

**Structure of self-Assembled monolayer of
decanethiol and C₆₀ on Au(111) studied by
scanning tunnelling microscope**

By

Chunqiu Xia

Supervised by Dr. Quanmin Guo

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Nanoscale Physics Research Laboratory

School of Physics & Astronomy

The University of Birmingham

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Abstract

This thesis presents the structure of decanethiol and C_{60} on Au(111) observed by scanning tunnelling microscope (STM). STM is a real space imaging technique with resolution high enough to directly view atoms and molecules.

Gold is a noble metal providing a large flat surface on its (111) for growing self-assembled monolayer of thiols and fullerenes, both of which would exhibit regular phases with long range order on Au(111) as studied previously. I choose decanethiol as an example of long chain thiols to mix with C_{60} and observe their structure on Au(111) by STM.

The interaction between decanethiol and C_{60} is of mainly Van der Waals in nature. This is in contrast to most of the bicomponent systems reported. The lack of directional bonding the two molecules favours the formation of a range of structures.

The mixture exhibits many different phases: sheer stripped phase of decanethiols, regular phases of thiol- C_{60} , heptamers of C_{60} , intermediate phase and irregular phase. Different phases provide various types of information. Regular phases and heptamers can be used to construct models to identify the positions of decanethiols and C_{60} molecules. For the irregular phases, I have performed some statistics analysis and found the average molecule-molecule distance. Intermediates, which exhibit semi-regular structures, provide a series of images about the motion of C_{60} and can be used to identify the how the molecules from the irregular regions get incorporated into the regular phase.

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I am pleased to present this thesis, which represents the fruits of my labour as well as the generous assistance and mentorship offered by those above.

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1 Introduction

Nano is the word meaning ‘dwarf’ in ancient Greek^[1] and nanometre is 10^{-9} m in modern science and technology. Nanoscience researches the structures and behaviours of matter having physical dimensions at least in one-dimension between 0.1-100 nm, while nanotechnology concentrates on the application of such materials. For historic reasons, the non-SI unit, Angstrom ($1 \text{ \AA} = 0.1\text{nm}$) is also used. For example, the Van der Waals radius of a gold atom is $0.166 \text{ nm} = 1.66 \text{ \AA}$. The Hepadnaviridae is the smallest double-stranded DNA virus with the size of 42 nm. Hence, nature is full of nanostructures.

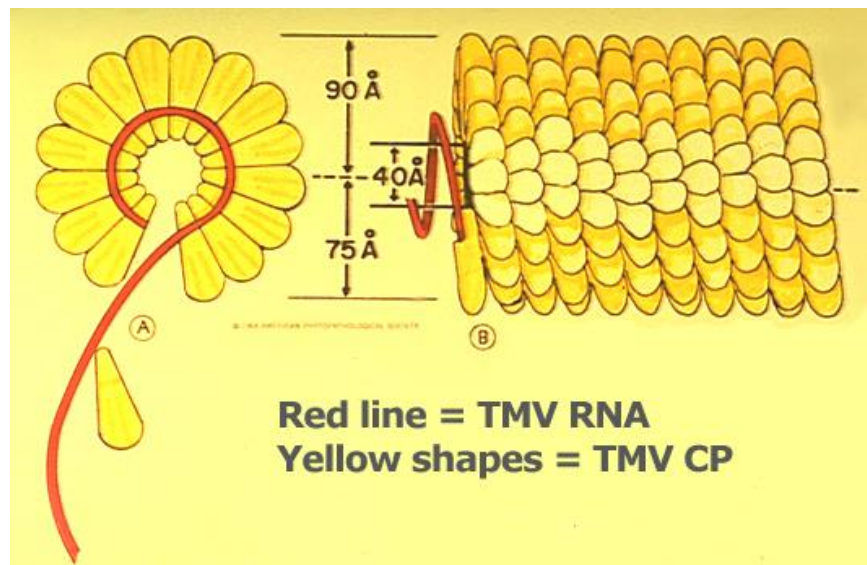


Fig 1.1. A schematic diagram Tobacco mosaic virus^[3], although its diameter is only 18nm, it has complex structure.

Although nano-scale structures are small, they have great impact on our life, such as Tobacco mosaic virus (TMV), it can infect tobacco, tomato, and other solanaceous plants, causing mosaic, mottling, necrosis, stunting, leaf curling, and yellowing of plant tissues^[3]. The structure was first revealed by Harrison in 1978 via X-ray crystallography^[2]. He reported that TMV is a rod-shaped virus with a length of about 300 nm and a width of about 18 nm. Its structure is composed of a single-stranded RNA genome surrounded by a helical capsid made up of identical protein subunits called coat proteins. The TMV capsid is formed by the assembly of 2130 coat protein subunits into a helical structure,

with each subunit arranged in a helix of 16.3 subunits per turn. The RNA genome of TMV is located inside the helix and is tightly associated with the coat protein.

However, artifact nano structures came into existence in relatively much more recent times, and they were in many cases fabricated accidentally. For example, in 4th century, a famous luxury Lycurgus Cup in the Roman Empire consists of nanoparticles which are responsible for its interesting optical properties.



Fig 1.2 The Lycurgus Cup. It shows green by reflected light or light from outside, and red by transmitted light or light from inside^{[4][5]}.

After research in 1990 by using the atomic force microscope (AFM), the reason of the two-colour phenomenon is found to be due to colloidal nanoparticles with diameter of 50-100 nm dispersed in this glass, which is composed of 66.2% silver, 31.2% gold and 2.6% copper. Although the detailed principles are complicated, the red-purple transmission can be mainly attributed to the absorption of green (500-600 nm) by Au nanoparticles, while green reflection is the result of scattering mainly by silver nano

particles, such scattering, called Rayleigh Scattering, depends on the number, size, refractive index of particles, refractive index of medium and wavelength^{[1][5]}.

Of course, ancient artisans knew nothing about nano-knowledge, since they could not directly or indirectly observe any structure less than 100nm, they just followed their manufacturing procedures with tiny different conditions and achieved such extraordinary features by accident.

In 1857, there was the milestone dividing random and engineered nanotechnology, when Michael Faraday firstly synthesised pure ruby gold colloids and studied how the reduction in size of metallic particles affects their optical properties^[6].

Since then, nanoscience and nanotechnology sprouted from many fields listed including microscopes, chemistry, molecular biology, manufacturing and commercial, and even in cosmology^[1].

On Dec. 29, 1959, the physicist Feynman suggested ‘there is plenty of room at the bottom’ and predicted the direct manipulation of individual particles^[7]. In 1974, a Japanese physicist Norio Taniguchi firstly define nanotechnology: “nanotechnology mainly consists of the processing of separation, consolidation, and deformation of materials by one atom or one molecule”^[8]. There are 2 main approaches to synthesis: top-down and bottom-up^[1].

Top-down has been industrialized to micro-electronics industry like lithography. The bottom-up is the method to manipulate atoms or molecules via self-assembly, by which atoms or molecules connect themselves into nano order via their chemical-physical interaction with each other.

However, before the invention of the phrase SAM, Langmuir and Blodgett developed a process to construct a monolayer of closed packed amphiphilic molecules (amphiphilic molecules) on water surface in 1935^{[103][110]}. Since 1980s, there have been a series of significant achievement in SAM, which will be expanded in Chapter 2.

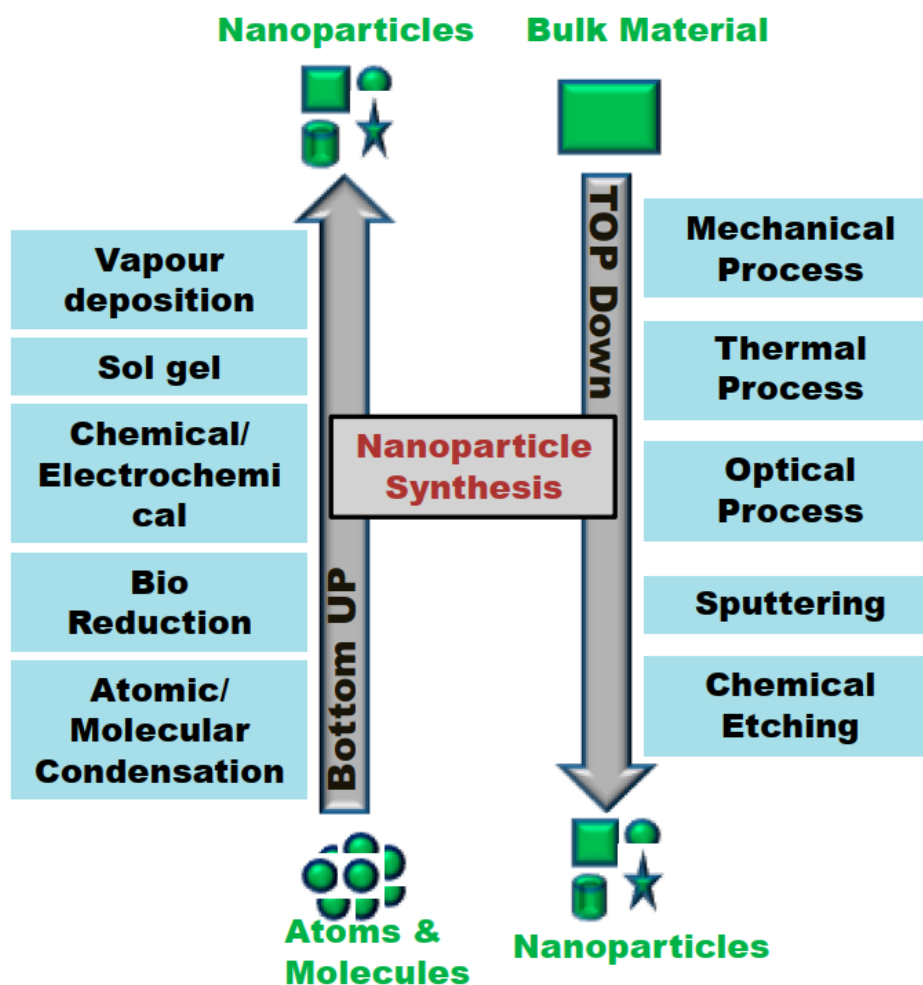


Fig 1.3 Two approaches to synthesis nano particles^[1]

My research is to investigate the structure of a SAM (self-assembled monolayer) of mixed C₆₀ and decanethiol on Au(111) by STM (scanning tunnelling microscope). Noted that the term ‘structure’ in science contains 2 inseparable types: electronic structures and geometric structures^[9]. However, to totally understand the whole structures, it requires mutual verification of different observations and models from many apparatuses. They are not in sync. For example, before the invention of the STM, the structure of Au(111) surface has been detected by LEED (low energy electron diffraction). So, my research is reasonable to focus only on geometrical structures. So, unless stated otherwise, the term ‘structures’ in the following contents are all classified as geometric structures.

Chapter 2 is the review of basic SAM, including the advantages and structure of Au(111) as a substrate on HOPG (highly oriented pyrolytic graphite), the formation and structure of long-chain thiolate on Au(111) and cluster of C₆₀ on Au(111).

Chapter 3 introduces the experimental techniques and equipment. The principle and operation of the STM, tip making, data acquisition, and imaging processing are discussed. We use Gwyddion as the main software for image analysis.

Chapter 4 is the introduction to my experiment, including procedures, making detecting tip and image distortion.

Chapter 5 introduces the known structures and exhibit my experimental results, including basic crystallography, structure of Au(111) and its reconstruction, decanethiol.

Chapter 6 consists of the detailed analysis of the mixed phase of C₆₀ and decanethiol. Based on the STM images, structural models are developed to describe how C₆₀ and decanethiol form different structural phases.

Chapter 7 draws the main conclusion and suggests further works.

2 Literature review

2.1 Introduction to self-assembly

Self-assembly is a process happened in both micro- and macroscale, where many basic elements form a complex ordered system via small-range interaction (rather than string external force) among them^{[17][18]}. In macroscale, such phenomenon can be raised in a school of fish^[19], a colony of ants^[20], where everyone doesn't consciously lead or organized the whole group but communicates with only a few neighbouring patterns. However, the whole group would emerge some degree of organization. However, such stories should be told by biologists or sociologists.

In the microscale, self-assembly is an important process for both creature and non-biological phenomenon such as the organization of protein^[21] or silica nanotubes^[22]. Only this alone is worth being research. The second reason is that self-assembly is a highly promising approach in the manufacturing of regular materials at the nanoscale, through which we don't need to control every atom or molecule.

2.2 Introduction to SAMs

Based on the shape and geometry of the materials, nano-matter can be described as 0-dimensional (0-D, particles), 1-D (nanowires), 2-D (films) or 3-D (nano crystals and nanotubes). At the nano-scale, quantum phenomenon takes effect like tunnelling^{[23][24][25]}, electron confinement, near-field optical effects, entanglement, ballistic transport. Such phenomena would be applied in materials, catalysts, medicine, and magnetic, electronic, and optical devices. Self-assembled monolayers hence belong to 2-D nanomaterials.

Since the beginning of 20th century, human society has been changed everywhere, one of the major contributions has been in the field of heterogeneous catalysis, particularly in the synthesis of ammonia and potassium-related industries. Such chemical industry requires heterogenous, which not only can reduce the temperature, energy, pressure and etc of corresponding reaction, but also strengthen desired reaction and weaken other sides

effects. A catalysis doesn't like a boss to supervise the reaction but is a part of reactants. During the corresponding reaction, reactants is meeting at the interface between them^[9]. So, interface or surface are playing an important role in our world.

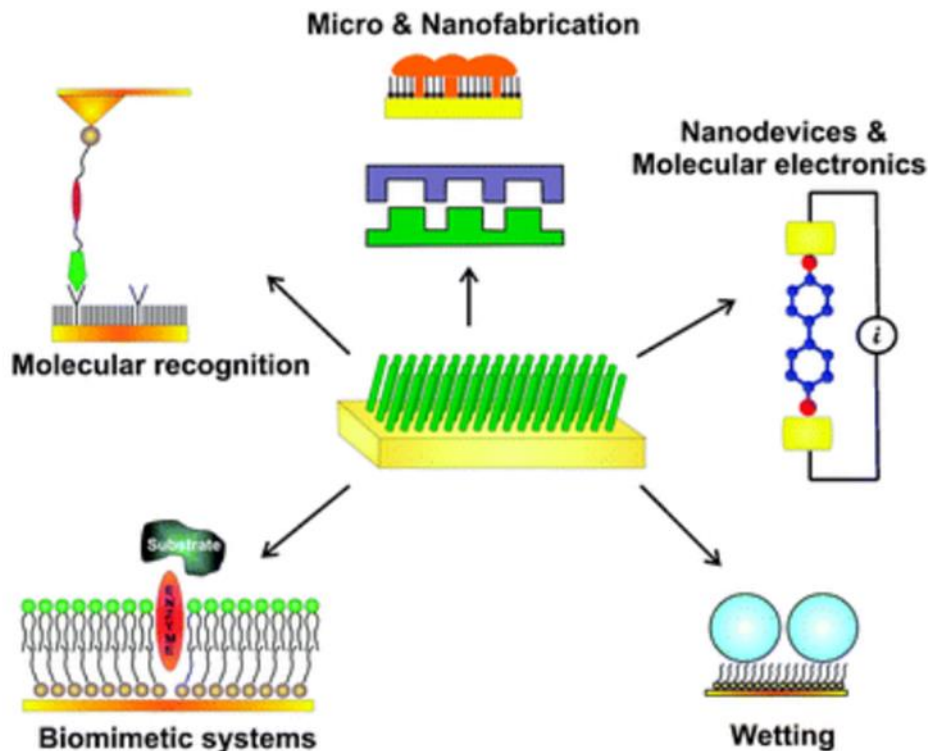


Fig 2.1 Some examples of application of SAMs^[14]. The tail ends of the chains (green bars in the middle image) could be functionalised to facilitate the formation of a particular bonding with a target molecule or particle. The bond can be covalent, Van der Waals, or hydrogen in nature. Such interaction can induce shifts in electronic or magnetic properties, these signals provide us the information of working results or the properties of analytes.

In micro & nanofabrication, molecules which can self-assemble play as inks, resists and anti-adherent layers in different technologies^{[15][16]}. In nanodevices, SAMs can be used in sensors, biosensors, actuators^{[23][24]}, nano alligator clips^[25] and molecular motors^[26]. In wetting, the degree of hydrophilicity of a surface can be modified by SAMs molecules with different functional groups^{[27][28][29]}. Biology is another field to attract nanoscience. Since cells or virus are highly organized nano machines. Our basic cell functions can be viewed as a system constructed beautifully by a large quantity of chemical pathways

regulated by many soft sub-cell machines like mitochondria, chloroplast (not in animal cell), ribosome (can recognize specific RNA segments and amino acid), Golgi, cell nucleus etc. Some current nano-physics research is influenced by development in biology science^{[27][30]}.

In general, S/V is the ratio of the numbers of atoms on surface to that in the bulk. This ratio is proportional to l^{-1} , where l is the characteristic length of the object. So as the size reduces to the nano-range, in some cases, most atoms or molecules are located on the surface instead of in bulk like macroscopic materials. For example, roughly speaking, a gold (atomic radius 0.166nm) nano particle of 1 nm in radius has 2/3 atoms on the surface. Atoms and molecules on the surface experience different environment. So, surfaces can be regarded as another state, not only because of the different fields but even in principle which 2-D liquid are totally different from 3-D liquid^[13].

Metal and its oxides are the materials that the bare surface is active, they tend to absorb organic molecules to lower the surface energy between atmospheres^[36]. The adsorbates would alter the surface properties and prevent metals from interacting with each other e.g., 2 bulks of iron would not welt together automatically in our daily life.

In materials science, it is a well-developed procedure to modify the surface properties by various treatments such as coating. Self-assembly monolayers (SAMs) are an example of surface modification with single layer of molecules. In general, such monolayers are formed by adsorption of organic molecules from solutions or gas phases to the surface of solids or sometimes liquid (mercury), these molecules would spontaneously assemble in some organized way that one of their functional groups binds with substrate, such group is called headgroup. From the view of chemical bonds, typical SAMs are the results of the equilibrium of Van Der Waals force, electrostatic force and even hydrogen bond or halogen bond. In addition, these molecules or ligands may have terminal functional group (or endgroup) displayed on the new surface. Not only do these groups have functions but can be altered (connection or other chemical reactions) to form other functional structures^[27].

Since the first SAM created by Blodgett in 1935, many followers such as Zisman, Blackman and Dewar also studied SAMs^{[111][112]}. During their eras, they focused on macroscopic properties of SAMs like surface tension and wetting due to lack of proper devices to detect microscopic properties, it is only with the advent of advanced tools like STM and AFM, that we can observe or even modify microscopic structures or properties^[110].

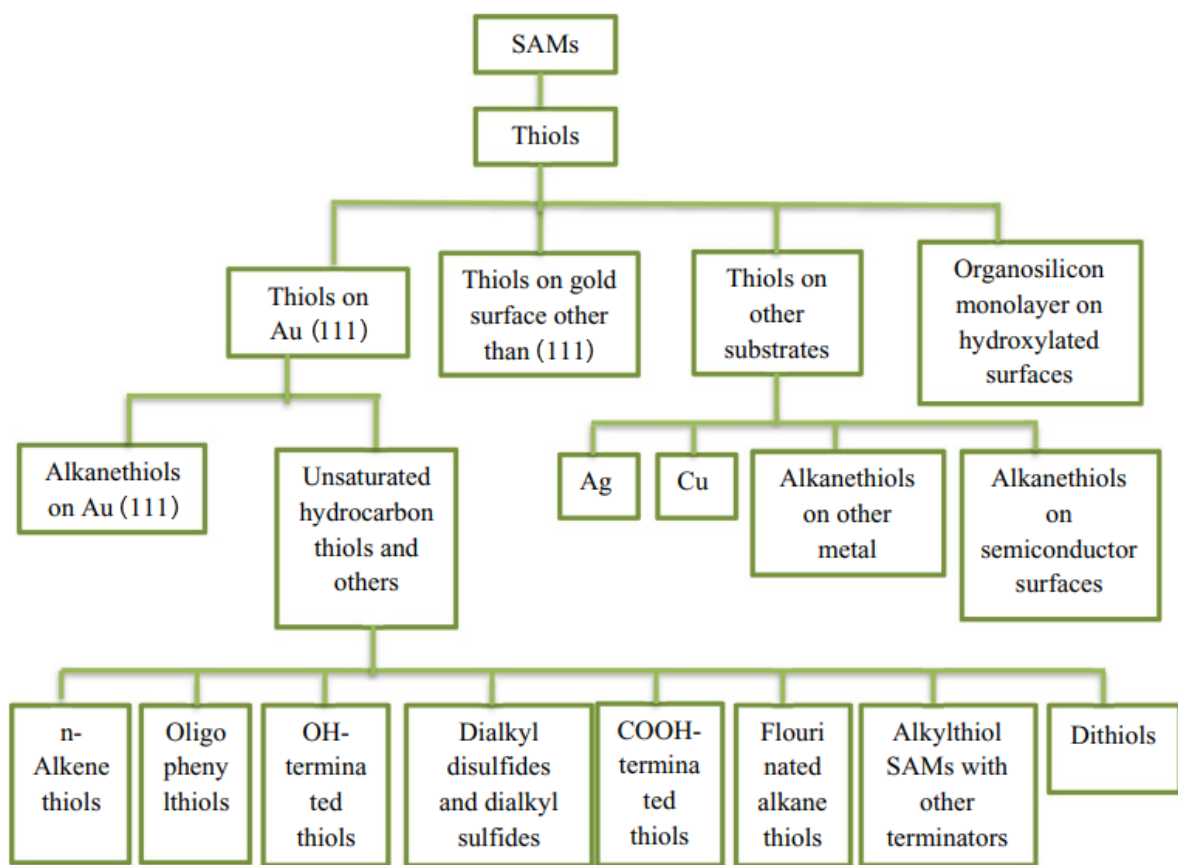


Fig 2.2. Classes of SAMs with thiols as a basic component

Early studies concentrated on simpler molecules with only headgroups such as thiols, silanes, and phosphonates^[114]. However, the most research focus on thiols on Au(111), the reasons are simple preparation, inert substrate and its rigidity^[115], the chemical bonding and formation of thiols will be introduced in section 2.5. Based on thiols, there are many developments and alteration to research, including dithiols, adding endgroups,

changing substrate components or planes, etc. The categories of thiol-based SAM are illustrated on Fig 2.2.

Another class of adsorbent of SAMs on Au(111) is fullerene and with endgroup, which can be used to photovoltaics or quantum computing^[116]. Section 2.6 will provide the basic information on C₆₀. The structure and properties of C₆₀ with endgroups can determine the applications to photovoltaics or quantum computing. There are two ways to alter these: selection of endgroups connected to C₆₀ and the geometrical distribution of C₆₀s on Au(111). Our group are familiar with thiols and fullerenes on Au(111), my focus will be on observing the geometrical distribution of C₆₀s and thiols.

