hydrolysis behaviour, under atmospheric moisture and controlled addition of water. Stabilisation behaviour was determined with triethanolamine. From this evaluation, two groups of behaviour were established. The isopropoxides were preferred for direct deposition of sol-gel coatings through *in-situ* hydrolysis and condensation, and being stabilised by the addition of TEA, whilst the ethyl hexanoates were preferred for the development of printable inks; this is discussed further in Chapter 10. The dimethyl indium acetylacetonate/dimethyl tin diacetate and dimethyl indium methoxide/dimethyl tin diacetate were identified as possible alternatives for ink fabrication, since they were suitably stabilised by TEA additions. Further processing was focussed on ink development and is therefore considered in Chapter 10.

8.4 Wet film coating process

8.4.1 Substrate preparation

Samples were prepared from 100mm squares of 1.1mm glass. These were cut down to 25mm square using a diamond scribe.

In order to produce a high quality coating, the surface required preparatory cleaning to remove particulates and organic and inorganic contaminants. This was necessary since particulates leave defects in the film; inorganic contaminants (particularly halides) are detrimental to the conductivity of the film and organic contaminants reduce surface wetting.

Mechanical abrasion was rejected since a smooth surface was required to retain optical clarity and plasma cleaning was considered unsuitable due to difficulties of scalability to in-line production on large area substrates. Liquid phase cleaning procedures were therefore considered. These are summarised below.

8.4.1.1 Cleaning procedure 1

A basic cleaning procedure was considered, as used in phase 1.

- Wipe with IMS using a low-lint tissue.
- Wash both sides with 10% IPA in water.
- Blow-dry with hot air.

8.4.1.2 Cleaning procedure 2

A more comprehensive cleaning procedure was also considered.

- 15mins ultrasonic clean in acetone.
- 15mins ultrasonic clean in ethanol.
- 15mins ultrasonic clean in HCl.
- Rinse in de-ionised water.
- Dry with filtered, compressed air.

8.4.1.3 Cleaning procedure 3

The procedure used by Maruyama and Kojima in their development of a sol-gel route to ITO (Maruyama and Kojima 1988) was replicated. No times were specified for the steps in the original procedure; for this work 5 minutes were used for each step.

- 5mins ultrasonic clean in warm, soapy water
- 5mins ultrasonic clean de-ionised water.
- 5mins ultrasonic clean in methanol.
- Dry with hot air just before use.

8.4.1.4 Cleaning procedure 4

Birch's procedure recommended for substrates to be sol-gel dip coated (Birch 2000) was replicated.

- 5-15mins ultrasonic clean in surfactant.
- Rinse in de-ionised water.

- 5-10mins ultrasonic clean in de-ionised water.
- 2mins immersion in de-ionised water.
- Dry with compressed nitrogen.

8.4.1.5 Cleaning procedure 5

The RCA cleaning procedure was developed by Kern at RCA laboratories in 1965 and reported in 1970 (Kern and Puotinen 1970). It still forms the basis for standard cleaning procedures in the semiconductor industry (Bachman 1999).

The procedure contains two cleaning steps, SC-1 and SC-2. SC-2 is based on peroxide/hydrochloric acid/water and was therefore not included due to the potential for contamination of the surface with residual chloride ions. The cleaning sequence for SC-1 is given below (Hull 1999).

- Mix 5 parts H_2O with 1part 27% NH_4OH.
- Heat to 70±5°C on a hotplate.
- Remove from heat.
- Add 1 part 30% H_2O_2.
- Soak substrate for 15mins.
- Rinse under running de-ionised water.

8.4.1.6 Cleaning procedure 6

A simplified procedure was adopted, based on the key elements of procedures 1, 2 and 4.

- 15mins ultrasonic clean in acetone.
- 15mins ultrasonic clean in 5% decon90 solution.
- Rinse under running de-ionised water.
- 15mins ultrasonic clean in 10% propan-2-ol in de-ionised water.
- Dry with filtered compressed air.

8.4.2 Assessment of effectiveness of cleaning procedures

The effectiveness of each procedure was assessed by comparison of contact angles with water on cleaned borosilicate glass. Contact angle was measured for a sessile drop, using a Kruss DSA100 contact angle and surface energy analyser. The results are shown in table 8.4.

Cleaning procedure	**Contact angle (°)**
Uncleaned	32
1	15
2	<10
3	12
4	18
5	<10
6	10

Table 8.4 Contact angle measurements between cleaned borosilicate glass surfaces and de-ionised water.

Since inorganic contaminants are known to be detrimental to ITO with respect to conductivity, cleaning procedures 2 and 3 were rejected due to their potential to introduce contamination.

Of the other procedures, 1, 4 and 6 rely on dissolution to remove organic contaminants, whilst 5 is based on sequential oxidative desorption and complexing with hydrogen peroxide, ammonium hydroxide and water. Procedure 5 resulted in the lowest contact angle, however the difference was relatively small between this and the solvent-based dissolution procedure 6, suggesting a relatively high effectiveness in dissolving organic contaminants. Procedure 4 was less effective.

Insoluble particulate contamination is more complex, since there is a distinction between particles which remain adhered throughout on-processing, effectively acting as surface roughness, and those which are removable during the cleaning process. It is desirable to remove the maximum possible number of particles, down to the smallest possible particle size. To this end, ultrasonic treatment was preferred, since it is known to result in the removal of particles down to 0.3µm in size (Busnaina and Kashkoush 1993).

Hydrogen peroxide solutions have a shelf life, since the peroxide decomposes. This complicates their use, since solution age becomes a variable. Cleaning procedure 6 was therefore preferred, since it combined stability and potential for particle removal, resulted in good wettability and did not introduce potential inorganic contaminants.

Cleaning procedure 6 was therefore adopted for the purposes of this work.

8.4.3 Initial coating trials

Although the objective of the project was to produce coatings by printing, dip coating was also required to produce coatings earlier in the development cycle, in order to characterise the material structure.

Dip coating was used where sufficient volume of material was available; otherwise flow coating was performed from a syringe, the substrate being held vertically.

In order to produce a coating, it was necessary to use sols which did not exhibit a high degree of agglomeration prior to coating deposition, *i.e.* did not show the formation of precipitates or gellation.

8.4.3.1 Initial dip coating of isopropoxide solution

An indium isopropoxide/tin isopropoxide, 15%w/w solution in isopropanol was applied to borosilicate glass, cleaned as described above, using a withdrawal rate of 50mm/s. Having established that hydrolysis proceeded rapidly; coating was initially performed without prior hydrolysis, relying on *in-situ* hydrolysis with atmospheric moisture and gellation due to solvent removal. Good wetting was observed and the dipped parts were then dried at room temperature for one hour followed by the following thermal profile:

- Ramp at 1°C/min from room temperature to 600°C
- Dwell for 12hrs
- Ramp at 1°C/min from 600°C to room temperature

The coatings formed showed good coverage and adhesion when tested using a peel tape test. Some cracking was observed in all films. The coatings were highly transparent (95%) and slightly conducting (resistance measured at between 0.6 and 3.1MΩ/square).

A further part was coated using the same procedure and immediately sealed in a glass vial on a hotplate. The part was heated from room temperature with a series of dwell steps. The coating was regularly observed, without removal from the vial. The results are summarised in table 8.5 below.

Time	**Temperature (°C)**	**Observation**
55mins	Room temperature	No cracking
35mins	50	No cracking
20mins	100	No cracking
10mins	140	Cracked

Table 8.5 Summary of observations on progressively heating an uncured film.

Further coatings were prepared, reducing withdrawal rate in increments of 10mm/s. After dipping, parts were initially dried at 50°C for 30mins, then heated on a hotplate to 140°C and inspected for cracking. Cracking was observed until the withdrawal rate was reduced to 10mm/s. The coating was then fired according to the above procedure.

Coating thickness was measured by locally etching the coating with a drop of concentrated (40%) hydrobromic acid. Initially, a single drop was applied to the coating, left for 5minutes and the substrate washed with de-ionised water and dried. The step height was then measured using atomic force microscopy (AFM). A second drop was then applied in the same location and thickness re-measured. The measurement was identical, indicating that a single cycle was sufficient to fully etch the coating.

Using this procedure, a film thickness of 50μm was measured.

8.4.3.2 Initial coating of dimethyl indium acetylacetonate/dimethyl tin diacetate solution

2.835g 9:1 propan-2-ol:water was added dropwise to 10ml of precursor solution. 0.95g TEA was added dropwise, maintaining stirring throughout. The resulting yellow solution was flow coated onto glass substrates and cured as above.

The highest performance achieved from a coated part was 0.33MΩ/square.

8.4.3.3 Initial coating of dimethyl indium methoxide/dimethyl tin diacetate solution

5.415g of 9:1 propan-2-ol:water was added dropwise to 10ml of precursor solution, followed by the dropwise addition of 1.8g TEA, maintaining stirring throughout. The gelatinous precipitate was then re-dissolved by the addition of 10ml propan-2-ol. Coatings were applied by flow coating and cured as above.

The highest performance achieved from a coated part was 38kΩ/square.

8.4.3.4 Initial coating of indium ethylhexanoate/tin ethylhexanoate solution

1.25g of 9:1 propan-2-ol:water was added dropwise to 10ml of precursor solution, maintaining stirring throughout. The resulting clear, colourless solution was then flow coated onto glass substrates and cured as above.

The highest performance achieved from a coated part was 2.3MΩ/square, the coating being incoherent.

1.25g of 9:1 propan-2-ol:water was added dropwise to 10ml of precursor solution. 0.35g TEA was added dropwise to the solution, maintaining stirring throughout. The resulting clear, colourless solution was then flow coated onto glass substrates and cured as above. The highest performance achieved from a coated part was 0.16MΩ/square.

8.4.4 Effect of varying thermal cycle conditions

The influence of thermal cycle was assessed using co-dissolved solutions of the isopropoxide precursors in propan-2-ol and the *tert*-butoxide precursors in butanol.

From analysis of the TGA and DSC results presented below, equivalent sets of three parts were prepared using both precursors, at a withdrawal rate of 10mm/s. The parts were dried at 50°C for 30mins and fired according to two schedules, the first as described above having a peak dwell temperature of 600°C, the second having a reduced dwell temperature of 500°C, for 18 hours. The parts were compared visually and the sheet resistance values measured. The lowest value recorded from three measurements of each substrate is recorded in table 8.6.

Precursor	**Firing temperature (°C)**	**Sheet resistance (MΩ/square)**
Isopropoxide	500	0.63, 0.75, 0.78
	600	0.58, 0.66, 0.82
Tert-butoxide	500	0.72, 0.72, 0.85
	600	0.75, 0.83, 0.92

Table 8.6 Summary of sheet resistance measurements from isopropoxide and *tert*-butoxide derived coatings, varying firing conditions.

The results showed no significant difference between firing at 600°C and 500°C. Since it was commercially preferable to reduce firing temperature, 500°C was adopted for further work.

In order to increase film thickness without causing cracking, different thermal cycles to promote structural evolution prior to high temperature conversion were evaluated. Parts were coated as above, using a withdrawal route of 50mm/s.

The results of the dip coating trials are summarised in table 8.7.

Precursor	**Pre-treatment**	**Cure**	**Sheet Resistance**
Isopropoxide	Room temperature, 1hr	500°C, 18hrs	20kΩ/square
Isopropoxide	50°C, 1hr	500°C, 18hrs	Open circuit (excessive cracking)
Isopropoxide	Nitrogen, 1hr	500°C, 18hrs	14kΩ/square
Butoxide	Room temperature, 1hr	500°C, 18hrs	Open circuit (excessive cracking)
Butoxide	50°C, 1hr	500°C, 18hrs	125kΩ/square
Butoxide	Nitrogen, 1hr	500°C, 18hrs	270kΩ/square

Table 8.7 Summary of effect of pre-treatment on sheet resistance.

For the isopropoxide precursor route, drying at room temperature resulted in less cracking than drying at elevated temperature. For the butoxide precursor route, drying at room temperature in air was least effective. Drying in nitrogen reduced cracking, as did drying at elevated temperature. Overall, the isopropoxide precursor route produced lower sheet resistance values than the butoxide precursor route.

A coating was prepared from the isopropoxide precursors, stabilised with TEA, using a drying/curing sequence of one hour in air at room temperature, followed by firing at 500°C for 18 hours. Sheet resistance was measured at 6kΩ/square. Film thickness was measured at 50nm. Transmission at 550nm was measured at 98%.

Secondary electron micrographs of the coating surface were taken using a scanning electron microscope. These are shown in figure 8.2.

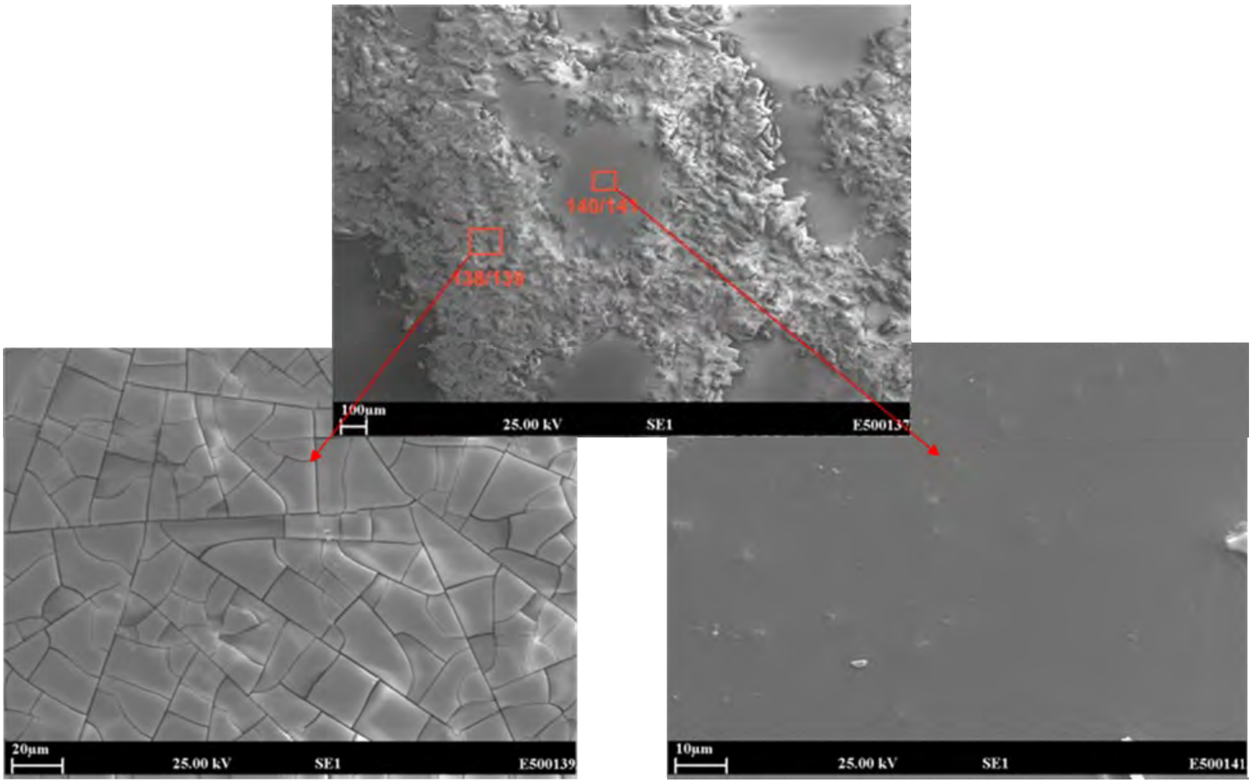


Fig.8.2. Secondary electron micrographs showing coating structure in isopropoxide derived ITO coating.

Micrographs of the coating show island structures on the scale of 20microns across large regions of the coating. It is likely that these islands are electrically isolated and account for the low conductivity. This is supported by the electrical charging observed under the SEM.

8.5 Development of firing regime

A firing regime was required which resulted in a continuous, well adhered coating of uniform thickness and with a crystalline microstructure. Phase 1 established firing conditions of 12hrs at 600°C in air to produce the best conductivity.

8.5.1 Isopropoxide route

In order to identify the thermal features of the isopropoxide material, thermogravimetric (TGA) analysis and differential scanning calorimetry (DSC) were performed simultaneously using a Netsch 4 combined instrument. Isopropoxide precursors were hydrolysed and the material evaporated to dryness, the powder being recovered for analysis. Scans were performed between 100 and 600°C and are shown in figure 8.3.

The TGA shows a loss of 19.6% mass, in two regions. The initial loss of approximately 4% during the initial dwell at 100°C corresponds to removal of residual entrapped solvent. The second region during the initial ramp between approximately 100 and 350°C corresponds to the loss of hydroxyl groups through condensation polymerisation. The loss in mass corresponds substantially to that expected from hydroxyl groups, indicating that hydrolysis was largely complete before the analysis commenced.

The DSC curve shows an initial exothermic event, associated with the peak region of mass loss and therefore likely to be associated with decomposition and condensation of the ligands. Three distinct endothermic events can be identified, assigned to ligand decomposition, glass transition temperature (T_g) and crystallisation temperature (T_c) in increasing temperature order. Onset of crystallisation was observed at approximately 340°C.

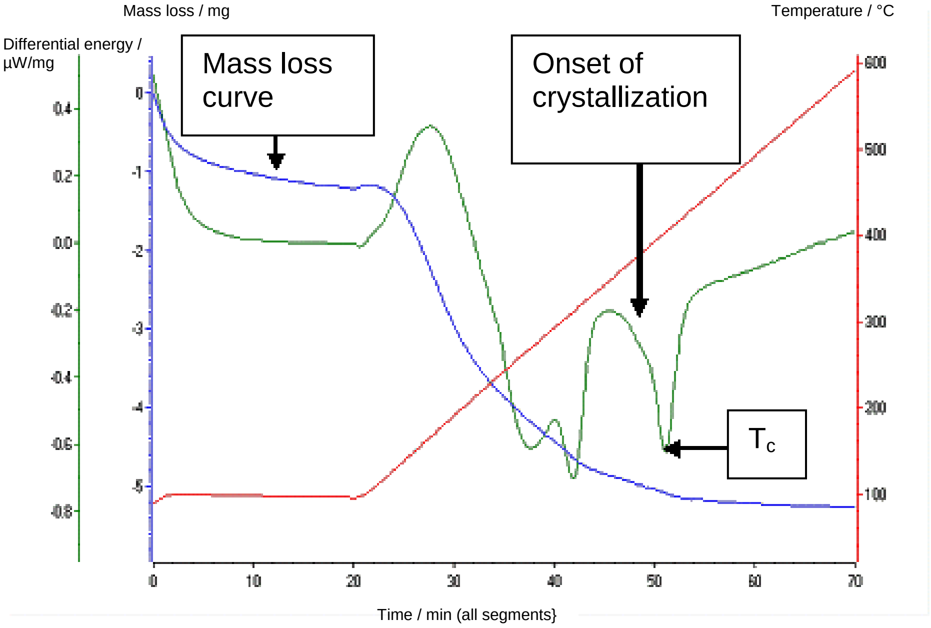


Fig.8.3. TGA and DSC of hydrolysed isopropoxide derived material, showing condensation and crystallization of the structure.

Crystallisation behaviour at 600°C was characterised by X-ray diffraction (XRD), using a dip-coated specimen prepared from the isopropoxide precursors on a glass substrate, with a firing sequence of 10hrs in air. The diffraction pattern is shown in figure 8.4(b). The diffraction pattern was compared with a reference pattern recorded from a piece of equivalent glass, shown in figure 8.4(a).

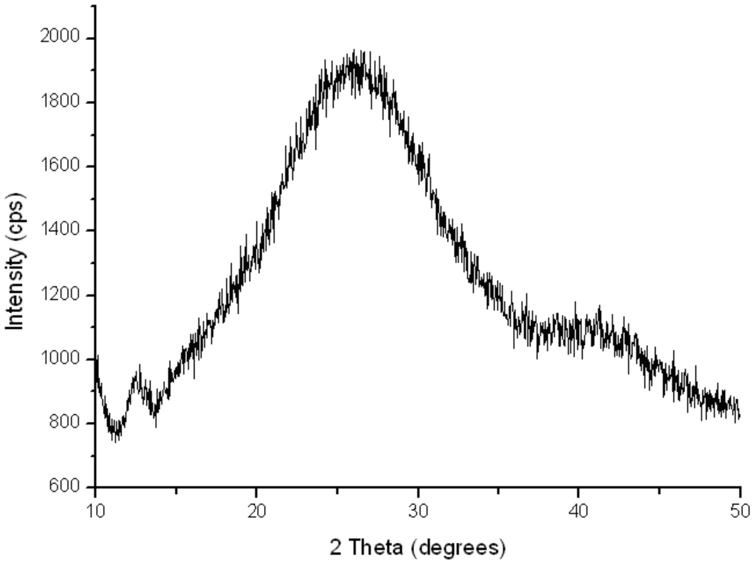


Fig.8.4(a) Reference diffraction pattern for glass substrate

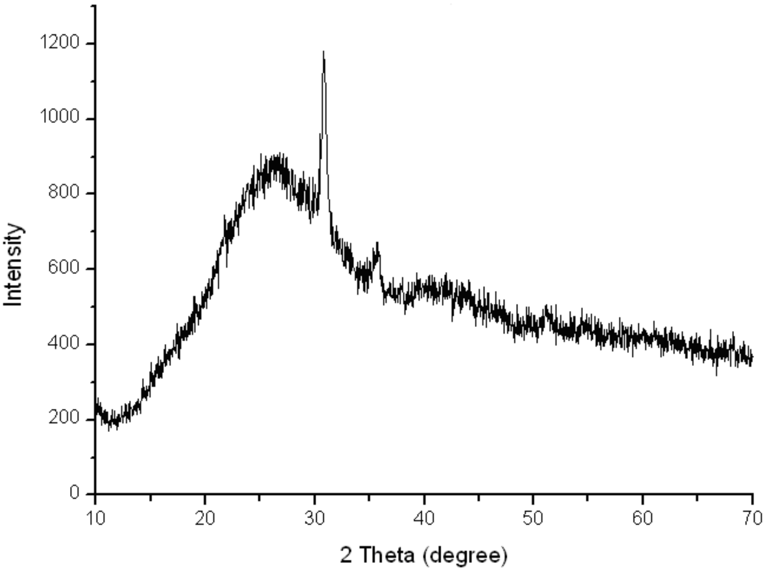


Fig.8.4(b) Diffraction pattern for the isopropoxide derived fired film, showing characteristic crystalline peak at 31°.

Comparison of the two diffraction patterns shows the presence of a crystalline peak at 31°, corresponding to crystallisation of the film. A further trace recorded after an additional 10hrs firing was identical to the first, indicating that crystallisation was complete after 10hrs treatment. It is also apparent that the background peak from the glass is dominant, since the sample was sufficiently thin for the X-rays to substantially interact with the substrate beneath.

In order to establish crystallisation time and temperature, trials were conducted using hot stage XRD, performed on powdered, hydrolysed material to alleviate the dominant glass peak. A sweep was recorded between 30 and 32 degrees (corresponding to the ITO peak (International Centre for Diffraction Data 1995)), each sweep taking approximately 55mins. Diffraction patterns were recorded at 300, 320, 330, 340, 500 and 600°C, against a reference, unfired pattern. These are shown in figure 8.5.

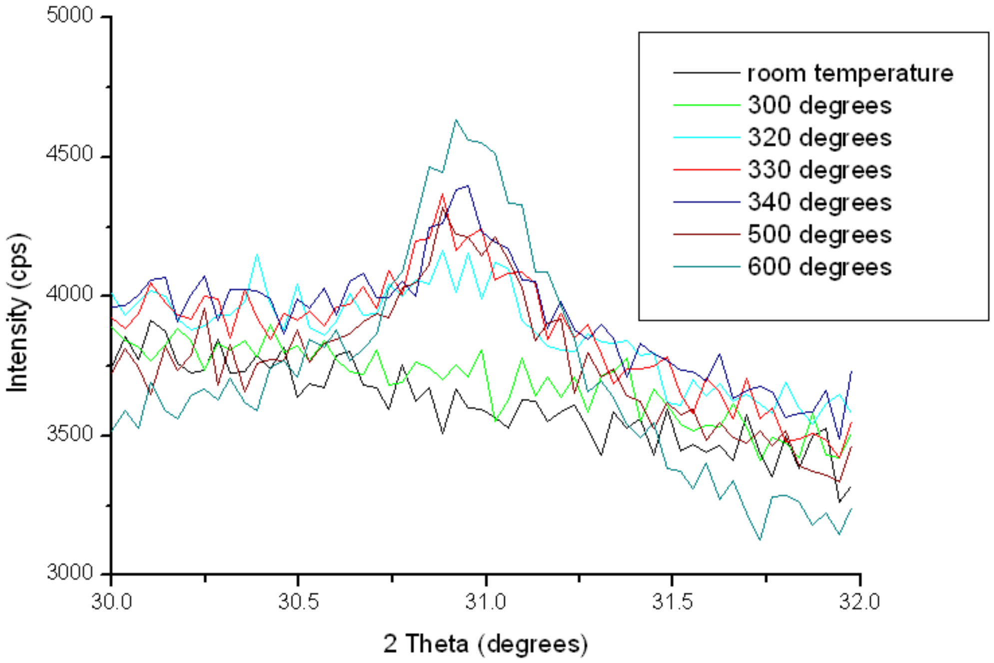


Fig.8.5. Diffraction patterns for powdered, hydrolysed ethylhexanoate precursor fired at a range of temperatures, showing increase in crystallisation peak intensity above 320°C.

The diffraction pattern shows no crystallinity below 320°C, with substantial crystallinity at 330°C. The onset of crystallisation therefore lies at approximately 320°C and firing at temperatures above 330°C results in substantial crystallinity. This is broadly consistent with the DSC data.

The experiment was repeated at 350°C to establish whether degree of crystallisation was influenced by additional firing time. The temperature was selected with reference to the TGA data, ensuring that mass loss events were complete. Diffraction patterns were recorded after 52 and 104 minutes (corresponding to single and double sweeps of the equipment). Equivalent patterns were also recorded for corresponding times at 600°C. These are shown in figure 8.6.