Pristine C₆₀ or thiols on Au(111) lack practical applications due to no endgroup. However, there are 2 reasons to combine C₆₀ and thiols.

1. The structures of SAMs mostly depend on headgroups, substrate and neighbouring monomers, rather than endgroups^[110]. To prevent the interference from endgroups, which may also interact with each other or the substrate, it is an appropriate option to use pristine C₆₀ and thiols. It is another story to study the influence of endgroups and the synthesis appropriate SAMs for practical use.

2. Sheer C₆₀s can only be closely packed on Au(111) without other molecules, it is extremely difficult to change the structures obviously. Thiols, acting as ‘walls’, can separate C₆₀ molecules. My work is to investigate the regularity of separations as well as the structure and even the dynamics of the formation of such structures.

2.3 The role of bonds in SAM

In the field of surface science, chemical bonds play a significant role, not only because they are the base for surface interaction and adsorption, but they can also determine the surface properties, interaction dynamics and choosing the methods for analysis. The structure of SAM is determined by the molecules and bonds between molecules - molecules, molecules-substrates, and in some cases molecules-environments (solvent of gas or liquid phases). On surface, there are 5 main types of bonds, from strongest to the weakest are electrostatic interactions, intermolecular π - π , halogen bonding, hydrogen bonding and Van der Waals interaction.

Electrostatic interactions: Permanent charges or dipoles/quadrupoles on a molecule can generate an electrostatic field that influences the self-assembly of ions, zwitterions, and donor-acceptor compounds. Ions with opposing charges are often found to construct a film, and zwitterions with charged centres are usually designed as electron-rich and electron-withdrawing entities. They adsorb on ionic crystal surfaces through strong electrostatic interactions. Dipolar interactions arise when two molecules exhibit a permanent dipole. The interaction is generally weak and varies as $1/r^3$. Dipole-dipole interaction was implicated as the driving force in the formation of the 2D porous honeycomb structure^{[17][32][33]}.

Intermolecular π - π : This type of bonding is generally raised between aromatic molecules, and hence is important in biology and chemistry. The strength of intermolecular π - π mostly depends on the distance and angles between 2 approaching aromatic rings. The interactions may be too weak to form a chemical bond if the geometry of 2 aromatic rings prevent them from maintaining at proper distances or angles. Such properties can be used to molecule recognition. Because of its directionality, molecules tend to growth linearly i.e., are stacked in one direction. As a result, in surface science aromatic molecules can self-form parallel to the substrate surface^[34].

Halogen bonding: A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity entities^[31]. It has multiple functions in surface science including surface modification, molecule recognition or control of molecule arrangement. 1. In surface modification, molecules with halogen bonding can introduce specific chemical functionalities, this leads to a change in wetness, hydrophobicity, and reactivity of SAM. 2. The directionality of halogen bonds can arrange the geometric structures of SAM and then alter their properties and functions. 3. Halogen-containing molecules can recognize some specific molecules through forming intermolecular interaction.

Hydrogen bonding: The most common form of hydrogen bond is $\text{XH}\cdots\text{Y}$, which is a type of noncovalent interaction occurring between a hydrogen atom covalently bonded to a highly electronegative atom (such as nitrogen, oxygen, or fluorine) and another electronegative atom in a nearby molecule ^[35]. Similar to halogen bonding, the directional nature of hydrogen bonding can lead to the formation of ordered structures, such as secondary structures in proteins or DNA. In addition, its selectivity can also play a key role in molecule recognition or capture specific molecules or groups.

Van der Waals interaction: it is a non-directional interaction because it arises from temporary fluctuations in electron density around atoms and molecules. There are 2 parts of VdW: repulsive and attractive force. The corresponding attractive potential is inversely proportional to r^6 , where r is the distance between 2 atoms or molecules, this can be derived from the Hamiltonian of 2 particles^[109]. The repulsive potential is inversely proportional to r^{12} , and it is much more difficult to derive from the first principle. The distance r_w is defined as Van der Waals radius, where these 2 parts of force are in equilibrium. Although VdW is the weakest in a small range, self-organization and large-scale structures are largely depends on Van der Waals interaction. The structure of SAM can always be closely packed on their substrate if it is dominated by VdW.

2.4 Structure of Au(111)

Gold is one of the favourite metal substrates used for self-assembly. This is mainly because it does not get oxidised in ambient conditions and it can be used in air and liquid. Gold can be made into reactive catalysis for the synthesis of many chemicals such as thiols^{[84][85]}. Thiol covered Au nanoparticles, known as passivated Au nanoparticle, has special optical properties. In surface science, it is relatively easy to manufacture clean and atomically flat Au(111) surfaces.

The Au(111) samples used in my experiment are gold thin films deposited on HOPG as described in Chapter 4. The thickness of gold film is about 200 nm, and the gold can form polycrystalline. The crystallites in the film share one orientation such that the (111) plane is parallel to the substrate surface of HOPG. Therefore, the Au film on HOPG is equivalent to a very large number of single crystals along (111).

Before the description of closed packed structure of Au(111), I need to review some basic knowledge in crystal. For crystals with closed-packed structure, there are two different stacking sequences which produce either face centred cubic (fcc) or hexagonal close packed (hcp). Under classic crystal model, gold atoms stack in the form of fcc.

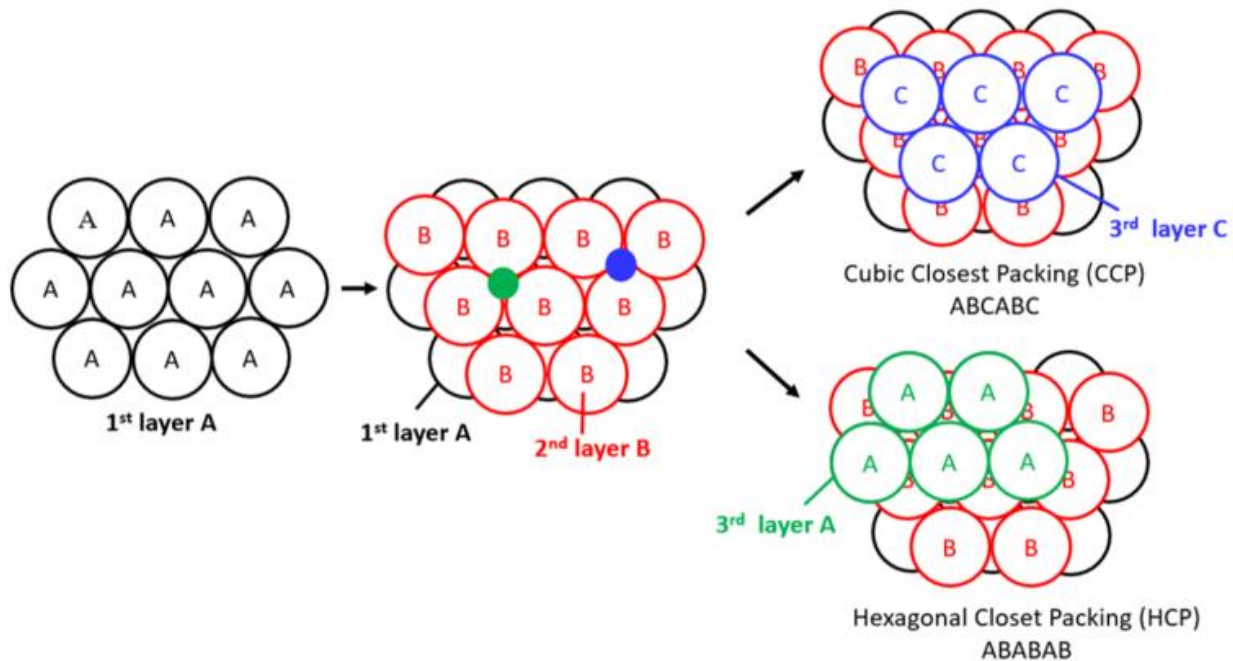


Fig 2.3. Two classic models of closest packed structure, fcc (top right) and hcp (bottom right)^[82].

On the 1st layer (A), each atom is surrounded by 6 nearest neighbour atoms and this agreement of atoms extends across the entire plane. On the 2nd (B) layer, each atom occupies a three-fold hollow site of layer A. On the 3rd (C), there are 2 options for atoms to occupy. One option is to occupy the three-fold hollow site sharing the same projection onto the plane with layer A, and then extending as the form of ABABA... in the direction perpendicular to the layers. This gives rise to a hcp crystal. Element such as cadmium, magnesium, titanium, zinc, and zirconium have the hcp structure. And side view is shown on Fig 2.5. If the 3rd layer atoms take the alternative three-fold hollow site, such that the positions of the atoms on the 3rd layer take a projection different those of A or B. This structure (ABCABC...) is the model of fcc, such as aluminium, calcium, nickel, copper, silver, iridium, platinum, gold or lead, and other views are shown in Fig 2.4. It has been proved there are only 2 such ways of closest stacking with volume occupation ratio 74%. Each unit cell of fcc is occupied by 4 net atoms, and of hcp is 6.

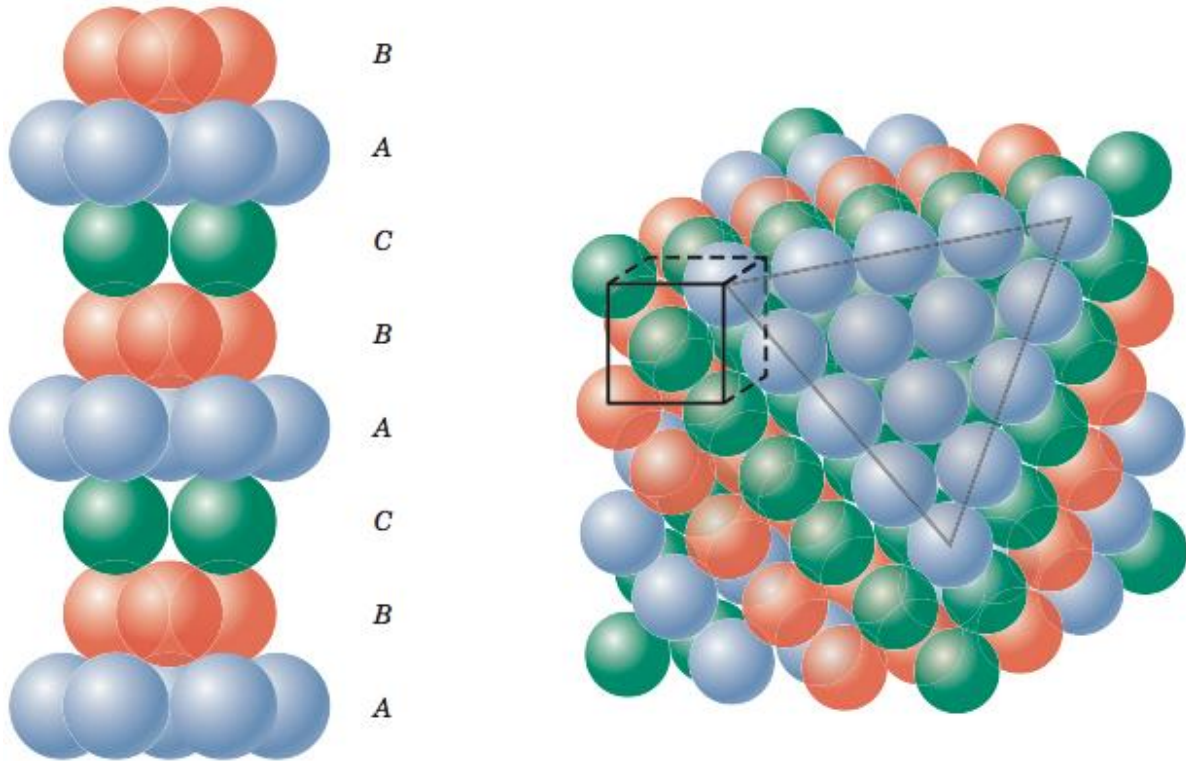


Fig 2.4. Side view of fcc (left), unit cell and section (111) (blue layer on the right)^[83].

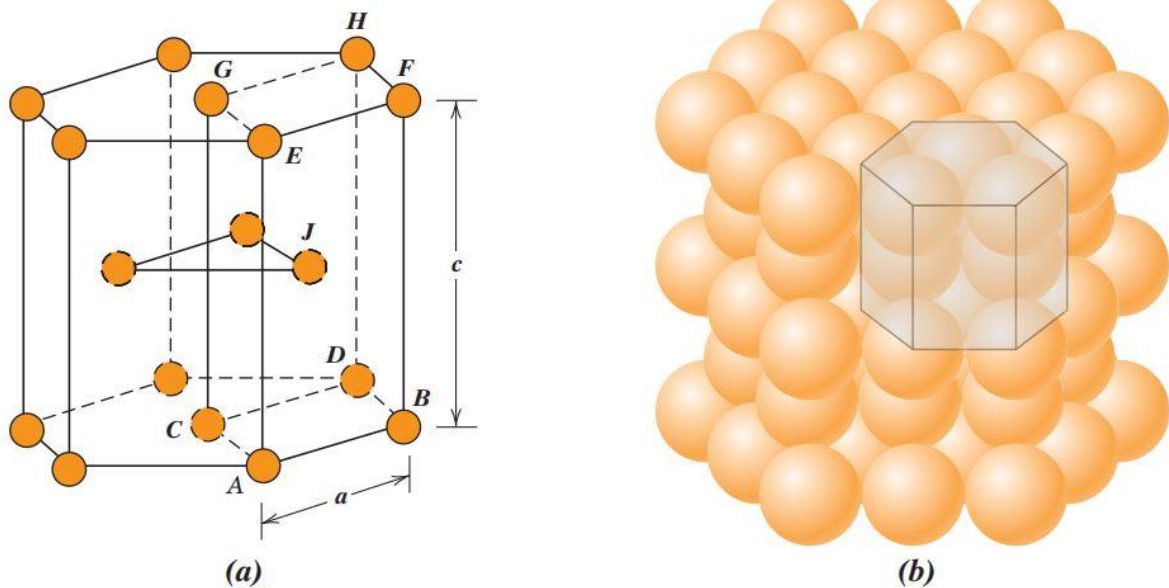


Fig 2.5. Side view of hcp. (a) is a unit cell of hcp structure and (b) is the position of a unit cell in a large model^[83].

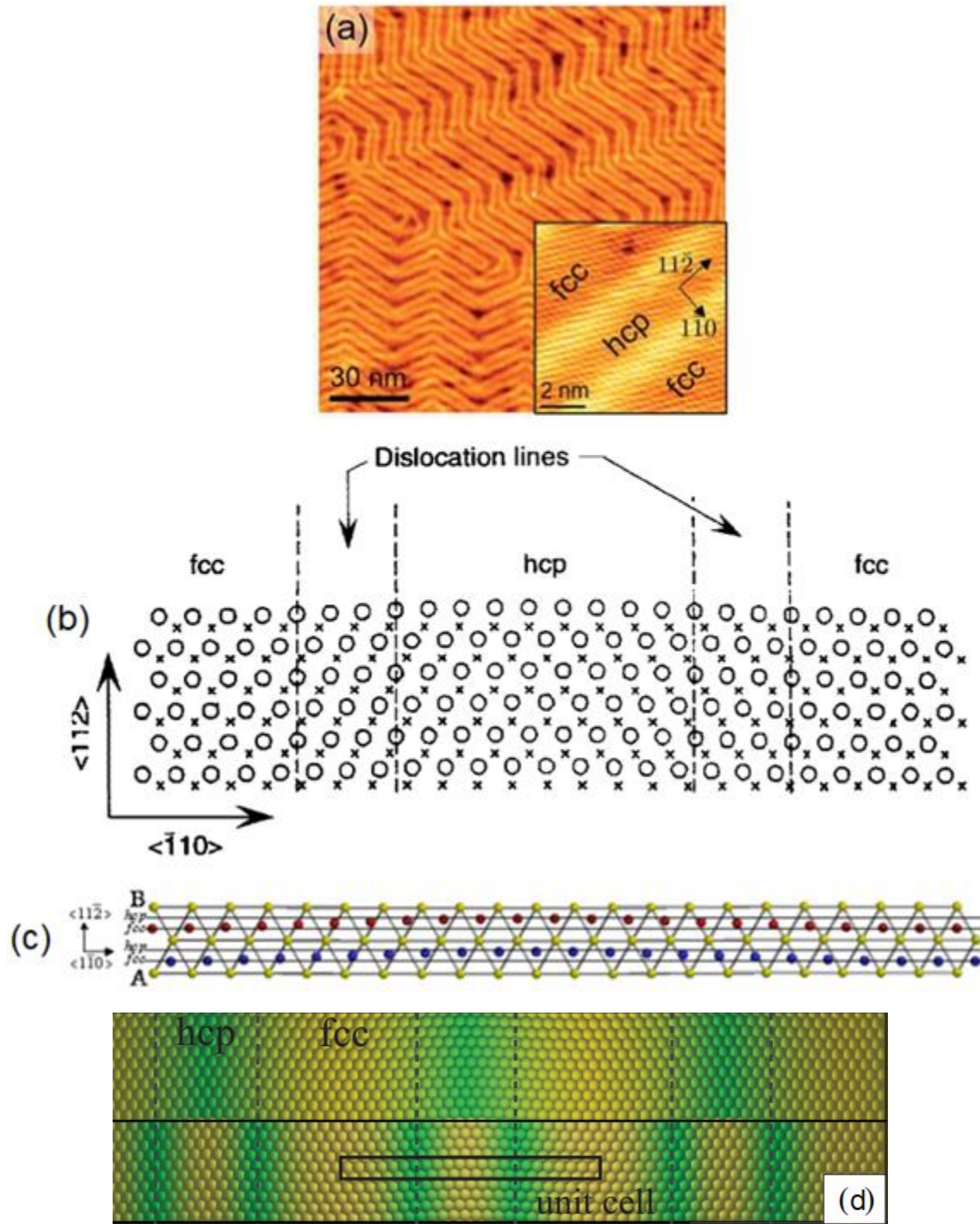


Fig 2.6. (a) A STM image of Au(111) surface with herringbone reconstruction and their details^[88]. (b) A model of Au(111) reconstruction, circles indicate the 2nd layer of atoms (fcc sites), and crosses correspond the 1st layer^[87]. (c) A unit cell of Au(111) reconstruction^[85]. (d) A ball model of reconstruction with a unit cell^[84]

In classic model, the lattice parameter (the length between two points on the corners of a unit cell) of Au fcc crystal is 4.08 Å, which means the distance between adjacent gold atoms in bulk is 2.88 Å. However, an atom is not a classic hard sphere, surrounding conditions of an atom on a surface are different from in the bulk. As a result, there is a competition between surface stress reducing the distance of Au-Au due to the conditions of surface atoms and the force between the first layer and the second which attracts the atoms on the first layer occupying the same positions of the bulk. As a result, gold surface, under this competition, is the only fcc metal which reconstructs its atoms from fcc to hcp on the surface. So, there are many transition regions like herringbones and ridges on the surface of gold crystal.

Fig 2.6. Shows the details and unit cell of Au(111) reconstruction. The unit cell of the reconstructed Au(111) surface can be represented by a rectangle ($22 \times \sqrt{3}$). From the first atom on a fcc site, along the $[1\bar{1}0]$ direction, one passes through a dislocation area, gradually transferring to a hcp site and finally back to the same fcc site. The whole repeating distance contains 23 Au atoms but covers 22 bulk sites. Furthermore, the distance of adjacent atoms is not the mean value (2.75 Å) but it oscillates along $[1\bar{1}0]$, thus a unit cell must contain all 23 gold atoms, this is so called reconstruction. Along $[11\bar{2}]$, the next line is the copy of the first one. However, in surface crystal, a unit cell must be a 2D structure, hence such 2 lines are in one unit cell as shown on (d)

Comparing (a) and (b), it is clear the bright lines i.e., dislocation lines are along $[11\bar{2}]$, however, the reconstruction is not along the one direction but is zigzag course. Since the directions of reconstructions on different region may be different, as the growth of both reconstructions, they would meet with each other, this results a bend in corrugation exhibited on Au(111)^[86].

2.5 SAMs of decanethiol on Au(111)

2.5.1 Introduction

SAMs of alkanethiols are one of the most studied 2-D materials, because of their stability and ease of preparation^[37]. They can form on the surface of gold^{[14][37][39]}, silver^{[38][39]}, copper^[39], palladium^[40], mercury^[41], and platinum^[42]. There are four main reasons to research SAMs in nano science and technology^[27]:

1. They are easily prepared without the need of extreme experimental conditions.
2. They can form functional materials in all sizes and are critical components in many fields like nanowires.
3. They can be used as molecular linkers in electronic and optical devices.
4. They can stabilise metal nanoparticles by forming a thin protecting layer. This protecting layer has the ability of making passivated nanoparticles either hydrophilic or hydrophobic.

In this review, I will briefly introduce important components of SAMs of thiolate, since the preparation, structure, properties, and application are determined by these components.

The first is the metal substrate. For alkanethiol SAMs, the most popular substrate is thin film of metal grown on glass, mica, plastic, silicon wafer or graphite^[27] by PVD (thermal / electron beam evaporation)^[43], electrodeposition^[44] or electroless deposition^[45]. SAMs can form on the surface of bulk materials as well. Thin films are used because of practical purpose. It is easy to prepare smooth films and costs less.

The shape of the substrate can be from flat to highly curved like in nanoparticles ^[27]. The most common types are planar surfaces, since such flat surfaces are easy to prepare and to be analysed with many techniques including XPS^[47] (X-ray photoelectron spectroscopy), HREELS^[47] (High resolution electron energy loss spectroscopy),

NEXAFS^[48] (near edge X-ray absorption fine structure), XRD^[49] (X-ray diffractometer), SPR^[50] (Surface plasmon resonance), SPM^[51] (Scanning probe microscopy), etc. The selection of shape of substrate is determined by the application of SAMs, for example, the etch resistance can be achieved by polycrystalline supported on a flat^[46].

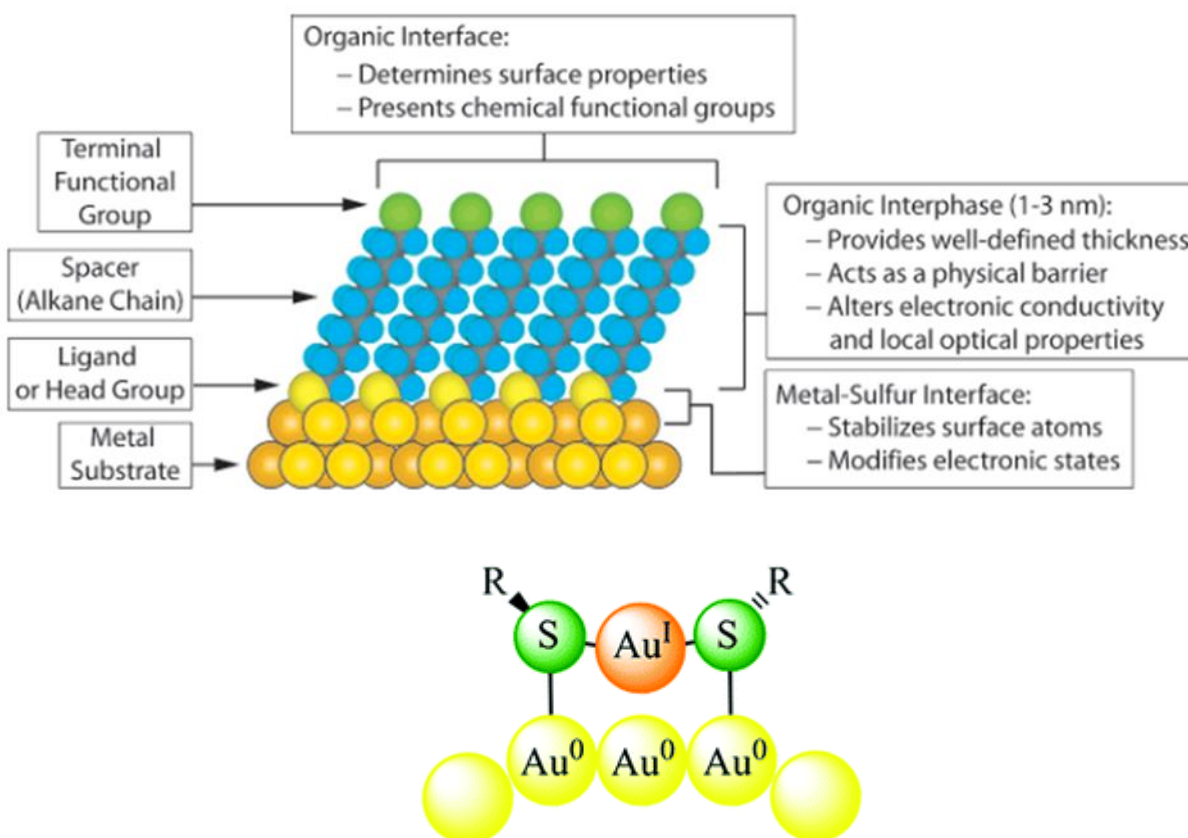


Fig 2.7 The ideal SAMs of closed packed alkanethiol on Au(111)^[27]. the spacing between neighbouring chains is typically around 0.54 nm. The tilt angle, or tilt angle, of the alkyl chains with respect to the surface normal is typically around 30 degrees.

There are many available proper metals, gold is well-attracted and studied. Although in some applications, gold is not an ideal substrate, there are five advantages to choose it^[27]:

1. It is easy to form thin film by PVD, electro (or electroless) deposition.
2. Gold is easy to be forming accompanied with other method like lithography or chemical etchants.

3. Gold can be prepared under atmosphere condition rather than limited under UHV condition, since gold is an inert metal, it does not interact with most chemical and would not be oxidized under its melting point^[52].

4. In modern spectroscopies and technologies including ellipsometry, quartz crystal microbalance, the thin film of gold is a common part. Such characteristic can be applied as interfaces to biology research. For instance, in ellipsometry a planar Au film contacting the sample can emit photonic sensing signals, these signals can be used to create dynamic images of entities such as cells, virus and DNA^[99]. Another example is that gold coated quartz crystal microbalance can monitor the adhesion and proliferation of cells on the sensor surface^[100].

5. Although gold is a heavy metal, it is compatible and non-toxic to cells, not only are the SAMs of thiolates stable for several weeks, but it is also a functional and adhesive group for cells.

Other metals share the same properties as above, but they are less studied as gold.

Silver is the second popular metal as a substrate in SAMs of thiols. Although the thiolates on silver can form simpler structure, but silver is less stable than gold, it can be oxidized instantly and is toxic to cells^[53].

Copper offer interesting properties and characters from technological perspective, but it is more active than silver^[39].

Palladium is another practical metal in SAMs and is better than gold in some application. As or even superior to gold, palladium can be fabricated to thinner film than gold^[55]. It is an appropriate metal in complementary metal oxide semiconductor processing, gold is not. Its catalytic properties can be applied to micro catalytic technology. It is also compatible to cells i.e., biocompatible^[54]. It is also an inert metal under room temperature. The cost of palladium is lower than gold in average with higher variance^[27]. But Pd oxidizes in air and its thin film is harder to prepare.

2.5.2 The formation of alkanethiol SAMs on Au(111)

Thiols are a group of molecules that alkane chain connects a -SH at its end. Thiols with lower molecular weight have strong and unpleasant odours, such property can be applied to detect gas leakage. The odours of long chain thiols are less intense but more complex, for example decanethiol smells like rotten vegetables. The solubility of thiols in water is poor, long chain thiols like decanethiol are insoluble. Hence to reduce its volatility, decanethiol is generally dissolved in ethanol at low concentrations.

Comparing with alcohol, they exhibit similar geometric structure except for O and S atoms. However, such 'little' difference leads that SAM use thiols rather than alcohol. The bonding energy of C-O in alcohols is 25kJ/mol higher than C-S in thiols, however, S-S is nearly twice as strong as O-O^[105]. So that organic compounds containing S atoms can form much more complex structures like proteins.

Another interesting chemical property of thiols is that it can interact with heavy metal atoms like Pb and Hg:



This is the main factor contributing to the toxicity of heavy metals. However, gold atom is inert and does not interact with thiols directly. This leads to non-toxicity of gold atom or nanoparticle to cells and hence gold is a good substrate for biochemical research. While oxidative gold ion can react with thiols and destruct proteins. Although general gold ions are gold(I) and (III), the structure of one unit of SAM is determined by complex conditions rather than gold ions alone.

In preparation of SAMs of organic sulphur on a metal substrate, there are 2 states of precursor solution: liquid or vapor phases^[27]. Most such SAMs assembly from liquid solution, since it is appropriate to interact with other solution for following experiments. While under extreme condition like UHV, gas solution is a better choice.

The precursor liquid in my experiment is the liquid solution of decanethiol in ethanol, the main steps are same as current popular method.

The annealed Au(111) supported on graphite (HOPG, highly oriented pyrolytic graphite) is immersed into ethanolic solution of decanethiol with rough concentration 0.1 mM (0.001 mol/L) under 4 °C for 24 hours. The immersion with similar conditions (concentration, time, Temp) are the most common method for preparation of thiolates. This is the famous method created by Langmuir and Blodgett in 1935^[103].

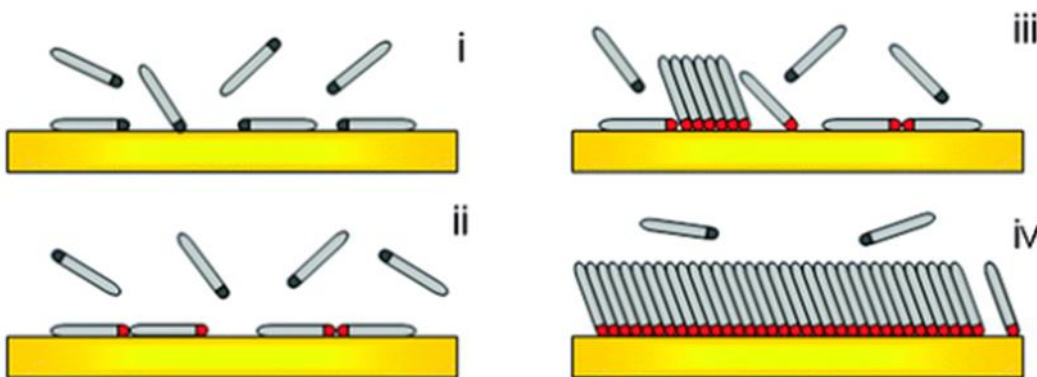


Fig 2.8 Schematic view of the process of SAMs of thiols on Au(111)^[14]

During the process, briefly speaking, there are 4 main steps. The first is physisorption, during which the coverage of thiolate increases quickly in at most a few minutes. Then (ii) the formation of laying down phase and followed by (iii) nucleation of dense phase (or standing up phase), until the completeness of dense phase.

In current stage, the mechanism of formation of alkanethiol on Au(111) is not fully understood, however there are some details have been exploited as shown on Fig 2.9.

The last 3 steps would take several hours to reorganize the structure (relative to (i)), maximize the density and reduce the defects. Hence it is a procedure affected by 8 main factors, solvents, temperature, purity of thiols, time, concentration, cleanness of substrate, the length of alkane and content of oxygen in solution.

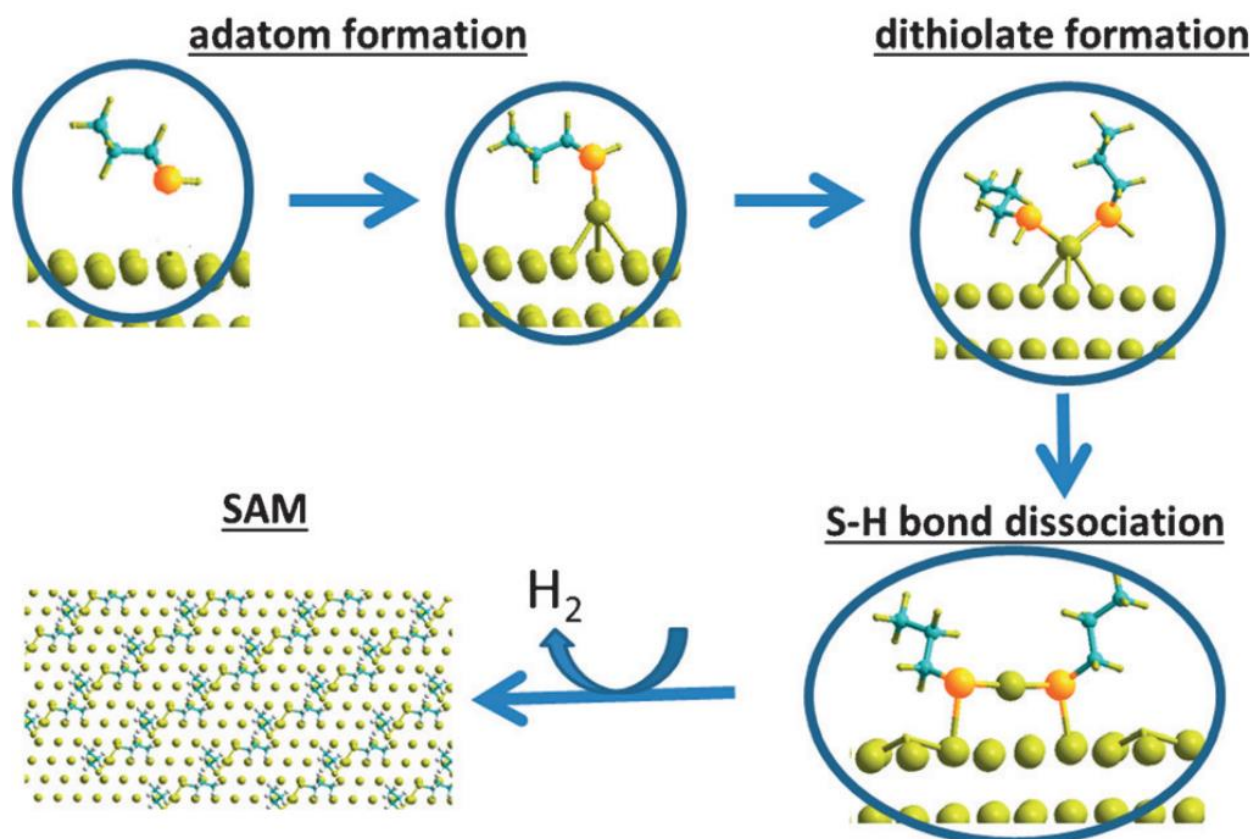


Fig 2.9. Thiol SAM formation. The first thiol is absorbed to a gold adatom from solution or vapor and begins the formation. Then the second thiol interacts with the same gold adatom and form dithiolate. Two sulphur atoms of dithiolate then connect a gold atom respectively on the second layer and release H_2 . Finally, the whole SAM is form regularly in this way^{[106][107]}.

The most popular solvent is ethanol, since it has low toxicity, easily achieve to high purity and compatible with most alkanethiols with inexpensive cost. Comparing with ethanol, it cost less time to form SAMs immersed in nonpolar solvents, but the structure is less organized, since polar solvents can reduce some defects^[56].

High temperature can, especially during the beginning minutes, optimize the kinetics, decrease the effects, and reorganize the structures^[57].

If the impurity of thiol which is generally oxide products is less than 5%, the structure of SAM would not be altered or at least unobservable in current technologies^{[40][56]}.

Generally speaking, the immersion time is inversely proportional to the concentration of thiols^{[56][58]}. For most cases, 1mM is a suitable concentration, 10^{-2} mM may also be applied some specific research, however when the concentration is as low as 10^{-3} mM, only imperfect monolayer can form after one-week immersion in higher concentration solution^[56].

Some theory suggested that the formation of SAMs is the process which alkanethiol replace other materials adsorbed onto the substrate before the immersion into the solution. Hence the kinetics of the formation of SMAs must be affected by the rate of desorption of impurities^[27].

The effect of oxygen on SAMs is little known quantitatively, but the reduction of oxygen in the solution by degassing with inert gas would increase the reproducibility of SAMs^{[39][40]}.

The length of alkanethiol would influences the structure, or sometimes even distort signals to create non-existent structures^[59].

2.5.3 The condensed structure of thiolate on Au(111)

After a 24-hour-immersion, the alkanethiolate has formed on Au(111) surface with many small pits. My research requires to mix C_{60} and decanethiol, hence I don't need fully condensed thiolate. The coverage of thiolate can be reduced by raising temperature from RT to 120°C. However, from RT to about 80°C, the coverage and main lattice structure remain constant, but the pits are being converged i.e., a reduction in their numbers and an increase in individual area while the sum of pits areas per unit area remains nearly constant, as illustrated on Fig 2.10 by Ryo Yamada, Hiromi Wano, and Kohei Uosaki, who observed and statistic the distribution of SAMs of saturated decanethiols on Au(111) by STM^[57]. The image (a) was detected from the sample 'annealed' (kept cooling) at -25°C for 1 hour. Image (b) to (e) were annealed at 5°C, 25°C, 60°C, and 78°C respectively for 1 hour. The distribution of pits remains relatively stable lower than the room temperature. At higher temperatures, there are changes as I mentioned above.

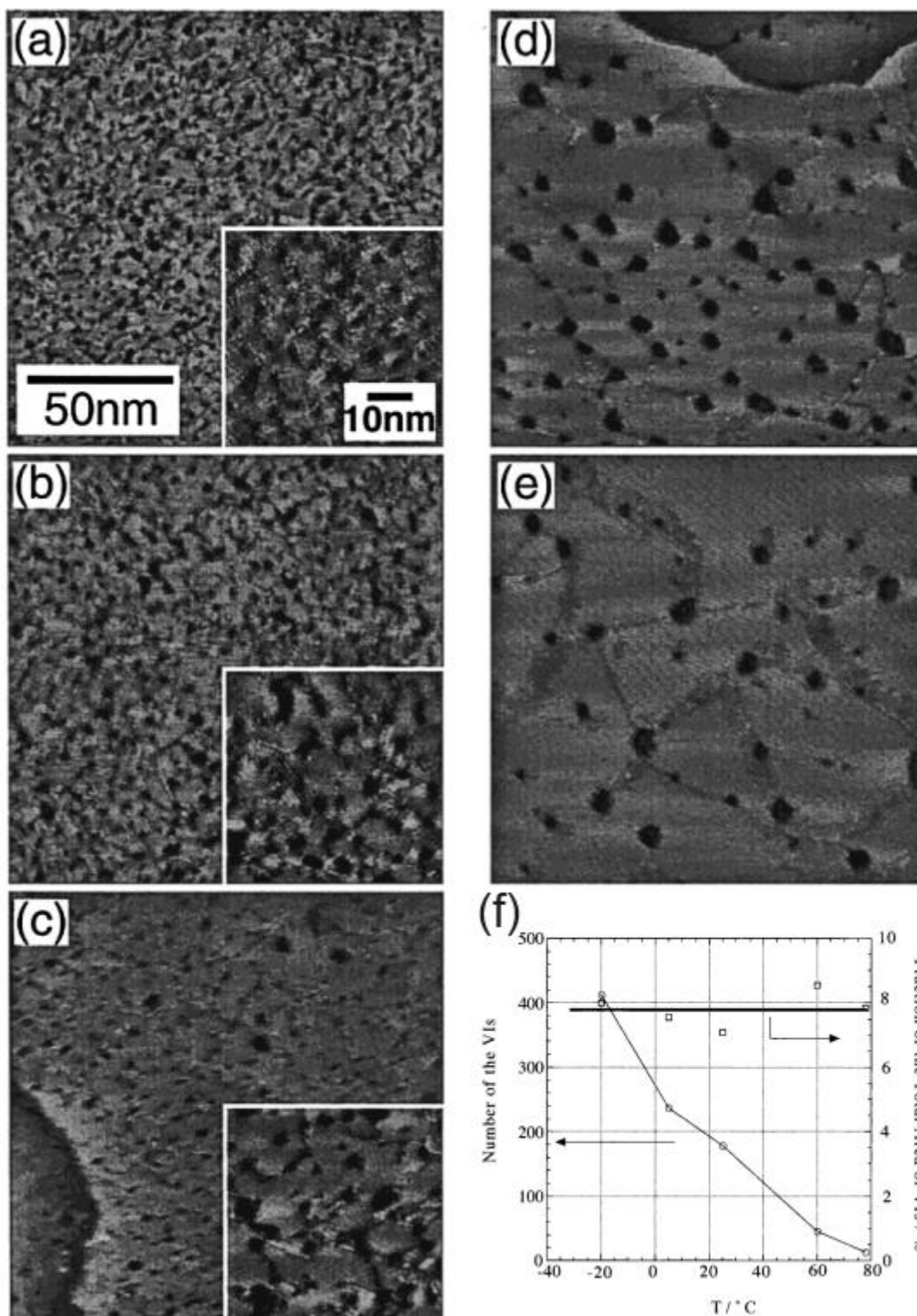


Fig 2.10. STM Images of decanethiol on Au(111) after annealing at (a) -25°C, (b) 5°C, (c) 25°C, (d) 60°C and (e) 78°C for 1 hour. (f) indicates the number of pits (thin line) and total area of pits (bold line) for (a) to (e)^[57].

Since gold is an inert metal, there is not corresponding oxide on it, so the formation of SAMs of thiol on gold is not complicated, But the main controversial problem includes the nature of Au-S bond and spatial arrangement^{[27][59]}.

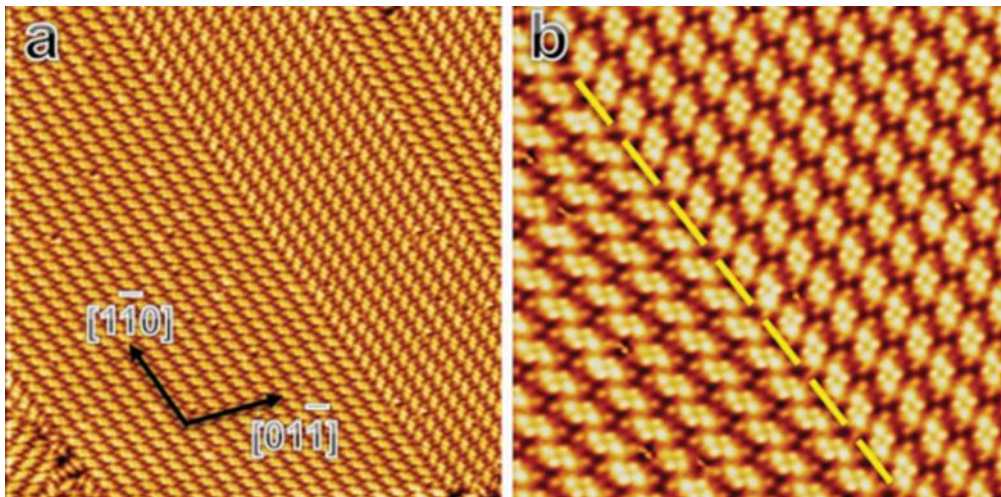


Fig 2.11 The STM image of SAMs of methyl thiol on Au(111), scanning condition is 77 K, -90 mV bias voltage, 1 nA tunnelling current. (a) The size is 30 nm× 30nm. (b) 11 nm× 11 nm the yellow is domain boundary similar to a grain boundary^[60].

Fig 2.11 is the images of STM of SAMs of closed packed methyl thiol on Au(111) with the coverage 1/3 ML, where ML means the number of molecules per Au atom on the surface. Several years ago, it was thought the basic motif of non-branched thiol SAMs was RS-Au where R is alkane chain^[61], but recently it was observed that RS-Au-SR is the basic motif by high resolution STM^[62] as shown on Fig 2.10, such structure is called ‘molecular alligator clip’ which is a stable bridge to link other function groups or even transfer electrical charge or current^[108].

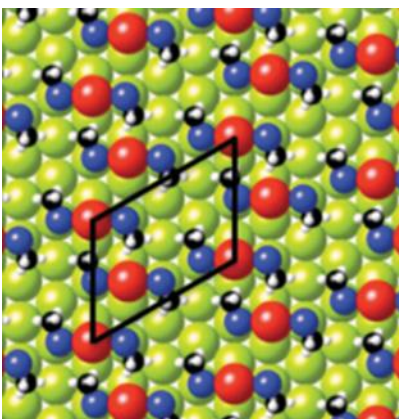


Fig 2.12 The model of SAMs of methyl thiol on Au(111) proposed by Voznyy et al. Green sphere: Au atom as substrate, Red sphere: Au atom as adatoms in thiolate, blue sphere: S atom, black sphere: C atom, white sphere: H atom^[60].

For short alkane chain, like methyl-, ethyl- and propyl thiol, the structure is 3×4 phase. In Fig 2.11 (b) each bright spot indicates a group of six molecules. This can be presented by Fig 2.12. The black parallelogram is the unit cell which, comparing with the unit cell of Au substrate, can be expressed as 3×4 ^{[60][63]}.