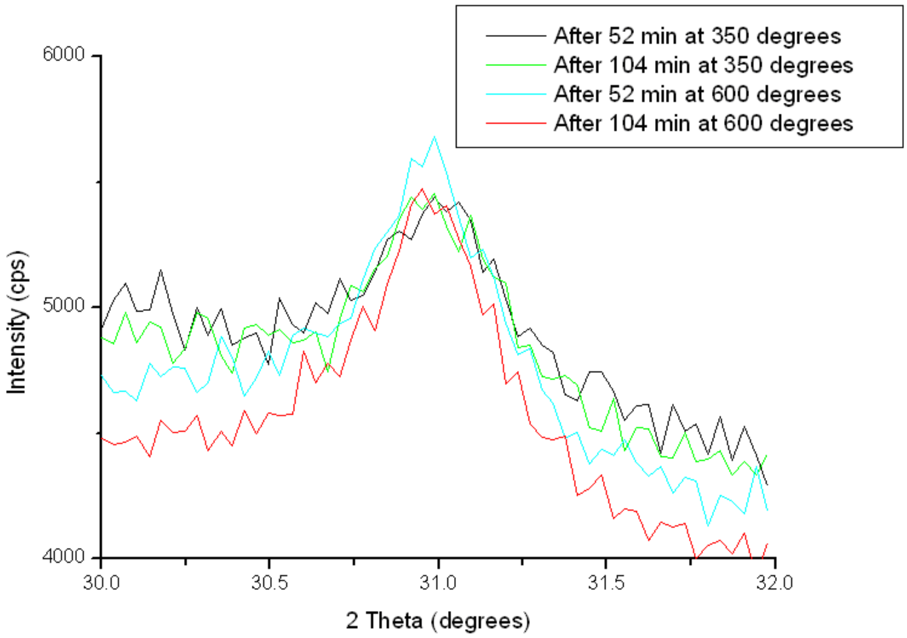


Fig.8.6. Diffraction patterns showing influence of time and temperature on crystallinity.

The diffraction patterns shown in figure 8.5 indicate that the extent of crystallization was not substantially altered by firing at temperatures above 330°C or for times in excess of 52 minutes.

This is substantially reduced when compared against the accepted bulk crystallisation temperature of 518°C (Gallagher, Scanlan et al. 1993).

8.5.2 Ethylhexanoate route

Since the ethylhexanoate route started from particulate rather than gelled films, the thermal cycle required that the particles coalesced in order to form a film, prior to crystallization.

A sample of the hydrolysed xerogel was heated on a hot stage optical microscope from room temperature to 300°C. A sharp transition from solid to liquid was identified at 285°C. This was assigned as T_g for the material. The sharp transition indicated very high purity.

Combined TGA/DSC was performed on the hydrolysed xerogel across the range 100 to 800°C. The TGA scan is shown in figure 8.7 and the DSC scan in figure 8.8.

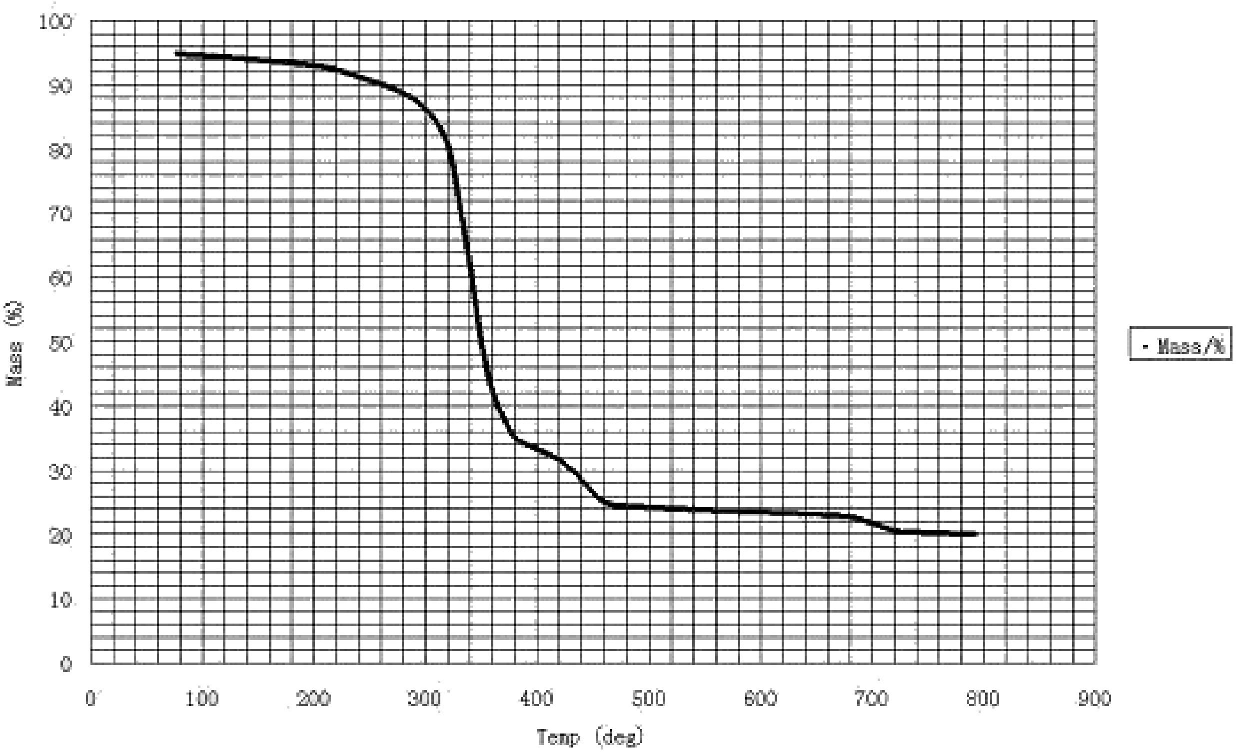


Fig.8.7. TGA of ethylhexanoate xerogel, showing decomposition between 300 and 460°C.

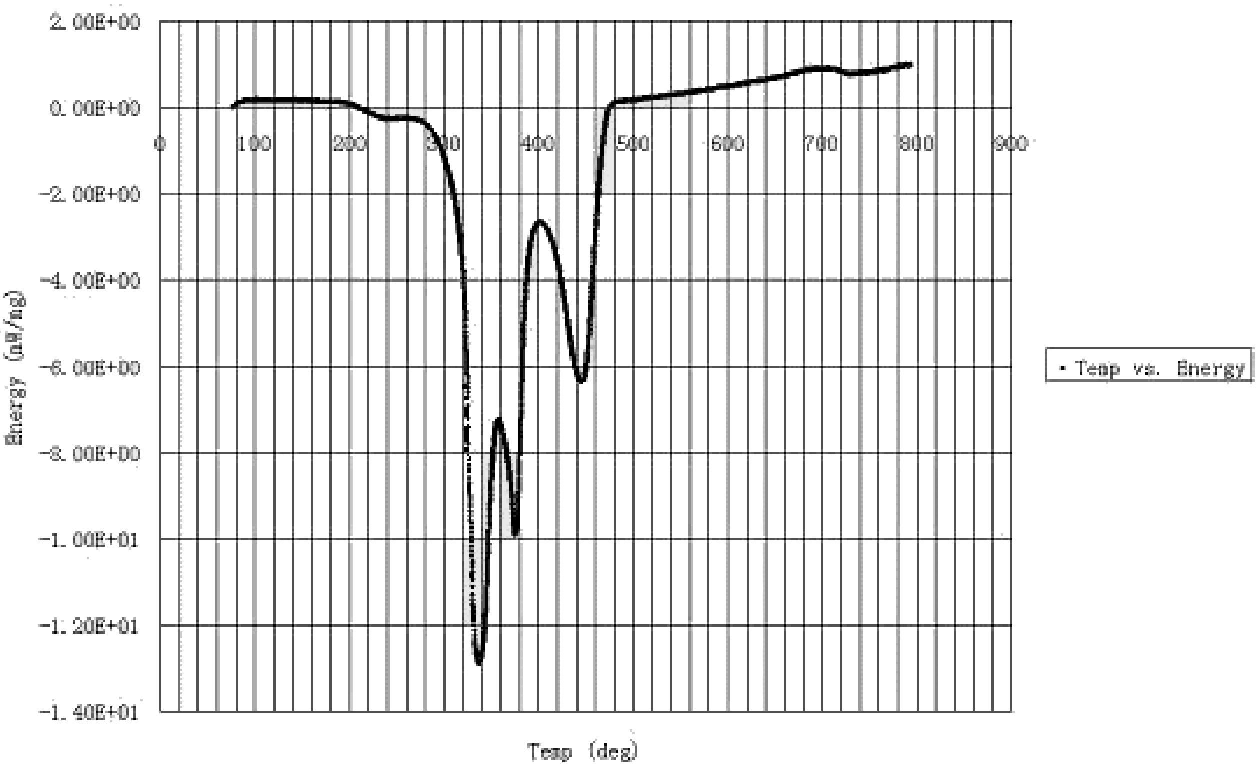


Fig.8.8. DSC of hydrolysed ethylhexanoate xerogel, showing peak trace corresponding to exothermal decomposition (340-380°C).

The TGA showed substantial mass loss of 63.5%, occurring primarily between 300 and 400°C and complete by 460°C. The mass loss indicates that a substantial percentage of the ethylhexanoate ligands remained unhydrolysed during the initial hydrolysis sequence. DSC showed three distinct events; the first two occurred during mass loss, suggesting the decomposition of two distinct groups. These are likely to correspond to the hydrolysed and unhydrolysed structures. The third event occured without associated mass loss and is therefore likely to correspond to crystallisation, determining a T_c of approximately 440°C.

XRD analysis was performed on a sample of xerogel material fired at 500°C to ensure that decomposition was complete. The pattern is shown in figure 8.9.

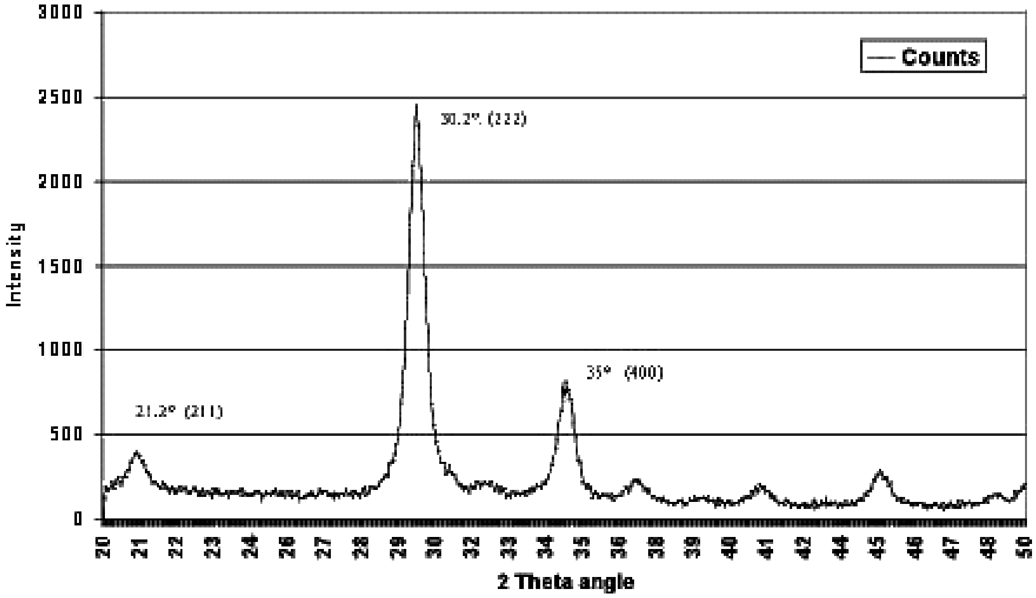


Fig.8.9. X-ray diffraction pattern for ethylhexanoate xerogel, showing full crystallization.

The XRD pattern confirmed that crystallisation was substantially complete after firing at 500°C.

Compared with bulk ITO values of T_g ~480°C and T_c being 518°C (Gallagher, Scanlan et al. 1993), the values obtained with the hydrolysed ethylhexanoate material were substantially lower.

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CHAPTER 9 - WP2: DEVELOPMENT OF INDIUM-FREE ANODE FILMS

9.1 Overview

A theoretical approach to the selection of In free materials was adopted. Working from first principles, candidate materials were identified with appropriate optical and electrical properties. Other physical parameters were considered, including material cost and hazard, both in processing and end use.

Suitable starting systems were investigated, both in bulk and as thin films, through a series of doping and processing experiments. The two most promising candidates were selected for preparation by a sol-gel route and developed following a similar strategy to that adopted for WP1.

9.2 Review of options for indium-free materials

As discussed in Chapter 5, since TCCs are semiconductors, conductivity is derived from promotion of electrons from the valence band (or donor levels) into the conduction band which, to be transparent in the visible region of the spectrum, requires a band gap of 3.75eV. For conductivity, the Mott criterion requires a minimum carrier density of $1x10^{19}cm^{-3}$, while the plasma edge defines an upper boundary to carrier density of $2x10^{21}cm^{-3}$, above which the material becomes optically reflecting.

The two routes to selecting a TCC are to start from a transparent material and dope it to produce a conductive band structure, or to start from a conducting material and make it transparent. The former is considerably more promising since a non-transparent semiconducting material would require alteration of the electron structure to prevent absorption, which would be likely to disrupt conductivity.

Suitable materials for consideration are concentrated in far and post transition metal systems, such as zinc, indium, cadmium and tin. These are known TCCs with good transparency and conductivity (high FOM). Of these systems, cadmium was rejected on grounds of toxicity and the project specifically sought to develop indium-free alternatives. Promising starting materials were therefore zinc oxide and tin oxide.

In order to achieve sufficient conductivity to meet the project objectives, doping was required. In order to achieve the maximum possible carrier concentration without adversely affecting carrier mobility, it is preferable to dope with a high valency cation. Aluminium doping has been extensively studied but is known to suffer performance degradation with time. A quadravalent cation substitution into the zinc oxide lattice was identified as a promising alternative. Titanium and silicon were identified as potential dopants.

An alternative is to use an anionic dopant, requiring the use of a monovalent anion, generally drawn from group VII of the periodic table. Tin oxide is commonly fluorinated to achieve conductivity. This may be achieved either by post-fluorination from vapour phase treatment, or potentially by incorporating a fluorinated group in the precursor.

Down-selection from the available materials indicated use of zinc and tin oxides with appropriate dopants. Since both offered potential benefits, they were developed in parallel.

9.3 Synthesis of alternative materials

Materials were prepared as bulk samples by microwave solid state synthesis and the bulk characterised by XRD to establish the phase(s) formed. Potential performance was also assessed, primarily through conductivity measurement.

PLD was developed as a screening tool to produce films from promising candidates, varying composition to determine optimum dopant level. Films were assessed to establish transparency and conductivity.

9.3.1 Synthesis of Ti-doped ZnO_2

Titanium doped zinc oxide was made using solid state preparation methods in the range

$Zn_{1-x}Ti_xO$ $0.0<x<0.1$

Powders were fired in air at 800ºC for 14hr. then 850ºC for 14hr. followed by subsequent annealing both in air and in nitrogen at 400ºC. X-ray diffraction showed some evidence of lattice shift with increasing concentration and sharp peaks, indicating a high degree of crystallinity. Microwave conductivity measurements were made on the bulk sample but no evidence was seen of change in performance with Ti doping and the work was discontinued.

9.3.2 Synthesis of Si-doped ZnO_2

The theoretical silicon doping level required in zinc oxide for optimum carrier density was calculated to be 10%. Solid state preparation was used to produce silicon doped zinc oxide in the compositional range

$Zn_{1-x}Si_xO$ $0<x<0.1$

Initial trials were performed using traditional solid state processing, firing in air up to1300ºC for 12 hours and in nitrogen up to 1200ºC for 12 hours. Primary structural characterization was performed using X-ray powder diffraction with a Philips X'Pert diffractometer.

It was established that the maximum concentration of silicon which could be incorporated into the zinc oxide lattice lay below 0.5wt% (0.7at%), with further addition resulting in the formation of zinc silicate.

Using microwave conductivity measurements, it was identified that conductivity dropped with incorporation of Si, however some increase was observed at 10wt% addition when fired in air.

Substantially higher concentrations of silicon were incorporated into the zinc oxide lattice using PLD. Targets were prepared using zinc oxide (purity 99.99%) and silicon dioxide (99.99%) powders. These were mixed in acetone and fired at 800°C for 12 hours in air, ground and fired again at 800°C for a further 7 hours in air. Films were then deposited onto borosilicate glass at 350°C in a 5mTorr oxygen atmosphere by ablation from the sintered pellets with a laser operating at a repetition frequency of 10Hz and 250-400mJ pulse energy for a total of 5000 pulses (Edwards, Jones et al. 2009).

Characterisation of the films by X-ray diffraction indicated that up to 10% silica could be integrated into the zinc oxide lattice.

Measurements of film sheet resistance were made using a 4-point probe. Thickness measurements were made using a Dektak 3 profilometer on the same film, across etched steps in the film. These results were used to calculate the conductivity of the material at each concentration of silicon dopant.

The Hall effect was used to determine carrier concentration. Application of a known, fixed magnetic field (B) perpendicular to the plane of measurement in the four point probe was used to measure the Hall voltage (V_H) and the carrier concentration (n) calculated according to the equation:

$$n = \frac{IB}{dq\left|V_H\right|} \tag{9.1}$$

where I and B are the applied current and magnetic field, d is the film thickness and q is the elementary charge, 1.602 x 10^{-19} C (National Institute of Standards and Technology 2009). The results are shown graphically in figure 9.1.

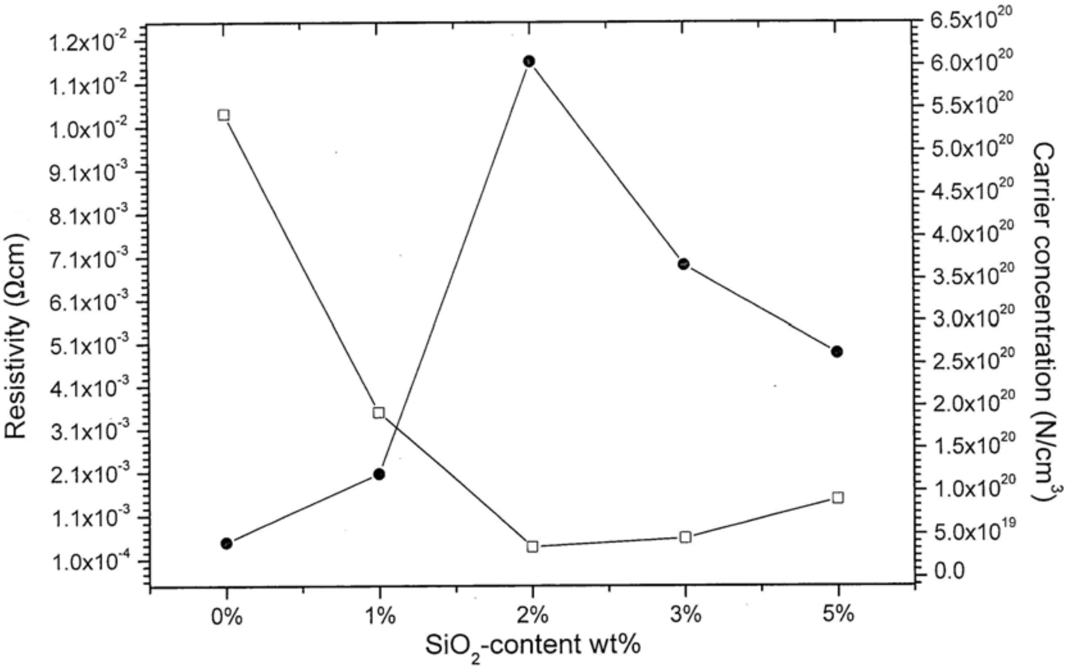


Fig.9.1. Resistivity of ZnO-SiO2 regime as a function of silicon dopant concentration (Edwards, Jones et al. 2009).

Si doping of ZnO reached a maximum performance at 2wt% (2.7at%), with an inherent resistivity of $6x10^{-4}\Omega$.cm.

9.3.3 Fluorine doping experiments

Fluorine doping of ZnO powders was attempted by three routes.

Solid state mixing was performed between ZnF_2 and ZnO (sealed in a quartz tube and fired at 700ºC/12hrs then 800ºC/7hrs). Powder X-ray diffraction showed formation of zinc silicate ($ZnSiO_4$).

NH_4F was mixed with ZnO in a quartz tube then sealed under vacuum; fired at 250ºC for 12hrs then at 500ºC for 7hrs. Analysis of the powder by X-ray diffraction similarly showed formation of $ZnSiO_4$.

Passing 5% fluorine gas over ZnO at 300ºC for one hour produced no change in the XRD pattern but resistivity was observed to decrease from $2.0\text{x}10^{-2}\Omega\text{cm}$ to $6.9\text{x}10^{-4}\Omega\text{cm}$, an improvement of nearly two orders of magnitude.

9.4 Precursor preparation

Precursors were prepared by Epichem for both zinc and tin-based systems.

9.4.1 Zinc precursors

The doped zinc oxide system required mixed precursors for zinc and for silicon. Tetraethyl orthosilicate was selected as the silicon precursor due to its well known tractability in sol-gel processing. The initial zinc precursor selected was the ethylhexanoate.

A range of alternative, more reactive, sources was considered. Diethyl zinc was rejected as too reactive, being pyrophoric. The alkylalkoxide compounds were deemed most suitable. A route was therefore developed to prepare an ethyl zinc ethoxide solution which was provided both as a single solution and as a mixed ethyl zinc ethoxide/tetraethyl orthosilicate solution, with a silicon loading of 2at% with respect to the zinc content. Structures for the ligands described above are shown in figure 9.2.

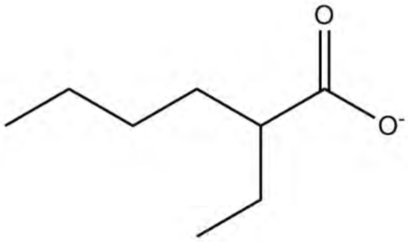
Ligand	Structure
Ethoxide	
Ethylhexanoate	

Fig.9.2. Structure of zinc and silicon precursor ligands.

The materials supplied were all clear colourless liquids. ICP indicated them to be of high purity and they appeared stable in their sample bottles for several weeks.

9.4.2 Tin precursor

Tin ethylhexanoate had been developed as a precursor to provide the dopant in the indium tin oxide system developed in Work Package 1, discussed in Chapter 8. This was prepared as the precursor for deposition of tin oxide films, to demonstrate feasibility prior to subsequent development of *ex-situ* fluorine doping.

9.5 Sol-gel processing of precursors

9.5.1 Processing of zinc ethylhexanoate precursor

Initial work was performed using the zinc analogue of the indium/tin system, *i.e.* the ethylhexanoate. This was assessed using a similar strategy to that adopted in the assessment of the indium tin system.

2g batches of the ethylhexanoate precursor were transferred into separate vials into an argon atmosphere. Amine additions were made to the solution and the effect observed. The specific amines identified were:

- Ammonium hydroxide
- Triethanolamine (TEA)
- Xylylenediamine (XLD)
- 3-(Dimethylamino)-1-propylamine (DMAP)
- 1,2-Diaminopropane (DAP)

All materials were supplied by Sigma Aldrich Corp. Structures for the above molecules are shown in figure 9.3.

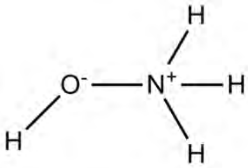
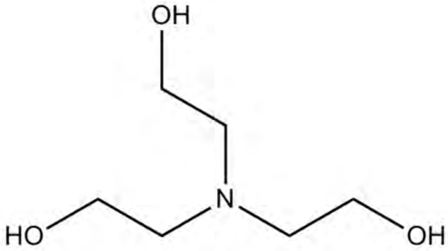
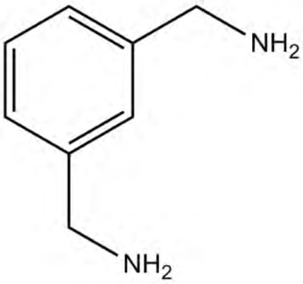
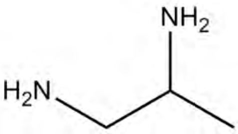
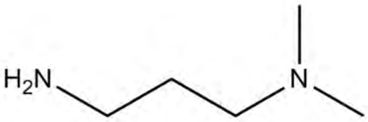
Amine	Structure
Ammonium hydroxide	
Triethanolamine	
Xylyenediamine	
1,2-Diaminopropane	
3-(Dimethylamino)-1-propylamine	

Fig.9.3. Structure of amines used for pH modification.

Each hydrolysis was performed using one of the above amines, mixed with deionised water to form a 28%w/v solution to facilitate direct comparison with the ammonium hydroxide with respect to water addition.

0.01ml of each amine was added to a separate batch of the precursor solution using a micro pipette, with vigorous shaking. A further 0.01ml was added after 20 minutes and a final 0.01ml after a further 20 minutes. The solution was then left under argon for 12 hours. The vials were inspected immediately before and after each addition for cloudiness or visible precipitate. The results are summarised in table 9.1.

Amine	**Observation of onset of reaction and subsequent changes with sequential 0.01ml additions at 20min intervals, followed by 11hrs standing**	**Observation of reaction following addition of 0.08ml followed by 1month standing**	**Observation of onset of gellation following 0.08ml addition and storage at 65°C**
Ammonium hydroxide	0.03ml addition, 12hrs, no change	Gelled	15 days
DAP	0.03ml addition, 12hrs, no change	Gelled	22 days
DMAP	0.03ml addition, 12hrs, no change	No change	-
XLD	0.03ml addition, 12hrs, no change	No change	-
TEA	0.03ml addition, 12hrs, no change	Gelled	27 days

Table 9.1 Summary of effect of amine additions on zinc ethylhexanoate precursor solution.

As can be seen from inspection of table 9.1, no visible effect could be observed from the addition of amine solutions to the zinc ethylhexanoate precursor. Subsequent addition of 0.08ml of each amine (equating to 2x stoichiometric water addition with respect to ligands) was made to fresh batches of the zinc ethylhexanoate precursor and allowed to stand for 24 hours. No effect was observed. The samples were then left for a month, resulting in gellation of all solutions except those treated with XLD and DMAP. The sequence was repeated, storing the sealed vials in an oven at 65°C. The samples were inspected daily. Ammonium hydroxide showed the most rapid gellation at 15 days, followed by DAP at 22 days and finally TEA at 27 days.

9.5.2 Processing of ethyl zinc ethoxide precursor

The ethyl zinc ethoxide solution was supplied in toluene/THF at 10w/v%.

Initial assessment was made by the addition of water. Working in an argon filled glovebox, 5ml of the precursor solution was transferred to a glass vial. De-ionised water was added dropwise, in 0.01ml quantities at 1 minute intervals, shaking well between drops. The effect of the additions was observed by studying the appearance of the solution. The results are summarised in table 9.2.

The precursor showed rapid reaction with water, even at sub-stoichiometric additions. The addition required to initiate reaction was a 0.01ml, approximately 0.25 stoichiometric with respect to ligands. The addition required to generate rapid full precipitation was 2x stoichiometric with respect to ligands.

Water addition (ml)	**Appearance**
0.01	Cloudy precipitate resembling snow
0.02	Fully cloudy
0.03	Increase in quantity of dispersed precipitate
0.04	Resembling milk
0.05	No change
0.06	No change
0.07	Precipitated powder observed
0.08	Increased level of powder on base
0.09	Fully precipitated
0.10	No change

Table 9.2. Summary of the effect of water addition on ethyl zinc ethoxide precursor solution.

9.5.2.1 Assessment of water content in IMS

A quantity of molecular sieve was dried in air overnight at 200°C. 3.522g of molecular sieve was added to 4.228g of IMS and left overnight. The liquid was then removed from the molecular sieve, which was re-weighed and dried at room temperature for 5 minutes to ensure removal of IMS from the surface. The molecular sieve was then re-weighed at 3.913g, indicating that the industrial IMS contained approximately 4.5% water.

9.5.2.2 Assessment of sensitivity of ethyl zinc ethoxide precursor

Water addition was repeated with decreased quantities performed over a longer time period to establish the sensitivity of the precursor to hydrolysis. pH was also increased by the addition of ammonium hydroxide, in order to establish the influence on hydrolysis rate.

A stock quantity of IMS was dried with molecular sieve for a minimum period of 24 hours. A quantity of the precursor solution was filtered at 1μm to remove the precipitate which had formed in the bottle. A series of solutions was then prepared with varying concentrations of ammonium hydroxide, water and dry IMS. These were added in 0.01ml quantities to 1g of filtered precursor solution and the effect observed. The results are summarised in table 9.3.

Addition (0.01ml)	**Observations**
De-ionised water	Immediately precipitated white particles
1:99 ammonium hydroxide:de-ionised water	Immediately became cloudy and white precipitate formed. Left overnight, precipitate settled.
1:99 ammonium hydroxide:IMS	Immediately became slightly cloudy with no visible precipitate. Left overnight, gelled completely
1:999 ammonium hydroxide: IMS	Immediately became slightly cloudy with no visible precipitate. Left overnight, gelled partially

Table 9.3. Summary of observations of reactive behaviour of ethyl zinc ethoxide precursor with small additions of ammonium hydroxide, water and IMS.

It was established that the reaction rate could be controlled by the addition of very low quantities of water, through ammonium hydroxide addition at 1:999 with dry IMS. This resulted in only partial gellation over a 12 hour period.

A further batch of this solution was prepared and parts coated after 1 hour, using dip coating with a withdrawal rate of 1mm/sec. Coating uniformity was poor, so further parts were flow coated from a pipette, resulting in improved coating uniformity. Parts were fired using the following firing sequence:

- 60°C for 10mins
- Room temperature to 500°C at 3°C/min
- Dwell for 40mins
- 500°C to room temperature at 5°C/min

The resulting coating was white and powdery.

The material was re-fired at 720°C (the annealing point of the 1737F substrate being 721°C (Coresix 2009), resulting in significantly improved coating adhesion. The coating structure is shown in figure 9.4. Further firing at 800°C improved adhesion still further but the glass showed significant distortion.

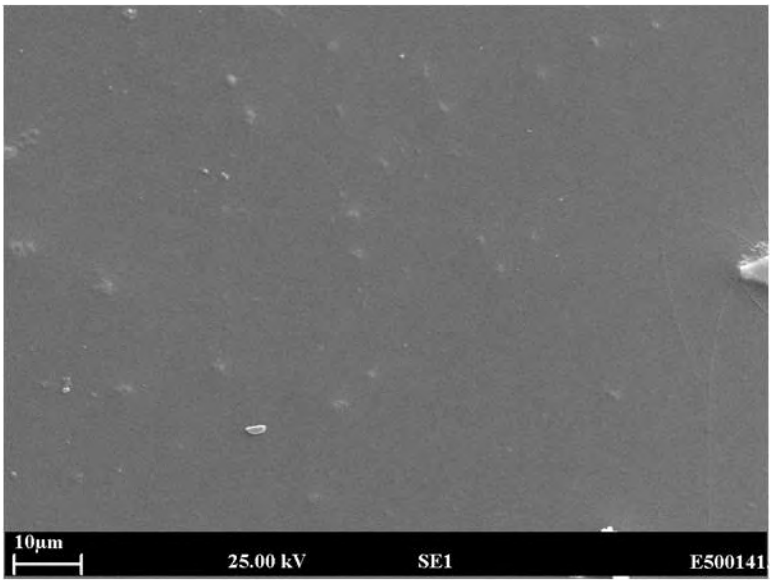


Fig.9.4. Coating structure of zinc oxide, showing poor homogeneity.

A further batch was prepared as above and fired according to the following sequence:

- 60°C for 10mins
- Room temperature to 720°C at 3°C/min
- Dwell for 40mins
- 500°C to room temperature at 5°C/min

Using a Surfcom profilometer the coating thickness was measured to be approximately 40nm. The coating showed poor transparency.

A further batch of material was hydrolysed according to the above procedure and dried at 65°C, resulting in a white, powdery material.

9.5.3 Processing of ethyl zinc ethoxide/tetraethyl orthosilicate precursor

The ethyl zinc ethoxide solution was also supplied with the silicon dopant integrated in the form of tetraethyl orthosilicate. This was supplied as:

EtZnOEt / $Si(OEt)_4$ 14:1 solution in Toluene THF 10%w/v

Similar additions were made to those in the undoped system. Initial work concentrated on understanding the formation of a suitable material from which to deposit a coating.

Working under argon, 0.01ml of de-ionised water/solvent was initially added to 2g of the precursor, the water being mixed with toluene and with dry IMS, at 1:99 in two separate experiments. No change was observed in the solution, which was then flow coated onto glass substrates. The solution did not wet in either case.

A further batch was prepared using 0.01ml of water added to 1g of precursor. No reaction was observed and the water was immiscible. 0.01ml of concentrated ammonium hydroxide was added and the solution immediately became cloudy.

A batch of solvent was prepared containing 9.8ml IMS, 0.1ml DI and 0.1ml ammonium hydroxide. To two separate batches of 1g of precursor, 0.01ml and 0.1ml of the above solution was added respectively. In neither case was any change observed in the solution, but both flow coated well onto a glass substrate.

An attempt was made to prepare a batch of xerogel for subsequent ink development. 20ml precursor was mixed with 5ml of the above solvent batch. No change was observed. 0.1ml of concentrated ammonium hydroxide was then added, resulting in initial cloudiness, followed by separation of the aqueous and organic phases. Both phases were then left to evaporate for 7 days at 50°C resulting in the formation of a viscous liquid. Further treatment at 80°C in a vacuum of 10^{-2}mbar for 36 hours did not result in the formation of a solid material.

9.5.4 Processing of tin precursor

Tin was supplied as an ethylhexanoate precursor, *i.e.* in similar form to the dopant material used in the development of the ITO system. Initial stability trials were performed in an argon filled glovebox. 2g of precursor solution was measured into a vial and left overnight. No change was observed.

0.01ml of 9:1 dry IMS:de-ionised water was added to a second vial and left overnight. This showed complete formation of a gel as a second phase, below the organic solvent phase.

The above experiment was repeated with monitoring at hourly intervals. No change was observed until 2 hours, at which point gelled material was observable at the rim of vial. Substantial gellation became visible after 4 hours progressed to complete gellation at 6 hours. The gelled material was present as a second phase. The supernatant liquid was removed and 8:1 toluene:THF added, which did not result in dispersion/dissolution of the gel.

A further batch was prepared and matured for 1.5 hours. This was then used to dip coat a glass slide which was fired according to the following schedule:

- 60°C for 10mins
- Room temperature to 200°C at 10°C/min
- Dwell for 120mins
- 200°C to 400°C at 10°C/min
- Dwell for 60mins
- 400°C to room temperature at 10°C/min

The coating was observed to be non-uniform but well adhered and transparent. No conductivity was measurable below 5MΩ/square.

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National Institute of Standards and Technology. (2009). "Hall Effect Measurements." Electronics and Electrical Engineering Laboratory, retrieved 12/12/2009, from http://www.eeel.nist.gov/812/intr.htm.

CHAPTER 10 - WP3: DEPOSITION OF ANODE MATERIALS

10.1 Overview

This work package examined the use of TCC inks, developing a specification for ink properties and determining printing parameters.

The development of a suitable ink required specification of properties required for screen printing, together with limited characterisation of the relationship between ink rheology and film performance.

Screen printing was selected for this programme on grounds of cost and achievable feature size. DEK designed screens to match agreed test patterns that investigated minimum track and gap width and film thickness and prepared screens of varying mesh sizes, materials and emulsion thicknesses to achieve this.

GEM established reflow temperatures, made a selection of binders based on prior expertise and prepared a series of ITO inks suitable for screen printing.

10.2 Development of test pattern

A test pattern (shown in figure 10.1) was designed to assess print uniformity, consisting of a series of track and gap patterns of varying track/gap width to test the minimum printable dimensions of track and gap. The test pattern also incorporated a 20mm square to test uniformity of printing on larger area features with potential for overprinting of busbars on two adjacent edges. The design also incorporated a linear track of decreasing width with pads inserted at various positions, to test track continuity and sheet resistance.

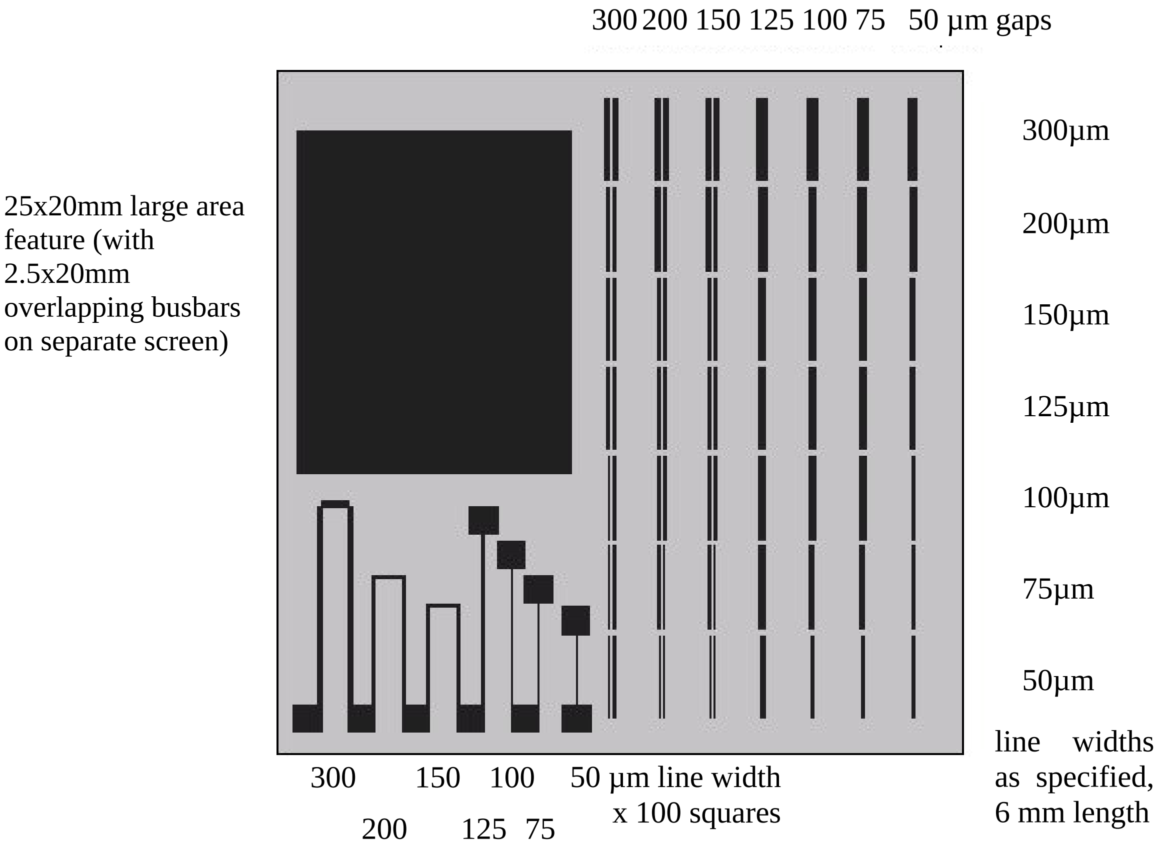


Fig.10.1 Layout drawing of test print component.

A second test pattern was subsequently developed with coarse pitch features to test conductivity. This incorporated a series to 10square ITO tracks of varying width, with larger squares, overprinted at the edges with silver to form electrode contacts. The second test pattern is shown in figure 10.2.

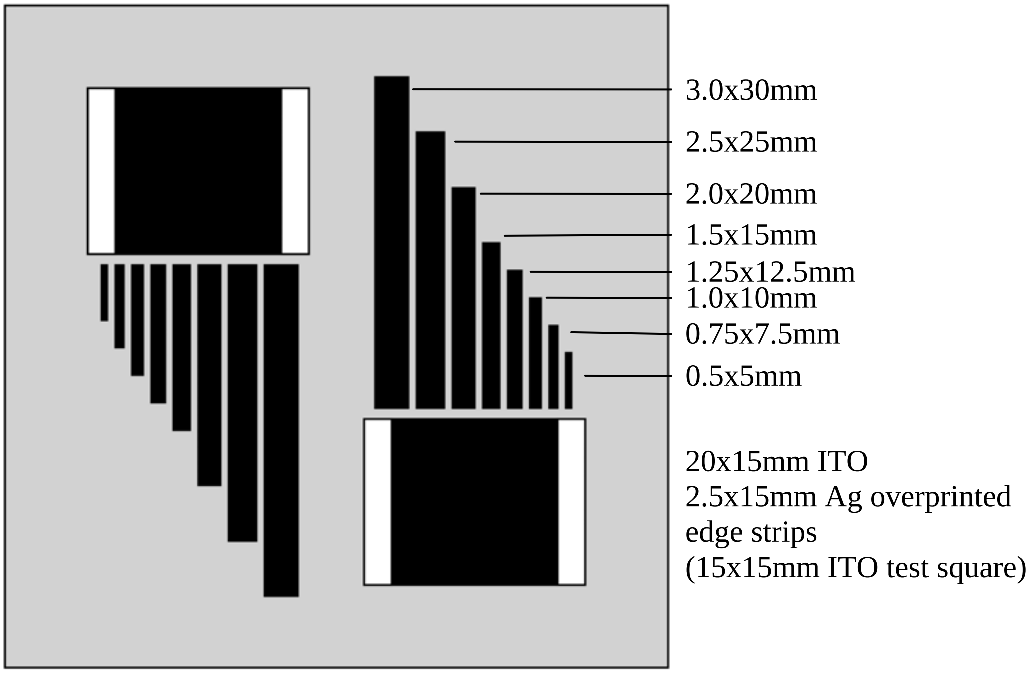


Fig.10.2. Final test print layout, incorporating large area test squares and 10square test lengths varying from 0.5-3.0mm in width.

10.3 Screen selection

Available screen types were reviewed and stainless steel and polyester mesh materials selected with the highest achievable resolution. The highest resolution polyester screen had a 27µm thread size and 380 threads per inch (150 thread/cm) pitch, capable of a nominal 80µm line width and 12µm wet film thickness. The highest resolution stainless steel screen available was theoretically capable of a 60µm line width at 25µm wet film thickness. Since it was desirable to minimise the wet film thickness to reduce the need for dilution, the polyester film was selected.

10.4 Ink requirements

As discussed in Chapter 3, the sol-gel process is a dynamic progression with metastable states at the precursor, the sol and the gel stages, each of which were assessed as to their potential for producing an ink. Although precursors have previously been used directly for preparing films

(Furusaki, Kodaira et al. 1986; Gallagher and Ring 1991) they were rejected for printing due to the high level of structural evolution required, making it unlikely that a suitable film thickness could be prepared to achieve the target conductivity.

The sol and gel states were therefore considered for ink fabrication.

In order to produce a satisfactory film, it was necessary that the ink should have the correct rheological characteristics, particularly shear and thixotropy (related to viscosity and gellation) and also form a coherent film such that, when a wet film was printed it would dry and adhere, curing to produce a film of the correct thickness with high definition of features. It was additionally required that the binders should remain in the system for sufficient time that the film did not powder or dust, but that ultimately they should be entirely removed during the firing cycle.

Additionally, for a commercial process, it was necessary that the ink be stable for at least six months. Whilst this could not be assessed within the scope of the project, systems which showed signs of instability within the project timeframe were noted and excluded.

10.4.1 Assessment of ink rheology

The ideal ink for this application would flow just sufficiently to bridge between the threads of the screen and would then self-level to present a uniform thickness layer. To achieve this is relatively complex, since inks range from highly structured trichromatics which do not flow after printing (Sericol 2009) to solvent based varnishes which flow rapidly to create a level, glossy surface. Whilst both these materials are screen printable, neither would be suited to this application, since the former would result in lack of connectivity and the latter would not be compatible with high resolution prints.

Full assessment of rheological properties was beyond the scope of this project, however, since wetting was required to be good and gellation was relatively rapid, viscosity was a relevant factor. Measurement conditions for inks are not commonly standardised, other than often including measurements at standard room temperature. Different equipment is used, fitted with different measurement cells under different conditions of speed and duration, not only from supplier to supplier but even within a supplier's product range. There are no useful conversions of viscosity measurement between systems. In addition, inks are rarely, if ever, simple Newtonian fluids and hence measured viscosity is highly dependent on measurement conditions.

Families of screen printable materials show a range of viscosity from around 100 to around 400 Pa.s (Todd 1998), although adhesives at around 50 Pa.s (RhinoTech 2006) and solder pastes at around 1300 Pa.s (Poon 1997) have been successfully screen printed.

10.5 Preparation of ink from sols

Following the initial assessment of sols described in Chapter 8, the stability of the precursors can be summarised as follows:

- The simple alkoxides were too reactive to be handled.
- The tetraglyme adduct was similarly reactive and precipitated.
- The methoxide and acetylacetonate could be handled. Addition of water caused cloudiness, but this could be reversed by addition of triethanolamine.
- The ethylhexanoate was highly stable.

The latter three materials were therefore considered suitable for further development work. The ethylhexanoate was preferred, since it did not need addition of triethanolamine for stabilisation.

Assessment of the sol showed a viscosity below the measurable limit of 5Pa.s with available equipment; however comparison with water, viscosity 1Pa.s, and industrial methylated spirits, viscosity 1.2Pa.s indicated a comparable viscosity, *i.e.* approximately two orders of magnitude below the target range.

The precursors were supplied at a concentration of 10wt% and water addition was sufficiently small to disregard with respect to concentration, since for larger volumes dilution with alcohols was not required for accurate control of the added volume. With a printed wet film thickness of 5µm and a target cured film thickness of 150nm, this indicated that a 5:1 dilution was required.

To achieve the necessary change in concentration and viscosity required the identification of solvents and viscosity modifiers which could be fired out during the thermal cycle and not react with the sol to destabilise it. Two routes were considered, the first being the addition of high viscosity solvents, the second being the addition of a proprietary commercial ink base.

10.5.1 Addition of viscosity modifier

Dry methylcellulose of particle size 0.2-0.045mm was mixed with dry IMS at a loading of 2wt%, according to the method of Schulz (Schulz 1994) to yield a high viscosity solution, in the region of 300Pa.s.

The solution was blended with the TEA-stabilised acetylacetonate-derived sol and the ethylhexanoate-derived sol in two separate batches, in the ratio 5:1. Test parts were then printed, using the test pattern and fired according to the schedule identified in Chapter 8. In each case, the resulting material was a white, incoherent powder.

10.5.2 Addition of a commercial ink base

Three proprietary ink bases were obtained from GEM with nominally high, medium and low viscosities. The formulation was not specified, but was known to be based on a large chain alcohol with a cellulosic viscosity modifier.

Test prints were prepared with each of the inks on glass substrates, using the screen and test pattern described above. The prints were assessed using light microscopy to establish whether tracks were intact or broken and whether the gaps between tracks remained separated. The assessment is summarised in table 10.1.

Ink Base	Relative viscosity	Assessment of tracks	Assessment of large square
R2050 408 R1	Low	Minimum track 150µm Minimum gap 200µm (evidence of poor wetting)	No defects observed
R2050 411 R1	Medium	Minimum track 100µm Minimum gap 100µm	No defects observed
R2050 309 R3	High	No continuous tracks No interconnected tracks	Bubbles visible in structure

Table 10.1 Summary of assessment of printability of features from commercially available ink bases.

The medium ink base produced the minimum track and gap dimensions of 100µm. The print is shown in figure 10.3.

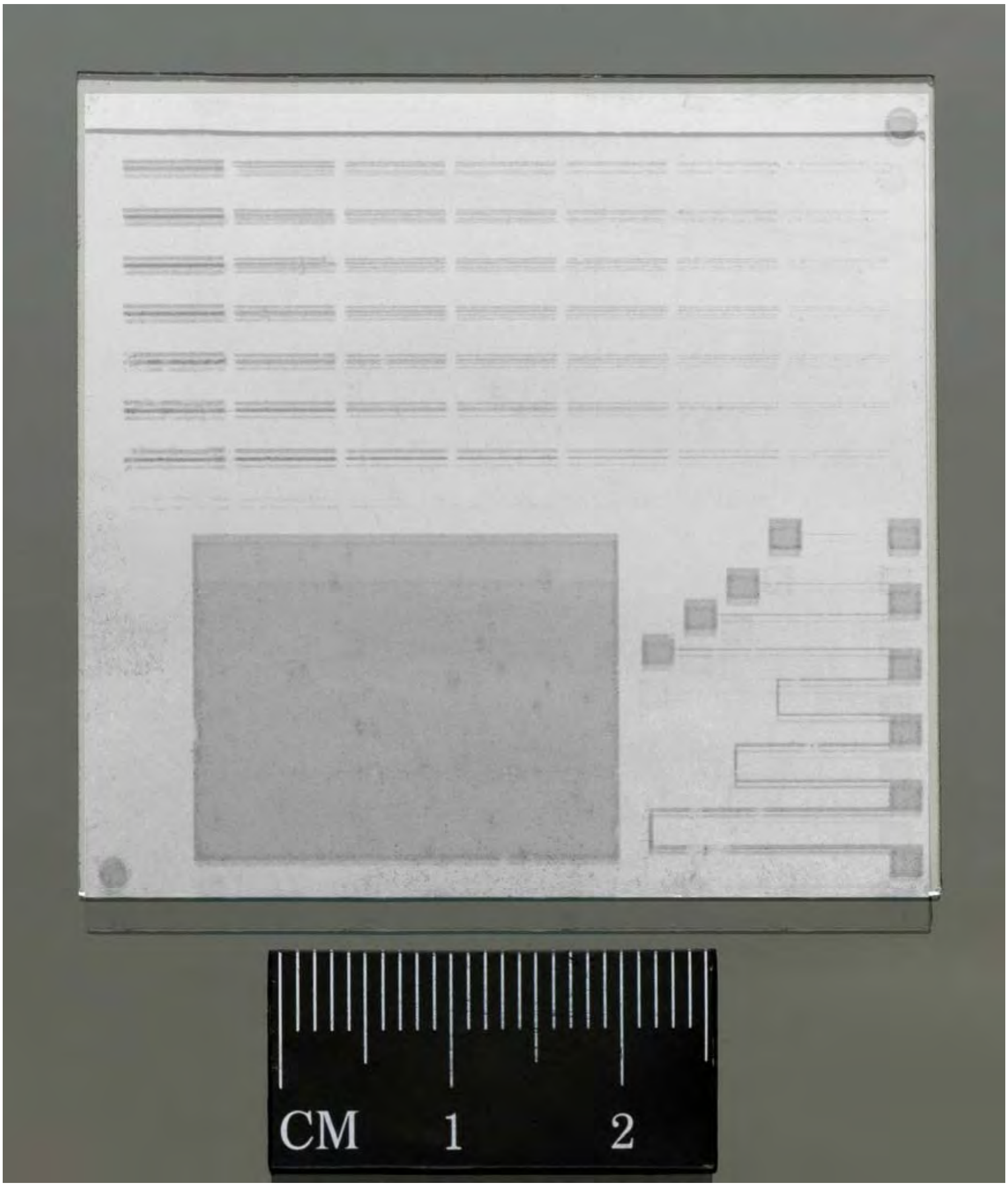


Fig.10.3. Test print prepared using medium ink base.

The viscosity of the ink base was measured using a Brookfield cone and plate viscometer. The machine was calibrated to 100Pa.s; the ink base was measured at 365Pa.s at 19.5°C. Based on the above results, the medium viscosity ink base was selected for further trials.

An ink was prepared, using the medium base and the hydrolysed ethylhexanoate sol. These were blended in the ratio 5:1 and further test patterns printed and fired according to the schedule described in Chapter 8.

The fired films were not coherent, appearing to form powders during processing. This was consistent with the observation that the addition of an alcohol to the hydrolysed/precipitated ethylhexanoate-derived material resulted in a white powder. It was confirmed by the supplier that the ink base included an alcohol.

10.6 Preparation of ink from gels

The alternative metastable state in the sol-gel process is the gel. To prepare an ink from the gel, the sol was precipitated as a xerogel after hydrolysis. This approach had the advantage of removing solvent sensitivity (provided the pH was maintained to prevent break-up of the alcogel particles). An ink could then be prepared by redispersing the xerogel in conventional solvents.

This approach was reliant on identifying T_g and ensuring that the firing sequence included a drying regime to promote slow, gradual shrinkage and sufficient time before crystallisation to produce a film from the colloidal material. The primary issues to be resolved were the development of a suitable xerogel and identification of a high purity solvent base which could be burned out during firing, promoting film stability.

It is known that the maximum suitable particle size for screen printing inks is approximately 1/3 of the hole diameter in the mesh. For this project, the hole diameter was 45microns, defining the maximum particle size as 15µm.

10.6.1 Initial trials

Initial trials were performed with the isopropoxide precursors. Following the observation during stability trials that when water was added to the isopropoxide precursors they were sufficiently unstable that the solution became immediately cloudy and the material rapidly precipitated, a procedure was adopted to form powder from these precursors.

Water was mixed with dry IMS in the ratio 9:1. This was added dropwise to 20ml of the precursor solution. 5ml of solution, *i.e.* 0.5ml water was added in total. The solution turned immediately cloudy and was left to precipitate for 48 hours. Further drops were added until no cloudiness was observed. The supernatant liquid was decanted and the powder evaporated to dryness at 65°C.

The mass loss from TGA measurements had previously been measured at 19.5% (as discussed in Chapter 8). The wet film thickness was anticipated to be 12µm, with a target cured film thickness of 150nm.

To prepare an ink to meet the above requirements, 2.25g of the xerogel was mixed with 20ml of the medium ink base.

The ink was printed onto glass in the test pattern. It was observed that the ink passed through the screen, indicating that the particle size lay below 15µm. The printed film was then fired according to the procedure described in Chapter 8. The resulting film was then inspected under a light microscope to determine film consistency and damage. The film was observed to be incoherent and powdery.

10.6.2 Fabrication of ethylhexanoate-derived ink precursor

The ethylhexanoate precursors were preferred for the sol route, due to the stability of the sol with respect to precipitation, however this required that the sol be destabilised in order to produce a precipitated material. This was initially approached by increasing concentration.

A sample of the mixed ethylhexanoate material was treated with water and evaporated to dryness. The dry powder was then subjected to thermogravimetric analysis, between 100 and 800°C (as shown in figure 8.6). This indicated a mass loss of 63.5% (cf. 19.6% for isopropoxides). Calculation of the ethylhexanoate mass indicated that the loss corresponded to thermal decomposition of the ethylhexanoate ligands and oxidation of the indium/tin network, *i.e.* hydrolysis did not proceed at a suitable rate prior to thermal treatment.