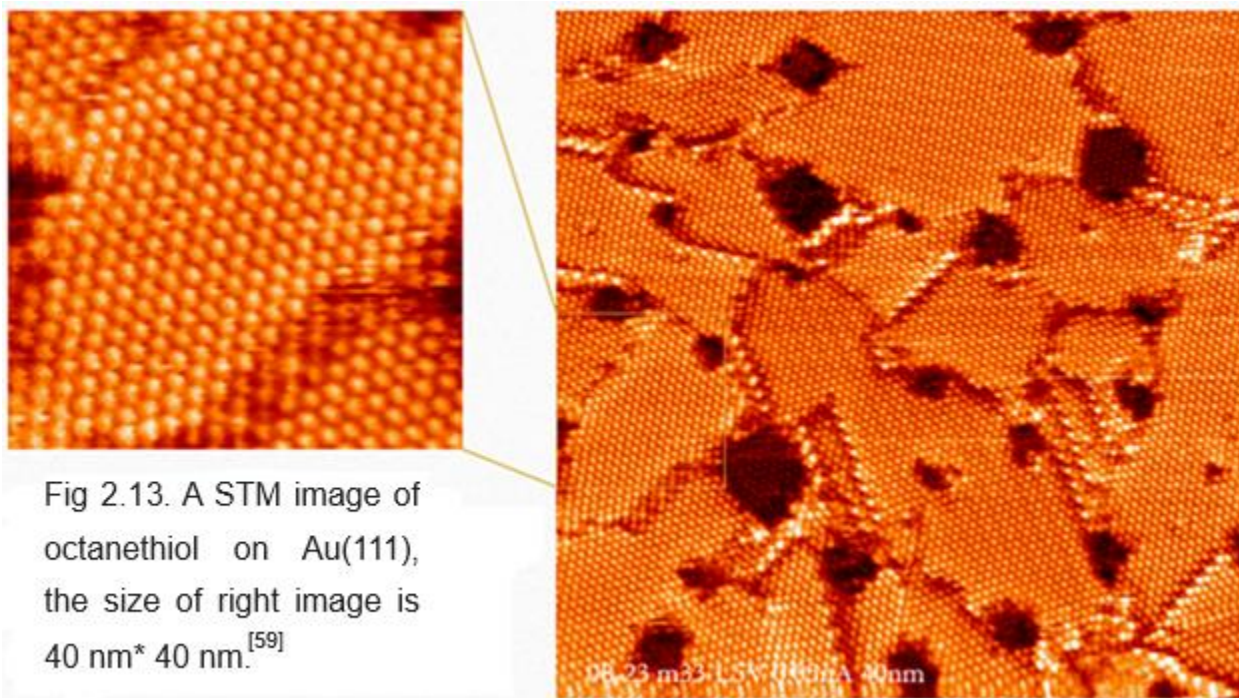


Fig 2.13. A STM image of octanethiol on Au(111), the size of right image is 40 nm* 40 nm.^[59]

For SAMs of thiolate with long alkane chain, the apparent structure is $(\sqrt{3} \times \sqrt{3})$ R30°, this was the thought in early stage. Although it cannot be observed directly due to long alkane chain, but 1:2 is the ratio of released Au adatoms to thiol when removing SAMs^{[64][65]}. Hence the basic motif should also be RS-Au-SR. From such basic motif, without consideration of van der Waals, the structure is 3×4 rather than $(\sqrt{3} \times \sqrt{3})$ R30°, the 2 chains are a little asymmetry rather than congruent i.e., the alkane chains are not equal spaced. As the increasing of chain, the van der Waals interaction tends to reduce such inequality and change the structure^[59], as shown in Fig 2.14.

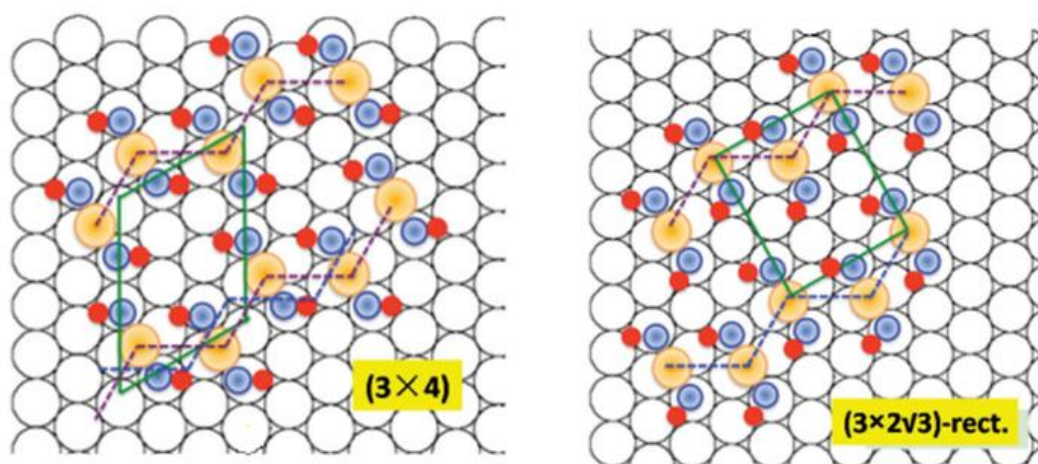


Fig 2.14 The influence of van der Waals on long chain alkane thiol ^[59]. Without changing coverage of alkanethiol, the lower chain on left image would translate along one of closed packed direction of Au, i.e., from purple line to blue line. The resulting structure is $(3 \times 2\sqrt{3})$ -rect.

$(3 \times 2\sqrt{3})$ -rect structure can also be 3×12 unit cell as shown in Fig 2.15. Each 3×12 unit cell contains 12 thiolates (-SR). According to early LEED experiment, long chain alkanethiol cannot form simple hexagonal symmetry^[66]. Accompanied with X-Ray^[67] and STM^[68], from interface to surface, the structure of long chain alkanethiol monolayer gradually transforms from $(3 \times 2\sqrt{3})$ -rect. to $(\sqrt{3} \times \sqrt{3})$ R30° as observed by STM.

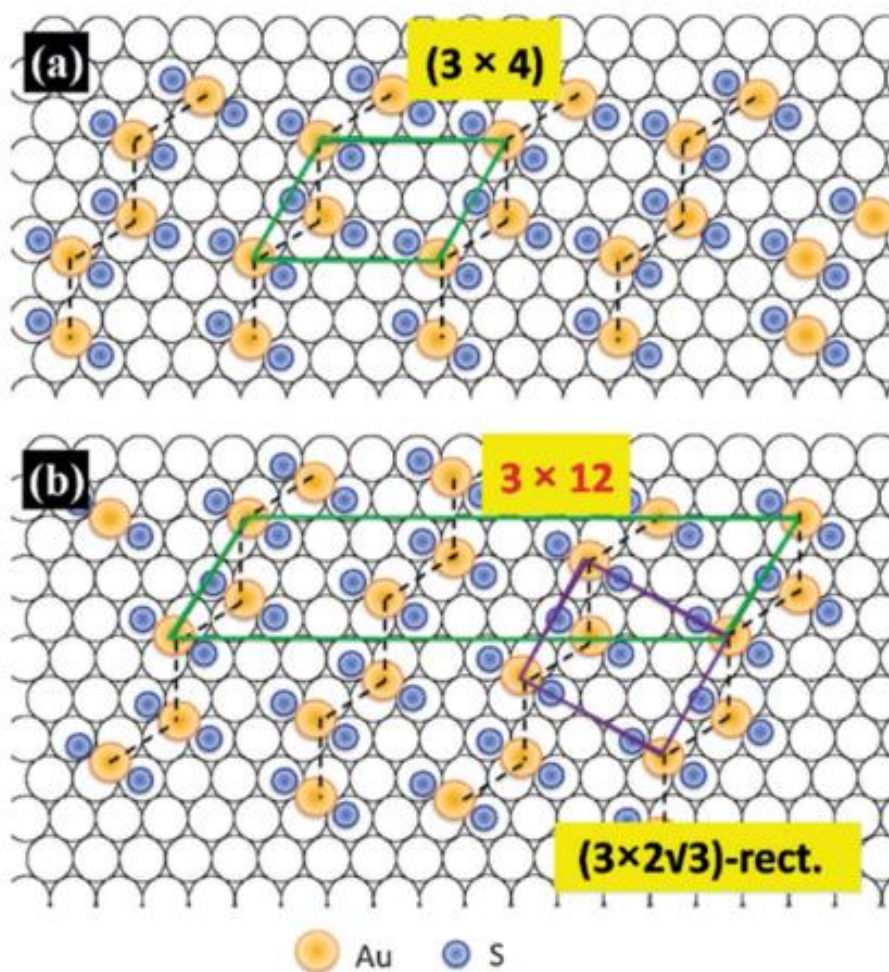


Fig 2.15 Another point of view of $(3 \times 2\sqrt{3})\text{-rect.}$, which is close relative to 3×4 ^[59].

2.5.4 Striped phase

The above structure can only form in $1/3\text{ML}$ coverage, the structure is sensitive to coverage. Since the SAM would form striped phase once the coverage only decreases by 3%^[59]. The striped phase consists of rows of alkanethiol along $[11\bar{2}]$ ^[49]. The spacing distance between ambient rows (or period) is various with coverage, and it can be expressed as pa where p is the ratio of vertical distance to a (gold atomic spacing on Au(111)). Apart from at extremely low coverage, the period is not relative to molecule length but depend on the coverage^{[66][69][70]}.

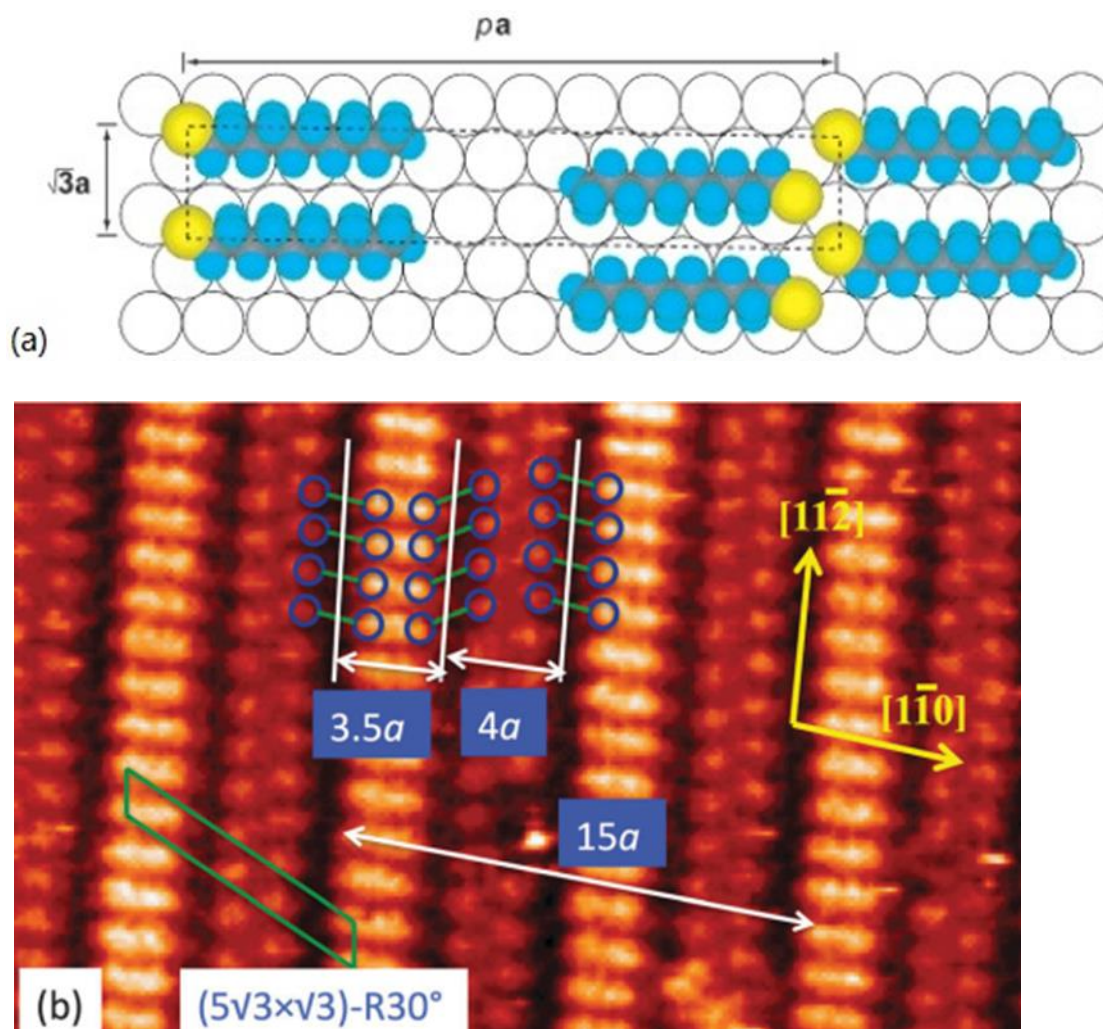


Fig 2.16 Images of striped phases. (a) the ball model of striped phase without gold adatoms shown^[27]. (b) The STM image of $(7.5 \times \sqrt{3})$ striped phase of $\text{CH}_3\text{CH}_2\text{S-Au-SCH}_2\text{CH}_3$, the unit cell can be expressed as $(5\sqrt{3} \times \sqrt{3}) \text{ R}30^\circ$ ^[59].

Although the striped phases are believed to be intermediate phase before saturate coverage, it can only be obtained in a control manner by heating saturated sample under set temperature^[59]. After this process, there is space for Au adatoms to form other SAMs with different molecules like C_{60} or C_{70} . In this case, there are 3 main regions, alkanethiolate, C_{60} and regular mixture of C_{60} and alkanethiol. Such structure is being observed recently.

2.6 C₆₀ on Au(111)

Another attracting adsorbate molecular is C₆₀ or Buckminsterfullerene, since its discovery in 1985^{[71][72]}, its interesting properties has been studied in catalysis^[117], superconductivity, electrical amplifier^[73], single-molecular transistor^[74], and molecular switch^[75]. Hence the interaction and structure of C₆₀ on electrode is the fundament to study and predict the application of C₆₀.

C₆₀ is a cage-like molecule consisting of 60 carbon atoms as shown on Fig 2.17., each carbon connects 3 nearest neighbouring carbon atoms. As a result, the whole C₆₀ molecule is constructed by 20 hexagons and 12 pentagons.

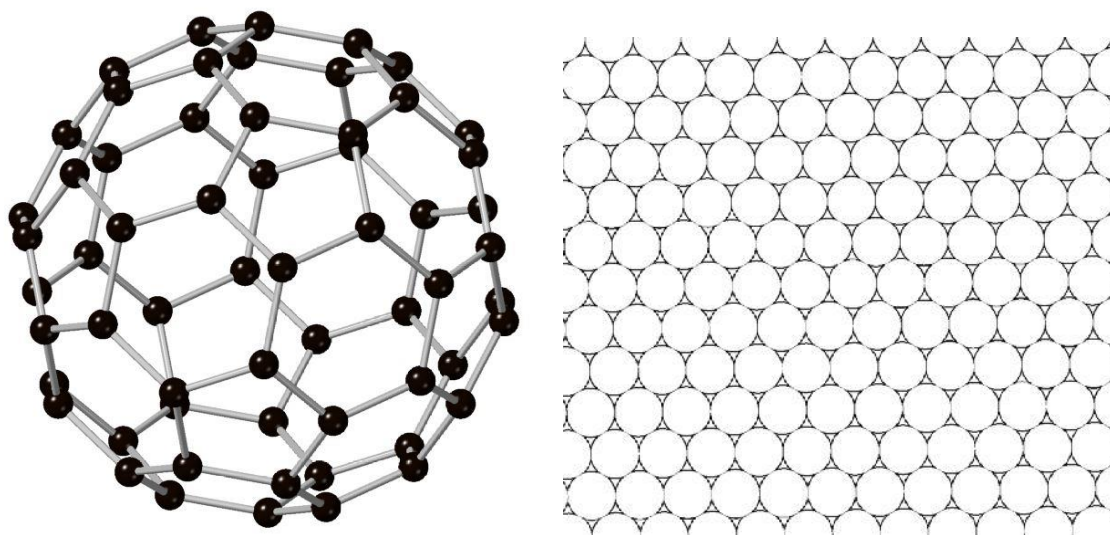


Fig 2.17. Left: a 3-D ball model of C₆₀ from ChemSpider^[77]. Right: a general ball model for 2D closed packed crystal, where each molecules or atoms (represented by circles) are surrounded by 6 identical entities, as C₆₀ on Au(111).

Although every carbon in C₆₀ is chemically identity, since each is a vertex of two hexagons and pentagon^[118], the chemical bonds are more complex. The bonds on edges of a hexagon are similar to those in a benzene ring, while bonds on edges of a pentagon are like the bonds in a 5-carbon ring of cyclopentadienyl.

For simplicity, we consider the bonds between two adjacent hexagons as 'double bonds' while the others are 'single bonds.' Based on this description, carbon atoms are considered

saturated because they are linked with 'four bonds'. Such complicated chemical bonds are applied to functionalized C_{60} , which can also self-assemble on Au(111) in practical use especially in electronic, with more complicated than pristine C_{60} as shown on Fig 2.18. Although only functionalized C_{60} is in practical use, the first step to research the structure of mixed SAMs is to observe pristine C_{60} and thiols on Au(111).

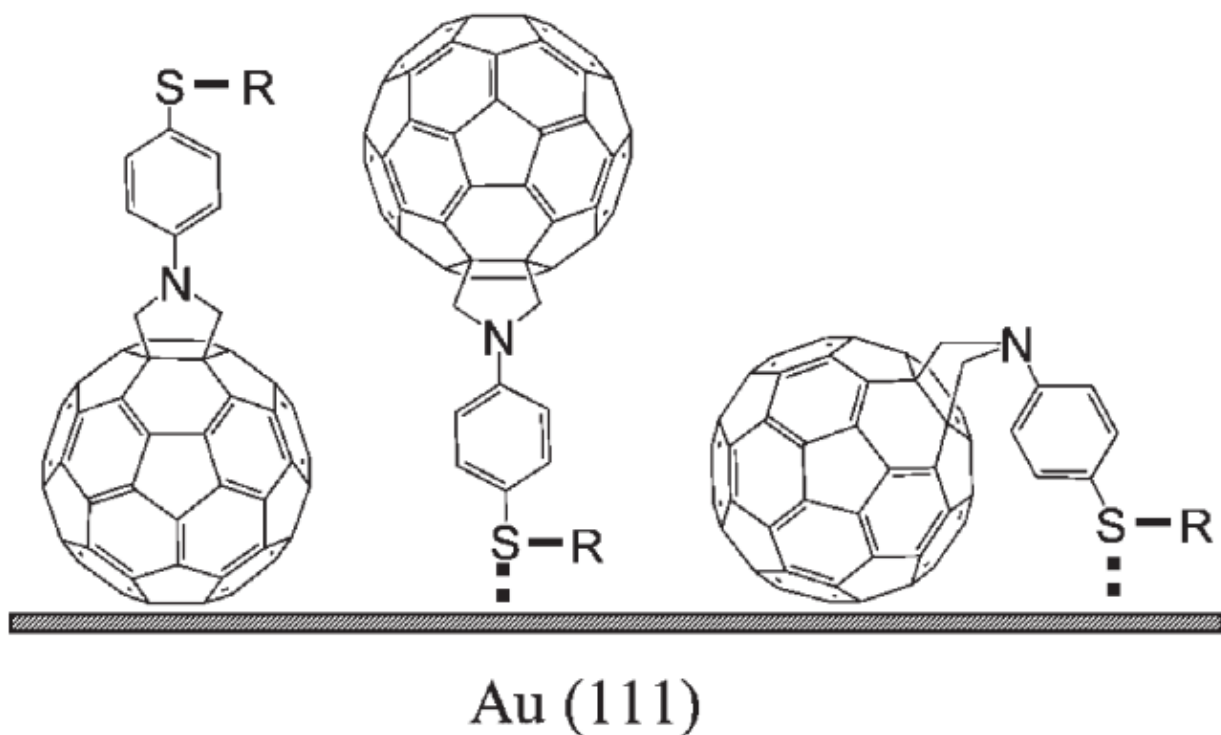


Fig 2.18. A functionalized C_{60} adsorbed on Au(111), there are three modes of connection^[116]. Since S-Au is also rigid, the last two cases are also stable.

However, in the case of C_{60} on Au(111), C_{60}/Au and C_{60}/C_{60} interaction are only controlled by van der Waals, which an unidirectional force, as a result, C_{60} would form close-packed structure on Au(111).

When deposited at room temperature, C_{60} form closed-packed layers. The molecule-substrate interaction is relatively weak, so the molecule-molecule interaction dominates the structures. A typical structure for closed-packed C_{60} is $2\sqrt{3} \times 2\sqrt{3}R30^\circ$. This is a commensurate structure with C_{60} molecules occupying the same surface site. The STM images do not give sufficient information to deduce if the adsorption site is the three-fold

hollow or atop. Within the $2\sqrt{3} \times 2\sqrt{3}R30^\circ$ structure, the nearest neighbour distance of C_{60} is $0.96 \text{ nm}^{[94]}$, which is smaller than the preferred C_{60} - C_{60} distance, $1 \text{ nm}^{[96]}$. Hence there is compressive stress in the layer. Other closed-packed C_{60} structures have been found with various degree of stress in the layers. The herringbone reconstruction is partially lifted upon C_{60} adsorption. This indicates that there are C_{60} molecules occupying less stable surface site in order to maintain an optimal C_{60} - C_{60} interaction.

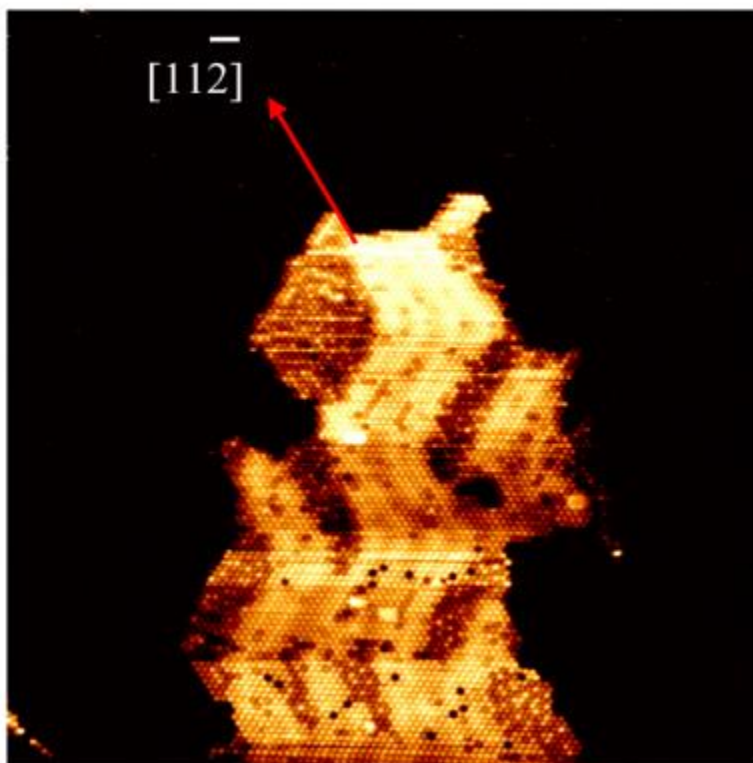


Fig 2.19. An STM image ($110 \text{ nm} \times 110 \text{ nm}$) of C_{60} island on Au(111), the background shows there is still partial reconstruction^[93].

Because of partial reconstruction, C_{60} molecules are not distributed on a plane but on light and dim position observed by STM. Such bright dim contrast arises from different adsorption site or different orientation of molecules. At room temperature, molecules are probably flipping. But, if a molecule appears constantly dim, it may indicate a constant, and more stable, orientation. Because of not strong interaction between C_{60} -Au, the molecules have freedom to move. This is desirable when C_{60} is added to a decanethiol

layer because the mobility of molecules is required to form a regular structure for mixed C_{60} and decanethiol.

Despite reconstruction, C_{60} are closed packed as $2\sqrt{3} \times 2\sqrt{3}R30^\circ$ and superstructure $7 \times 7 R14^\circ$, in phase 38×38 and $3 \times 3 R34^\circ$ or disorder domain, the neighbouring distances of C_{60} are listed on the table 2.1 and shown on Fig 2.20 and 2.21.

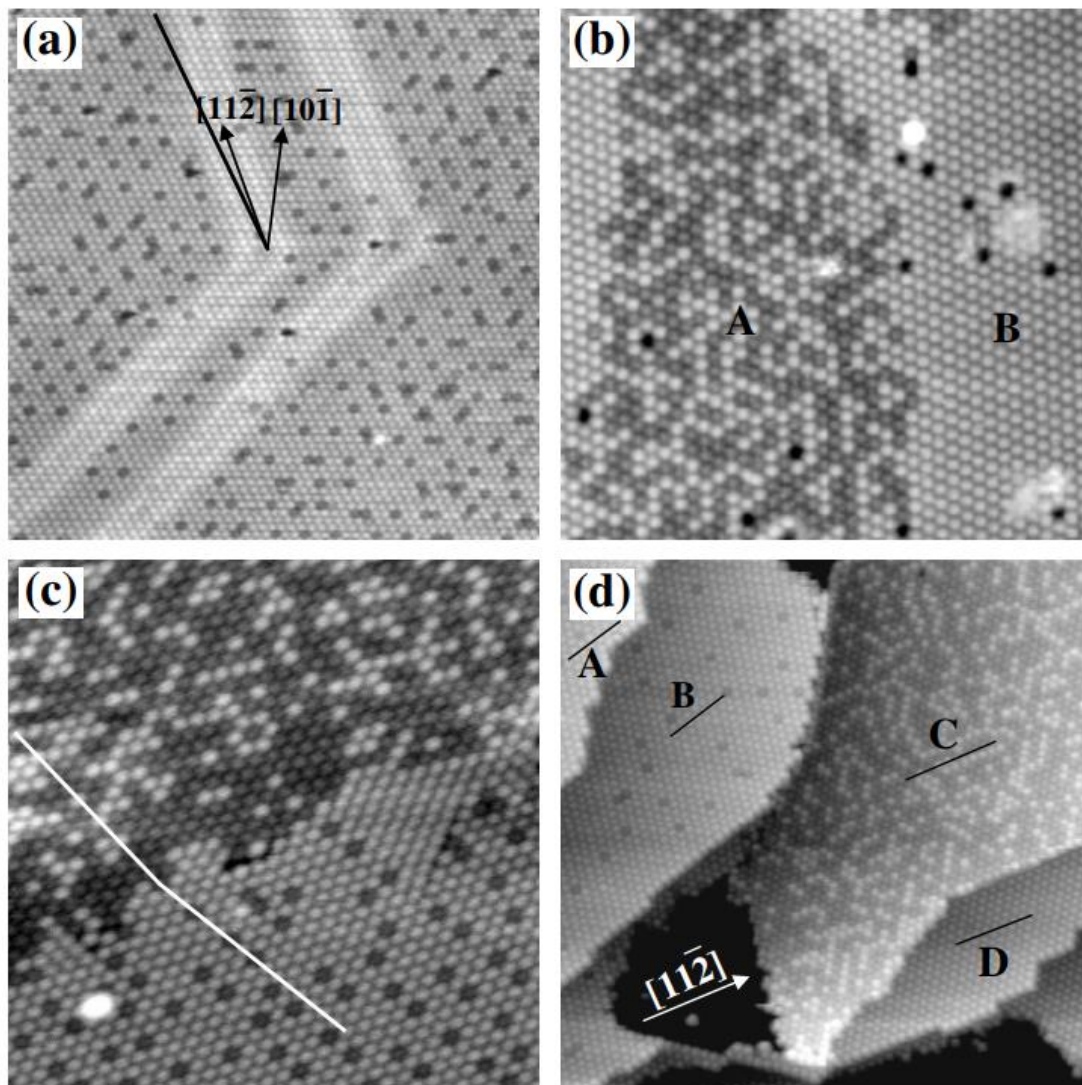


Fig 2.20. STM images of C_{60} on Au(111)^[95]. (a) C_{60} of $3 \times 3 R34^\circ$, there are 2 partial reconstructions hidden under C_{60} , the black line is the direction of closed packed C_{60} which rotates 34° relative to $[10\bar{1}]$. (b) disordered domain (A) on the uniform domain (B). (c) disordered (top) and quasiperiodic (bottom) C_{60} . (d) An image of different gold platform with different domain of C_{60} .

Table 2.1: Various structures of C₆₀ on Au(111) and corresponding distance of nearest C₆₀

Structure	Neighbouring distance of C ₆₀
$2\sqrt{3} \times 2\sqrt{3} R30^\circ$	0.96 nm ^[94]
7×7 R14°	1.1 nm ^[97]
In phase 38×38	0.99 nm ^[98]
3×3 R34°	1 nm ^[95]

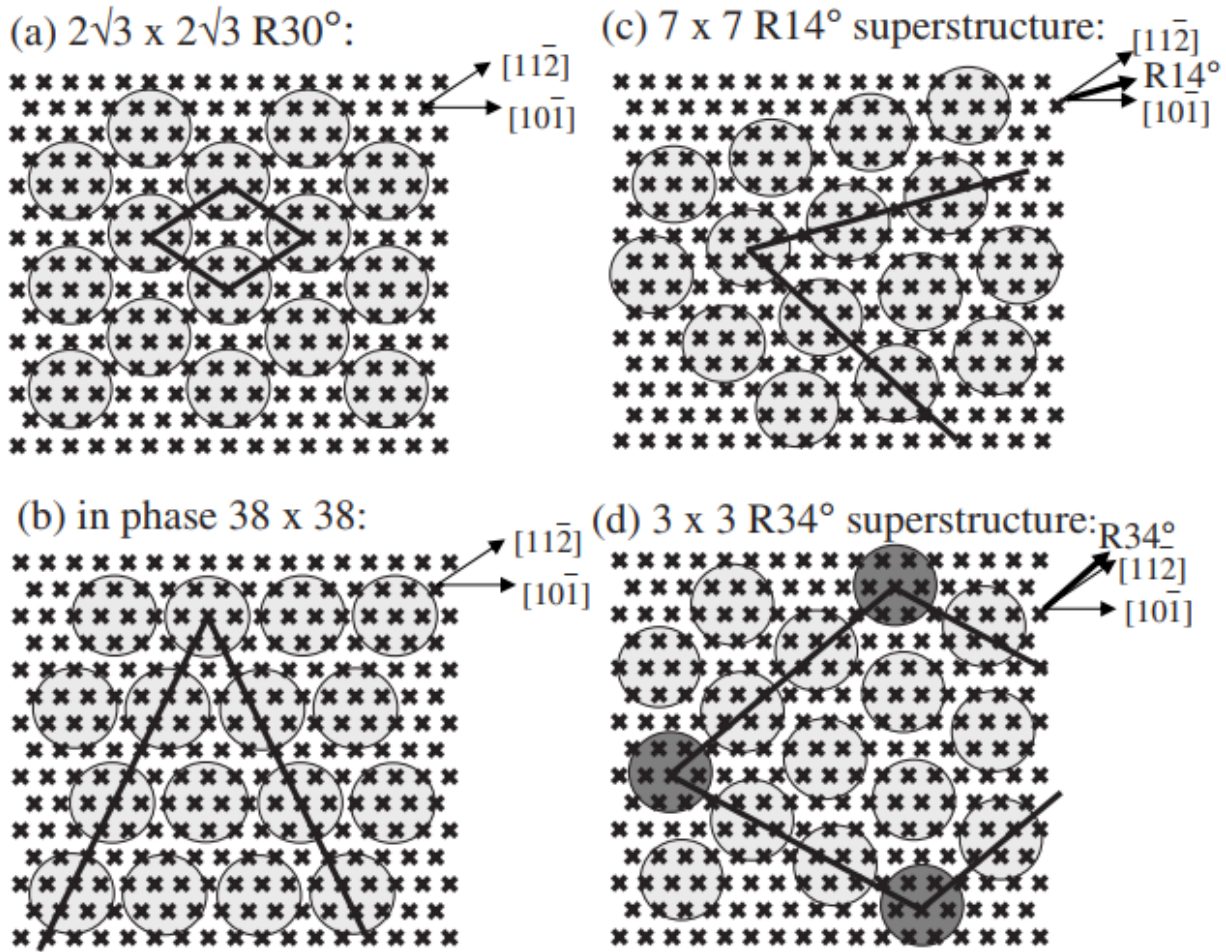


Fig 2.21. Models of different close-packed C₆₀ layers on Au(111). Crosses represent first layer of Au atoms, Open circles represent C₆₀ molecules^[95].

At room temperature, the strength between Au and C_{60} exhibits special properties, such that It is weak enough to permit a diffusion of C_{60} on Au(111) and is strong enough to organize a more complex structures like the cluster of $(C_{60})_m(Au)_n$, where m and n cannot be arbitrary but some constants called Magic Number. The smallest cluster is $(C_{60})_7(Au)_{19}$ ^[78].

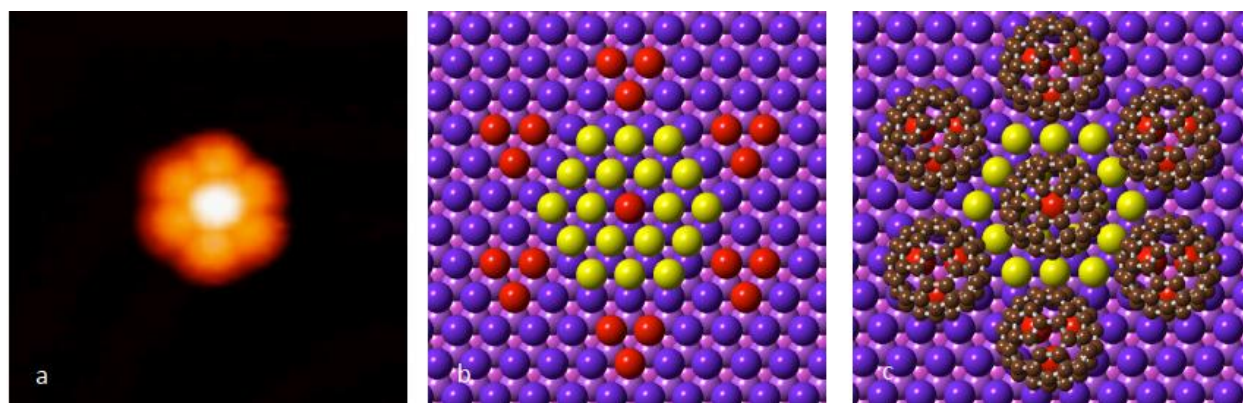


Fig 2.22 STM image and ball model of $(C_{60})_7(Au)_{19}$. Image a is a STM image. In b, purples balls represent atoms of substrate Au(111), the gold atoms forming the cluster are 18 yellow ones and the centre red one, the other 18 red balls on out shell are the substrate atoms supporting six C_{60} molecules as shown in c^[78].

3 Introduction to STM

This chapter introduces the basic principles of STM. Except for the last section, these are characteristics common to all types of STMs. The features and operation of the LT-STM I used will be discussed in Chapter 4

3.1 General working principle

Scanning Tunnelling Microscopy was invented by Gerd Binnig, Heinrich Rohrer, Christoph Gerber, and Edmund Weibel in 1981^[81]. Since then, single atom became visible and hence STM became one of the most useful instruments in experimental physics.

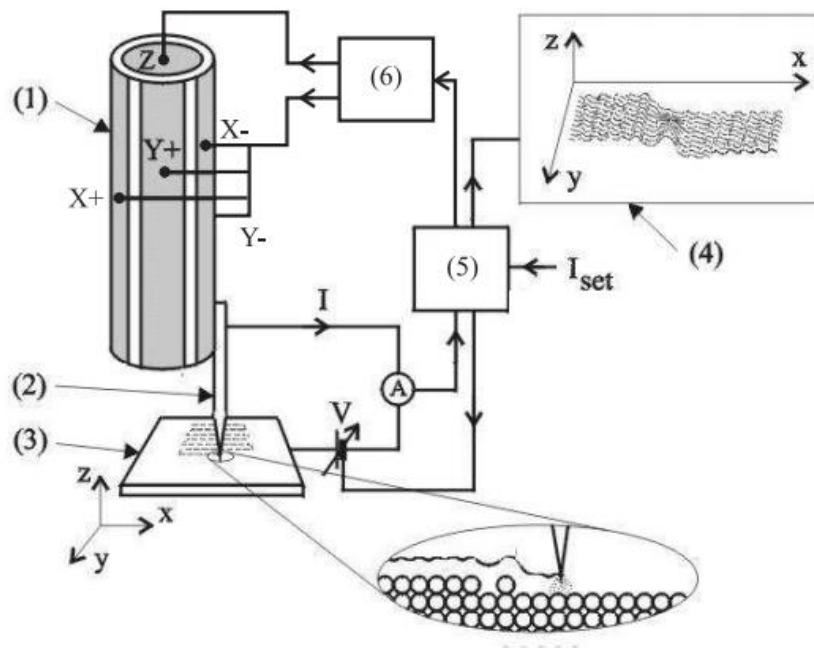


Fig 3.1 The scheme of the core system of STM^[79]. (1) Piezo tube. (2) Tunneling Tip. (3) Sample. (4) Image. (5) Control unit. (6) Piezo power supply

Fig 3.1 is the core system of an STM. The tunnelling tip (2) scans the sample (3) line by line, the signal collected by the tip is transferred into the control system or unit (5). After a complex progress including conversion of current-voltage, voltage-digital signal and comparing the difference from I_{set} . The digital signal is transferred to some software to be

inverted to images (4). The difference of signal (actual current and I_{set}) is transmitted into piezo power supply (6) which can ‘tell’ the piezo tube the next motion in x, y, z direction by inserting corresponding voltages onto the piezo tube.

3.2 Effect of oscillation

Before the introduction to the system of STM, one factor which is neglected in regular life would be considered first, vibration. For example, normal floor vibration (noise) has amplitude of 100 nm which is 10^4 times larger than the signal (0.01 nm or 10 pm) detected by STM^[80]. Hence the amplitude of noise should be reduced to less than 1pm which is 1/10 of tip-sample distance.

In design, there are 2 types of noise: outer and inner noise^[80]. Out noise is transmitted from ground and air to STM which can be considered as a rigid system. The reduction of noise can be obtained, briefly speaking, by suspending the system onto a spring. According to oscillation theory, the lower quality factor Q_1 of the spring the less vibration. However, the resulting $Q_1 \approx 2-5$ comprised from many factors such as large resonance enhancement and good damping at high frequency.

The inner noise stem from considering STM itself as an oscillation system. The quality factor STM (Q_2 , typically is 100) is determined by the softest part i.e., piezo material which is an important component for the motion of tip and will be introduced in the next part^[80].

In compromised 2 types of noise, the spring suspension can transmit a little noise with frequency lower than its natural frequency and damp the noise at larger frequency, while the STM can pass higher frequency (relative to natural frequency of STM) noise and damp lower frequency vibrations^[80].

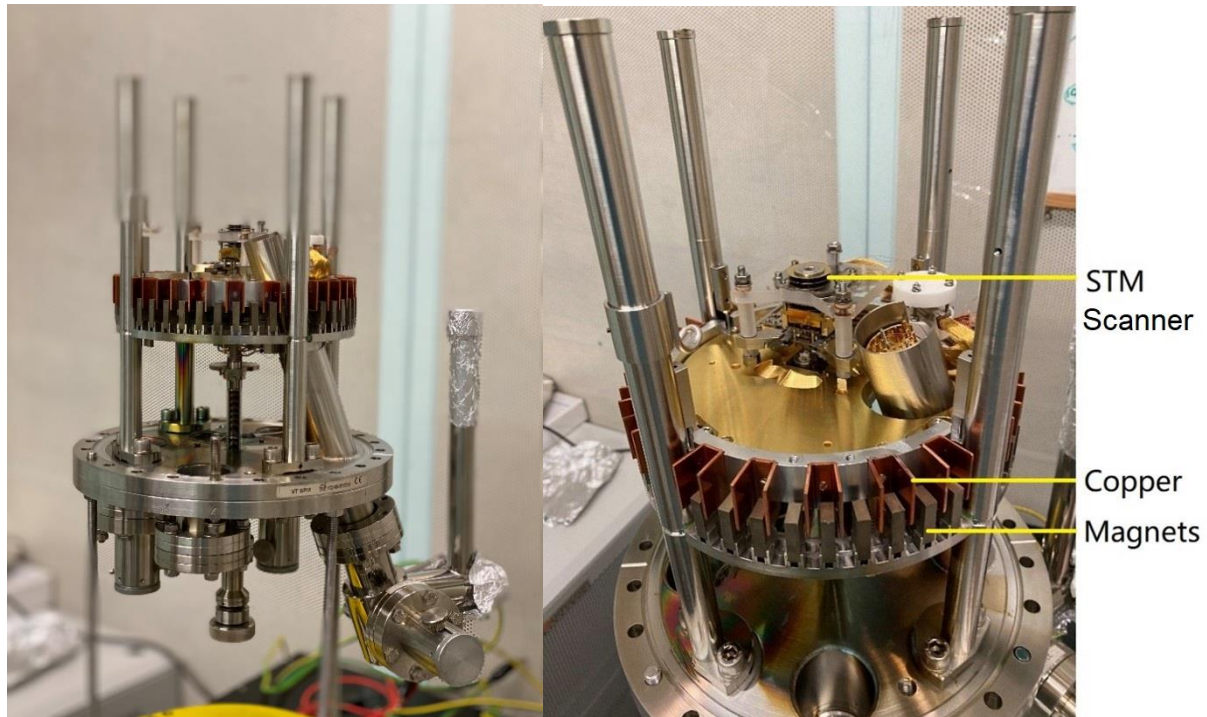


Fig 3.2. Photos of eddy-current damping system of a Varied Temperature STM (VT-STM). Although my STM is Low-Temperature-STM (LT-STM). Both STM systems are manufactured by Omicron, sharing similarities in their scanner and damping components. The main distinction is temperature control system. The picture of whole LT-STM is on Fig 4.2.

The STM in this fig is the inversion of Fig 3.1 i.e., the sample is above the tip. The inner structure is an eddy-current damping system, the eddy-current can generate damping force inside the copper conductor which moves in a magnetic field.

The whole microscopy is suspended in the basement to reduce building vibrations with frequency always below 10Hz. The expected tip-sample vibration which is calculated from experimental data and some oscillation functions is shown in Fig 3.3. The green line is the resulting amplitude of noise, in this case the noise is less than 1pm.

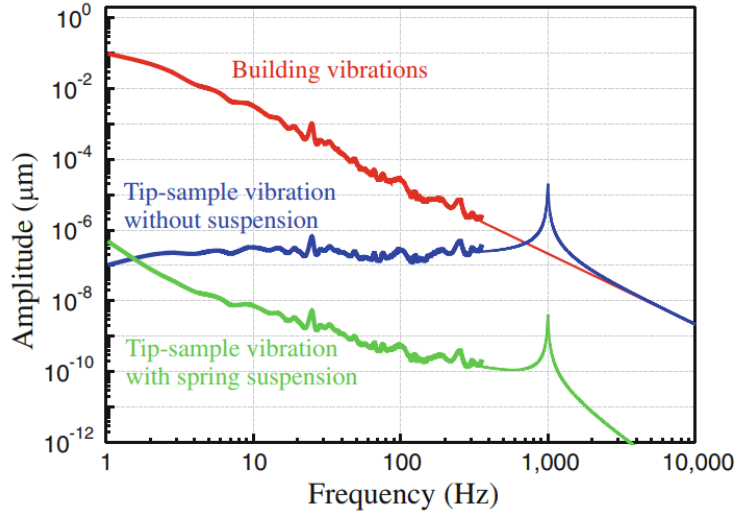


Fig 3.3 the ideal tip-sample vibrations^[80]. There is a peak at 25 Hz, however for my STM, the frequency of this peak is 49.2 Hz.

3.3 Basic theoretical principle

The basic principle of STM is quantum mechanical tunnelling i.e., there is possibility for particles to tunnel through a barrier which cannot be overcome in classical mechanical theory.

In quantum mechanics, the particles like electrons in a solid (which is the tip in STM) can be described as wave function which indicates the probability density of the electron in the space of the solid. Briefly speaking, 1-D wave function of an electron with energy E in Z -axis can be expressed (unnormalized)^[80]

$$\psi(z) \propto e^{\pm ikz}, k = \sqrt{\frac{2m_e E}{\hbar^2}}$$

and such function in uniform potential field and another solid (sample) which is gapped by a vacuum can be qualitatively expressed as Fig 3.4.

The amplitude of wave function of electron in sample is determined by the distance between the tip and the sample^[80]

$$T = \frac{|\psi(d)|^2}{|\psi(0)|^2} \approx \exp(-2\kappa d), \kappa = \sqrt{\frac{2m_e\phi}{\hbar^2}}$$

Where T is the transmission factor, d is the distance, Φ is work function which is the minimum energy for removing an electron from the solid to infinity.

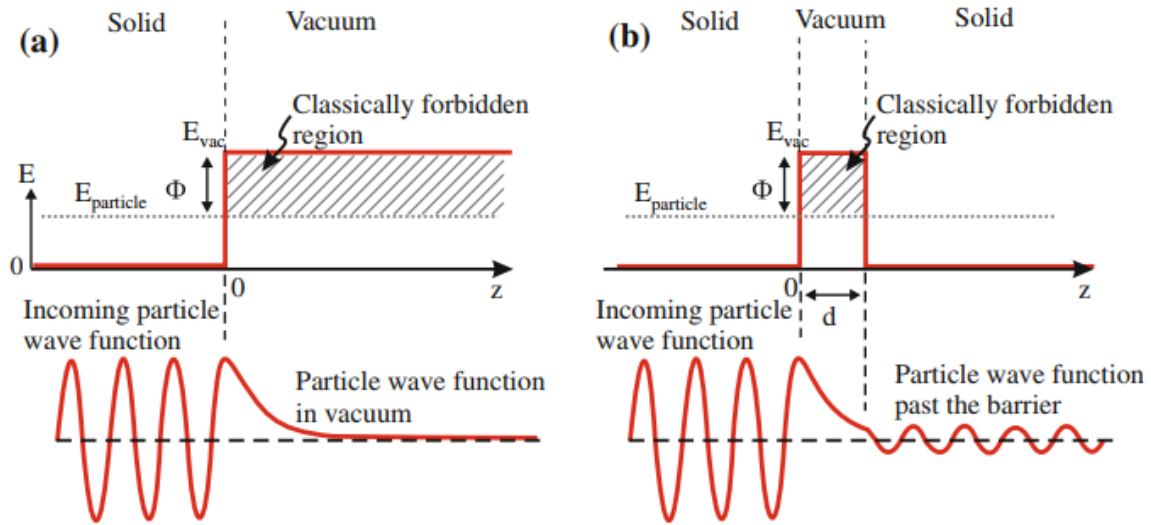


Fig 3.4 Brief qualitative description of wave function in STM, in vacuum the wave function decreases exponentially^[80].