This finding indicated that ethylhexanoates showed considerably higher stability than the other precursors assessed, requiring destabilisation in order to initiate hydrolysis. As previously discussed, stability is most readily altered via pH change. In order to produce a high purity coating (required for good conductivity) any addition to alter the pH needed to either evaporate or be decomposed in the subsequent thermal treatment. Initial trials were therefore performed with nitric acid and ammonium hydroxide.

Two drops of concentrated nitric acid (70%w/v) were added to 2g of precursor solution. The acid proved immiscible and did not produce a precipitate.

Two drops of concentrated ammonium hydroxide (28%w/v) were added to 2g of precursor solution. The ammonium hydroxide proved miscible and rapidly produced a cloudy precipitate. Ammonium hydroxide was mixed with IMS to form a 1M solution. Two drops were added to 3g of the precursor solution. The two solutions proved readily miscible and immediately formed a precipitated which rapidly settled.

10.6.2.1 Assessment of effect of amines on initiation of hydrolysis of ethylhexanoates

Since ammonium hydroxide was effective in facilitating the hydrolysis of a mixed In/Sn ethylhexanoate precursor, alternative amines were comparatively evaluated, in order to assess their potential to produce particulate material of varying size. Amines were selected to provide a range of polarity and molecular size in order to vary reactivity and steric hindrance. The specific amines identified were:

- Ammonium hydroxide
- Triethanolamine (TEA)
- Xylylenediamine (XLD)
- 3-(Dimethylamino)-1-propylamine (DMAP)
- 1,2-Diaminopropane (DAP)

All materials were supplied by Sigma Aldrich Corp.

Each hydrolysis was performed using one of the above amines, mixed with deionised water to form a 28%w/v solution to facilitate direct comparison with the ammonium hydroxide with respect to water addition.

The pH of each of the above solutions was recorded. The results are summarised in table 10.2.

Amine	pH
Ammonium hydroxide	11.0
Triethanolamine	9.1
Xylylenediamine	10.0
3-(Dimethylamino)-1-propylamine	9.2
1,2-Diaminopropane	11.3

Table 10.2 pH for each amine solution used to facilitate precipitation of ethylhexanoate precursors.

Working under an argon atmosphere, 2g of ethylhexanoate precursor solution was weighed into a vial and 0.1ml of the amine solution was added using a micro-pipette, with vigorous shaking to ensure thorough mixing. The solution was observed for an hour and a further addition of 0.1ml made if no precipitation was observed (either as cloudiness or as a settled powder). This sequence was repeated for a third time if required, *i.e.* a maximum addition of three drops.

The results of the assessment are summarised in table 10.3.

Amine	Result
Ammonium hydroxide	0.1ml addition, 1min, production of a cloudy precipitate
DAP	0.1ml addition, 5min production of a cloudy precipitate
DMAP	0.3ml addition, 1.5hrs, slight cloudiness
XLD	0.3ml addition, 1.5hrs, very slight cloudiness
TEA	No effect following additions

Table 10.3 Effect of amine additions on ethylhexanoate precursor solutions.

Treatment with ammonium hydroxide and DAP resulted in the precipitation of solid material; treatment with the other amines did not. Both solid materials were allowed to precipitate and the supernatant liquid decanted, the remainder being evaporated to dryness at 65°C.

Particle size distribution measurements were made on each of the resulting xerogels. The distribution is shown in figure 10.4.

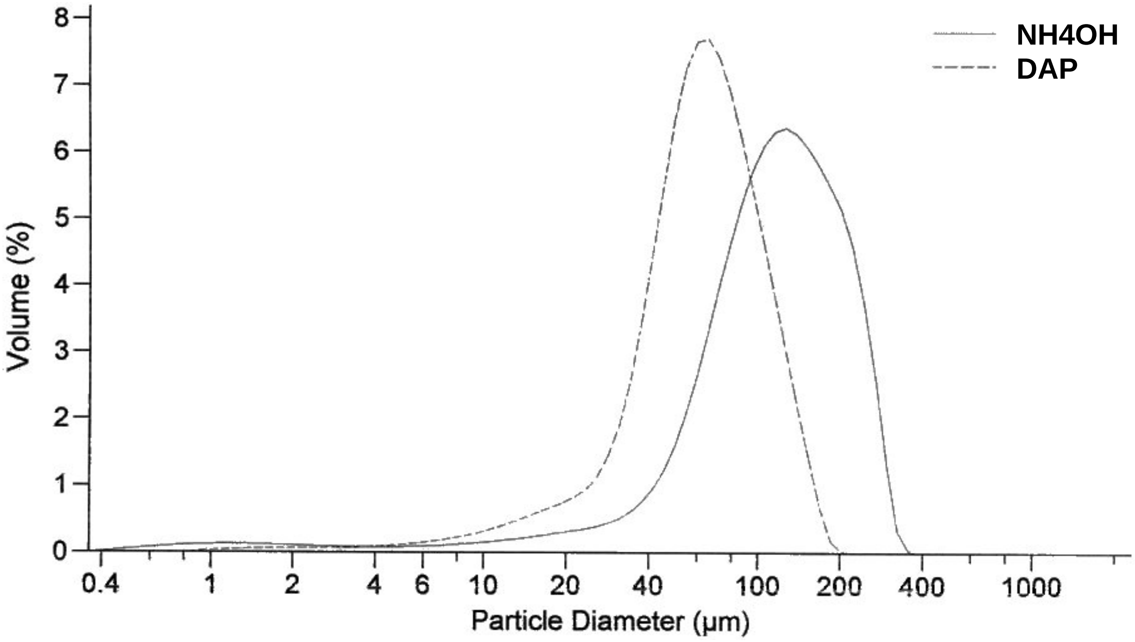


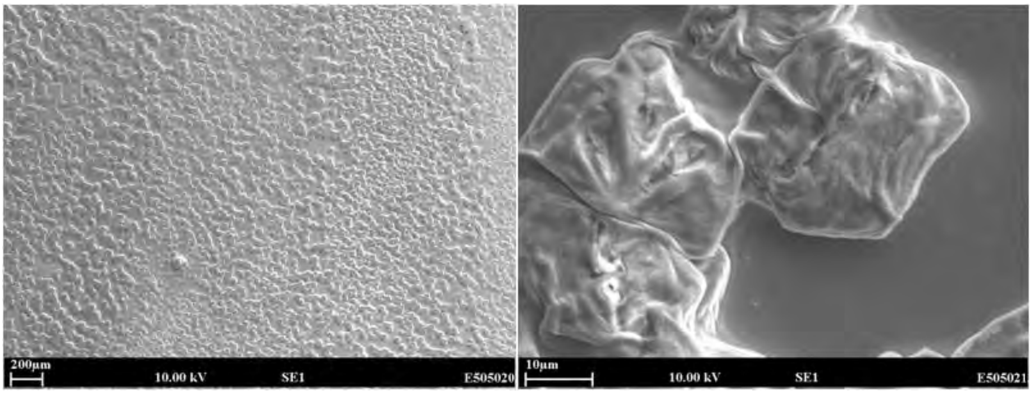
Fig.10.4. Particle size assessment for ethylhexanoate-derived xerogels precipitated by DAP and ammonium hydroxide, showing narrower distribution of smaller particles for material precipitated with DAP.

The particle size distribution of the DAP-precipitated material lay predominantly between 20 and 200µm, centred at 60µm, with a tail into the smaller end, down to 5µm. The mean particle size was 57µm.

The particle size distribution of the ammonium hydroxide precipitated material was broader, lying predominantly between 40 and 350µm, with the peak centred at 125µm. The mean particle size was 100µm.

Further samples of each powder were analysed using environmental scanning electron microscopy to assess the structure of the primary particles and establish the level of agglomeration. Micrographs of each xerogel are shown in figure 10.5 below.

Ammonia



DAP

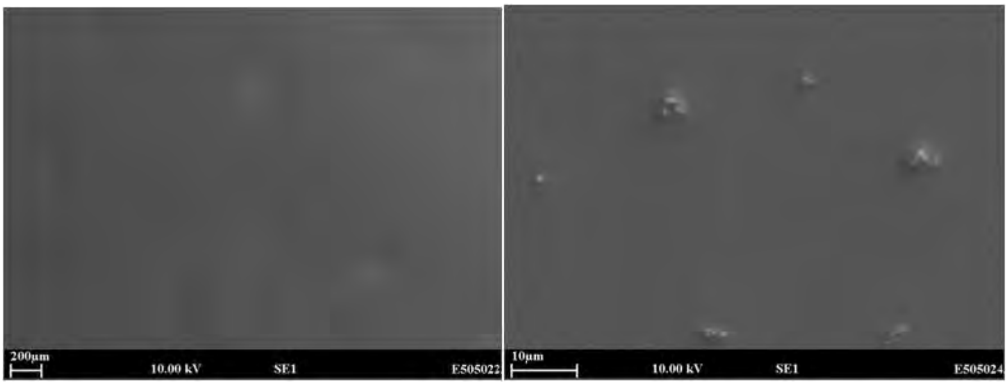


Fig.10.5. Electron micrographs showing the particulate structure of the ammonium hydroxide and DAP precipitated xerogels.

The xerogel precipitated with DAP showed no distinct primary particles and that precipitated with ammonium hydroxide showed a primary particle size of 20µm.

Further material was assessed to establish the dynamic behaviour of the system with sufficient sensitivity to detect nanoscale primary particles. Particle size was measured as a function of time and additive. Particles showed initial growth, to a maximum, followed by reduction with further time. The more polar the amine, the larger the peak particle size measured and the longer the time to peak size. Of the materials assessed, ammonium hydroxide produced the largest particles - peaking at 700nm after 150mins.

10.6.3 Printing trials with xerogel-based ink

A large batch (0.5l ethylhexanoate precursor solution) of ITO precursor xerogel was hydrolysed using 25ml of 28%w/v DAP in de-ionised water and dried at 65°C, resulting in a waxy material. It was observed that this material could be altered to a white powder with IMS.

The material was dispersed using three roll milling. A proprietary binder was added, consisting of a mixture of an ester alcohol and castor oil-derived hydrocarbon solvents with an alkyl cellulose thixogen. The binder was designed to fire out cleanly, resulting in densification of the residual material, rather than leaving residual organics or forming a loose, unbound powder.

Using the data derived from TGA analysis of the ethylhexanoate material, showing mass loss of 63.5% and the predicted wet film thickness of 12µm with a target cured film thickness of 150nm, the ink was calculated to require a concentration of 14.2%w/v. The final formulation contained 15% ethylhexanoate-derived xerogel.

The examples were printed using a 380 mesh polyester screen and fired by heating to 495ºC over 15 minutes, holding at 495ºC for 15 minutes and cooling to below 200ºC over 60 minutes. One print from each screen was overprinted, after firing, with a low temperature heat cure silver ink to provide electrical contact points. The films were characterised for transparency, conductivity and thickness. The printed layout is shown in figure 10.6.

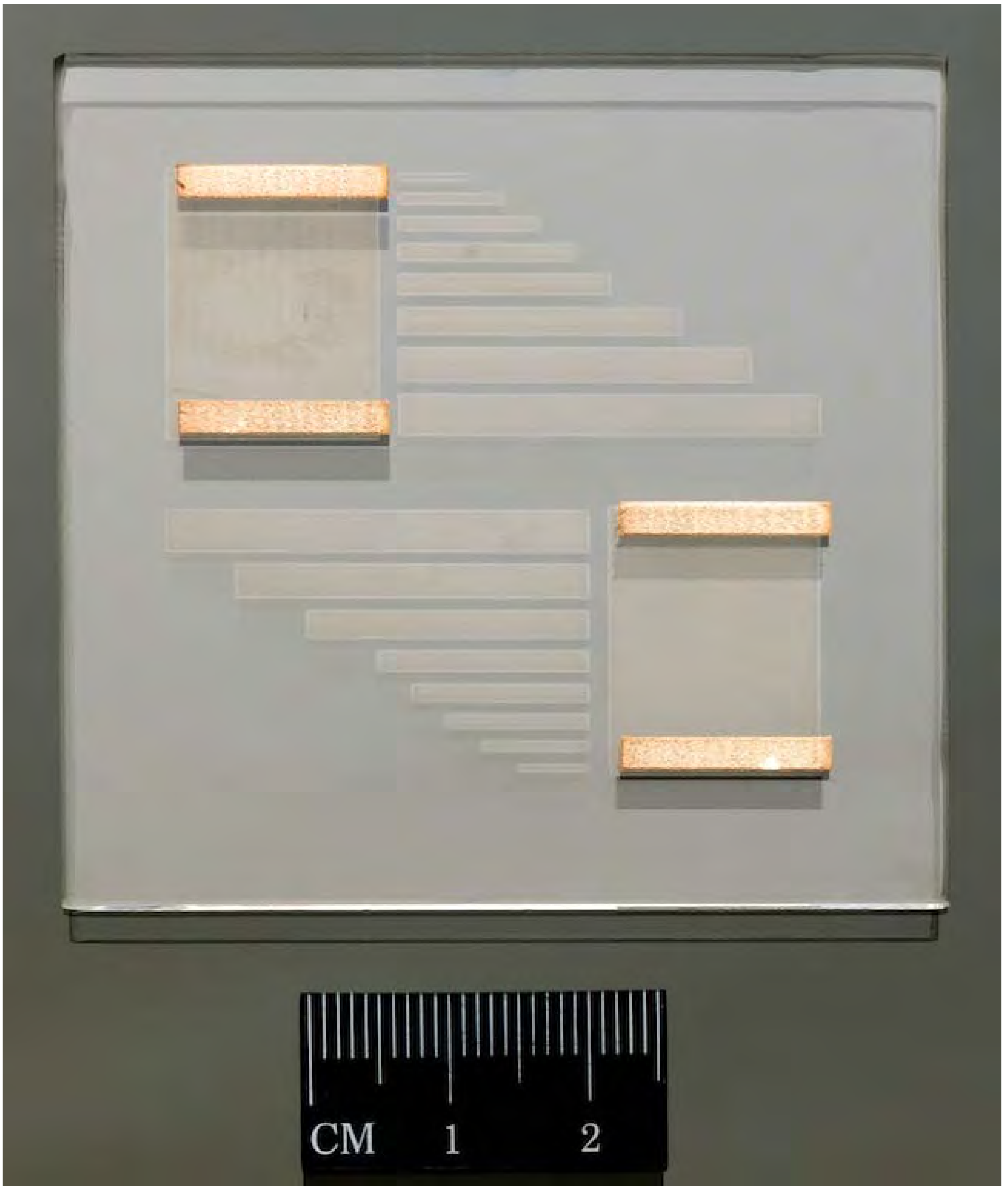


Fig.10.6. Printed ITO structure using second test print layout.

The film thickness was measured to be 140nm across an etched step. The profile is shown in figure 10.7.

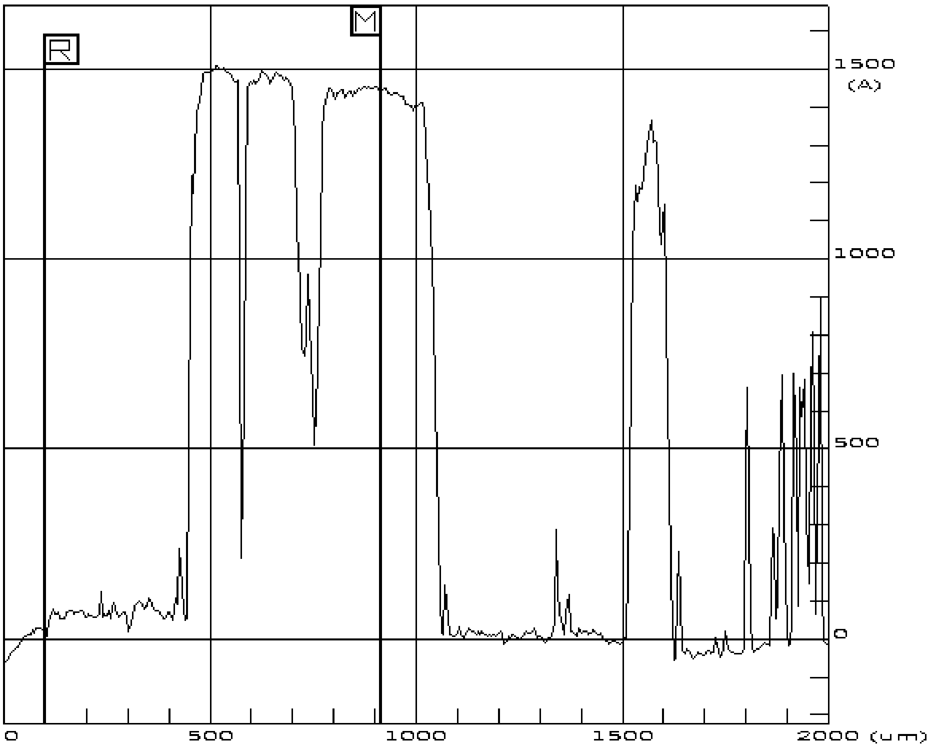


Fig.10.7. Profile across etched step in film, showing thickness of 140nm (recorded between points R and M).

Sheet resistance was measured across the printed square directly between the printed silver contact points. The results are shown in table 10.4. These showed a wide range of variation in sheet resistance value.

Printed specimen	**Sheet Resistance (MΩ/square)**
Sample 1	9
Sample 2	17
Sample 3	13
Sample 4	11

Table 10.4. Summary of sheet resistance from ITO films printed on glass, showing wide range of variation in nominally identical specimens.

X-ray diffraction was used to establish the crystalline phase; the diffraction pattern is shown in figure 10.8.

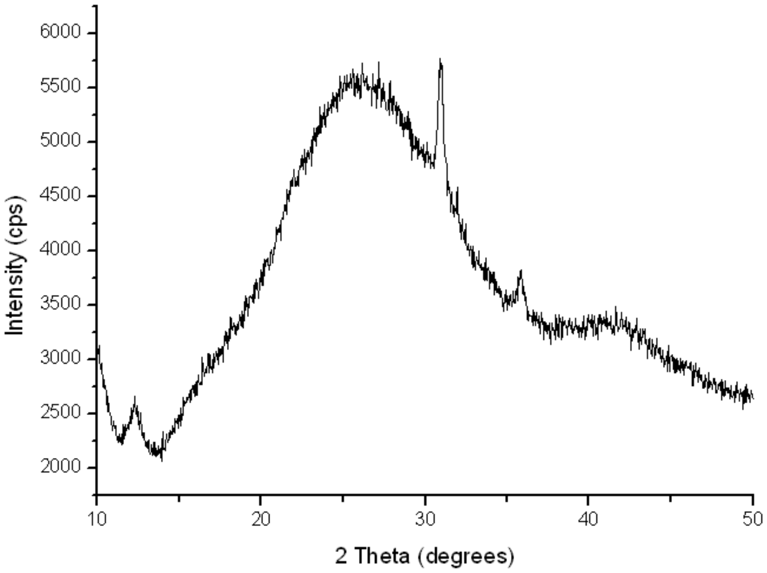


Fig.10.8. Diffraction pattern for the ethylhexanoate-derived, printed film, showing characteristic crystalline peak at 31° after firing.

Compared with the reference glass slide shown in figure 8.3(a) in Chapter 8, the material showed the characteristic crystalline ITO peak at 31°.

Transparency was measured across the ultraviolet and visible range. The printed film was compared with commercial ITO film and the lowest sheet resistance dip-coated material, prepared from a TEA stabilised, isopropoxide derived sol. The three spectra are shown in figure 10.9.

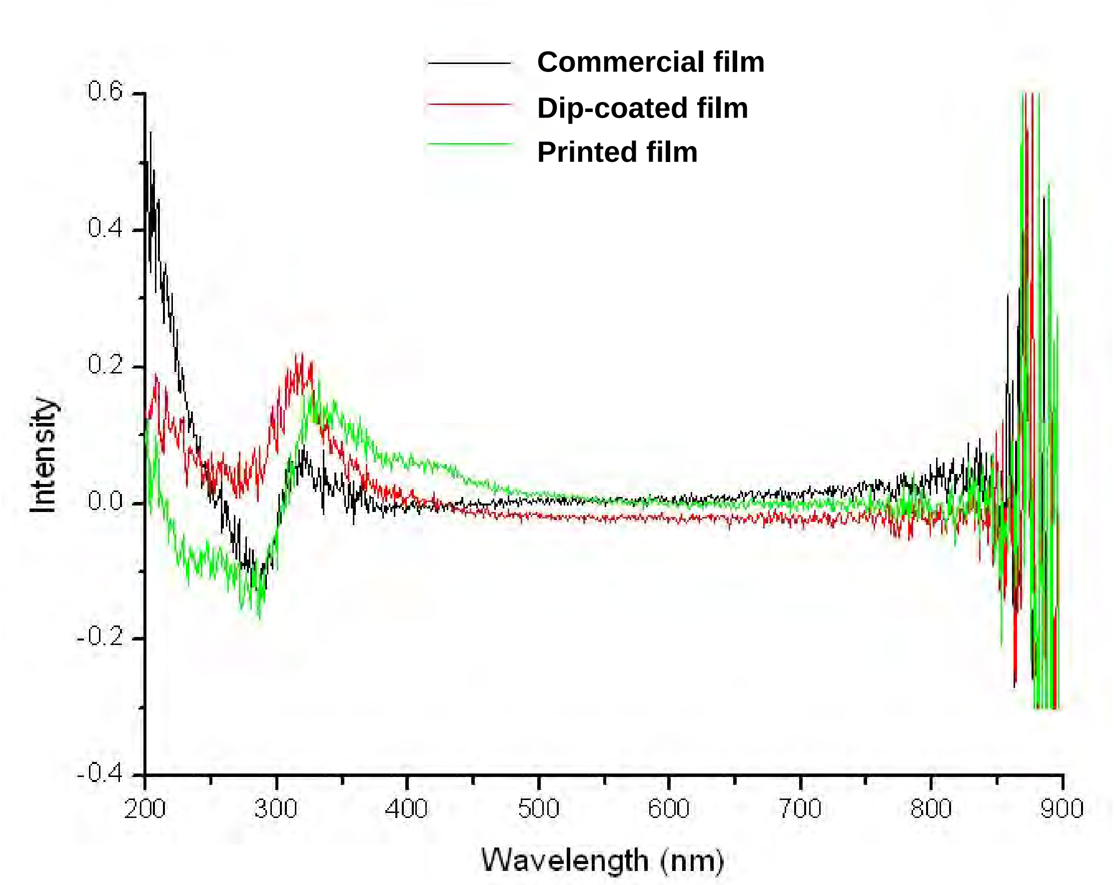


Fig.10.9. Absorbtion spectra of a commercial film, dip-coated film and printed film, showing high transparency across the visible range.

The three spectra are similar, all showing high transparency across the visible region. The dip-coated film showed higher transparency, whilst the printed and commercial films showed comparable transparency. The commercial film showed slightly higher transparency in the blue region of the spectrum, associated with particle size. The plasma edge lies beyond the measurable range, however the onset appears near the upper end of the range measured and is comparable in all three films, indicating a similar level of doping.

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CHAPTER 11 - DISCUSSION

11.1 Introduction

The overall objective of the case study was to develop a liquid phase (printable) route to transparent conductors. This contained within it scientific, engineering and commercial objectives.

In summary, the work performed advanced the state of the art through development of greater understanding of the reaction sequence associated with hydrolysis and condensation of indium and tin precursors. This was correlated with an understanding of the requirements for structural evolution in order that a practical coating could be deposited.

The results of the work are considered below from the scientific and engineering perspectives; also in terms of their commercial implications. The case study is then assessed in its broader context as an approach to commercial R&D.

11.2 Processing factors for transparent conducting coatings

Consideration of the requirements indicated that:

- The end result required was a high purity, inorganic coating
- The coating required two components to be intimately mixed in the correct ratio within a crystalline lattice
- The coating needed to be continuously interconnected, of uniform thickness and without cracks

The sol-gel route was selected for a number of reasons:

- It starts with a liquid phase
- It results in ceramic materials
- By control of reaction conditions, intimate mixing can be achieved at an atomic scale
- Sol-gel is particularly suited to forming thin coatings, since this form allows the drying stresses to be accommodated

The deposition of a sol-gel coating is best considered in respect of structural evolution. As the material progresses from precursor to sol to alcogel, xerogel, fully dense amorphous coating and finally fully dense, crystalline coating, the associated transitions result in decreased degrees of freedom. With progressive evolution, two factors interact.

Firstly, the average distance between atoms decreases. Consequently, the subsequent bond formation (and corresponding shrinkage) required to complete the coating is reduced. In any given step, if the atoms are free to move, the structure is less likely to become stressed in subsequent constrained steps, since the total additional movement to be achieved is reduced. This reduces the likelihood of cracks developing within the coating during subsequent drying and curing. However, once the system becomes constrained, subsequent structural evolution results in reduced inter-atomic distance (and constrained bond angles) and hence stress is generated. From this point on, the system may accommodate the stress if the film strength and substrate strength are sufficient to allow this, or if a subsequent stress relaxation event occurs. If the system does not accommodate the stress intact, it breaks, relieving the stress.

Secondly, the strength of bonding increases (and consequently the kinetic barrier to reversal increases). The consequence of decreased reversibility of bond formation is that, if defects do arise, the facility to alleviate them is reduced and they are therefore more likely to remain as residual cracks within the film, forming discontinuities for electrical conductivity. It also follows that, whilst sintering of a coherent coating is relatively facile; sintering of separate entities (e.g. colloids) into a coherent coating requires greater energy input.

The starting point in the process was with indium and tin precursors in solution. The desired output from this stage was a material with facility for deposition as a wet film. In order to achieve this, it was necessary to process the precursors to the point where sufficient structural evolution had occurred that the resulting material was capable of withstanding the stresses associated with drying and curing as a film. The process challenge can therefore be stated as identifying conditions which facilitated a metastable state where reaction proceeded beyond the precursor but did not reach full condensation.

11.2.1 Consideration of stable states of material for incorporation in an ink

Previous work has considered the use of pyrolytic decomposition of precursors (Xu, Shaikh et al. 1987; Maruyama and Kojima 1988; Furusaki and Kodaira 1991) and sol-gel processing (Mattox 1991; Bel Hadj Tahar, Ban et al. 1998; Burgard, Goebbert et al. 1998). In order to reduce the additional structural evolution required, a sol is a preferable starting point to unhydrolysed precursors. This can be seen from the relative tendency of coatings to show macrostructural failure, with the unhydrolysed ethylhexanoate material forming a powder whilst the formation of a coating was enhanced by using the hydrolysable isopropoxide material .

Indium and tin could be associated in the appropriate ratio from monomeric species under conditions of equal rate of reaction, for example very rapid evolution as in drying. This route would however be limiting to the extent of structural evolution which could be achieved prior to deposition. Ideally, a degree of condensation would also occur, forming larger structures than monomeric hydrolysed species, in order to incorporate the indium and tin species in the appropriate ratio within the structure prior to deposition. Indium alkoxides are known to form five-coordinate ring structures in solution (Mehrotra and Bohra 1983) hence effects of proximity are likely to increase the probability of reaction between indium species if the hydrolysis to condensation transition is too rapid for the hydrolysed species to spatially separate, reducing the likelihood of achieving microstructural homogeneity.

Reaction was necessarily limited to a point beyond which particulate sintering would be required, since the sintering temperature for indium tin oxide is 1650°C (Nakajima and Sato 1992), above that of the useable temperature of the 1737F glass substrate at 721°C (Corning Incorporated 2006). Consideration of available metastable states between these end points implied that the material precursors required processing into either a sol or gel state.

Consideration of the target ratio of indium to tin (19:1) indicated that, for the sol state, intimate mixing was a viable approach to ensuring atomic level homogeneity, whilst for the gel state it was necessary to ensure uniform condensation *in-situ*. For the gel state, it was also necessary to understand the extent of reaction in order to limit it, since a fully hydrolysed colloidal material would require significantly more energy, *i.e.* higher temperature to produce a fully dense coating.

11.2.2 Precursor considerations

Precursors were prepared in the form of an inorganic ionic solution with a range of ligands, varying in polarity and steric hindrance, in order to investigate routes to control of reactivity. High purity was required in the precursors since residual contaminants in the film would reduce performance. Anything which would not be removed during firing, *i.e.* any inorganic components, would therefore not be acceptable in the precursor. The majority of precursor preparation routes are based on halide chemistry, which means that commercial precursors are not generally suitable for high performance applications. This issue was overcome for the project by the fabrication of bespoke, ultra-high purity precursors, confirmed by ICP analysis.

This approach was, however, limiting to the range of precursors which could be evaluated on commercial grounds.

11.2.3 Controlling precursor reactivity

The preferred method for controlling reaction was the use of minimum addition of water, calculated with respect to the ligands present in the system. This approach had the advantage of not being selective with respect to reaction rate between the indium and tin. In order for the reaction to proceed, it was theoretically necessary to add water at a half stoichiometric quantity with respect to ligands. However, initial assessment indicated that all of the precursors, with the exception of the ethylhexanoates, showed high sensitivity to water, with the formation of precipitates even on exposure to atmospheric moisture. This indicated that under room conditions, reaction proceeded rapidly from hydrolysis to condensation, such that hydrolysis was not complete before condensation began. Consequently, the sol was highly inhomogenous, which was limiting with regard to formation of high quality material. This may be compared with previous work based on dip and flow coating, where hydrolysis and gellation may be allowed to occur rapidly within the wet coating. In this project, more control was needed since formation of the coating during printing would be relatively slow and stability was therefore required within the ink. The initial instability was overcome by handling under dry, inert gas, either nitrogen or argon, in a glovebox. The requirement to transfer the material to air for subsequent processing necessitated the pre-hydrolysis of the precursors.

Observation of the reactivity of simple alkoxide precursors (both isopropoxide and tert-butoxide) showed them to be highly reactive, with gellation occurring almost within 5 minutes of addition of water in all cases. This presented difficulty in limiting the extent of reaction prior to coating deposition, in order to make subsequent sintering practical, observed in the initial study where dip coating initially produced a white, powdery coating. Further development of alkoxide sols produced a coating material (Sol 1) with high purity, capable of depositing an ITO material and subsequent development established that it was possible to form a good coating via direct *in-situ* hydrolysis and condensation of the precursor. This approach was not transferrable to a printing process. It was therefore necessary to decrease the rate, and extent, of reaction.

The first approach taken was the incorporation of more sterically hindering ligands. As discussed in Chapter 3, larger ligands decrease reaction rate. Since the alkoxide solution can undergo ligand exchange with available –OH groups in solution, addition of alternative ligands such as 2,4-pentanedione was considered. This ligand chelates across the cation, reducing reactivity. The ligand also alters polarity of the bond, changing the point zero charge value and necessitating adjustment of the pH, ideally without the addition of water (since water concentration also affects reaction rate). This could be observed with the isopropoxide precursors, where the addition of 2,4-pentanedione reduced reaction rate when the pH was decreased with glacial acetic acid. 2,4-pentanedione was also added to the indium methoxide/tin diacetate precursor solution and showed a similar effect in reducing reaction rate at reduced pH.

Reducing reaction rate was beneficial in achieving comparable reactivity between the tin and indium precursors. Steric hindrance alone was however, insufficient, since the precursor route which resulted in the highest performance (lowest sheet resistance) had a lifetime of 30mins before precipitation which was still insufficient to allow ink fabrication and printing.

An alternative approach to ligand exchange was to use alternative precursors, *i.e.* to exchange the ligands during precursor fabrication, prior to initial hydrolysis. Alternative approaches considered were the methylation of two of the indium sites, with the third site being occupied by either a methoxide, *tert*-butoxide or an acetylacetonate ligand, the latter being isostructural to the 2,4-pentanedione substitution. With simple addition of water, reaction rates were observed to decrease, with time to gellation being >6days for stoichiometric addition to the methoxide, 2hrs for minimum addition to the *tert*-butoxide and 3days for the equivalent addition to the acetylacetonate. The methoxide showed higher stability than may be anticipated with respect to direct hydrolysis and condensation, however it also showed ongoing evolution of methane, suggesting that gellation may be inhibited by this evolution.

The greatest stability was exhibited by the ethylhexanoate precursors, which showed no visible reaction with water addition at neutral pH. The ethylhexanoate ligand had significantly more steric hindrance than any of the other ligands, limiting both the reaction rate and extent. Consequently, coatings prepared from this material, even after exposure to water, effectively underwent pyrolytic decomposition, resulting in an excessive degree of structural evolution and consequent lack of cohesion due to failure to withstand the curing stresses.

11.2.4 Stabilisation of the evolved state

The high sensitivity of the precursors to water meant that, although it was possible to reduce the rate of reaction, it was not possible to reach a satisfactory equilibrium position for the formation of a stable sol under conditions of neutral pH. pH was therefore varied in order to produce conditions under which an equilibrium point was maintained, effectively the point zero charge value for the material.

A number of factors required consideration to ensure correct network formation after coating. The addition of a pH modifier results in a compositional change to the sol. Since retention of the modifier within the fired crystalline structure would reduce conductivity, the range of additives which were available for consideration was limited to those which evaporate or decompose and do not have the potential for incorporation within the lattice (such as halide acids). It was also necessary to consider that many potentially suitable pH modifiers, such as ammonium hydroxide and mineral acids, are most conveniently handled as aqueous solutions, hence the water addition from the pH modifier itself had to be taken into account when calculating the water concentration, and in some instances it was not possible to achieve the desired minimum water addition if the concentration of the pH modifier was low and a minimum addition of this material was required.

It was necessary for the additive to be present in stable form within the sol to stabilise it, however after coating the objective was to form a network, which required that the sol became destabilised. This was predominantly through increase in sol concentration, however the concentration of solvent and concentration of pH modifier were simultaneously changed, the former decreasing, the latter either decreasing or increasing, depending on its volatility under the drying conditions.

This complex interaction was difficult to anticipate and not possible to deconvolute in real terms. Practically however the approach adopted was to establish conditions where the sol was marginally stable with respect to precipitation at the starting concentration, so that, so far as possible, precipitation began once the concentration increased during drying from the wet film.

11.2.4.1 Decreasing pH

The addition of weak acids to the precursors had the advantage that both acetic and acrylic acids could be added independently of water. Both weak acids had the effect of reversing precipitation within the isopropoxide and dimethyl indium acetylacetonate/dimethyl tin diacetate sols, resulting in solutions with continuing turbidity but no gellation over a period of days. The use of a weak acid therefore resulted in stabilisation. The addition of strong acids (hydrochloric and nitric) similarly showed reversal, but the solution to which nitric acid had been added became yellow. It is postulated that the addition of strong acids resulted in dissolution through reaction to form the corresponding salts. Whilst the thermal decomposition of nitrate solutions has been successfully used to form an ITO coating, this approach has similar drawbacks to the other pyrolytic decomposition routes discussed above.

11.2.4.2 Increasing pH

The use of TEA to vary reaction rate had previously been reported. TEA was found to successfully stabilise sols derived from the isopropoxides, the dimethyl indium acetylacetonate/dimethyl tin diacetate and the dimethyl indium methoxide/dimethyl tin diacetate precursors. Since, the hydrolysis step of each of the precursors results in an essentially similar hydroxide-bonded structure, the similarity in stabilisation behaviour observed with the hydrolysed isopropoxide and dimethyl indium methoxide/dimethyl tin diacetate suggests that the TEA acted to stabilise an essentially fully hydrolysed state. This is in contrast to the dimethyl indium acetylacetonate/dimethyl tin diacetate derived sol, which became yellow, indicating a different structure. Since the principal difference was the presence of the chelating ligand, it is postulated that in this structure the indium precursor contained a stable hydrolysed ligand, with a chelated 2,4-pentanedione ligand, *i.e.* a mixed structure which, having only one single cross-linkable bond was not suited to network formation.

11.2.5 Influence of controlled evolution on coatings

The various additions made to alter the pH had an influence on coating performance. The use of simply hydrolysed precursors was generally ineffective, since the reaction proceeded too rapidly and to a greater extent than desirable for subsequent network formation. By varying the pH, it proved possible to stabilise the liquid state, *i.e.* to arrest reaction before gel formation. On forming coatings from these materials, it was apparent that the coating quality was improved, in respect of continuity and sheet resistance. Coatings where strong acids had been used to stabilise the solution did not wet glass well, forming droplets. This suggests an incompatibility between the surface energy of the liquid phase and the solid substrate. By contrast, solutions that were stabilised with weak acids wetted the glass slides well, indicating combatibility between the point zero charge value of the substrate and the solution.

The coatings prepared from sols stabilised with TEA showed considerable improvement over unstabilised sols, indicating that pre-hydrolysis was successful in increasing the extent of structural evolution to a controlled extent. This approach resulted in material with a sheet resistance value of 6kΩ/square, the lowest achieved within the project.

11.3 Approaches to printing

The project sought to develop a screen printing route to TCCs. Screen printing was selected for this project on grounds of cost and achievable feature size. The targets for this project were analogous to the decorative pottery industry, where final film thicknesses of 150-200nm are achieved by using a simple organic carrier with additives which fire out.

The difference between the printing of electrically functional materials and conventional graphic printing is that the material in the latter is functional only from the top surface. So long as the layer provides good coverage, features such as holes, cracks and non-uniformity of thickness are largely irrelevant with respect to performance (considering the large discontinuities in newsprint pictures for example). By comparison, an electrically functional material is dependent for its performance on continuity of connection and cross sectional area. A device with varying thickness will show high conductivity in thick regions and low conductivity in thin regions.

In order to produce a satisfactory film it was necessary that the ink should have the correct characteristics (viscosity, concentration and gellation primarily) that, when a wet film was printed it would spread to a uniform thickness in the regions obscured during ink application by the threads of the screen; then dry and mechanically adhere, curing to produce a film of the correct thickness with high definition of features. It was additionally required that the binders should remain in the system for sufficient time that the film did not powder or dust, but that ultimately they should be entirely removed during the firing cycle.

The processing routes discussed above resulted in a material with stability over a sufficient time period to produce an ink, however additional requirements needed to be met to make the system printable, since the viscosity was well below that needed for printing and the requirement for good wetting to achieve good adhesion had the counterproductive effect of causing the ink to flow beyond the boundaries of the printed pattern.

Two routes were considered, the first being the addition of high viscosity solvents, the second being the addition of a proprietary commercial ink base. The former offered the potential for control of purity; the latter offered known design for printability but little opportunity for control of purity.

11.3.1 Sol vs. Gel state as an ink additive

Two alternative approaches were identified to the development of a printable ink.

The first was to use a stable sol (as described above) and change viscosity and concentration to allow printability. This route was attractive for commercialisation since it was based on relatively simple processing steps and minimised contamination. The difficulty arose in finding suitable solvents to achieve printability which did not react with the sol to destabilise it.

The alternative approach was to use a gel to increase stability via increased structural evolution. The principal issue to resolve was the need to create a coherent layer with a minimum of energy input. This indicated the need for partial hydrolysis/condensation, rather than full condensation to a colloidal material.

11.3.1.1 Sol

In order to formulate a suitable ink, methyl cellulose was used to increase viscosity. Methyl cellulose was selected, since it is available at high purity and thermally decomposes. It is a solid, soluble in water and small chain alcohols. Dry IMS was therefore used, in order to avoid addition of excess water. The ink was observed to print well, producing a uniform wet film, but the cured film became powdery and did not adhere. This is postulated to be due to a combination of three factors.

Firstly, the addition of IMS, required to dissolve the methyl cellulose, is anticipated to result in ligand exchange. The resulting methoxide and ethoxide groups are likely to be considerably less stable, promoting early network formation. Secondly, the volume of methyl cellulose required to increase the viscosity sufficiently resulted in considerable dilution, requiring the printing of a wet film thickness of 2µm to form a cured film thickness of 150nm. Gellation of the sol can occur at concentrations as low as 1%, hence a volumetric reduction of approximately a factor of 20 was required. This was likely to result in high levels of stress in the coating, leading to failure. Thirdly, the methyl cellulose itself forms a gel. It is likely that the methyl cellulose gel would disrupt formation of the inorganic gel.

Curing of films printed from inks formulated from the sol and a commercial ink base showed similar results with regard to formation of a powdery film. It was not possible to reverse engineer the ink base, but it is postulated that the factors described above are likely to be relevant, particularly since it is known to contain an alcohol. More significantly, the lack of facility to vary the system meant that this approach was unsatisfactory.

It was concluded that the likelihood of developing a solvent system which combined all the necessary attributes of reactivity in the precursor to achieve hydrolysis and stabilise the resulting sol, with the necessary attributes for printing was very low.

11.3.1.2 Gel

The advantage of a gelled system was reduced reactivity with respect to the ink base, due to increased structural evolution. Coincidentally, the use of a gelled system increased the likelihood of forming a high integrity coating, due to the decrease in further structural evolution required to form the cured film. The work discussed above did not identify any stable gel structures; therefore an alternative approach was required. The ethylhexanoate system was the only option identified which did not proceed rapidly beyond the required gel state, since the lack of precipitate formation suggested that it was unlikely to proceed to full hydrolysis. The challenge was finding a suitable method to activate it.

The work discussed above indicated that varying pH was successful in changing hydrolysis behaviour, particularly with TEA. A similar approach was used with the ethylhexanoate precursors. A range of amines was used to vary the pH. The behaviour of the precursor when exposed to various amines showed reactivity at higher pH; ammonium hydroxide and DAP being preferred, with a pH of 11.0 and 11.3 respectively. This was successful in forming a precipitated material, whilst the addition of other amines with lower pH (for example XLD at 10.0) did not form similar precipitated material.

The objective was to form a partially hydrolysed material, in contrast to the fully hydrolysed colloidal precipitate produced during work with the more reactive precursors. This was confirmed through TGA, which showed the precipitated material to have a relatively high mass loss of 63.5%, attributed to residual alkoxide ligands within the structure.

The ethylhexanoate derived material was shown to have reactivity with small chain alcohols, through reaction with IMS, which resulted in a powdery structure with similar characteristics to the precipitates discussed above. This also indicated that there are structural differences between the material which has been re-dispersed with IMS. These probably correlate to an alcohol exchange mechanism, indicating promising reactivity for the formation of a fully reacted structure, but also necessitated the formulation of an ink without the inclusion of such alcohols. The particular ink base selected therefore used larger ester alcohols.

The screen used had 380 threads per inch (150/cm) with 27µm diameter threads. This leaves a gap spacing of 40µm. Theoretically, this would limit particle size to 1/3 of the spacing, *i.e.* 15µm. However, practical experience indicated that the threads experience some lateral movement and printing would be likely to be satisfactory with particles up to 100µm diameter. Evaluation of particle size in the material treated with ammonium hydroxide and DAP indicated a smaller particle size from the latter, with a mean value of 57µm. Primary particles were established to be considerably smaller, however the degree of attrition of the waxy particles was anticipated to be limited, hence DAP was selected due to compatibility with the printing screen. An ink was successfully prepared, producing a satisfactory print pattern for the demonstrators.

Since the gelled material required sintering to form a network, the thermal processability was assessed, using HTXRD and hot stage microscopy. Analysis indicated that, on heating, the material underwent, sequentially, a sharp liquification and flow point at 285°C, thermal decomposition between 300°C and 460°C and crystallisation at 440°C. Assignment of the liquification event is complicated, since the structure contained both hydrolysed and organic elements. The latter would conventionally be described as melting, while the former would be described as a glass transition. In this case, the event incorporated both, but in practical terms it resulted in reflow, which facilitated homogenisation of the printed layer.

Crystallinity was confirmed by powder XRD after firing at 500°C, indicating the peak temperature for processing.

No cracks were observed in the fired film. Since the reflow event occurred before decomposition, it is indicated that sufficient structural evolution was achieved in the gelled structure to facilitate subsequent processing without excessive additional shrinkage. The principal issue lay with the low conductivity of the film, at 5MΩ/square. Film thickness was measured on tracks at 140nm, lying close to the optimum thickness, indicating that the screen was satisfactory, but considerable variation in thickness was measured between edge and centre of open regions, the former corresponding to the track thickness and the latter lying below measurable range. The thickness at the edge of screen printed areas is controlled by the emulsion, while the central region is not similarly controlled. This is an inherent factor in screen printing and it was therefore concluded that, whilst good results were achieved in the x and y plane, the technique was inherently unsuited to the level of control required for the z direction across open areas. Distinct translucency was observable in the film, indicating that the curing conditions resulted in a considerable degree of internal refraction, corresponding to lack of connectivity. It is likely that these factors combined to limit conductivity.

11.3.2 Comparison between dip/flow coating and screen printing

Three approaches were taken to deposition within the scope of this project; direct coating of the precursor, direct coating from the sol and screen printing from an ink.

Direct coating from the precursor was limited in scope. No structural evolution occurred prior to deposition and the resulting coatings were either dependent on *in-situ* hydrolysis and condensation, as in the case of the isopropoxide precursors, or dependent wholly on subsequent pyrolysis, as in the case of the ethylhexanoates. The latter was dependent on high temperature sintering for film formation, which was not practical within the thermal budget allowable for the substrates. The first phase of the work demonstrated that it was possible to form conductive films from the former, with the best performance achieved being transparency of 98% and resistivity of 1.5×10^{-2}Ωcm by firing in nitrogen. Thickness was, however, limited without severe cracking. This was limiting to performance, since the coating thickness was below the threshold required to overcome grain boundary effects. Additionally, for these films the composition ratio was not ideal and the sol precursors were known to contain impurities that have an adverse effect on resistivity. The surface finish when sintered under inert atmosphere was however superior to that of the commercially sputter coated sample.

Direct coating from the sol, via dip and flow methods, was a logical starting point for the second phase of the work. Performance was measured in respect of transparency and conductivity. Resistivity of $3.0\text{x}10^{-2}\Omega\text{cm}$ was achieved with firing in air within the second phase of the project, through a combination of higher purity precursors, enhanced stabilisation of the sol, facilitating greater structural evolution prior to deposition, and an improved curing procedure. Transparency was measured at 98% at 550nm. It was also found that structural evolution was further promoted by a longer delay between coating and firing. Film thickness at 60nm was, however, still limited, lying well below the critical threshold value of 100nm to overcome grain boundary effects. The films also showed considerable cracking.

With a screen printed film it was possible to use a gelled material, incorporating a higher degree of structural evolution prior to coating deposition. This resulted in a thicker film without gross defects (cracks or holidays) at the target thickness of 140nm. Whilst overall transmission at 550nm was equivalent to that of the dip coated specimens, the observable haziness of the coating meant that the high resistivity figure of 7.0Ωcm was attributed to poor internal connectivity within the structure.

A correlation could also be observed between crystallisation temperature, T_c and processing route. The quoted bulk value for T_c of ITO is 560°C. In the gelled ethylhexanoate material this was reduced to 440°C whilst for the isopropoxide material crystallisation was observed above

340°C. Thus crystallisation temperature can be correlated to particle size, with smaller particles resulting in a lower T_c.

11.3.3 Alternatives to ITO

Within the programme, F-doped tin oxide and Si-doped zinc oxide were identified as alternatives to ITO. FTO is well known, being generally prepared via CVD directly onto a float glass surface during manufacture. By extrapolation from the development of ITO, tin oxide precursors were necessarily compatible with processing as discussed above. This was validated by assessment of the tin ethylhexanoate precursor.

Si-doped zinc oxide showed comparable performance to ITO, with inherent resistivity of $6x10^{-4}\Omega^{-1}cm^{-1}$ when prepared by PLD. The development of a synthesis route via sol-gel was progressed through early stage development to show proof of concept.

The system had the advantage that the fabrication of silica is the most widely studied area of sol-gel processing. Tetraethylorthosilicate (TEOS) is a well known precursor which is readily hydrolysed. The requirement within this programme was therefore to identify a zinc oxide precursor with comparable reactivity. The majority of previous work with zinc oxide indicated that reaction rates are generally too high, so a sterically hindered precursor was initially considered.

Assessment was made of the zinc ethylhexanoate precursor, which was analogous to the indium and tin precursors. Reaction proved to be considerably slower than with the indium and zinc analogues, with gellation observed in a minimum of 15 days with ammonium hydroxide addition. This made the zinc ethylhexanoate precursor incompatible with the tetraethylorthosilicate dopant, where reaction would be expected to occur under comparable conditions in a few hours.

A more reactive precursor was therefore required. An ethoxide group was selected, being compatible with similar solvents to TEOS, since ligand exchange would be equivalent. By analogy with the indium and tin precursors, one of the ligands was substituted with an unhydrolysable alkyl group, in this case an ethyl group, in order to limit the extent of reaction. This material showed high sensitivity to water, gelling even with very low concentrations. The reactivity was considerably higher than that of the dopant, however by use of a very low water concentration, reaction with either species became probabilistic, resulting in comparable rates of reaction.

The production of an undoped zinc oxide xerogel resulted in a white powder, indicating that hydrolysis progressed substantially and was not successfully stabilised as a partially hydrolysed gel. This was consistent with the high firing temperatures (720°C) required to sinter zinc oxide coatings prepared from the ethyl zinc ethoxide precursor. By contrast, the silica-doped zinc oxide remained liquid even under vacuum at 80°C for 36 hours. This result was surprising, however it is consistent with the behaviour of some zinc complexes such as zinc ammonium chloride, which decomposes before drying. It is therefore postulated that a zinc silicon complex was formed. This would require confirmation by silicon NMR, which was not available within the scope of this project. The material would, however, necessitate a different approach to formulation of an ink to that employed with a solid or gel-forming material. It is also apparent that the indium-free system was developed to a considerably less advanced state than the ITO system and it was therefore not possible to consider its commercial viability at the end of the project.

11.4 Relationship between project results and industrial need

The commercial drivers which led to the development undertaken in this project were discussed in Chapters 4 and 5, hence it has been established that there is demand for a product which meets certain requirements. In order for the process to be commercially applicable it had to meet a technical need in a cost effective manner. The process developed can therefore be considered relative to currently available materials in respect of technical performance, correlated to industrial applications. Consideration is also given to the process aspects relevant to cost.

11.4.1 Comparison with commercial ITO

The conductivity observed in the dip coated specimen was approximately an order of magnitude below the commercial sample.

The two central issues to achieving the target of a transparent conductive coating are:
1) The inherent material properties of the coating.
2) Achieving a coating morphology which is continuous, as opposed to discrete islands of material separated by cracks.

Considering these in turn:

1) Material properties

The principal target material was ITO which, when produced by other routes, gives the required properties. The material characteristics of sputtered ITO are those of a homogeneous, fully crystalline material with a specific level of tin doping. Failure to achieve the desired properties may stem from:

a) Inappropriate doping levels

b) Inhomogeneous network formation with discrete tin-rich and tin-poor zones

c) Inappropriate lattice siting of the tin

d) Contamination affecting the conduction bands

Crystallographic analysis indicated that the material was crystalline and showed an appropriate structure to indicate the formation of ITO. Assay indicated that the dopant level was correct and showed no residual impurities.

2) Coating quality

Should the fabrication route yield the desired material, this may not be readily recognised if the processing route yields a heavily cracked coating. Electrical measurement of such a coating will indicate low or zero conductivity if the probes are set at a distance greater than the mean island size.

The coating structure was too thin to facilitate microwave measurement of inherent conductivity; however physical observation indicated that the most likely reason for this result was lack of connectivity. This was observable in the combined effects of the coating thickness lying below the threshold required to overcome grain boundary effects and the coating containing defects in the form of cracks.

In the printed coating, no gross cracks were observed, but the coating showed poor clarity, associated with a high level of internal refraction. This indicated that the high resistivity observed was associated with poor connectivity.

A typical ITO coating for use as a substrate in a thin film display would be prepared by sputter coating. Transparency and conductivity are a function of coating thickness and, since deposition rate is constant, a function of deposition time.

By contrast, a sol-gel coating deposition (be it dip, flow or printed) uses a single pass process to produce a given thickness. Since it is not a cumulative coating, the drying process requires a high level of control to produce a suitable thickness of sintered film from the wet film without cracking or powdering due to residual internal stress.

In all cases, transparency exceeded the target. The commercial material, dip coated film and printed film all showed equivalent transparency, at approximately 93%.

As described in Chapter 5, transparency (α) and conductivity (σ) are dependent on thickness and can be related as a quantitative figure of merit (FOM) for TCC performance proposed by Gordon (Gordon 2000):

$$\sigma/\alpha = -\{R_r \ln T\}^{-1} \qquad (11.1)$$

where R_r is the sheet resistance in Ω/square and T is the total visible transmission. This can be used as a quantitative FOM for TCC performance.

By this metric, using supplier's data, as shown in table 5.1 in Chapter 5, commercial ITO achieves a value of 0.73, with a peak performance of 4 for research grade materials produced by CVD. The air-fired dip coated sample produced within this project achieved a figure of 8.2×10^{-3}. The printed part achieved a figure of 2.8×10^{-6}.

Surface roughness and grain size measurements indicated that the nitrogen-sintered sol-gel derived film had a lower average roughness value (both R_a and R_z) and smaller grain size than the commercial reference sample, whilst the air fired sample showed greater average roughness. None of the samples showed significant individual features since the R_q value was proportionate to the average peak to trough value (R_a). This suggests a smaller initial grain size in the sol-gel film than in the sputtered film, but with grain growth promoted under oxidizing conditions.

No spikes were detected in any of the samples, but they are known to be formed intermittently in sputtered films, through sputtering of nodules from the target surface. The absence of spikes in the sol-gel process and the potential for a smoother surface when firing under nitrogen offers substantial advantages for applications where thin layers are to be deposited on the ITO surface, such as thin film displays.

11.4.2 Commercial considerations of process

In order for the process to attract commercial interest, it would be necessary for each process step to be cost effective. Factors affecting cost effectiveness include:

- Cost of materials
- Time of process
- Energy requirements
- Yield

Considering each of these factors in turn, in comparison to conventional sputter deposition, the viability of producing precursors was established. Whilst the production route for isopropoxide and *tert*-butoxide precursors was not viable due to poor yield, the ethylhexanoates and the indium 2,4-pentanedione with tin acetate were established to be viable for manufacture on a similar commercial basis to CVD precursors. The process time for printing and firing was greater than that for sputter coating, but without the cost of equipment. Energy costs for firing at elevated temperature are likely to be comparable in order of magnitude to those for the operation of large vacuum equipment. It is therefore likely that the process becomes more competitive when patterning is required, since removing the etch patterning steps represents a major saving in time, materials and energy costs. Coincidentally, the products with patterning requirements also have higher performance targets, so at this stage are further from realisation.