The work function of a metal is $\sim 4.5\text{eV}$, hence $2\kappa \approx 20\text{ nm}^{-1}$, the effect of difference in distance is listed below,

Table 3.1 the relation between distance difference and transmission factor difference

Distance difference	Transmission factor difference
0.1 Å	20%
1 Å	7.4 times
2.5 Å (~1 atom)	150 times

This is the reason that the resolution of STM can be sensitive to 0.1 Å. Based on such data, STM can be designed in 2 ways: detection one of current or z-coordinate of the tip

while keeps another fixed. In experiment, it is safer to keep current fixed, since the tip may collide with some large cluster under fixed z-coordinate.

However, the above is only the partial-quantitative description, different electronic types of materials display specific profiles around their Fermi energy. Such profiles can be described by I-V curves of the sample. For metal, there is not gap between its valence and conduction bands, hence I-V curve is almost linear and dI/dV curve is nearly a horizontal line. For semimetal, although there is not band gap, a gap in momentum space will distort the I-V curve at low voltage. Both semiconductors and insulators have band gaps. The band gap of a semiconductor is less than 3 eV, while that of an insulator is greater than 3 eV. As a result, a larger band gap leads to a broader distortion in I-V curve. So, it is required large voltage (exceeding 1 V) to detect semiconductors or thin insulators, or the tip may crush to the sample to achieve the set current.

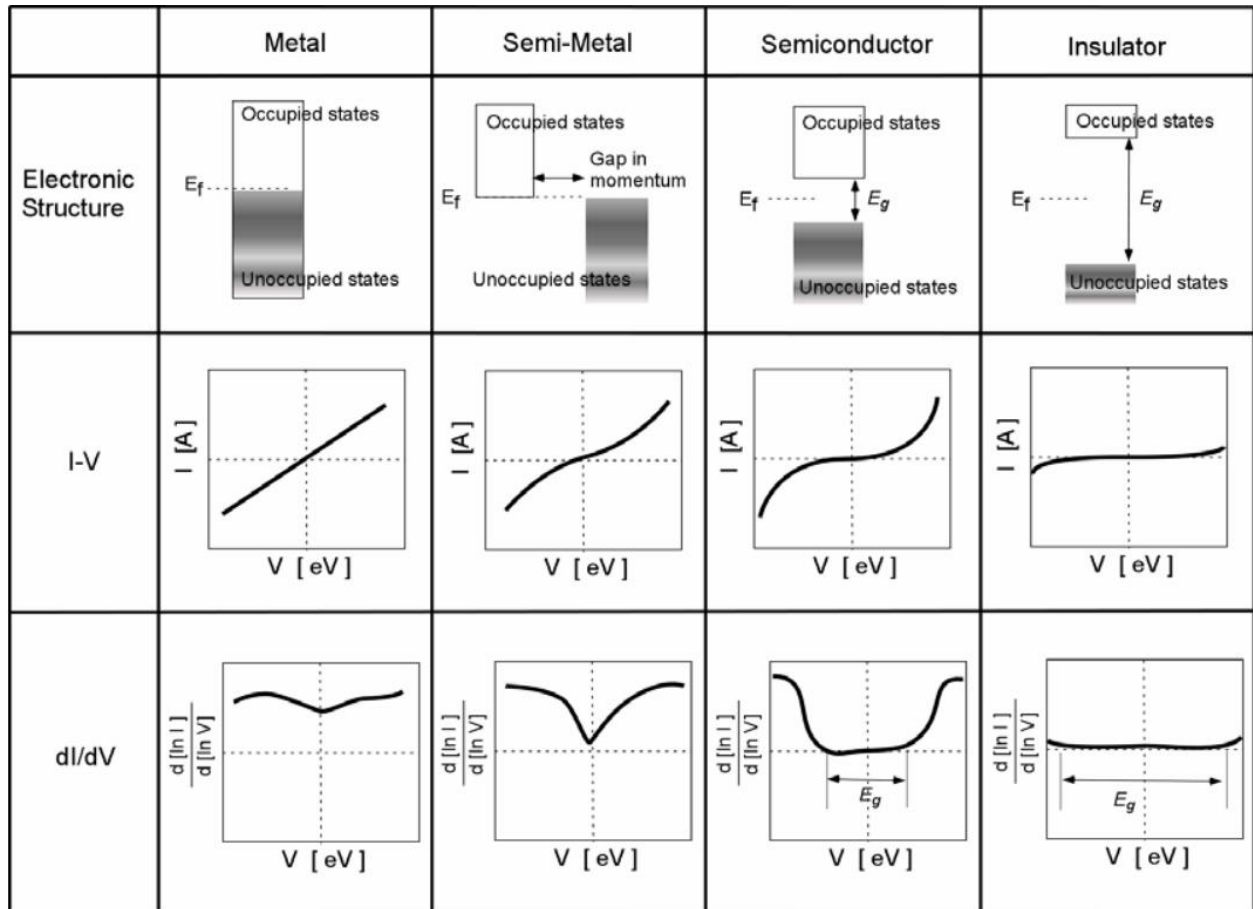


Fig 3.5 Electronic structures and their corresponding I-V, dI/dV curves^[102].

3.4 The piezo element controlling fine movement.

Since manipulation at atomic range is too small to control by ordinary machine, the only choice is piezoelectric (ceramic) materials. Briefly speaking, the deformation of piezo materials is continual and can achieve less than 1 Å by exerted voltage in mV. This material was first discovered by Curie brothers in 1880. The standard piezoelectric element is PZT (Lead Zirconate Titanate $\text{Pb}[\text{Zr}_x\text{Ti}_{1-x}]\text{O}_3$), Fig 3.6 (a) shows a unit cell of PZT with temperature $T < T_c$ which is Curie temperature, such that the Ti^{4+} is not located at the center of an unit cell.

The net charge of one PZT unit cell is not neutral but poled as Fig 3.6 (b). But there is 0 net charge on a bulk of directly sintered PZT. Since such ceramic is polycrystalline, the net charge is offset by randomly polarized crystallite. And even a single crystallite consists by differently oriented domains. So, a macroscopically polarized PZT ceramic is fabricated in special condition, under which the ceramic is applied a large electronic field ($>2000 \text{ V/mm}$) at temperature closely below T_c , such that the electric dipoles of most domains switch to 1 of 6 possible directions, this macro-polarization became remnant after cooling to room temperature in the electronic field.

Piezo materials have piezoelectric and converse piezoelectric effect,

1. Longitudinal effect, voltage aligned z-direction induced by a normal strain in z-axis.
2. Transverse effect, voltage aligned z-axis induced by a normal strain perpendicular to z-axis.
3. Shear effect, voltage perpendicular to z-axis induced by a shear strain along z-axis.
4. Converse piezoelectric effect, a strain induced by externally applied electric field.

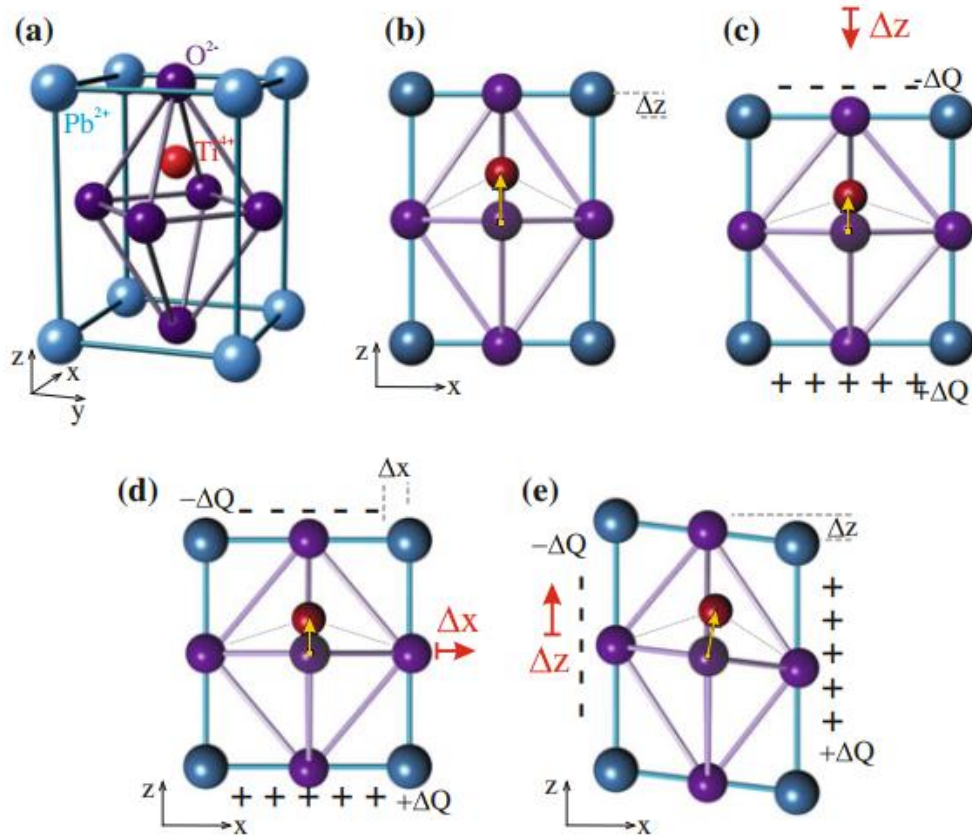


Fig 3.6. A ball model of PZT in 3D and 2D, the polarization is along z-axis. In c, d, e, red symbols represent external strain, + and – represent corresponding induced charges^[80].

In STM, the core system is not actuated by a bar of piezo material but a tube piezo element to keep fine motion. As shown in Fig 3.7, the inner and outer tube are covered with metal electrodes. Applying voltage between these electrodes can induce a motion along z-axis. The outer electrode is divided to 4 uniform parts. 2 pairs of opposite parts can exert voltage along x or y direction respectively. The tube would be bent in such applied voltage.

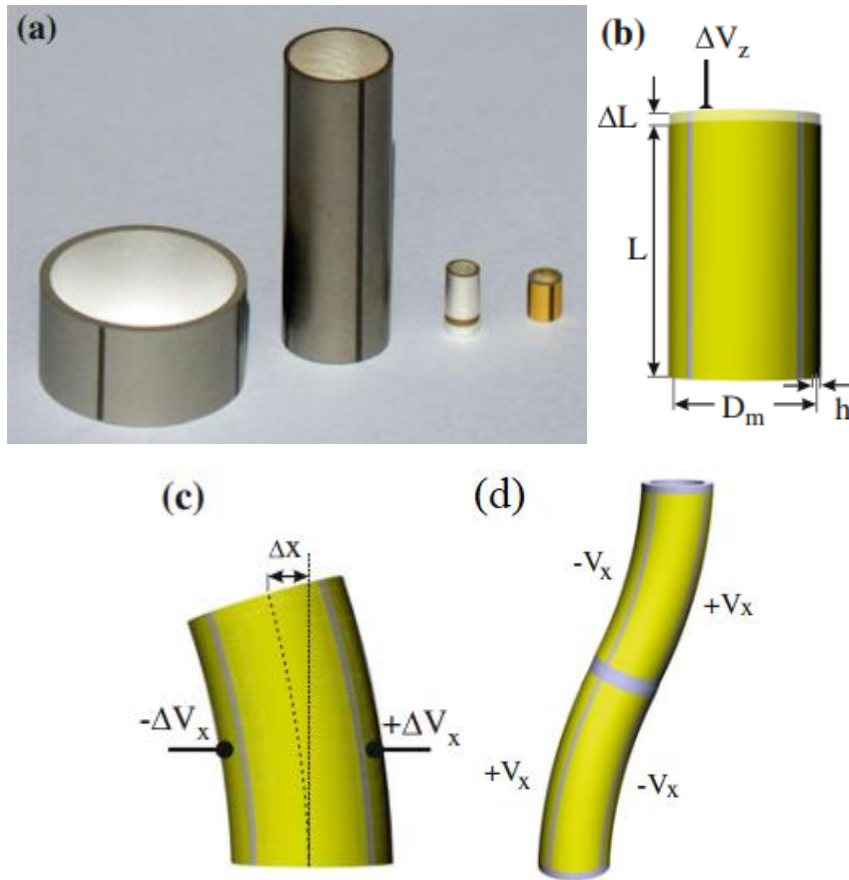


Fig 3.7 A photo and models (b, c, d) of tube piezo element^[80]. (a) A photo of tube piezo elements. (b) A piezo tube exhibits expansion or contraction along Z-axis, under voltage in Z direction. (c) Exhibiting bending along X-axis, with voltage applied in X-direction, but the upper plane is not perfectly parallel to XY plane. (d) Two piezo tubes connecting end-to-end are applied opposite voltages along X direction, this can ensure the upper plane is parallel to XY plane.

One disadvantage of a single tube is that x, y and z are partially coupled i.e., later motion may have a little effect in z-direction and vice versa. A trick to tackle is to couple 2 single tubes end to end with one rotated 180°. The disadvantage of coupled tubes is a half of the x and y scanning range.

3.5 Feedback controller

During scanning, the piezo is generally not controlled manually but automatically according to its feedback signal.

Fig 3.8 shows the model of an STM feedback loop. We generally set w current as a desired setpoint. In software (such as Nanonis), the unit of w is often ampere (like 100pA), which is transformed by the software defaultly. The output signal of an STM is tunneling current which is detected by STM circuit loop, through the current amplifier, the output is converted to corresponding voltage x . The error signal $w-x$ is sent to PI Controller. The PI controller has two parts: Proportional Controller and Integral Controller.

The principle of proportional Controller is like a shower. We turn cool the water when it is hotter than our expectation, and generally the new is cooler and we turn it hot. After some times, the water temperature is close to our expectation. Our expected temperature is like w , our feeling is like x , and according to $w-x$ we choose turn cool or hot the water, which is like an output signal from P-controller to the system. This signal (denoted by y) is proportional to $w-x$, as $y(t) = Kp (w-x)$, where Kp is proportional gain which determines the degree of reaction, this reaction is also limited by power supply.

In STM, the P-controller continuously receives the error signal and inputs voltage to the system to draw back or approach the tip corresponding to reduce or increase the next output voltage. Since the tip is scanning on uneven plane, there is a permanent deviation between setpoint and actual output, but the reaction time in STM is faster than Integral Controller.

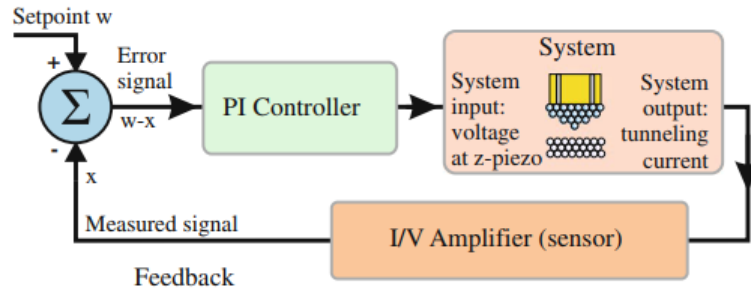


Fig 3.8 A schematic of an STM feedback loop^[80]

If the system is only tuned by P-controller, the result voltage and the motion of the tip are large vibration, hence this requires Integral Controller. It can accumulate deviations from the setpoint over some time. The output signal is proportional to the time and magnitude of error during such time, that is $y(t) = K_I \int_{t_0}^t (w - x(\tau)) d\tau$. The I-Controller can reduce the residual steady-state error occurred from P-Controller with longer reaction time than P-Controller.

The controller combined P and I controller, called PI Controller, has both advantages and avoid disadvantages. The output signal from PI Controller is written as

$y(t) = K_p (w - x(t)) + K_I \int_{t_0}^t (w - x(\tau)) d\tau$. Short-term error is eliminated by P-controller while long-term error by I-Controller. The general performance of these controllers are shown in Fig 3.9, the setpoint in it is a step response, that is it changes from 0 to 1 at time 0. The output signal cannot coincide with setpoint due to steady-state error of P Controller.

In practical experiment, the parameters K_p and K_I are important parameters. They are required to be tuned to appropriate values to get a fair image, such progress may take several days.

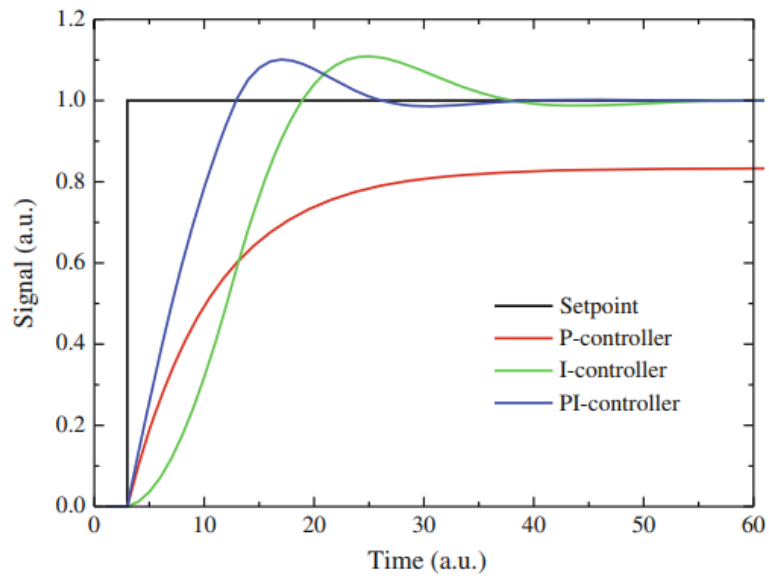


Fig 3.9 The performance of various controllers comparing with actual signal^[80]

3.6 Inertial slider for coarse movement

However, the range of motion of such piezo is limited to at most several micrometres. Before scanning, the distance of tip and the sample can be 1 centimetre for safe storage. So, the coarse movement of the tip is controlled by alternative ways, mainly inertial sliders, stepper motor, beetle STM, pan slider and Koala drive. This part, which controls the coarse position of the piezo tube, is not shown in Fig 3.1.

My STM uses inertial sliders. This is a very common design. The principle is easily understood, place a piece of paper on a table with a cell phone on it. If we drag the paper slowly, the cell phone would move together with the paper, if we drag the paper quickly, the cell phone would disengage from the paper due to its inertial and also move slightly relative to the table.

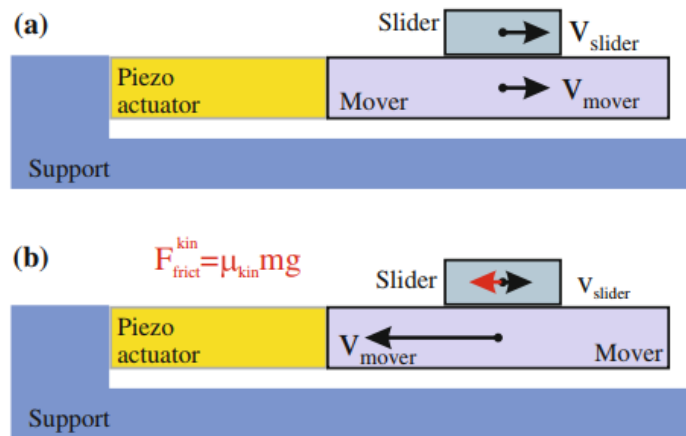


Fig 3.10 Model of an inertial slider^[80]:

a. riding phase: $ma_{mover} < \text{max friction}$. **b.** Sliding phase: $ma_{mover} > \text{max friction}$, where m is the mass of the slider.

An inertial slider consists of 2 main parts: a mover and a slider. The mover is moved by piezo actuator and the slider is the object to be moved. In STM, the piezo tube is the slider.

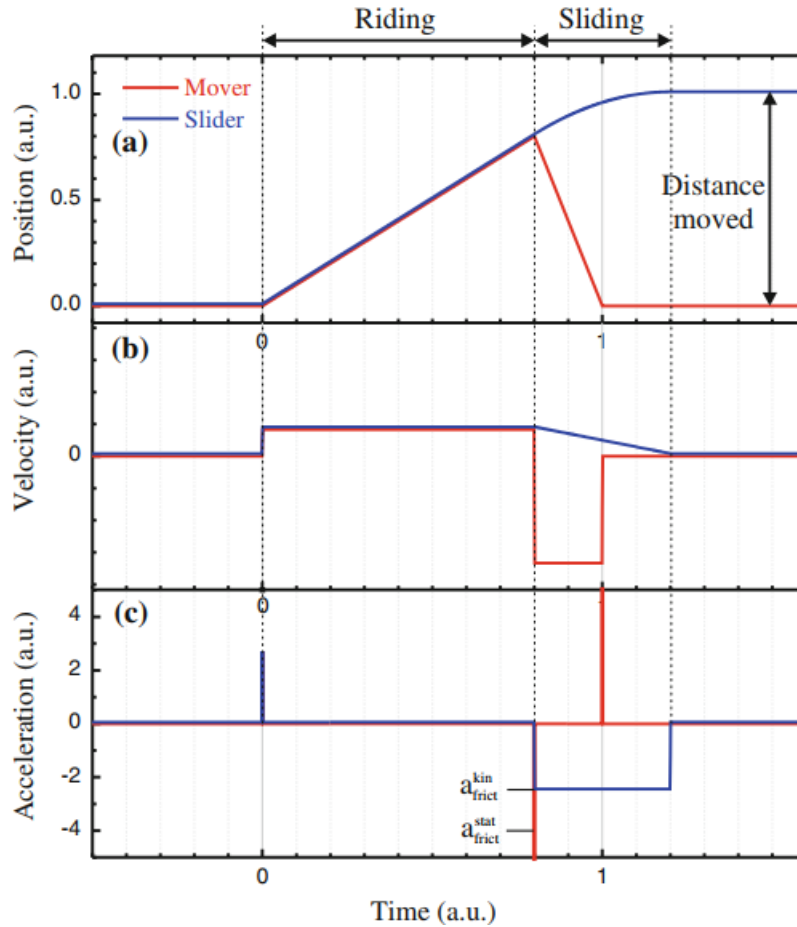


Fig 3.11 The position, velocity and acceleration of the mover and slider relative to external inertial reference frame (like the ground)^[80].