It was established (in line with results reported in previous work) that firing in nitrogen produced a better surface finish and a lower sheet resistance. The cost of firing in an inert atmosphere was, however, regarded as commercially prohibitive. Additionally, it is known that achieving low sheet resistance in an inert atmosphere is a result of anionic non-stoichiometry through lattice defects. This effect is reduced under a voltage bias, hence is not preferred for practical devices. Hence the work was not continued in the second phase

The area which requires greatest consideration in respect of its viability is therefore the handling of the precursors. The processes involved in sol-gel processing do not require high cost equipment or materials, however there are many process variables to control as discussed above, including process times, and the timing and quantity of additions. These show a high level of process sensitivity, which is likely to have an adverse effect on yield. Achieving a suitable level of process control is likely to add substantially to process cost.

11.4.3 Performance relative to device requirements

As discussed in Chapter 4, applications have a wide range of requirements, both physical and commercial. In each application, the prioritisation of these requirements determines material selection. Parameters in which improvement has been made within this project are as follows:

- Integrity of thin film, as observed by SEM.
- Surface roughness.
- Potential for elimination of post deposition patterning (potential material saving of up to 60% vs. a typical etching process).

Transparency and conductivity are most appropriately considered as FOM values for each application, compared with that achieved in this project. These figures are shown in table 11.1.

For non-conducting applications such as solar control glazing, UV shielding and anti-graffiti coatings the principal requirement is cost per unit area, with no patterning requirement. Sol-gel deposited ITO, as prepared within this project, would meet the physical requirements, however the raw material cost for the precursors may preclude its commercial introduction. The sol-gel method is, however, suitable for large area continuous coatings. The use of a lower cost coating material based on tin oxide may be a practical route.

For non-current carrying applications such as touch panels and static dissipation, low conductivity is required, with sheet resistance in the region of $1x10^3\Omega$/square and a FOM of approximately $9x10^{-6}$. This performance is likely to be achieved by the ITO coating developed in this project, however the raw material cost would probably preclude commercial introduction.

The liquid crystal in an LCD also carries essentially no current and has a similar FOM requirement. The route developed within this project would be eminently suited to PMLCD use, since directly printed patterning would reduce cost. Deposition of thin films with high transparency and good surface finish has been demonstrated, meeting the key requirements for LCD devices. The material is also suitable for AMLCD electrodes, but if the capacitor and source or gate lines were to be constructed from the ITO layer then the material would be unsuitable.

Application	Transparency (%)	Sheet resistance (Ω/square)	FOM
Solar control glazing	70	-	-
Anti-graffiti coating	70	-	-
UV shielding	70	-	-
Dichroic filter	70	-	-
EMF/RFI shielding	70	$1x10^3$	$2.8x10^{-3}$
LCD electrode	90	$1x10^3$	$9.4\ x10^{-3}$
Touch panel	90	$1x10^3$	$9.4\ x10^{-3}$
Static dissipation	90	$1x10^3$	$9.4\ x10^{-3}$
EL display	90	200	$4.7x10^{-2}$
Resistive heater	70	80	$3.5x10^{-2}$
PV electrode	90	30	0.31
LED electrode	90	15	0.63
Commercial ITO	90	13	0.73
Dip coated ITO from project (nitrogen fired)	98	$2.1x10^3$	$2.3x10^{-3}$
Dip coated ITO from project (air fired)	98	$6.0x10^3$	$8.2x10^{-3}$
Printed ITO from project	93	$5.0x10^6$	$2.8x10^{-6}$

Table 11.1 Transparency and conductivity requirements for a range of example applications for TCCs, compared with project results.

Resistive heaters require a lower sheet resistance, with a FOM of approximately 3.5×10^{-2} and are generally patterned. ITO prepared within this project has a FOM which approaches that for this application, the order of improvement required being likely to arise from increasing film thickness above the threshold value of 100nm. Significant economic advantage would be gained by the ability to directly pattern the heater element.

The ITO prepared within this project would not meet the resistance requirements for thin film displays. The ability to produce a directly written pattern would, however, meet key cost requirements and the improved surface finish would be highly desirable. Further work would be required to increase connectivity within the ITO film.

11.5 The research process and its place in the R&D landscape

The industrial need for the work performed within this project was identified through internal strategic roadmapping within TWI. This was confirmed with reference to wider government strategy, identifiable from the funding of the LINK ISD programme by the DTI. At the start of the first phase, the literature indicated that work had progressed beyond conceptual, but had not yet progressed to proof of concept, indicating a TRL of 2. Phase 1 was performed using internal funding, since it required only a modest programme. The first phase moved it forward to demonstration of principal, *i.e.* to a TRL of 3. This was the appropriate level for collaborative public funding, since the aim here is to support developments through TRLs 4-6.

This necessitated collaboration, which was appropriate, since input was required to integrate academic development with industrial need via technology translation. It was also apparent that benefits could be derived by all partners from participating in such a project. The work conducted within the collaborative project developed the concept further to validation within a laboratory environment, *i.e.* TRL 4.

A consequence of the collaborative approach adopted was that it sought to develop a route to the production of ITO which had sufficiently good performance to make it a worthwhile route for commercial adoption. In this sense, the objective differed from a purely analytical project, in that it did not seek solely to develop an understanding of observed phenomena, but also to deliver a practical result, *i.e.* it constituted synthetic rather than wholly analytical work.

The challenge to be addressed in performing a synthetic project on a defined timescale with finite resources is that of satisfying the scientific, engineering and commercial requirements simultaneously. Development was therefore sequential, with a repeating cycle of hypothesis/synthesis/analysis. Thus, the sequence of investigation required that analytical work was restricted to that which facilitated formation of a new hypothesis from which to progress to the next development cycle.

The indium free aspect has very strong commercial drivers, but was initially based only on basic principles, *i.e.* TRL 1. Within the scope of the project, the initial phase of reduction to practice was performed through academic institutions, in keeping with their capability for fundamental research. The work was then reduced to practical materials, showing proof of concept. At the conclusion of the project, the work had been developed to show critical function, *i.e.* TRL 3. It therefore corresponded in terms of technology maturity with the starting point of the second phase of the ITO development project.

A key feature of performing the work in collaboration with industrial partners is that, in the long term, delivery of analysis alone is insufficient to satisfy their needs. Research of this type should therefore be correctly considered as an ongoing continuum of development towards the end goal, performed in a series of discrete steps or projects. The completion of a well executed project represents a step towards the goal, since the route taken is logical based on the available knowledge at the start of the project. The development of further knowledge indicates the correct direction for the subsequent project, until either the goal is reached or it becomes apparent that it is not possible to reach it. Either point constitutes the completion of the research for the stated application requirements.

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CHAPTER 12 - CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

12.1 Summary of conclusions

During this investigation a method has been developed for preparing a transparent conducting coating which can be deposited by screen printing. The route is based on sol-gel processing and allows patterned electrodes to be directly written, rather than etched from a continuous film, with consequent cost and waste savings.

It has been shown that a sol-gel route can be used to create a thin, conductive coating on a glass substrate. It has also been shown that composition of the sol is critical to conductivity, whilst the coating and firing method are critical to formation of a continuous coating.

The field of sol-gel derived TCCs is still embryonic. The research conducted in this programme has advanced capability across the supply chain. Working in a collaborative fashion, high purity precursors were developed, with suitable sol-gel processing routes to produce a material suitable for formulating as a screen printable ink. Inks were developed in conjunction with screen printing, to ensure suitable film-forming properties on a glass substrate. Firing conditions were established which resulted in a crystalline ITO film.

The use of simple sols was generally ineffective in respect of printing, since although the isopropoxide precursors showed rapid hydrolysis and good network formation *in-situ* following dip coating, the reaction proceeded too rapidly and the structure evolved too far to allow coating densification from a printed ink.

It proved possible to stabilise sols derived from the indium acetylacetonate/dimethyl tin diacetate and dimethyl indium methoxide/dimethyl tin diacetate precursors by the addition of triethanolamine. The metastable sol state reacted with the additions needed to formulate an ink.

The ethylhexanoate was inherently stable with respect to hydrolysis. It proved possible to hydrolyse the material under conditions of increased pH. The addition of 1,2-diaminopropane followed by drying resulted in a partially hydrolysed, xerogel material which was sufficiently stable to formulate an ink from.

It was feasible to add rheology modifiers with sufficiently low evaporation/decomposition temperature to facilitate removal during firing. These were based on alkyl cellulose and castor oil derivatives.

A screen printed pattern was produced to a resolution of 100µm track and gap width.

Characterisation of the solid state material was performed using TGA, DSC and XRD to interpret the reaction sequence. It was established that the material produced by the sol route crystallized at a lower temperature than that produced by the gel route. Both showed lower crystallisation temperatures than that reported for the bulk material. This is indicative of a relationship between crystallisation temperature and particle size.

The TCCs were characterised for thickness, surface roughness, transparency and conductivity. Thickness measurement required the development of an etching technique to create a step edge for measurement. The necessary edge was successfully created by etching the ITO film using concentrated hydrobromic acid.

A coating was produced with transparency of 98% and resistivity of $1.5 \times 10^{-2}\Omega$cm fired in nitrogen and 98% transparency, $3.0 \times 10^{-2}\Omega$cm resistivity fired in air. A printed coating was produced with 93% transparency and 7.0Ωcm resistivity.

The conductivity observed in the dip coated films is approximately two orders of magnitude below the commercial sample. The conductivity of the printed film is approximately four orders of magnitude below the commercial sample. This is likely to be related to coating morphology. The thickness of the dip coated specimens is below the threshold required to overcome grain boundary effects and cracks were observed within the structure. The printed sample was transluscent, indicating a high level of internal reflection. In both cases, this indicates a lack of connectivity.

The printed material meets the requirements for non-conducting applications such as solar control glazing, UV shielding and anti-graffiti coatings. The inherent material properties approach those required for non-current carrying applications such as touch panels and static dissipation. The best commercial fit is with LCD electrodes, since directly printed patterning would reduce cost and deposition of thin films with high transparency and good surface finish has been demonstrated, meeting the key requirements for LCD devices.

Specific capabilities developed within this programme include:

- A unique series of precursor materials suitable for sol-gel TCC development.
- Hydrolysis routes for previously unexplored materials.
- Ink formulation expertise for full decomposition of binder systems at appropriate temperature ranges.
- Firing schedules for sol-gel TCC crystallisation.

12.2 Recommendations for further work

The industrial requirement for improved transparent conducting coatings has increased since this work was initiated (House of Commons 2009). The predominant need lies within the fields of thin film displays and thin film photovoltaic devices, both of which require higher conductivity than was achieved within the present project. Further work is therefore required to optimise the deposition process and heat treatment schedule in order to improve connectivity within the structure.

The coating thickness targeted lies significantly below what is conventionally accepted as the upper thickness threshold of 0.5microns for sol-gel coatings. Further work is therefore required to focus on drying, shrinking and network formation in the sol and gel materials prior to deposition.

It is also notable that the printing technique used deposits a minimum wet film thickness of approximately 3µm, relative to a target cured film thickness of 150nm, a factor of 20 reduction. Since gellation may occur at concentrations above 1%, further work is required to examine alternative printing processes, such as gravure and flexographic printing, which can deposit significantly lower thickness coatings, at approximately 0.5µm. This would reduce shrinkage during curing, decreasing the likelihood of defects within the film due to drying stresses.

An alternative engineering approach would be to produce multiple layers. The overcoats would be aimed at providing conduction pathways by "filling" the cracks. This would require repeat coating, drying and curing steps, increasing process complexity and hence cost, particularly if depositing a pattern, where it would be necessary to align the substrate and mask in register in successive cycles.

The present project has relied on measurement of the solid phase and the cured film to establish material properties. The principal limitation of this technique is that resistivity measurement (one of the two fundamental properties of interest within this project) has been limited to bulk specimens, measurable by microwave conductivity, and thin films. In the latter, it is not possible to deconvolute material and morphological effects. Research is therefore required to develop a test method capable of measuring inherent conductivity in thin films.

The recent review by the House of Commons Innovation, Universities, Science and Skills Committee identified the emerging plastic electronics market to be of key strategic importance to the UK (House of Commons 2009). Whilst the crystallisation temperature has been significantly reduced in the present project, it remains above that suitable for all but ultra-high temperature polymers. Further work would be needed to develop precursor materials with lower processing temperatures. This could be approached by using a direct thermal process with lower firing temperature precursors and rheology modifiers, removed by thermal decomposition rather evaporation or oxidation. Alternatively, non-thermal energy processes could be used, for example laser, electron beam or ultraviolet initiation.

Mechanical assessment would also be required, including buckle and bend tests, to establish the maximum strain exhibited by the coated substrates before a significant loss of conductivity.

If realised, the combination of a non-vacuum printing process compatible with plastic substrates would remove one of the major barriers to flexible device manufacture. The principal advantage would be in facilitating reel-to-reel production, with additional benefits in reduced weight and component cost, increased area and conformability of devices to surfaces.

The need for alternative transparent conducting materials has also increased significantly, due to recognition of the potential importance of thin film photovoltaic devices, which will consume large quantities due to the surface area required, and limited indium reserves, most of which are under Chinese control. Further work is therefore required to develop understanding of the hydrolysis and condensation behaviour of silicon-doped zinc oxide. This material is very attractive since its constituents are readily available at low cost. Results developed by partners within the project indicate it has considerable promise.

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APPENDIX – COATING PROCESSES

A.1 Introduction

From an industrial perspective, a coating represents a particular approach to meeting a performance requirement. The alternative approach would be to use a monolithic component. The relative complexity of a manufacturing process to make a monolithic component in a particular material, compared with that of developing a suitable coating process, may not be immediately apparent. The factors involved are discussed below. If a coating process is to be used then a wide range of options is available and these are discussed in sufficient detail to indicate the factors which influence the decision to use a particular process. The practical work described in this thesis relates to sol-gel coatings; the sol-gel process being of sufficient complexity to warrant a chapter. Within this appendix, particular attention is paid to vapour deposition processes, since these produce coatings with similar characteristics to sol-gel processes; and to liquid phase coatings such as paints, lacquers and varnishes, since sol-gel follows a similar deposition route.

A.2 Definition of Coatings

In a coating process, a component with one material composition and structure, the substrate, has a layer of a different composition and/or structure applied to some or all of its surface, The exception is in the case of a repair overlay, for example by weld cladding or thermal spraying, where the material may be identical, however the remainder of this appendix considers new build rather than repair.

The reason for this difference between coating and substrate is immediately apparent, in that no advantage would otherwise be gained from the application of the coating. In this respect, coating differs from joining, in that a joint may be formed between similar materials with no inherent difference in either composition or microstructure between the two components (Kazakov 1985).

Although the concept of a coating on a substrate is clear, the definition is less precise. At what point does a layer cease to be a coating and become part of a composite? The paint film on a steel girder is clearly a coating, while the individual layers in a piece of plywood clearly form a composite, but if the outer layer of a piece of plywood is formed from a different timber for decorative effect does this class as a composite or a coating?

There is no strict definition by which a system may be determined to consist of a coated substrate, rather than two joined components. As a general rule though, the factors to be considered include a combination of relative thickness (when the ‘coating’ thickness is above or below a certain percentage of the substrate thickness), of process (whether the ‘coating’ is applied as a pre-constructed layer or by manufacture of the layer *in-situ*), and of function (whether the surface layer is present to perform a function which is distinct from that of the substrate). Pre-constructed layers would technically be regarded as cladding rather than coating and for the purpose of the present work will not be considered further. Semantically, weld cladding processes are not cladding according to the definition, but they do generally produce a coating of substantial thickness, in the order of several millimetres. Only coatings which are thin relative to the substrate and are produced *in-situ* will be discussed, since sol-gel coatings follow this distinction.

Likewise, at the opposite end of the scale, the surface of a material may be chemically altered by processes other than coating. These can include deliberate chemical reaction of the surface under particular conditions, for example the growth of an oxide scale on a chromium or aluminium-bearing alloy under controlled conditions to impart corrosion resistance (Haynes International Inc 2008). Similarly, a material can be dissolved into the surface to form a different composition with desirable properties, as in carburising or nitriding (Gunner 2000). Alternatively, a completely different material can be incorporated into the surface layer by a process of ion implantation or coating followed by diffusion, as found in platinum aluminide surface treatment of turbine blades (Wing and McGill 1981). Whilst these treatments undoubtedly offer performance enhancement, many of the factors relating to coatings are not relevant here and hence they too will not be considered further.

A.3 Reasons for applying coatings

There are many reasons why a coating is selected as part of a fabrication process. The purpose can be as simple as decoration (frequently the purpose of applying paints or lacquers), or as intricate as the multi-layer stack of sub-micron layers to be found in a silicon semiconductor device. In all cases, the objective of applying a coating remains the same; to provide an enhancement to the properties of a bulk material.

The question should be addressed as to why the coating material is not used as the bulk, however this is easily answered, since the correct approach is to consider the system as a whole, rather than considering the properties of the individual layers. The functionality of the system may then be addressed with respect to the combination of properties attained from the individual components.

In this context, either the substrate or the coating material may be the subject of primary interest. The substrate may be chosen for its desirable features and the coating selected to overcome its deficiencies or enhance its attributes. Alternatively, the volume of coating material required to deliver the function may be less than the total volume required for structural stability, in which case the function of the substrate is to provide support.

The application of a coating to a product requires at least one additional process step, and in the case of a coating such as the Vitex Barix™ barrier structure, designed to provide oxygen and moisture permeation protection for thin film displays, it may require up to 50 individual layers (Burrows and al. 2000). Consequently, the decision to apply a coating carries a significant cost and therefore must necessarily offer a substantial benefit. This in itself demonstrates that the commonly used term 'functional coating' is a misnomer – all coatings must fulfil a function in order to justify the cost of the process and the materials.

The cost of the coating process necessitates that application of a coating achieves a result which could not be technically or economically achieved by the use of a monolithic material. The function to be fulfilled by a coating may be one, or more often several combined, from a broad range. Coatings functions are summarised in table A.1 and specific functions are considered below.

Protective Coatings	Corrosion barrier Scratch and wear resistance Passivation Thermal barrier
Electronic/Magnetic	Photo anodic Conducting/semiconducting/insulating Superconducting Ferromagnetic Piezoelectric
Optical Coatings	Coloured Antireflective Optoelectronic Optical memory Photocatalytic

Table A.1 Functions of coatings (Brinker and Scherer 1990; Holmberg and Matthews 1994)

A.3.1 Protective functions

Compatibility between a material and its operating environment is essential in order for a component to function effectively throughout its design life. The bulk of the component must inherently have suitable mechanical properties, however the surface provides its protection from the environment. Protective functions include thermal protection, chemical protection, both from electrochemical and oxidative corrosion and from dissolution. Mechanical protection may be provided against scuff, scratch and wear, whilst non-stick or self-cleaning coatings may be used to retain operating efficiency.

The surface forms the point of interaction between a component and its environment. The requirements placed on the surface may therefore be different from those placed on the bulk; consequently there may be commercial advantage to be achieved in combining a substrate material which has the necessary bulk properties with a coating which achieves the necessary surface properties. The alternative is to use a monolithic material which is capable of meeting both the bulk and surface requirements, and hence is over-engineered in some aspects. The relative costs of the two approaches determine which is more satisfactory in a given application.

For example, whilst stainless steel I-beams could technically be used in the construction of buildings, no benefit would be derived in terms of corrosion resistance except by the surface layer and this feature would therefore be redundant throughout the bulk of the structure. A beam of sufficient section to function as structural beam would be three times more expensive than a carbon steel beam with a paint coating, (Roberge 1999) the performance of which would be fit for purpose in most construction projects.

Heat exchangers are required in the chemical process industry for condensing vapours, cooling or heating liquids and gases and for steam generation. The service conditions and wide range of fluids, which include abrasive or corrosive fluids such as acids, alkalis and oxidising agents render heat exchangers prone to corrosion, fouling and scaling. This decreases the rate of heat transfer and hence performance of the heat exchangers. In addition, these factors may have a significant influence on the operating and maintenance costs. One solution is to choose a suitable construction material such as stainless steel, Monel or titanium (Perry and Green 1998). Despite its limited corrosion resistance, carbon steel is still frequently used industrially for large tube and plate heat exchangers, due to its availability, low cost and ease of fabrication (Perry and Green 1998)**,** in which case a coating may be applied to extend service life and enhance performance.

Likewise in pipelines, with an uncoated material the difference in operating conditions between the internal and external surfaces implies that, in order to obtain compatibility with one environment, the material is over specified for the other. Overspecification results in many knock-on complications including additional weight and size but the fundamental result is increased cost. The alternative is to use a substrate material which is specified for its mechanical properties and may be compatible with the conditions at one of the surfaces and apply a coating to one or both surfaces to ensure environmental compatibility.

A similar situation arises with the use of thermal barrier coatings on turbine blades. Here, the thermal barrier coating facilitates operation of the blades at higher temperature than would otherwise be achievable due to excessive creep during service life. The higher operating temperature improves operating efficiency.

A.3.2 Electronic/magnetic functions

The majority of semiconductor devices are constructed as thin coated layers on a substrate. An example would be the fabrication of electronic devices with conductive, semiconductor and dielectric components, built up through a series of coatings (Doering and Nishi 2007). Silicon chips are fabricated in this fashion, as are liquid crystal and light emitting diode (LED) displays and photovoltaic cells. Both display and photovoltaic devices use either polycrystalline silicon or glass as substrates, depending on the type. Likewise, sensors are manufactured by thick-film deposition (Patranabis 2004).

A.3.3 Optical functions

Most optical devices are manufactured on transparent substrates. The use of plastic substrates is still limited, beyond application to spectacle lenses, due to dimensional stability. Consequently glass is the preferred substrate. Additional optical function is frequently added to glass through the application of a coating. For example, by applying coatings which absorb or reflect particular ultra-violet (UV) or infra-red (IR) wavelengths, glazing can be tuned to retain or radiate heat to improve building efficiency (Pilkington K Glass 2008). Anti-reflective coatings may be applied to increase transmission in the visible range, improving the operating efficiency of photovoltaic and solar-thermal panels. Active coatings include photochromic and electrochromic materials which change colour in response to light or applied voltage. Such coatings are increasingly found in applications such as light-reactive sunglasses and mirrors on high-end cars to improve night vision (Gentex Corporation 2008).

A.3.4 Coating selection

From an engineering perspective, the function of the coating is its most important feature – the industrialist is unlikely to be interested in coating processes or compositions, except in respect of features which influence cost. These factors include, in addition to raw materials cost, the costs associated with achieving a satisfactory product (such as processing considerations, compatibility with existing equipment and cost of new equipment). These considerations are balanced against the coating's function, *i.e.* a techno-economic consideration, although increasingly environmental consideration is also a substantial element.

It therefore falls to the technology provider to interpret the functional requirements and offer the best solution in terms of coating composition, structure and deposition process. The available options are considered below, however in order to interpret the functional requirements, consideration should be given to the nature of a coating. The way in which a coating performs is dependent both on its internal properties and its interaction with the substrate and the environment. These regions are therefore considered in detail below.

A.4 Consideration of the regions within a coating

In considering the generic functions required of a coating, it is apparent that three regions within the coating structure affect its performance. These may be identified as:

1. The interface between coating and substrate
2. The bulk of the coating
3. The interface between the coating and the environment

The significance of each of these regions may be considered in respect of the generic functionalities considered above.

A.4.1 The coating-substrate interface

As explained above, the coating and the substrate are inherently dissimilar materials. The interface between the coating and the substrate is governed by adhesion. The American Society for Testing and Materials (ASTM) Definition of Terms Relating to Adhesives (D 907-70) defines adhesion as “the state in which two surfaces are held together by interfacial forces which may consist of valence forces or interlocking forces or both” (Rickerby 1988)**.** In order to achieve satisfactory adhesion between dissimilar materials, two competing factors must be considered, the first being the adhesive forces which hold the materials together and the second being the stresses arising from the dissimilar material properties and the coating process. If the stresses exceed the bonding forces then the coating will fail, either at the interface or in the bulk, depending on the relative strengths of these two regions.

Four principal theories have been proposed for the origin of adhesive forces; these can be classified as two generic types, mechanical or chemical, the latter comprising adsorption, diffusional and electrostatic (von Fraunhofer and Boxall 1976).

Mechanical bonding originates from keying of the coating into features on the substrate surface. Increasing the number of features by roughening the substrate surface has been shown to increase adhesion strength (Ye, Delplancke et al. 1998; Chae, Baik et al. 1999). More recent understanding indicates that the improved adhesion is predominantly based on the increase in surface area available for bonding, rather than from mechanical interlocking (Watts and Castle 1984).

Chemical bonding arises from forces between the atoms and molecules at the interface. The adsorption theory is based on either primary or secondary forces. Primary forces such as ionic, covalent and metallic bonds generate the strongest adhesive forces; an effect which is seen in functionalised adhesion promoters based on phosphonate and silane species (Cotton and Wilkinson 1988). Secondary forces such as Van der Waals forces and hydrogen bonds are associated with polarisation of bonds. These are the dominant mechanism in the formation of organic/inorganic interfaces. Increasing asymmetry in the organic component increases polarity, generally resulting in stronger adhesion (Plueddemann 1991). Secondary forces are substantially weaker than primary forces and hence operate only over short ranges. It is therefore important to ensure a high degree of surface preparation (cleanliness) to allow the forces between the coating and substrate to act directly (Mayne 1979).

The diffusional theory is based on interfacial diffusion between coating and substrate creating a boundary layer. In general diffusion is relatively slow, the rate being temperature dominated according to the Arrhenius equation (McNaught and Wilkinson 1997):

$D = D_0 \exp(-Q_d/RT)$ (A.1)

where

D_0 = a material dependent pre-exponential (m^2s^{-1})

Q_d = activation energy for diffusion ($Jmol^{-1}$)

R = gas constant ($8.31Jmol^{-1}K^{-1}$)

T = temperature (K)

It is not anticipated that the majority of coating processes would maintain temperature for sufficiently long to produce significant diffusion (Mayne 1979), with the exception of deliberate diffusional processes. Such processes, for example carburising, nitriding and platinum aluminide formation create a surface layer of different composition to the bulk, however they are not strictly coatings and will not be considered further.

The electrostatic theory assumes coulombic attraction at the interface is generated from an electric double layer. It is anticipated that electrostatic attraction would be insufficiently strong to produce meaningful bonding.

The stresses generated at the interface between the coating and the substrate arise from a combination of the stresses induced by the deposition process and the subsequent stresses induced by service conditions. Coating processes will be considered in detail below, but the principal factors which influence stress are the dimensional change of the coating material relative to the substrate throughout the process at both a general (coating bulk) and local (discrete coating particle) scale and the elastic modulus of the coating and substrate materials.

The composition determines the scale of the relative strain, via the coefficient of thermal expansion (CTE). The overall strain is governed by the relative CTE of the coating and substrate and the temperature change between maximum and minimum temperature. The stress is determined from the strain and the elastic moduli of the coating and substrate.

Dimensional changes in the coating are determined by the process, which in turn influences the stresses induced at the interface between coating and substrate. Large dimensional changes are associated with coatings which undergo densification in the solid phase. These are typically deposited from a liquid or gaseous phase and undergo chemical reaction, either through compositional reaction *in-situ*, or through cross-linking. The impact is maximised when the entire coating is deposited as a complete film before densification, for example in a paint, and correspondingly minimised when the coating is built up from either a series of layers, or discrete particles (or ions), as in a sprayed powder, vapour deposition or ionic plating process.

In respect of coating functionality, adhesion is a significant property in respect of coating durability – for example a coating bonded to a substrate solely by mechanical forces would have significantly lower mechanical strength than one which is chemically bonded.

A.4.2 Bulk properties of coatings

Whether a coating is satisfactory is determined by its morphology. This is a property of the coating bulk, dependent on a combination of composition and structure; the latter being heavily influenced by processing history. Coating morphology may be considered in respect of the plane of the coating (x and y directions) and through its thickness. Inhomogeneity in the x and y on the macro-scale is always undesirable, while the desirability of variation in the z direction is dependent on the functional requirements of the coating.

Defectivity in the x and y directions has the greatest impact on coating performance. Defect types include cracks, inclusions and holidays. The extent of the impact is determined by defect density, percentage of the thickness (z direction) affected and coating function. For example, a small inclusion, less than, say, 10% of the coating thickness, may have negligible impact on abrasion resistance, whilst a holiday inherently compromises corrosion resistance.

In a single phase coating, any inhomogeneity is undesirable. In a multi-phase coating a degree of inhomogeneity is inherent if the scale considered is sufficiently small. On a macro-scale, inhomogeneity is to be regarded as a defect – thus areas of variation in thickness or composition result in variation in performance which necessarily deviates from the optimum. As an example, the pigment particles held in an organic binder in a conventional paint may be regarded as inhomogeneity at the scale of the particle, yet these are inherent to its performance. Conversely, at the macro-scale (i.e. substantially greater than that of the pigment particles) inhomogeneity could be a consequence of poor mixing (composition) or poor application (processing).

In respect of functionality, the bulk properties of a coating influence factors such as electromagnetic and optical properties, for example transparency/opacity and resistivity. It would generally be desirable for a coating to be homogenous in the z direction to optimise these properties. The bulk permeability to oxygen and moisture is the primary factor in determining the barrier properties of a coating; the principal factor in corrosion resistance. Homogeneity in the z direction is not necessary for permeability – however x-y homogeneity is critical.

In a multi-layer coating, the whole structure cannot be homogenous but the structure can be considered as a series of individual layers and interfaces. The above discussion therefore applies to each individual layer and each interface, between substrate and coating and between each individual coating layer; only the final layer presenting an interface with the environment.

A.4.3 The interface between coating and environment

As described above, in many cases the objective in applying a coating is to change how an object interacts with its environment, predominantly in a protective role. Even when this is not the primary objective, it remains a consequence of applying a coating. Surface properties therefore have the greatest influence on chemical and mechanical interactions.

Surface energy is the property with the greatest influence over adhesive or chemical factors in environmental interaction. The surface is directly responsible for hydrophilic/hydrophobic properties, being a feature of high/low polar component of surface energy respectively. Low total surface energy is a feature of anti-fouling coatings, making deposition less thermodynamically favourable.

Mechanical interaction, *i.e.* the tribological properties of a material, is also essentially a surface property. Tribological properties are associated with the surface energy, combined with the bond strength and stiffness, which on a macro-scale give rise to properties such as friction and wear. The interaction here is not straightforward; for example titanium in contact with titanium presents two relatively hard surfaces but the high interaction energy results in galling and hence rapid surface wear, whilst tin/lead bearing alloys are relatively soft but do not wear rapidly against steel due to the low chemical interaction (Bhushan and Gupta 1997).

Abrasion resistance is more complex, taking into account factors including hardness, geometry and energy of the impinging part, with the equivalent properties of the coating and substrate. Whether abrasion is a surface or bulk property depends on the above factors and the consequent effect on the coating. If the substrate is sufficiently soft, the impinging energy is sufficiently low and the geometry does not generate a sufficiently high local concentration to cause damage to the bulk of the coating, then only the surface of the coating is altered. This is seen as scuffing or marring, measurable by increased haze (in transparent coating/substrate systems) (ASTM Standards Panel 2008) which cause surface movement without bulk loss, or abrasion, which is measurable by weight loss (ASTM Standards Panel 2008). These relate to surface properties. If however these conditions are not met then scratching or cracking result. Scratching is defined by the penetration of a single point load into the surface, measured by the pencil hardness test (ASTM Standards Panel 2005). Scratching and cracking relate to bulk properties. Thus plastic spectacle lenses, being soft, are easily scuffed, but having a relatively low modulus are resilient to bulk deformation and hence do not easily break compared with glass lenses, which are more resistant to scuffing but more easily broken.

Whilst the surface of a coating provides the point of interaction with the environment, the operating conditions determine whether that surface remains constant or is altered during service life. Thus if no wear or abrasion is anticipated, as for example where the coating is used in an electronics application, the minimum thickness of the surface layer need only be that required to meet functional requirements. By contrast, if material loss is anticipated, the bulk of the coating will gradually become the surface layer. This has two consequences. Firstly, the initial thickness required may be calculated from the wear rate, service life and required final thickness as per equation 4.2.

$$\text{Initial thickness} = (\text{wear rate x service life}) + \text{final thickness} \qquad \text{(A.2)}$$

Secondly, any inhomogeneity in the bulk in the z direction will result in varying performance characteristics with time. A typical example would be the use of fluorinated silanes as a paint additive to reduce fouling. The silane is not chemically bound within the paint structure and therefore tends to be repelled by the remainder of the composition, moving it predominantly to the surface. Whilst this is where the effect is desired, once the surface has been worn away, no further benefit is derived from the remainder of the coating.

A.5 Coating process selection

When a coating is specified for a given application it is predominantly on grounds of function; the majority of industrialists would have little or no interest in the underlying materials (chemistry and microstructure). As discussed above, their principal interests are likely to be techno-economic, *i.e.* function and cost-effectiveness. This places a requirement on those specifying the coating to understand the options available to produce the desired functionality. Consequently, a contextual understanding of available deposition processes and compositions is required, with a detailed understanding of the subtleties of their interaction.

A bewildering array of different coating types is available to the average industrialist. This is made more confusing by the fact that many materials can be deposited using one of several different processes, rendering process selection significantly more challenging. Certain properties, such as good adhesion, are almost universally desirable. Selection of process can however be influenced by which other properties are required and whether they are surface or bulk properties.

The fact that coating selection can be approached either from the perspective of the composition or of the process makes its presentation challenging. In this present work, discussion is focussed on the process, since this provides a better context for identifying where sol-gel is an appropriate process. From an industrial perspective it is also more appropriate since, whilst considering material properties may facilitate identification of an *ideal* coating, the limitations of what is *practical* are more readily identified by consideration of the process requirements. Table A.2 summarises the range of processes in industrial use, the materials for which they are used and the applications to which they are applied.

Figure A.1 shows the typical thickness of coating produced by each process. The subtleties of each process are considerable, however the key points for each process, in respect of physical properties and suitable material types, are presented below, together with some typical example applications.

Coating Process	**Materials**	**Typical Applications**
Sol-gel	Oxide, nitride and carbide ceramics	High purity semiconductors, abrasion protection, advanced materials
Electro/Electroless plating	Pure metals	Electrical/electronics
PVD	Ti/Cr/N/O compounds, high purity ceramics	Wear resistance, thermal barriers, semiconductor devices
CVD	Carbides/Nitrides/Oxides	Wear resistance, semiconductor devices
Lacquer	Solvent soluble organic resins	Decorative, corrosion resistance
Varnish	Soluble organic pre-polymers	Abrasion resistance, oxidation resistance, barrier, decorative
Powder Coating	Thermoplastics	Corrosion protection, decorative
Galvanising	Zinc	Corrosion protection
Paint	Pigmented resins	Decorative, corrosion protection
Enamel	Glass	Corrosion protection, decorative
Japan	Organic resins	Decorative, corrosion protection
Mastic	Organic resins	Corrosion protection, barrier
Thermal spraying	Alloys, ceramics	Corrosion protection, wear resistance, thermal barrier
Slurry	Ceramics, metals	Corrosion protection

Table A.2. Coating processes in use in industrial applications.

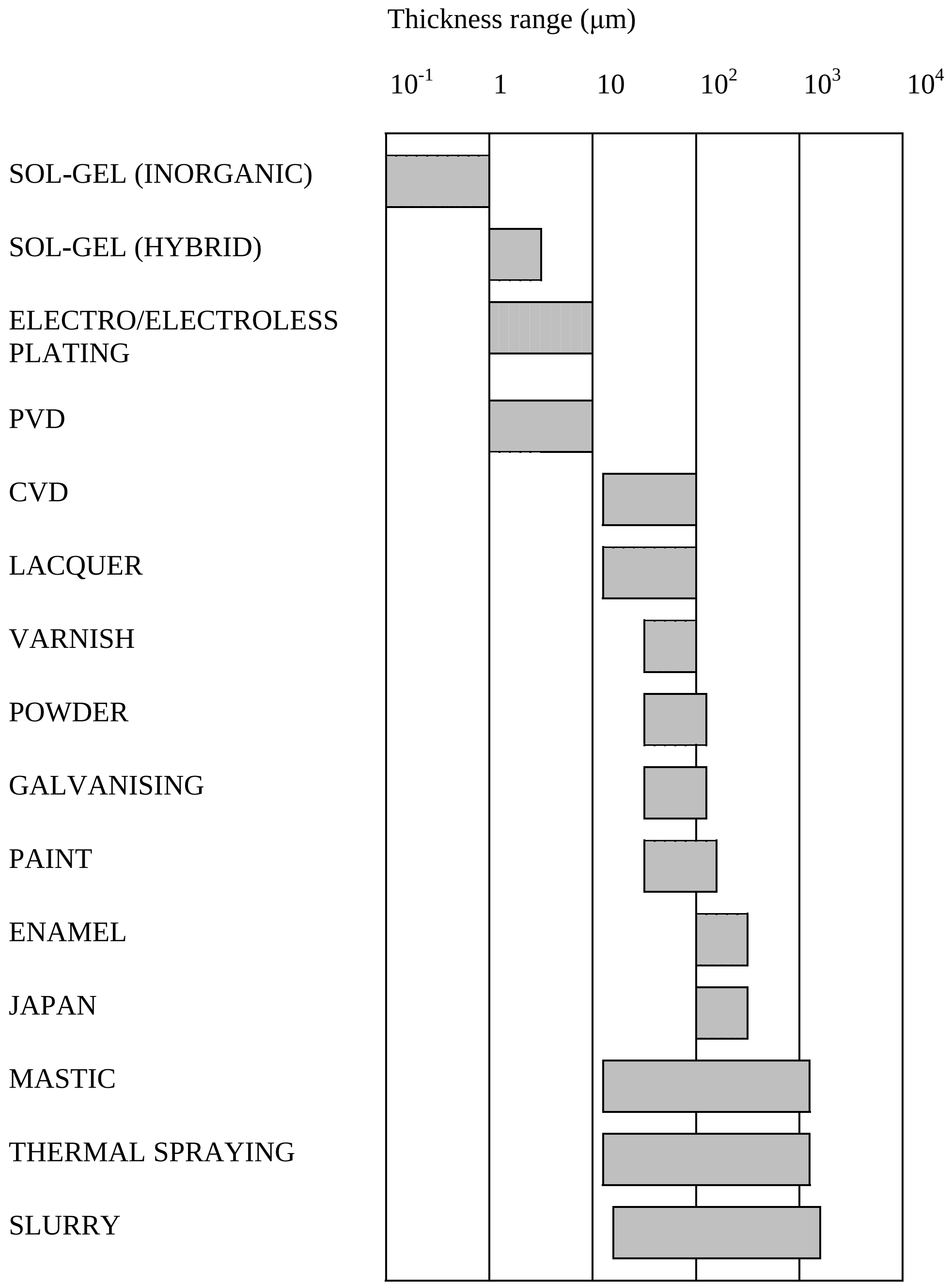


Fig.A.1. Typical thicknesses of surface coatings, after Bell (Bell 1990).

A.6 Coating processes

Any attempt to classify coating processes must necessarily be somewhat artificial. In the context of the present work, a logical distinction is in respect of the phase (solid, liquid or gas) of the material being deposited. Specifically, this refers to the phase of the particles impinging upon the surface. Since cladding has been excluded, coatings can be considered as being built up from the binding together of particles. This view is consistent with the above discussion in respect of bulk properties. The binding process may be via sintering in the solid phase, chemical reaction or phase change. In coating systems with an inhomogenous composition, where multiple phases are present, these may best be categorized by the binding phase. Thus paints, consisting of solid pigment fillers in a liquid binder, will be considered as liquid phase coatings rather than solid.

Coatings which are built up on the surface tend to be conformal to the existing surface. Coatings which are applied in a flowable condition, i.e. are either liquid or sintered from suspension, tend to have a planarising effect on the surface, although the extent of this effect is dependent on the roughness of the substrate relative to the coating thickness.

A.6.1 Solid phase processes

Solid phase processes are dependent on the sintering of particles. The only practical means for dispersing and applying such a coating is as a slurry dispersed in a liquid vehicle, with or without an additional, fugitive, organic binder to confer green strength. Suitable coating deposition processes are therefore similar to those used for depositing liquid phase coatings and are described below.

In order to achieve sintering, the coating material must be taken to a high proportion of its melting point, typically $0.8T_M$ (Kang 2005). Sintering may be used where residual porosity is required, as for example in cobalt-chromium or titanium coatings to facilitate bone growth into medical implants (ASM International 2003). The long process time required to produce a dense coating by sintering, compared with a liquid process, restricts its use to circumstances where the coating materials have low chemical reactivity and a higher melting point than the substrate, or to conditions where the substrate cannot withstand the higher processing temperature of other processes.

The above factors mean that coating formation by sintering applies primarily to ceramic materials and its use is restricted to high melting point substrates. Sintering is performed either directly as in boron nitride (Precision Ceramics 2008) or oxide ceramic coatings (Singh, Singh et al. 1997) or by chemical conversion (Milaniank, Orzel et al. 1994). The latter case applies when metal coatings are applied to components with complex geometry, or to avoid altering the microstructure and converted *in-situ*. A specific example is the coating of turbine compressor blades with sacrificial aluminium coatings for corrosion protection, since the allowable temperature to avoid microstructural change in the blade alloy is too low to facilitate the curing of higher temperature coatings (Indestructible Paint Ltd 2009). The aluminium is converted to an alumina barrier layer in service.

A.6.2 Vapour and ionic phase processes

Vapour and ionic phase coating processes will be considered together. In the former, the coating material is carried as either an atomic dispersion or ionised plasma, in a gaseous atmosphere, or under reduced pressure to increase mean free path length in order to improve transportation rate. In the latter, the carrier is a solvating liquid.

In all cases, deposition is driven either by varying surface conditions relative to the dispersion, for example by varying the temperature, or by using an electromagnetic field. The coating is therefore built up at an atomic or molecular scale, hence such processes are generally used for relatively thin coatings, in the order of nanometres to microns.

In respect of binding considerations, this constitutes a phase change, which may be from highly energetic species, so high density coatings may be produced. This renders such processes suitable for applications where bulk properties of the coating are significant, while the minimal particle size minimises stress generation within the coating. Thus vapour and ionic phase processes are commonly used for depositing both metal and ceramic materials on almost any substrate, including a wide range of plastics.

The details of specific processes are considered below.

A.6.2.1 Chemical vapour deposition

Chemical vapour deposition (CVD) processes use a volatile precursor material which is transported in a gas stream to a reaction chamber. In order to achieve a CVD coating of a particular material, a suitable precursor must be available. The precursor then chemically decomposes on the substrate surface to leave a coating.

The decomposition process generally requires a considerably elevated temperature, typically in the region of 600-1100°C (Bunshah 1994). The species is highly reactive and is therefore likely to combine with the carrier gas. Decomposition and combination reactions may be exothermic, in which case deposition will occur preferentially at the substrate if it is cooled relative to the chamber walls (hot wall) or endothermic, in which case deposition will occur preferentially at the substrate if it is heated relative to the chamber walls (cold wall) (Bunshah 1994).

The high cost of suitable precursors and the requirement for good control of the vapour flow over the substrate surface to ensure uniformity make the process best suited to high specification materials where the components are relatively small and uniform. One example is for depositing semiconductor layers on silicon wafers in the electronics sector, where a wide range of precursors have been developed (Epichem Group 2006; SAFC Hitech 2008). The potential for reaction with the carrier gas makes CVD a suitable process for depositing semiconductors such as gallium nitride, as used in light emitting diodes (LEDs) (Axitron 2008).

By suitable process selection, a hard graphite coating may be deposited (Teer Coatings Ltd 2008). With plasma assistance a diamond-like coating may be deposited (May 1995). Alternatively, a tungsten carbide deposit may be formed (Hardide Coatings 2006).

A.6.2.2 Spray Pyrolysis

Spray pyrolysis is dependent on the thermal decomposition of metal salt to an oxide. In forming a coating, the salt solution is sprayed onto a substrate under evaporating conditions, building up a coating of the metal salt. This is then thermally decomposed and sintered to form an oxide coating. The process is shown sequentially in figure A.2. Under laboratory conditions, high purity acetates may be used but these have limited solubility, reducing deposition rate. For commercial deposition, either nitrates, sulphates or chlorides may be used since they show higher solubility. The former result in relatively low purity coatings since residues are frequently included, whilst the latter results in chlorine gas, presenting an issue for safe handling (Rahaman 2003).

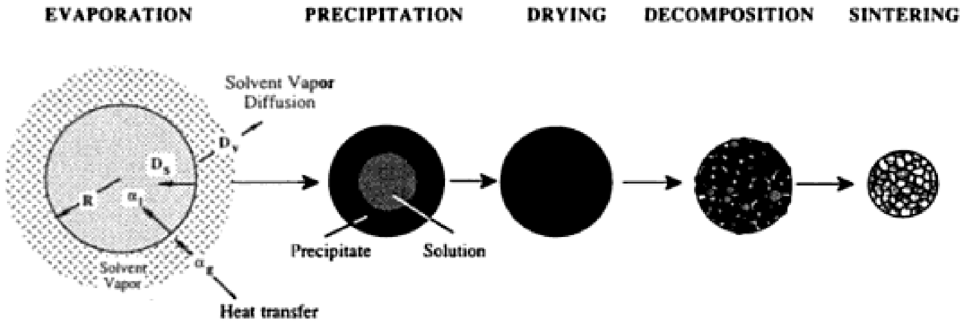


Fig.A.2 Schematic representation of the stages in the spray pyrolysis process (Messing, Zhang et al. 1993).

A.6.2.3 Physical vapour deposition

Physical vapour deposition (PVD) processes are dependent on the formation of a vapour, which requires the input of energy. Reducing atmospheric pressure shifts the equilibrium according to Le Chatelier’s principle, increasing the rate of evaporation and reducing the total energy input required. Consequently, PVD processes are carried out under vacuum. This makes them relatively costly, since a pumped chamber system and high energy power supply are required. The requirement for a chamber also imposes a limit on the maximum size of component which may be coated. It should be noted that, since the melting point of metals are lower than their oxides or nitride, this can make it desirable to use a reactive process where the metal vapour reacts with the process gas to form the compound *in-situ*.

A.6.2.3.1 Evaporation

Evaporation is a relatively simple process. Any material which boils without decomposing can be coated by evaporation. Both the material to be deposited (target) and the article to be coated (substrate), are placed in a vacuum chamber. The material to be deposited is heated above its boiling point, either by placing it in a boat or coil of a material such as tungsten or carbon, which is heated electrically via resistance, or via an impinging power beam of either electromagnetic energy (laser) or electrons. The vapour is then emitted from the target and travels to the substrate, forming a coating.

Since there is no driving force between the target and the substrate, molecular material is transported in a uniform solid angle in linear fashion from the target. To obtain a relatively even coating, the target must be a considerable distance from the substrate, coating thickness following a sinusoidal relationship. The mean free path must therefore be on a comparable length scale and consequently a high vacuum, typically 10^{-7}mbar, is required for commercial scale substrates.

The low impinging energy of an evaporated molecule results in little or no subsequent movement on the substrate. Consequently, evaporated films tend to have a relatively poor microstructure and correspondingly low strength (Efunda Engineering Fundamentals 2008). The deposition rate is low, in the order of 10nm/min and hence the process is not generally used to deposit films thicker than a few hundred nanometres.

Evaporative deposition is therefore widely used in the semiconductor industry, to deposit a range of metals and ceramic compounds. This is usually performed at ultra-low deposition rates, in the order of one monolayer per second to ensure the growth of an epitaxial deposit (Farrow 1995) termed molecular beam epitaxy (MBE). The process is also used to deposit aluminium, which has a low boiling point, on plastic films to provide an oxygen and moisture barrier for food packaging such as crisp bags.

A.6.2.3.2 Sputter coating

A sputter coating process has some similarities with evaporative coating, in that it takes place in a vacuum chamber and material is transferred from the target to the substrate. The significant difference lies in the energy used to effect transfer. Whilst evaporation occurs in high vacuum, sputter coating requires a process gas to be present in the chamber. The gas is ionised to form a plasma. A bias is applied between the substrate and the target, which causes the plasma to bombard the target. The resulting particles removed from the surface are then driven by the bias towards the substrate where they are deposited.

The bias applied between the substrate and the target may be either continuous, as in direct current (d.c.) sputtering, or alternating, radio frequency (r.f.) sputtering. The former requires an electrically conducting (metallic) target, whilst the latter may also be used to deposit electrically insulating materials.

An additional process variation is via selection of the process gas. At its simplest, a noble gas is used, which plays no role in the process beyond the initial removal of particles. If a reactive gas is also introduced to the process then this may combine with the coating material, resulting in a compound deposit. Thus d.c. sputtering may be used to deposit metal oxides or nitrides, at either stoichiometric or non-stoichiometric ratios, depending on the process parameters used.

The higher energy of the impinging particles results in more movement of particles on the substrate and hence a better microstructure. Conditions may be changed to vary the impinging energy and create films with tensile, compressive or neutral stress.

Sputter coating is still a relatively slow process, capable of depositing low stress films at rates in the order of microns per minute. It is therefore typically used to produce relatively thin coatings, in the order of microns in thickness. The relatively high process cost limits the process to high value industries, such as the electronics sector, being used to deposit indium tin oxide (ITO) on glass for use as display substrates (Applied Films Corporation 2008); the deposition of ceramic coatings such as titanium nitride, carbide and combined coatings such as titanium aluminium nitride and titanium nitride/vanadium nitride (PVD 2005; Richter Precision Inc 2006) (Bloyce 2000; ANC Ion Coating Inc 2009) and diamond-like coatings (Field, Yang et al. 2005) for use on cutting tools and in the aerospace sector for depositing thermal barrier coatings (Padture, Gell et al. 2002).

A.6.2.3.3 Pulsed laser deposition

Pulsed laser deposition (PLD), is an evaporation process wherein short pulses (in the order of a few nanoseconds) of high intensity laser light are focused on a solid target. The high peak power density results in rapid heating of the target, ejecting a plume of evaporated material. The process is performed in a vacuum such that the mean free path length is sufficient for the plume to transfer to the substrate. Deposition rates are relatively low and the plume transfers only to a relatively small area.

With a compound target, the plume contains both cations and anions with a stoichiometric ratio similar to that of the target. This provides the principal advantage of the technique over CVD and MBE (Edwards, Jones et al. 2009).

These process features mean that PLD is a highly successful materials screening technique for laboratory use, since it does not require the complexity of target needed for sputter coating.

A.6.2.4 Plating

Whilst the vapour phase processes described above are performed in vacuum, plating processes take place in solution. The equipment therefore consists of baths, usually with heating and plating solution. Plating processes are therefore considerably more straightforward and much lower cost than vapour phase processes. Two distinct alternatives types may be used; electro- and electroless plating. Electroplating additionally requires a d.c. power supply but low cost soluble metal salts may be used. Electroless plating uses an autocatalytic chemical reaction. Its principal advantage is that it gives coatings of almost constant thickness over complex shapes. The coating thickness is usually less than 50 μm (Efunda Engineering Fundamentals 2008). However, only a few metals are readily deposited in this way, predominantly nickel, copper and to some extent gold. In addition, the reducing agents used are mostly expensive and solution lives are short (Edwards 1997).

Plating processes are restricted to metal deposition. Electroplating requires that the substrate is electrically conductive, i.e. metallic, while electroless plating may be applied to non-conductive substrates. In order to achieve suitable chemical conditions for plating a particular material onto a given substrate, a series of plating layers may be required, to achieve chemical compatibility.

Thus an initial nickel deposit is frequently used to facilitate overplating with the desired chromium or gold surface layer.

Plating is not dependent on line of sight; a satisfactory film being produced continuously over the surface of immersed parts. Typically, electroplated layer thicknesses may vary from 0.1 to 30 μm, though nothing prevents the deposition of thicker or thinner layers, as desired (Schlesinger 2002).

Plating is therefore used in the electronics sector to provide solderable connections and to provide passivation/aesthetic improvement by chromium plating of steel and plastic parts in consumer goods.

Hard chromium plating is a long established process. Chromium is deposited at a temperature of 200°C. The coating formed is hard, smooth, wear-resistant and reduces the coefficient of friction significantly. It is used industrially for wear resistant coatings (Chandler 1997). Chromium plating is currently declining due to the rising cost of chromium and environmental legislation associated with the use of CrVI salts and disposal of the contents of plating baths.

A.6.3 Liquid phase processes

The liquid phase processes considered below fall into a series of groups. Thermal spraying is discussed under this heading, although the particles may not be fully molten, but the particles flow plastically and hence their behaviour has more in common with liquids than solids. As a process it has more in common with the vapour deposition processes. Galvanising is a highly specific process relating to a single substrate and coating material, however its industrial importance warrants discussion. Enamelling and powder coating use a solid powder which is then heated to the liquid phase and reflowed. The final group contains the coating processes based on materials which are liquid at room temperature. This group contains both conventional materials such as paints and varnishes, and more recent developments including sol-gel materials. Whereas the other groups are effectively defined by coating process, this latter group has a wide range of applicable processes which are covered specifically below.

Liquid phase coating processes have one marked distinction from vapour phase processes in that, with the exception of thermal spraying, the entire coating layer is usually deposited as a single layer. As a consequence, homogeneity is more readily achieved within the coating bulk, however the simultaneous binding of the entire coating, either by phase change or chemical reaction, almost universally results in the generation of stresses within the coating bulk. Mechanisms for the accommodation of these stresses are dependent on the specific coating process and material involved. These will be discussed within the consideration of each individual process below.