Fig 3.11 (a) shows the distances moved in one step. In this way, the slider can be moved to a designed distance relative to resting reference frame.

In most cases, it is not the gravitation supply the normal force $F_{\perp}$ between the mover and the slider which determines friction, but magnets or springs since they can be much larger than gravitation. The advantage is that the slider can be moved in all orientations.

However, there is some disadvantages of inertial sliders

1. The frequency of a mover must be less than its resonance frequency.
2. The difficulty in designing the mass of a slider, since the acceleration of the mover is limited by charge pumped by power supply to the piezo element, it is acquired larger mass of slider such that $ma_{mover} > \max \text{ friction}$. But a higher mass of slider would

introduce lower eigenfrequency and nano-positioning system requires every part as small as possible. So, it is difficult to find the proper mass of the slider to satisfy such demands.

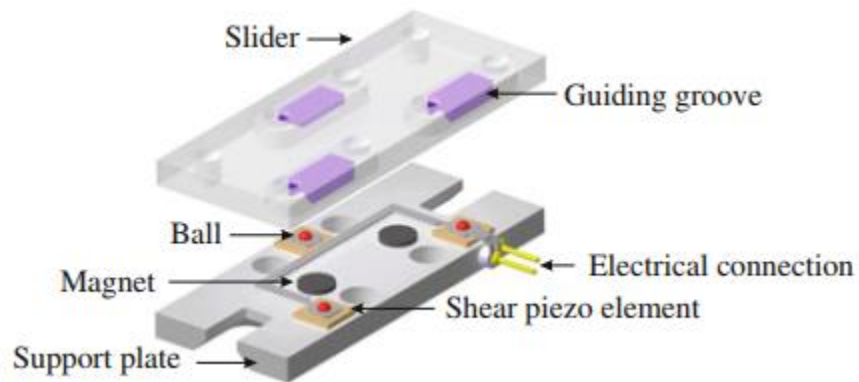


Fig 3.12 The sketch of inertial slider^[80].

Fig 3.12 shows the practical sketch of an inertial slider. The 3 shear piezo elements can supply up to 1 μm in 1 direction. On the top of the elements, 3 red hemispherical balls are movers which are mainly made of ruby, sapphire, or stainless steel. The slider which is mounted onto the balls is rested firmly by magnet force. The direction of slider motion is guided by one groove in the slider while the other 2 of 3 balls are resting.

Inertial slider as discussed above is specific for my LT-STM manufactured by Omicron. In addition, there are 4 more designs for: stepper motor, beetle STM, Pan slider and KoalaDrive for other types STM. Each has its applications and disadvantages^[80].

4. Experiment

4.1 Sample preparation

The sample of my project is the structure of combination of C₆₀ and decanethiol on Au(111). This Au(111) is a 2-D nano plane on graphite. The preparation is as follow (it's essential to use tweezers that have been cleaned and air-dried after an ethanol wash when transferring the sample in room conditions between the following steps. Some parts of STM are shown on Fig 4.2 and 4.3):

1. Obtaining a smooth graphite surface: This can be achieved in a standard laboratory setting. Start by cutting a rectangular prism of graphite along the crystallographic direction, approximately 0.5-1 cm in length and width, with a thickness of about 0.5-1.5 mm. Ensure that all faces appear smooth to the naked eye. Gently apply the tape along a diagonal to the largest surface, which is roughly parallel to the plane of graphite. Ensuring no air bubbles, and lightly press the tape with fingers to adhere it closely to the graphite surface. Allow it to sit for approximately 1 minute. Slowly peel off the tape along one corner, making sure that no flakes are visible in the central region of the plane, to obtain a monolayer graphite surface, this is Highly Oriented Pyrolytic Graphite (HOPG). If flakes are observed, repeat this step.

2. Evaporation Au atoms onto HOPG: Fixing HOPG onto a sample holder and place it inside the evaporator. The instrument presets the evaporation direction and sample orientation within the evaporator. Lock the evaporator and pump out gas with its turbo to reduce the pressure to $\sim 10^{-6}$ mbar (usually requiring about 20 hours). Adjust the evaporation rate, taking approximately 3-5 hours to evaporate gold atoms onto the HOPG, achieving a thickness between 120 nm to 220 nm. Once the sample is cooled, gradually increase the evaporator pressure back to atmospheric levels by slowly pumping nitrogen into it.

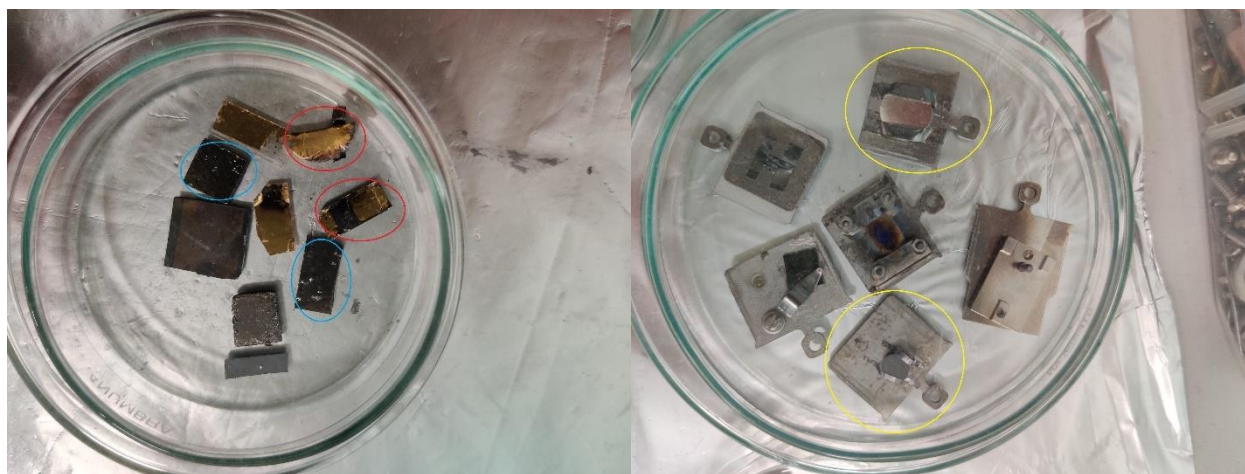


Fig 4.1. Left: A collection of various samples, with Au(111) on HOPG circled in red and HOPG circled in blue. Right: Fixed samples onto sample plates, I always fixed my sample by tantalum foil as indicated by yellow circles.

3. Transferring the sample into STM: My STM operates under Ultra-High Vacuum (UHV) conditions, maintaining a low pressure within both the analysis chamber (typically 10^{-12} mbar) and the preparation chamber (usually 10^{-10} mbar). These chambers are usually isolated from each other. UHV conditions are achieved through a combination of a turbo pump, ion pump, and a Titanium sublimation pump (TSP). To begin, the sample is initially placed into the fast entry lock (load lock), a small isolatable chamber that connects to the preparation chamber. The load lock is then sealed, and the pressure is reduced to approximately 10^{-7} mbar using the turbo pump, a process that takes roughly 0.5-1 hour. Subsequently, carefully connecting load lock and preparation chamber, the sample is then transferred into the preparation chamber using a manipulator. Then isolating the load lock. Based on the specific sample conditions, a decision is made regarding whether to connect the preparation and analysis chambers. The sample may then be transferred into the analysis chamber using another manipulator, facilitating further analysis.

4. Cleaning and condensing gold layers. The fresh gold planes are loosely packed with impurities. The impurities on top of gold layers can be cleaned by Ar atoms emitted from an Ar gun connected into the preparation chamber of STM. Shooting the Ar rays onto the Au sample with the pressure increasing to about 4×10^{-6} mbar for 5 mins. Then by

annealing the sample to about 500 °C for 1 hour and slowly cooling with 0.1°C/min to room temperature, some inner impurities would transfer to the surface and the gold structure becomes more condensed, and then cool the sample. Such 2-step-cycle is repeated over 10 times. The whole progress would take at least 1 week.

5. Detection of Au(111). The new sample should be detected by STM in analysis chamber. If there is obvious reconstruction of Au(111) on flat plane (section 2.5.2), the decanethiol can be added onto Au(111). If there are more defects like sharp steps, peaks, or holes on Au(111), the sample needs more 2-step-cycles.

6. Detection of closed packed decanethiol. There are only planes and pits of closed packed decanethiol on the images of the new sample of STM image. Since the gold reconstruction disappears by adding decanethiol onto it.

7. Reduction of the coverage of decanethiol. This can offer enough space for C₆₀ to construct with decanethiol or C₆₀ only accumulates at some defects instead of interacting with thiols. The sample is transferred back into preparation chamber and then subjected to heating and annealing at 50°C, 70°C, 90°C, 100°C, 110°C and 120°C separately, each for a duration of 30 mins. Detection is required after each annealing step for the changing in morphology of the surface.

8. Evaporation of C₆₀. C₆₀ can be evaporated onto the sample in preparation chamber of STM with C₆₀ gun. The surface of the sample is shot by C₆₀ source heated to 330-350 °C for 5 or 10 mins.

4.2 Practical Scanning Process

Although the fundamental principles of every STM are constant, each type of STM has its unique operational processes. In the case of the Omicron LT-STM, the scanning process is listed as follows:

Before scanning, a sample is stored in a carousel within the analysis chamber. First step is to transfer the sample into the STM sample holder using a wobbler-stick. Following

this, the spring connected to the STM scanner is released. The spring is normally anchored to prevent unnecessary movement when the STM is not in use. During operation, it needs to be released to minimize noise (the spring is not visible from the outside unless the analysis chamber is opened).

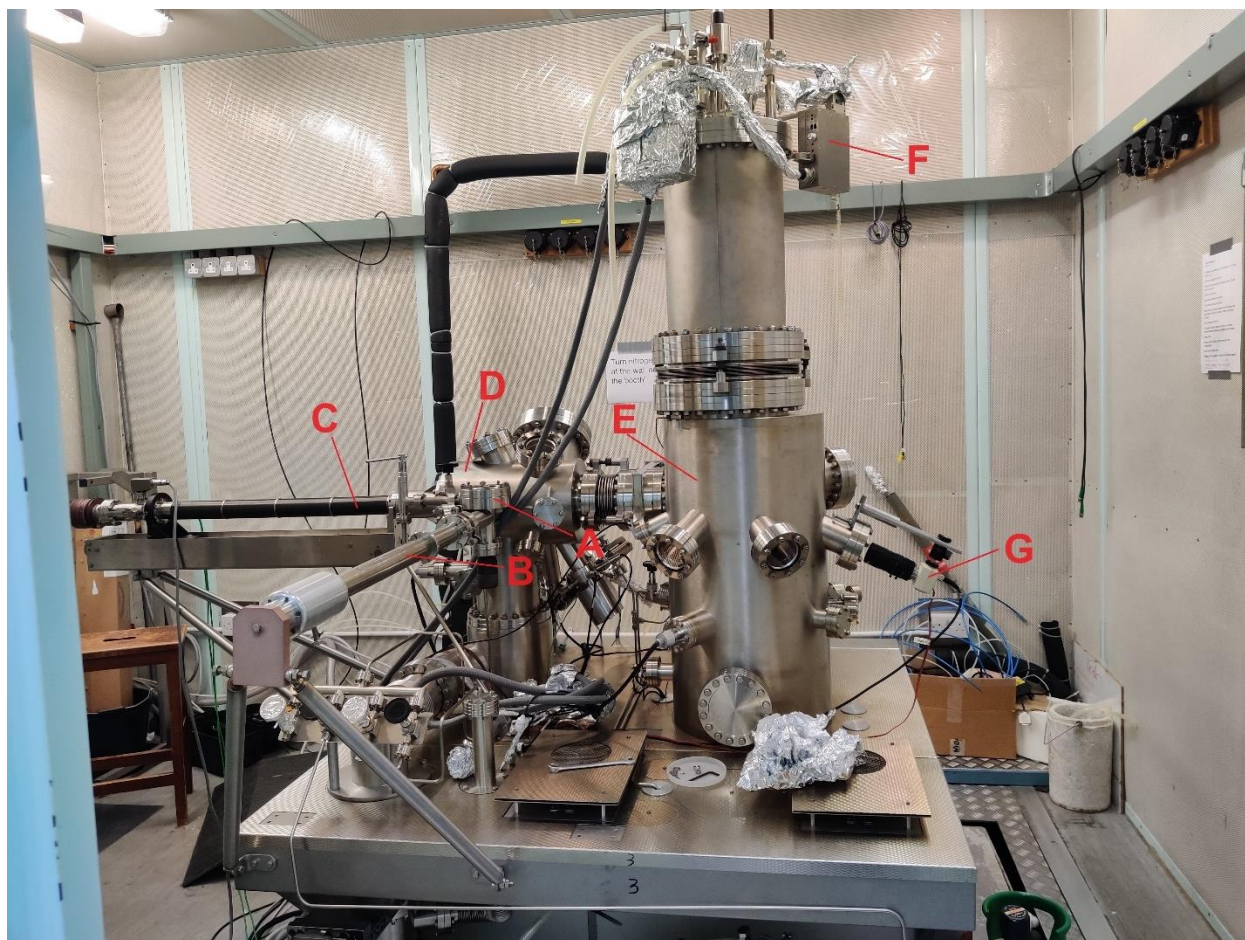


Fig 4.2. A picture of rear view of LT-STM. A: Fast entry lock (load lock). B: Manipulator 1, which is to transfer a sample between preparation chamber and the load lock. C: Manipulator 2, connecting external controller, can treat a sample in various manners such as heating, cooling, sputtering etc. D: Preparation chamber, enabling longitudinal motion and $\pm 180^\circ$ rotation of manipulator 2. E: Analysis chamber. F: Preamplifier. G: A camera is used to magnify the distance between a tip and a sample on a screen.

At this point, the distance between the tip and the sample is approximately 2-3 mm (depending on the length of the tip). The tip is coarsely approached to the sample using an externally connected control box. Subsequently, a fine approach is performed using a

feedback loop, controlled by Nanonis-produced equipment. Once approached, we can set some parameters for scanning, including set current, bias voltage, proportional gain K_p and time constant K_I , as shown on Fig 4.4.

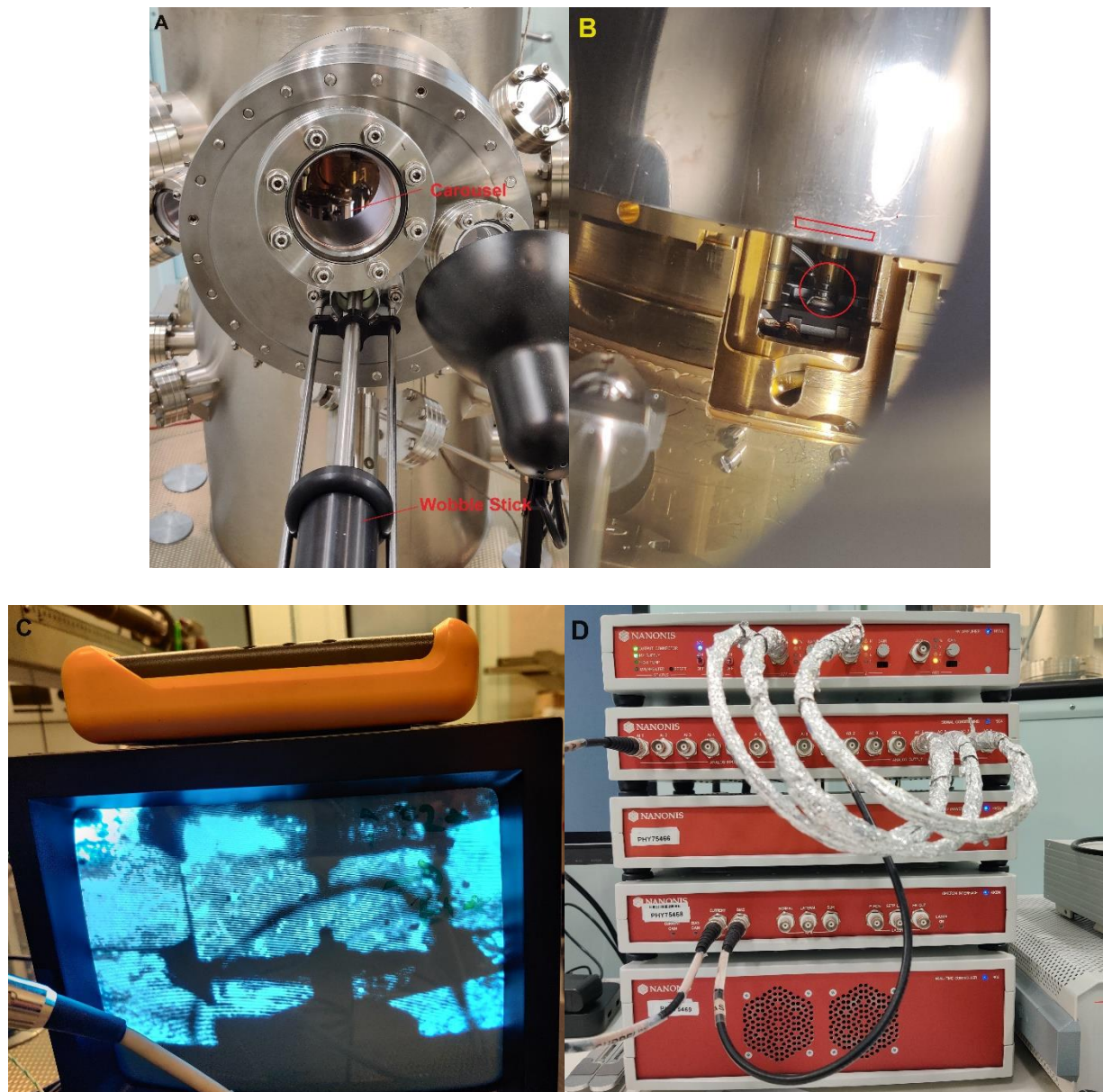


Fig 4.3. A: a front view of partial analysis chamber with wobble stick and carousel. B: a picture of my LT-STM scanner with a tip circled in red and sample hidden behind a protective shell indicated by the red rectangle, the visible distance between the tip and the scanner allows for a coarse approach. C: a screen view of coarse approached tip, the very tip is invisible due to screen quality, it is easy to crush the tip for a first-time STM user. D: Control system produced by Nanonis.

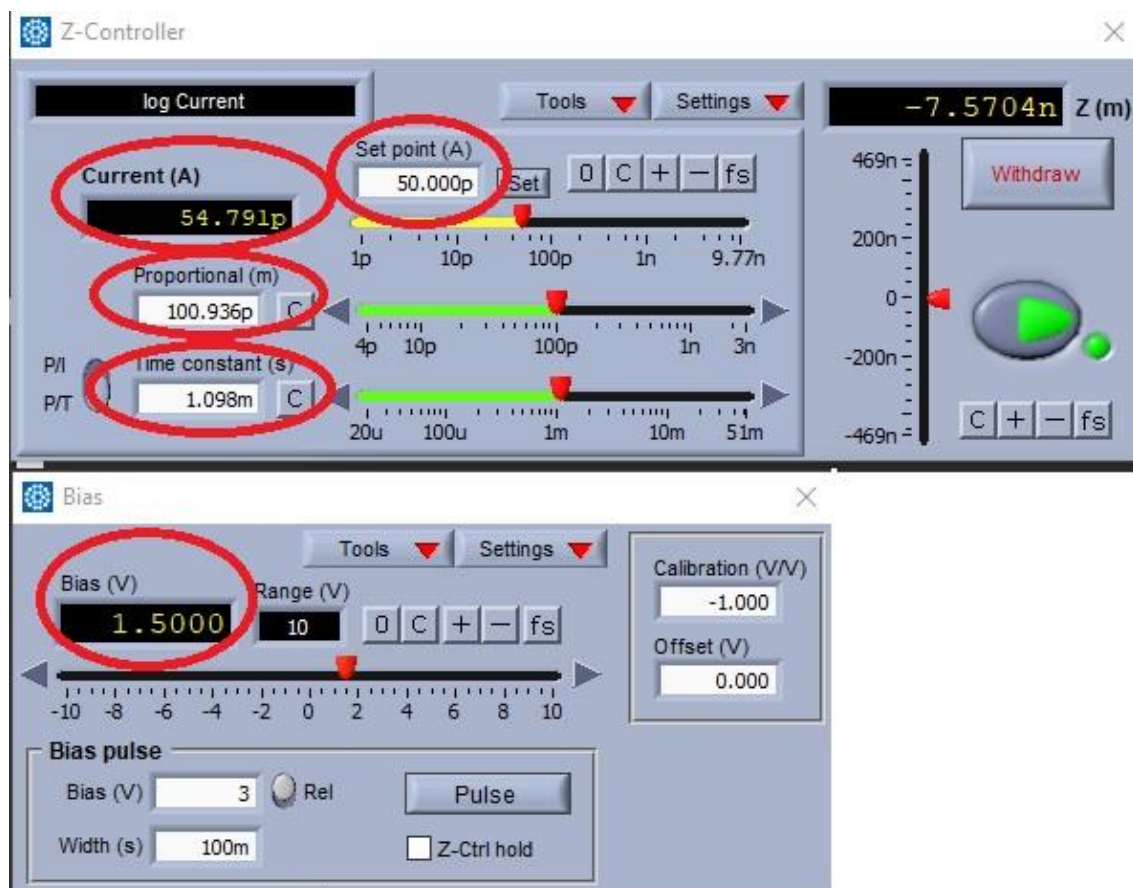


Fig 4.4. A screenshot of Nanonis software setting key parameters indicated by red circles. Set point is set current, typically 10 pA – 1nA. Current is real time current detected from the tip.

4.2 Tip condition

In STM as well as other probes, all data are detected and collected by the tip, so image quality is totally determined by the tip conditions. The tip quality is mainly attributed to 2 factors: materials and shapes.

In ordinary STM system, there are 2 sorts of materials of the tip: Pt-Ir (Platinum-Iridium) and Tungsten. Pt is inert and Ir can make tip harder, but it is mechanically unstable. So, Pt-Ir tip can be used under ambient condition only for spectroscopic measurement. W is a more widely used material. Since my sample is scanning under ultra-high vacuum, W is not oxidized in several months. In addition, crystalized W becomes superconduct only

under 10 mK and it is a mechanical stable and hard element, so it can be used for topology and spectroscopic measurements under low (4.2 K, liquid helium) and room temperature. For these reasons, my experiment focuses on W tip.