A.6.3.1 Thermal spraying

In thermal spraying processes the coating material in the form of a powder or wire is fed into a gun where it is rapidly heated using a flame, electrical arc or plasma (Herman, Sampath et al. 2000). The material is projected by a gas flow as a stream of small particles, in the region of 1-20µm in size (Davis 2004) against the substrate where it cools almost instantaneously. As alluded to above, the condition of the particles is not fully liquid, but the combination of thermal and kinetic energy results in plastic flow and hence behaviour has more in common with a liquid than a solid. With continuing deposition, the layer builds up as a series of ‘splats’ landing on one another to form a coating (Bodycote Metallurgical Coatings 2008). Bonding both to the substrates and between the individual splats is through mechanical interlocking and hence bond strengths tend to be low compared to chemically bonded coatings, although good mechanical properties are achieved in compression.

With the range of heating processes available and the high energy density which can be achieved, thermal spraying can be used to deposit any material which can be melted without subliming or decomposing; thus a wide range of metals, plastics and ceramics may be deposited.

Flame spraying is the original process, having been invented by Dr. M.U. Schoop of Zurich, Switzerland in the early 20th century (Spray-Itsa) who developed the first process for spraying metal. Early applications included coating the original Waterloo bridge (Newnes' 1946). This process uses simple, portable equipment, requiring a fuel gas such as propane or acetylene which is mixed with air and delivered to the gun. It may therefore be transported to the structure and has been used for applying corrosion protective aluminium coatings to ships whilst still afloat (Rogers 1997). Coating properties are modest, with relatively high porosity up to 10 – 20% (although this can approach zero in self-fluxing coatings) and a bond strength of 30MPa for metals and 15MPa for ceramic materials. Typical deposit thicknesses are 100-2500μm (Pawlowski 1995).

In detonation flame spraying, a mixture of oxygen, acetylene, and powdered feedstock material are detonated by sparks in a gun chamber several times per second. The coating material is deposited at very high velocities to produce very dense coatings. The particle velocity is reported to reach 750 m/s in the D-gun^{TM} and about 900 m/s in the Super D-gun^{TM} (Irving, Knight et al. 1993). Typical applications include wear resistant ceramic coatings for high-temperature use. The porosities of D-gun^{TM} coatings are about 0.5% for WC-Co coatings and about 2% for Al_2O_3 coatings with a bond strength of approximately 70MPa (Tucker 1982). D-gun^{TM} coatings are typically about 300μm in thickness (Pawlowski 1995).

A more recent variant, high velocity oxy-fuel (HVOF) spraying introduces oxygen and the fuel gas at high pressure. The burning gas mixture is accelerated to supersonic speeds, and a powdered feedstock is injected into the flame. The process minimizes thermal input and maximizes particle kinetic energy to produce coatings that are very dense, with low porosity (less than 1%) and high bond strength. The bond strength of HVOF sprayed carbides can be as high as 90 MPa (Kreye 1991). Typical coating thicknesses are in the range of 100 – 300 μm (Pawlowski 1995). HVOF has been used extensively to apply wear resistant thermal barrier coatings for applications such as jet engine combustors and nozzle guide vanes to protect them against extreme heat in the combustion stream (Harrison 2000; Poeton 2008).

In arc spraying two wires are continuously fed into the gun and an electric arc is struck between them. The two wires may be of identical or different materials to produce composite coatings. Compressed gas, usually air, is used to atomize and propel the molten material to the substrate. Arc spraying may be used to apply electrically conductive materials including metals, alloys, and metal-metal oxide mixtures. The process provides very high deposition rates (up to 15 kg/h), but it is noisier and gives off more fume than the flame wire process (Edwards 1997). The bond strength is in the range of 10 – 30 MPa for Zn and Al coatings (Gwie 2005) and may be as high as 70 MPa for NiAl coatings (Pawlowski 1995). The porosity and thickness of the coatings are in the range of 10 – 20% and 100 – 1500 μm respectively (Pawlowski 1995).

Plasma spraying produces the highest quality coatings. Typical working gases are hydrogen, nitrogen, argon and helium (Pawlowski 1995; Edwards 1997), most frequently containing a percentage of reducing gas in an inert carrier (Pawlowski 1995). Gas temperatures of 4000 – 8000 °C are achieved with hydrogen or nitrogen plasmas, 15,000 °C with argon and 20,000 °C with helium plasmas (Edwards 1997). These high temperatures make plasma spraying the most suitable technique for depositing ceramic materials. The porosity and thickness of deposits are typically in the range of 1 – 7% and 50 – 500 μm respectively (Pawlowski 1995). In the case of vacuum plasma spraying, the porosity is usually lower than 1 – 2% with a typical coating thickness of 150 – 500 μm (Pawlowski 1995).

Thermally sprayed coatings are limited to line of sight and are sensitive to impinging angle; therefore they are not suited to complex internal geometries. The process provides only mechanical adhesion, so resistance to shear and tensile loads is poor and their use is restricted to applications which are not subject to high forces in these planes. When the material to be deposited can react with the deposition environment, for example through oxidation, the surface of the splats is likely to be reacted, resulting in inclusions. The latter issue can be resolved to some extent by use of cold spraying techniques (Marrocco 2008) where the input energy is reduced sufficiently to avoid reaction.

A.6.3.2 Galvanising

In contrast to thermal spraying which can be used with an extremely broad range of substrates and coatings, galvanising only applies to a single combination; that of zinc coatings on steel. The zinc is melted in baths and the components to be galvanised are immersed, whereupon the zinc reacts with the surface, forming a zinc/iron intermetallic on which a further layer of approximately 50 – 200 μm of zinc is deposited (Edwards 1997).

Although the combination is highly specific, the dominance of steel as an engineering construction material and the passivating properties of zinc, in contrast to the majority of corrosion control coatings which act only as barriers, galvanising is still a highly utilised process for structural steelwork. The relatively simple process equipment and modest energy requirements due to the low melting point of zinc at 420°C (Lide 2008) make galvanising the industrial standard for environmental protection of exterior components which are sufficiently small to be fitted in a dip bath (the largest of which in the UK is 21.0m x 1.5m x 2.78m (Galvanizers Association 1999).

A.6.3.3 Enamels

Enamelling is the application of a fused glass layer as a coating. The glass is applied as a powder and then heated above the glass transition temperature, T_g causing the particles to flow and fuse together into a continuous layer. Enamelling is a long established process, being used for aesthetic purposes in decorative work and watch dials (Spon 1875) and as a protective coating for ironwork operating at elevated temperature, such as stoves, chemical vessels and pipework, particularly due to its chemical inertness and barrier properties (Spon 1875; Yong-Taeg, Fujino et al. 2002; Collins 2008).

Enamel coatings are relatively thick, in the order of hundreds of microns, partly due to the need for a thick layer to achieve opacity (Spon 1875). Issues therefore arise with CTE mismatch, since metals typically have much higher CTEs than ceramics. This is addressed by a combination of reducing processing temperatures and specific additions to the composition to increase CTE. Many oxides with useful properties in this respect, such as lead and arseneous oxide (Spon 1875), are technically satisfactory but raise issues with safety, both in processing and use. Alternative options are limited, therefore enamelling is restricted to a range of smaller or lower CTE metallic components.

A.6.3.4 Powder-coating

Powder coating is a similar process to enamelling, but uses a powdered plastic rather than glass. The plastic is usually applied to a pre-heated metal surface.

The use of plastic rather than glass has many advantages. Plastics have a lower melting point and a higher CTE. These properties combined with higher toughness make the application of powder coatings considerably easier than enamel coatings. They are therefore used for protective coating of large volumes of decorative and structural iron and steelwork. The relatively high permeability of plastics to oxygen and water, combined with the weak bond formed between the coating and the surface, results in relatively short coating lifetimes in corrosive environments, e.g. approximately 5 years compared with galvanised coatings which can last in excess of 50 years; the coating failing through delamination and hence accelerated electrochemical corrosion in the crevice (Rawat and Mallik 2005).

A.6.3.5 Room-temperature liquid phase processes

A.6.3.5.1 Compositions of liquid phase coatings

A.6.3.5.1.1 Lacquers and mastics, varnishes, japans and paints

Varnishes, japans, lacquers and mastics have in common the compositional basis of an organic resin, in some cases with additional solvent, particularly when the resin is otherwise solid. In paints, the composition contains a binder which may be an organic resin and additionally contains a pigment.

Although in common parlance the terms ‘varnish’ and ‘lacquer’ are interchanged, the distinction lies in the nature of the resin. In lacquers, the resin does not form formal chemical bonds during the drying process (Wicks, Jones et al. 1994). The resin must therefore necessarily be solid and dissolved in an appropriate solvent. A coating is therefore formed by application of the solution and subsequent drying. Given the lack of chemical bonding, lacquers may be surprisingly hard, their properties being largely dependent on the resin from which they are made (Wicks, Jones et al. 1994). Likewise in mastics, the removal of volatile components, usually with associated cooling, results in a non-bonded, high viscosity coating. Mastics such as coal tar, asphalt and bitumen are commonly used for lining steel pipes for corrosion protection (Liu 2003).

Varnishes, by contrast, undergo chemical bonding during curing. Varnishes may be based on natural or synthetic oils or resins. They are applied as a liquid phase, any solvent is then removed by evaporation and the curing mechanism proceeds via cross-linking. The chemical bonding mechanisms are the same polymerisations as those found in thermosetting plastics; many resin types, such as epoxies and acrylates, having variants used for both purposes (Allen and Edge 1993). Polymerisation improves coating durability of varnishes relative to lacquers, particularly in respect of toughness and hence abrasion resistance. Since the base material polymerises, it need not be solid. Consequently, solvents, or thinners, may be reduced or eliminated, reducing the volatile organic content (VOC). This has significant benefits in respect of health-related legislation (Crown Copyright 2005).

The reactions by which varnishes cure are free radical addition or condensation, the latter generating small molecules, usually water, which must be eliminated from the coating structure for full properties to be developed. The extent of reaction is never complete and therefore residual solvent further limits coating performance. Properties can be enhanced by heating the uncured material above the melting point of the resin. This removes solvent, including that formed during condensation reactions, facilitates reflow of the coating, eliminating holidays, and increases cross-linking. These factors influence coating durability. The process of treating varnishes in this fashion is japanning (Spon 1875). It is substantially obsolete following improvements in synthetic resins (Colorcraft Art Craft and Needlework Supplies 2008), but provides useful indications as to how to promote enhanced performance in other systems.

Both lacquers and varnishes are predominantly transparent, being specifically used for aesthetic protection of underlying surfaces with a desirable appearance. The addition of fillers is therefore limited to fused silica, which has negligible effect on transparency, having a similar refractive index (Drinberg, Gurevich et al. 1960). Both lacquers and varnishes therefore have the relatively high permeability associated with organic materials, although brass lacquered with shellac resin in the 19th century and kept in relatively dry (indoor) conditions may frequently still be found to be well protected.

Paints (with the exception of artists' watercolours (Gottsegen 1993) consist of a varnish-type polymerisable resin blended with pigment, which is a fine, insoluble powder which may be organic or inorganic in nature (Gottsegen 1993). As well as providing opacity for aesthetic reasons, the addition of a pigment may confer other functional advantages, including enhanced bonding, as seen in the use of glass flake bearing paints used for protection of steelwork (Greenwood-Sole 2005) enhanced UV resistance by virtue of the inert nature of inorganic (ceramic) pigment materials and facilitating the formation of a thicker protective layer by virtue of the composite performance of the bulk of the coating.

Although paints have enhanced performance compared with pure resin coatings, the permeability and weatherability of organic systems are inherent limitations to their long-term durability as protective coatings.

A.6.3.5.1.2 Sol-gel

Sol-gel processing is a technique for fabricating ceramics from a liquid phase. Since the process forms the subject of the experimental work discussed in this thesis, it is discussed separately. Thin film or coating deposition represents the oldest commercial application of sol-gel technology and the most widespread commercial uses of sol-gel techniques at present are in the fabrication and deposition of coatings.

In comparison with the other coatings discussed in this appendix, the principal features of sol-gel coatings are those of fully dense oxide, carbide or nitride ceramics. They may therefore be tailored to provide mechanical protection for soft materials (polymers and metals), chemical protection for reactive materials, or semiconducting/magnetic properties. Using sol-gel methods, protective organic-inorganic hybrid coatings can be produced at temperatures below 150°C.

The principal limitations of sol-gel coatings are in thickness, which for fully ceramic coatings is limited to below 1 micron and for hybrid coatings does not typically exceed 5 microns when predominantly ceramic-like properties are required.

A.6.3.5.2 Coating processes specific to room temperature liquid phase coatings

There are numerous methods for applying room temperature liquid coatings (ASM International 1994). The principal features of the most common methods are described in this section. Coating methods can be divided into contact methods, including brush and roller coating, and non-contact methods. The latter either form continuous wet films, as in dip, flow and spin coating, or are built up from a series of sprayed droplets which may be patterned or random in placement.

A.6.3.5.2.1 Brush and squeegee coating

In brush coating a brush (or sponge) is immersed in the coating liquid and absorbs a quantity of liquid through absorption and capilliary action. The liquid is forced out onto the substrate by a combination of a wiping action and pressure. Brush coating has advantages of simplicity and portability of equipment, unrestricted area of coating and approaching 100% efficiency of transfer of material. There are limitations as to the properties of the coating composition, since the process is not continuous and a wet edge must be retained between successive regions brush strokes. Considerable variation in film thickness must be expected so the film must flow to self level to remove inconsistencies and the process is not suited to coating materials with critical thickness ranges. Ideally the film should wet the substrate easily to eliminate holidays in the coating, although the mechanical action of the brush does provide additional energy which tends to enhance wetting. The material must therefore have a relatively long drying or gellation time.

Brush coating is entirely manual and therefore very flexible in respect of coating geometry but highly labour intensive.

The process may be automated by using a squeegee (a flexible rubber blade) to apply the coating. This requires that the substrate is flat and that a stand-off distance is maintained between the squeegee and the substrate. This is typically achieved by using a mesh screen, in which case the process is described as screen printing. The mesh size determines the amount of material which passes through the screen and hence the film thickness. The screen may have regions masked to form a pattern by filling in the mesh with an emulsion.

A.6.3.5.2.2 Roll coating

In roll coating a thin liquid film is formed on a surface by one or more rotating rolls. This facilitates either the rapid manual deposition of a more even film than achievable with a brush, or the coating of a continuously moving web or substrate in a reel-to-reel process. By patterning the roll surface a printed pattern may be transferred to the substrate. When the coating material is of high viscosity the film thickness can be controlled by using two rollers and controlling the gap between them. The upper roller (metering roller) is moved relative to the application roller as the schematic diagram shows in figure A.3. The surfaces of these two rollers can move either in the same direction (forward coating process) or opposite directions (reverse coating process). The excess coating on the roller is wiped off by the doctor blade and the coating is then deposited onto the substrate as it passes between the application roller and the support roller. Typical coatings are 1-50 μm thick, and the coating speed can be up to 15 metres per second. This technique is used for painting, printing of magnetic media, adhesive tape, film and newspaper and magazine printing (Han 2006). The details of the print roller determine whether the process is lithographic or gravure. The resultant coating is uniform and shows good mechanical performance.

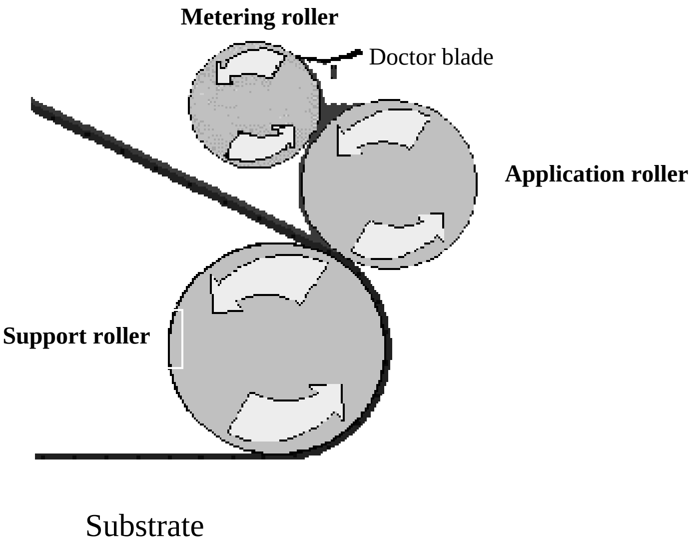
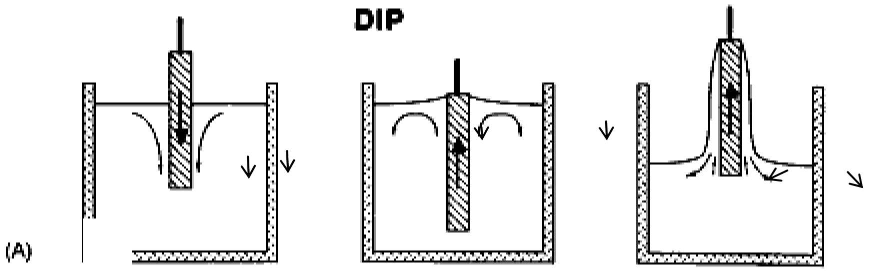


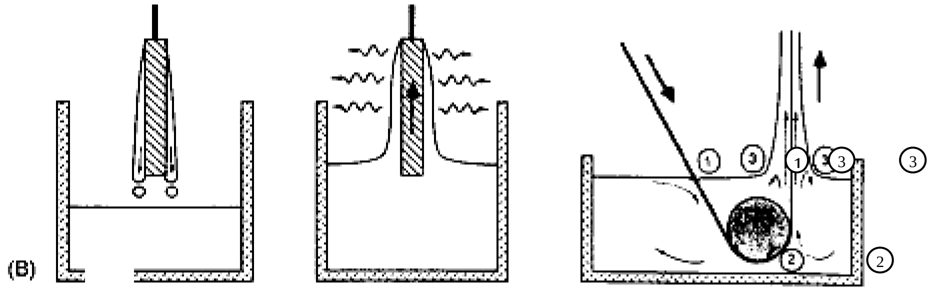
Fig.A.3. A schematic diagram of 3-roll reverse coating process (Technical Coating International Inc 2005).

A.6.3.5.2.3 Dip coating

Dip coating is the simplest process for applying a liquid phase material. The substrate is immersed, either completely or to a predetermined depth in a bath containing the coating composition. The substrate is then removed from the coating, either by withdrawing the substrate or draining the bath. The process is then dependent on the coating material having a sufficiently low viscosity to flow from the surface of the substrate back into the bath, leaving a residual film on the surface. The process is shown schematically in figure A.4. The thickness of the wet film is dependent on the withdrawal speed of the substrate, the viscosity of the coating material and the time between withdrawal and either gellation or solidification of the coating, or reorientation of the substrate, resulting in no further flow in the coating. In general, the faster the substrate is withdrawn, the thicker the deposited coating.



(a) immersion (b) start-up (c) deposition & drainage



(d) drainage (e) evaporation (f) continuous

Fig.A.4. Dip coating process for a sol batch production (a-e) and continuous process (f) (Scriven 1988).

The coating thickness can be calculated by the Landau-Levich equation when the substrate withdrawal speed is such that the shear rates keep the system in the Newtonian regime (Landau and Levich 1942).

$$h = 0.94 \frac{(\eta v)^{\frac{2}{3}}}{(\gamma_{LV})^{\frac{1}{6}}(\rho g)^{\frac{1}{2}}} \qquad \text{(A.3)}$$

where h is coating thickness, η is viscosity of the coating material, v is the substrate velocity relative to the liquid meniscus, γ_{LV} is liquid-vapour surface tension, ρ is density and g is gravity.

An accurate and uniform coating thickness can be obtained if the withdrawal speed is controlled precisely and the vibration of the substrate and fluid surface is minimised. The wet-film coating thickness can be varied between 20 nm and 500 µm, spanning the range of most liquid compositions. The dip coating technique is used where a continuous coating is required, as for optical coatings on components such as bulbs, car body pretreatments, and protective coatings for printed circuit boards. Dip coating can also be used on porous substrates and complex shapes.

Dip coating presents difficulties in coating components with concave geometry or internal cavities, where the liquid may be trapped. The component may require suspension in a bath and the suspension parts will not achieve an even film thickness. Parts with lower density than the coating liquid may float and the coating thickness can vary from top to bottom of parts if the flow rate of the film is comparable to the withdrawal rate.

If the geometry is appropriate, internal coatings may be applied to components by sealing the external orifices and filling them completely with the coating solution, followed by subsequent draining. This technique has been successfully used to coat the inner wall of carbon steel heat exchanger tubes in the geothermal power plant. Tubes 6m in length and 24mm in diameter were coated with poly-phenylenesulphide (PPS)-based and phenolic materials. The thickness of the coating, excluding the primer (8 to 60 µm thick) ranged from 300 to 330 µm (Gawlik, Kelley et al. 2000; Sugama, Elling et al. 2002).

In this case, the coating requires subsequent curing at elevated temperature and the process is known as ‘fill-drain-baking’. The primed tube is inserted into the vertical furnace and the coating material is poured into the tube until it is filled. It is then slowly drained from the tube. The tube is then left for at least twelve hours to allow the solvent to volatilize at room temperature. Finally, the tube is baked for 2 hours at 320 °C and then is cooled off to room temperature. The process is repeated several times to build up the coating to the desired thickness. In the case of phenolic coatings, the curing temperature is at 200 °C.

One factor which must be taken into account in dip coating is that whilst the volume of material required to form the coating is dependent on the surface area of the component, the volume required to carry out the process is dependent on the volume of the component or the bath. Thus coating small numbers of parts or coating parts with a small surface area to volume ratio can be very costly compared with other processes.

A.6.3.5.2.4 Flow coating

In flow coating, the coating material is dispensed as a continuous liquid stream onto the top edge of the inclined substrate component. This may be manual using gravity feed, or for larger volumes pumped from a reservoir through hoses and a nozzle. The coating material deposits on the upper face of the substrate at a controlled speed. The deposition point is advanced across and down the substrate to create a continuous wet film. The process is shown schematically in figure A.5. As in many other wet film processes, the coating thickness is dependent on the viscosity of the liquid, also the speed at which the liquid front is advanced and the angle of inclination of the substrate.

Flow coating is suitable for coating complex products and also large components which are impractical or too large to dip, since no bath is required. In addition, the efficiency is much improved since the coating volume relates to the area rather than volume of the component. The issue of leaving suspension points uncoated is reduced, since the component can usually be supported from the under side, which is not simultaneously coated. Unlike a dip coating however, it is not practical to coat the entire item simultaneously and nor is it possible to maintain a wet edge. This inherently gives rise to discontinuities within the coating. The spinning of the substrate after flow coating may be useful to obtain homogenous coatings, reducing the tendency of the film thickness to increase from top to bottom of the substrate.

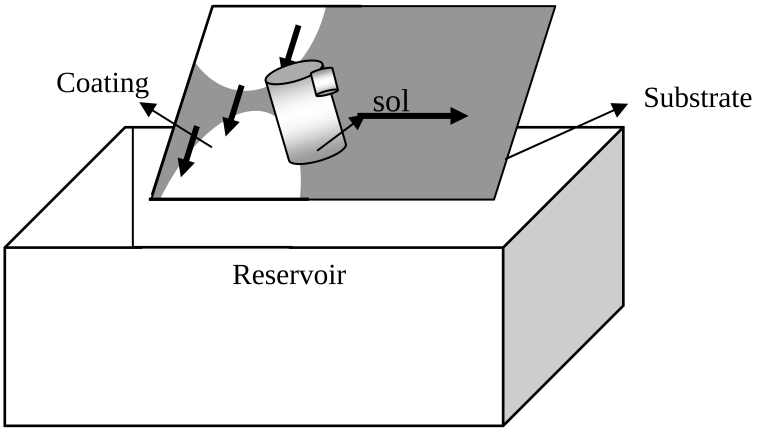
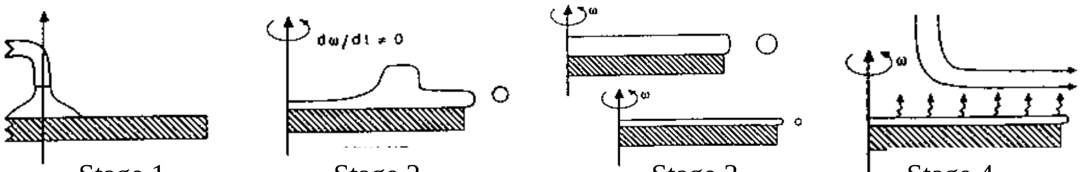


Fig.A.5. Schematic diagram of a flowing coating process (Han 2006).

A.6.3.5.2.5 Spin coating

The spin coating process introduces a greater degree of control over coating thickness compared with dip and flow coating. The process, shown schematically in figure A.6, has four key steps. The substrate is placed on a chuck and an excess of the fluid is initially dispensed at the centre of the substrate, the substrate is then spun at low speed to flow the fluid across its surface by centripetal acceleration, the spin speed is then increased to throw the surplus fluid from the edges of the substrate as droplets and finally the film dries through evaporation. In practice, evaporation occurs to some extent throughout the process.



Stage 1 Stage 2 Stage 3 Stage 4

Fig.A.6. The four stages of spin coating. Stage 1: deposition, Stage 2: spin-up, Stage 3: spin-off and Stage 4: evaporation (Bornside, Macosko et al. 1987).

Coating thickness and uniformity depend on the rotation speed and the evaporation rate. Spin coating is restricted to flat substrates but additional variation is experienced at the edges where air flow is disrupted from the planar. Uniformity can be enhanced by increasing laminar flow; by using round substrates, by rebating the substrate to its thickness into the chuck and by placing a flat plate over the chuck to create a constant narrow gap, the plate being spun with the chuck. In addition, the properties of the coating liquid, such as viscosity and concentration, also affect resultant coating thickness. The typical coating thickness range is from several hundred nanometres up to 10 microns.

The method is used for many applications where a continuous, uniform coating on a flat substrate is required and where the edges may subsequently be discarded. It is therefore particularly suited to the semiconductor industry.

A.6.3.5.2.6 Sprayed coatings

Spray coatings are formed from individual droplets which are formed above the substrate and propelled onto it either singly in a controlled pattern or simultaneously in a random pattern.

The deposition of controlled droplets is achieved either by electrophoresis or mechanical pulses; the latter being used in ink-jet printing where the droplet is expelled from the print head using a piezoelectric effect. The nozzle design for what is essentially a mechanical process results in considerable challenges to avoid blocking around the nozzle end by evaporation of ink when not printing. Placement is usually controlled by an x-y table. The principal advantage of ink-jet printing is its ability to deposit.

Spraying is also used to deposit large quantities of semi-randomly formed droplets. These may be formed using a pressurised gas, usually compressed air, to form the droplets and propel them to the substrate. Alternatively the drops may be formed mechanically using automated equipment such as the internal pipe painting device called the Orbiter, supplied by Clemco Industries Corp. This uses a rotating head powered by an air motor to throw paint by centripetal acceleration at an evenly metered flow against the surface. It can be used to coat pipes with an internal diameter in the range 100mm – 1m and up to 10m long and produces a uniform coating at approximately 3m/min.

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