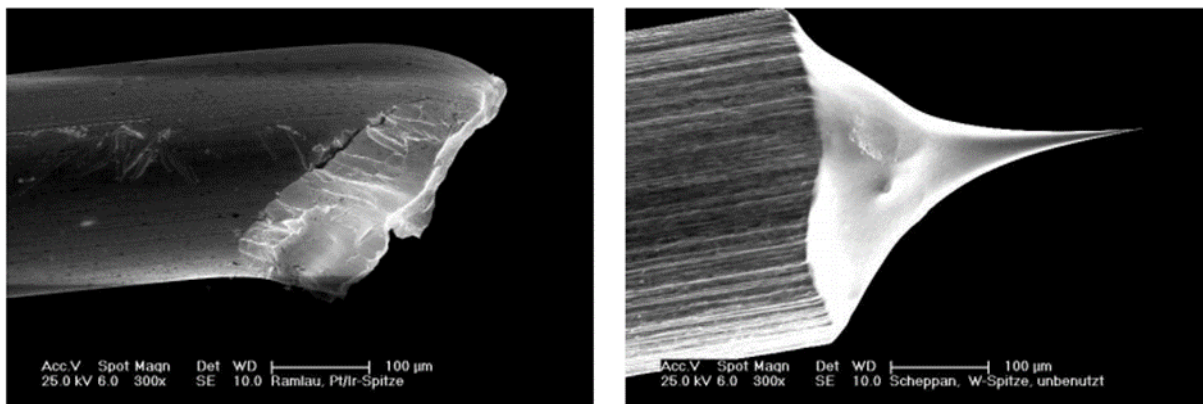


Fig 4.5. Left: Pt-Ir tip with some pincers, and Right: polycrystalline W tip^[80]

In my experiment, the preparation of W tip is as follows:

1. Cutting a piece of W wire. It is easily cut a piece of polycrystalline W wire from a long original W wire with perimeter 0.75 mm due to mechanical stability.
2. Etching W wire. As right image of Fig 4.5, the W tip needs to be electrochemical etched to sharpness. The W tip is an anode, and another metal wire is cathode within NaOH solution of concentration 1-2 mol/L. Fig 4.6 is schematic of etching process and corresponding chemical reaction.

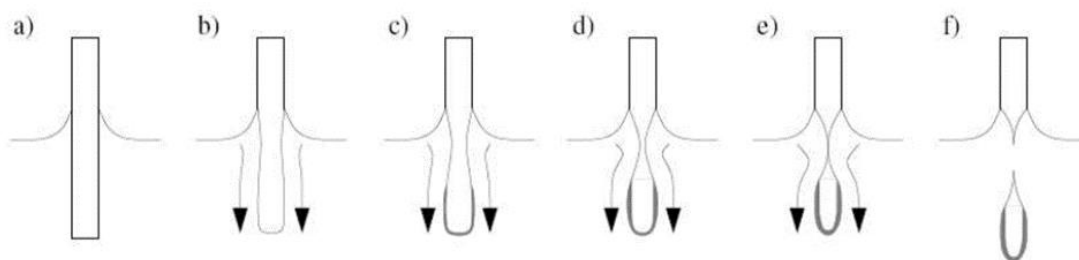
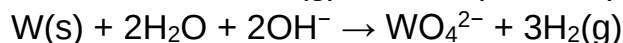
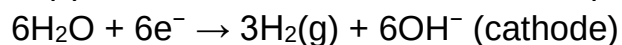
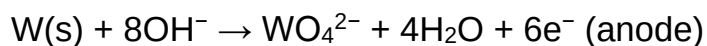


Fig 4.6 The etching process for W tip in NaOH solution and corresponding chemical reaction is as follow^[80]:



3. Cleansing and annealing W tip. After etching, the tip head is not clean but attached by many contamination including bubbles and meniscus formed from H_2 and $NaOH$ respectively. The first is to rinse the tip into distilled water. The cleaner tip is cut to 4-5 mm and installed into a tip holder, then sent into the preparation chamber of STM and annealed at $100^\circ C$ for 1 hour to evaporate some contamination.

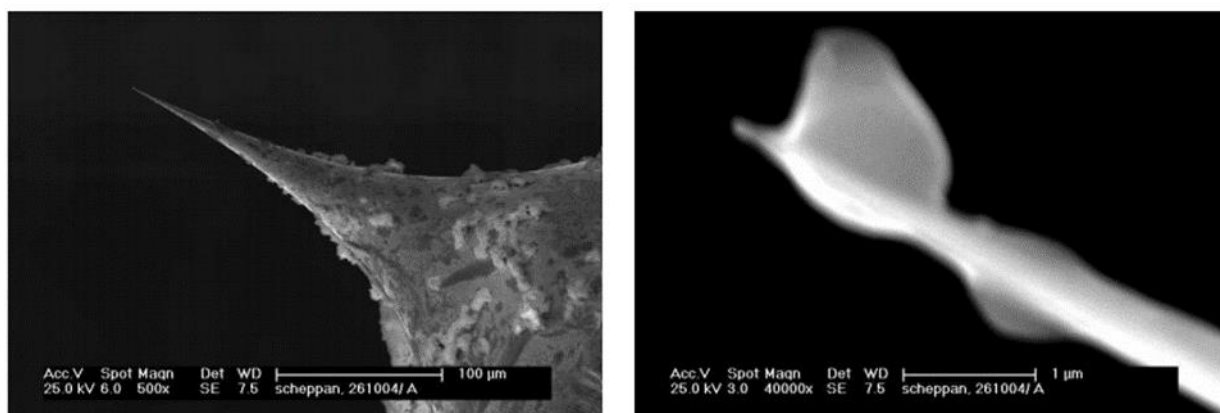


Fig 4.7. SEM Images of W tip without being rinsed^[80].

The above pictures are obtained under SEM. So, the apparently sharp and smooth tip is not so perfect. This (the shape of tip) would be reflected onto the resulting images. Fig

4.8 shows how an image is affected by a tip.

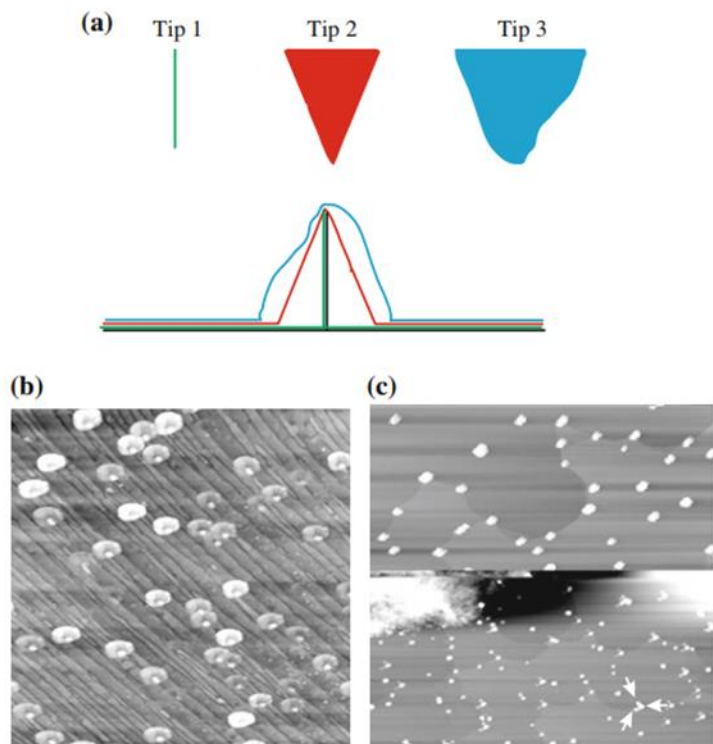


Fig 4.8. Images influenced by tip shape. The colored lines in (a) are the trajectory of corresponding tip, this is transformed into images. (a) The real structure is a sharp asperity on a surface. (b), (c) The real structure is carbide cluster^[80].

In (a), Tip 1 is perfect only for imaging, although it can image the asperity faithfully, such tip would introduce larger vibration. Tip 2 is a perfect tip practically. Tip 3 is a blunt tip which is reflected in the image of the asperity. In addition, blunt tip is not only formed by tip element structure but often by attached unexpected atoms or molecules. In (b) and (c) all the carbide clusters have similar shape-the tip shape. And in the middle of (c), there is a change in tip shape, this phenomenon often appears in every 3 images. During scanning, we are waiting for such a change until the appearance of perfect tip shape like tip 2 in (a).

Apart from reflecting its shape, blunt tip may introduce many deformed images, such as dead zones and multiple tip.

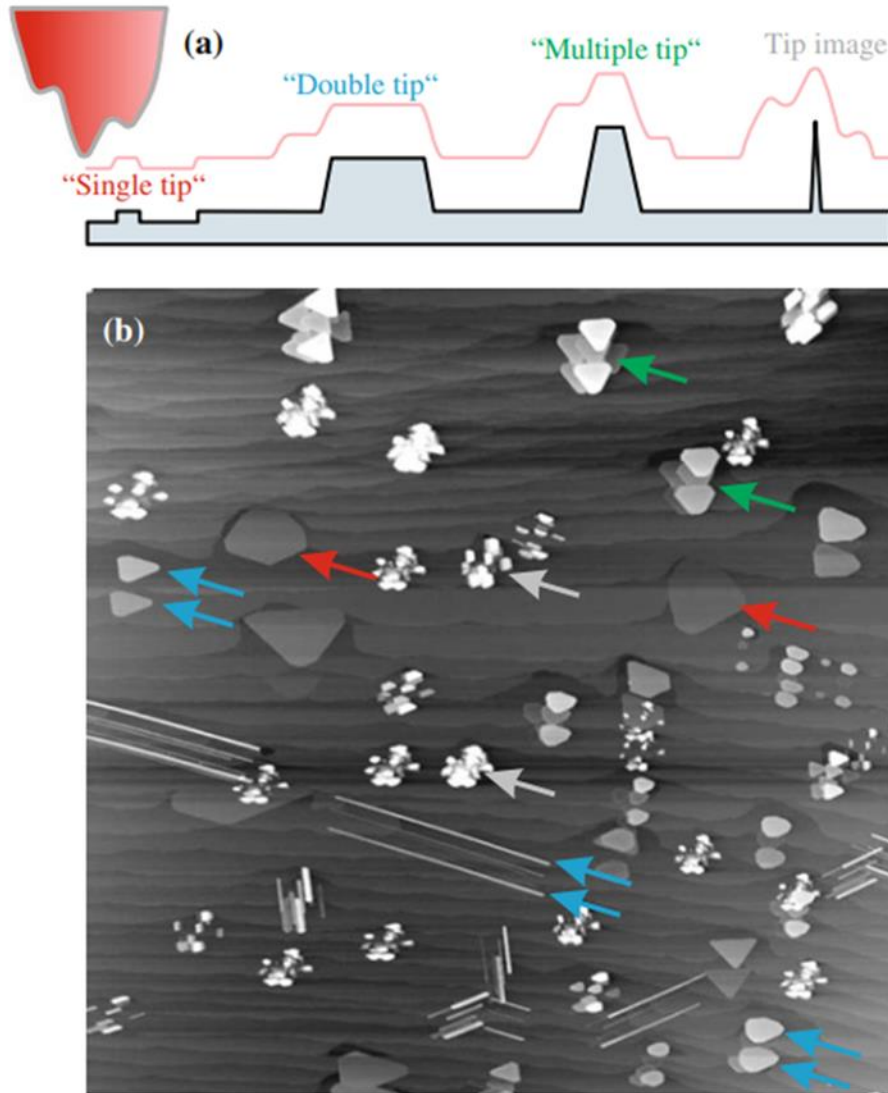


Fig 4.9. Multiple tip formed by blunt tip and surface structure. (a) the red line is the trace of the tip. (b) The image of silicide nano-island scanned by blunt tip. The higher the structures, the more tendency being imaged multiple images. The red arrows indicate a single image corresponding to an atom higher. The blue arrows are double tip apex, the green is multiple tip apex, these correspond higher and higher structures. The grey lines indicate narrow and high structure, the resulting images are tip shape rather than real structure^[80].

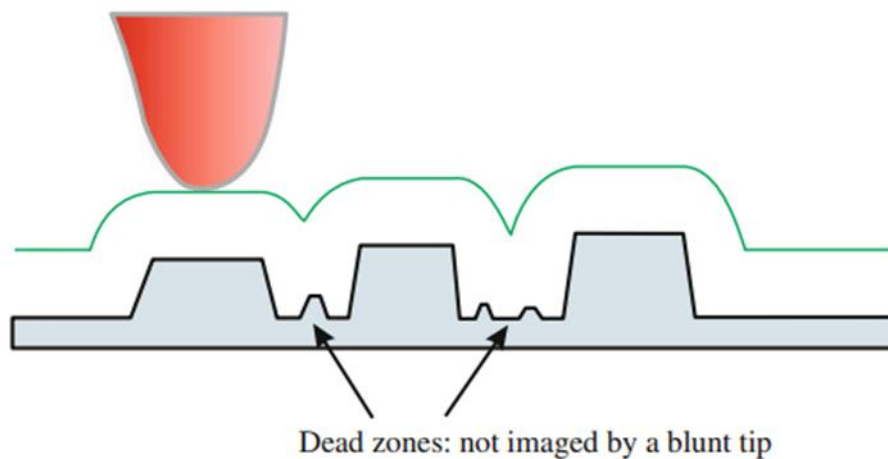


Fig 4.10. Dead zone due to topological radius of curvature is smaller than the tip. These zones would not be shown in images^[80].

Practically the perfect tip should be like tip2 in Fig 4.8, the endpoint is only one atom. However, this is hard to achieve, because of uncertainty principle and interaction between particles, blunt tip is more general, the experiment is waiting for such perfect tip by scanning or some modification for the tip including pulse and oscillation.

4.3 Image Processing

The raw images or data gained by STM cannot be analyzed quantitatively. So, I need to process them for further research. The most common free software to do this is Gwyddion. Its main menu and effect to process an image of Au(111) is shown below.

Gwyddion is a specific software to process images gained from STM, AFM or other microscopes. Although there are many functions in this menu. The basic functions are numbered 1 to 8.

In addition, this software can also do Fourier transformation in 1-D and 2-D. The following Fig 4.12 is a comparison of raw and filter data.

The above image is raw data, brightness indicates depth, the darker the deeper. Since the sample plane is not perfectly horizontal, the image is gradually deepening from up to

down. After mean plane subtraction (No. 3 in Fig 4.11), the basic features are shown in the bottom image. There are many black pits, this is corresponding to a part of 2.2.3. I will discuss briefly in the following chapter.

Since raw data cannot be seen by naked eyes, I will only attach filtered images in the following chapter for analysis.

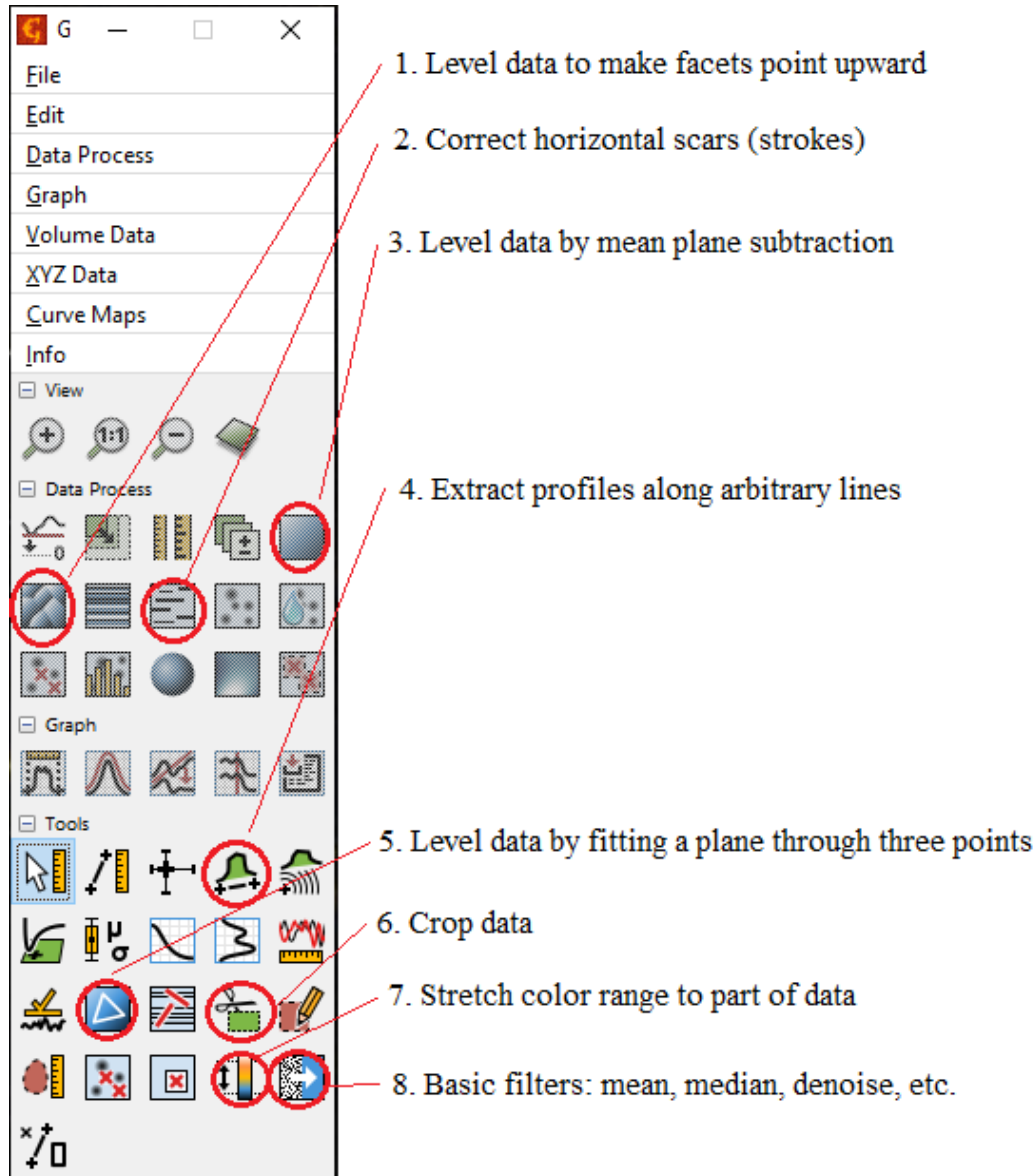


Fig 4.11. The main menu of Gwyddion and numerated important functions with numbered important functions. Although I don't programme myself, this can help readers to navigate and utilize this Gwyddion.

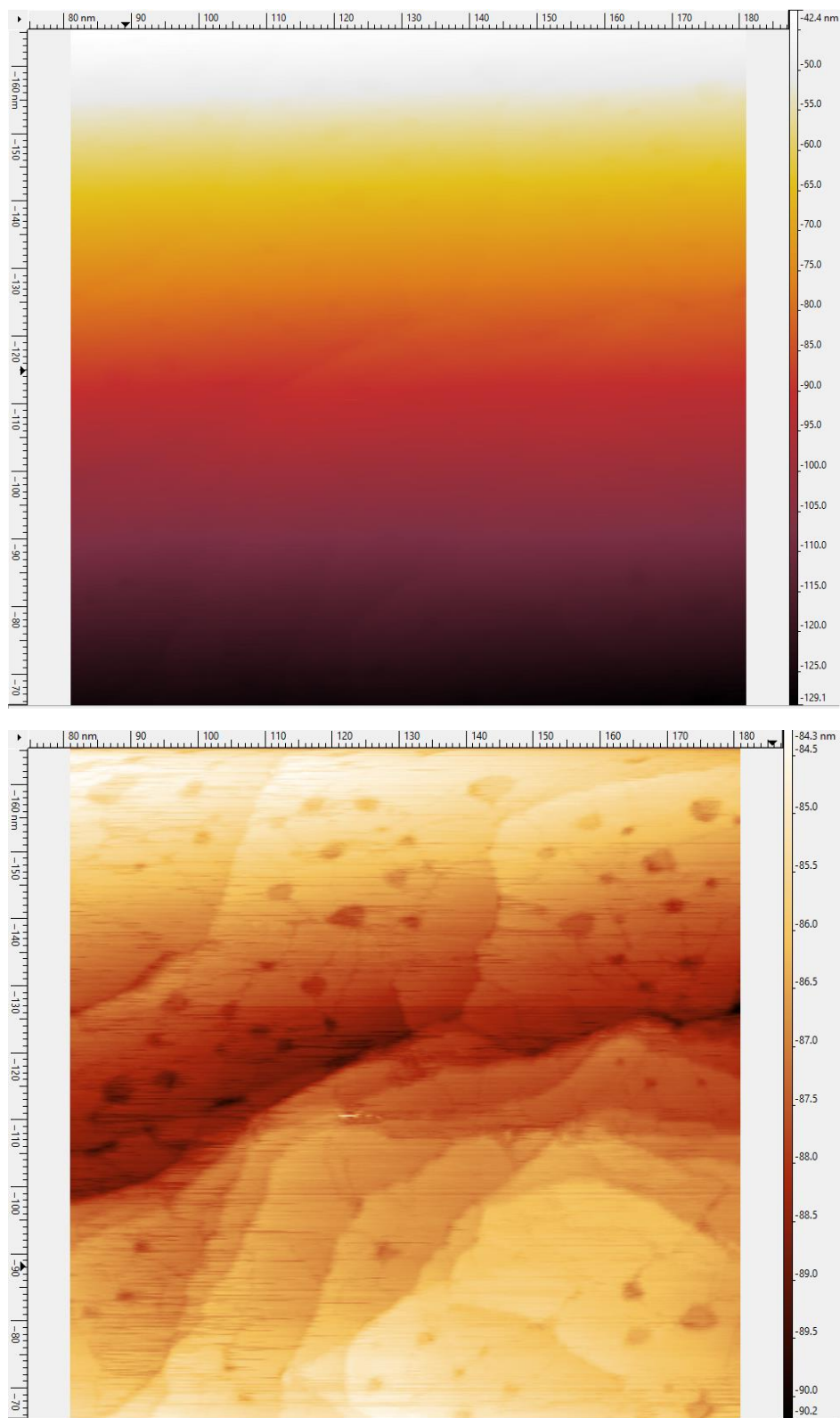


Fig 4.12. A Comparison of raw and basically processed images of decanethiol on Au(111)

5 Decanethiol on Au(111)

In this chapter, I will discuss the structure of decanethiol/Au(111) and C₆₀/Au(111). I will start from the basic knowledges and rules of crystal, which provides notation for further description. The result of my sample performed that the monolayer of decanethiol on Au(111) is consistent with those reported in literature^{[27][57][59][60]}. I will pay more attention on striped phase of decanethiol, since such phase will be used to make mixed thiol-C₆₀ on Au(111). The structure of C₆₀ monolayer on Au(111) is discussed in this chapter using data from literature^{[93][95]}. Hence this chapter provides necessary information and knowledge before detailed discussion of structures of thiol-C₆₀ phase in Chapter 6.

5.1 Au(111) and its reconstruction

Fig 5.1. is a STM image of my Au(111) sample. Although it is not very clear due to noise, the reconstruction is shown with uniform and parallel corrugation and with little defects. This indicates the Au(111) surface is well-prepared for the next procedures.

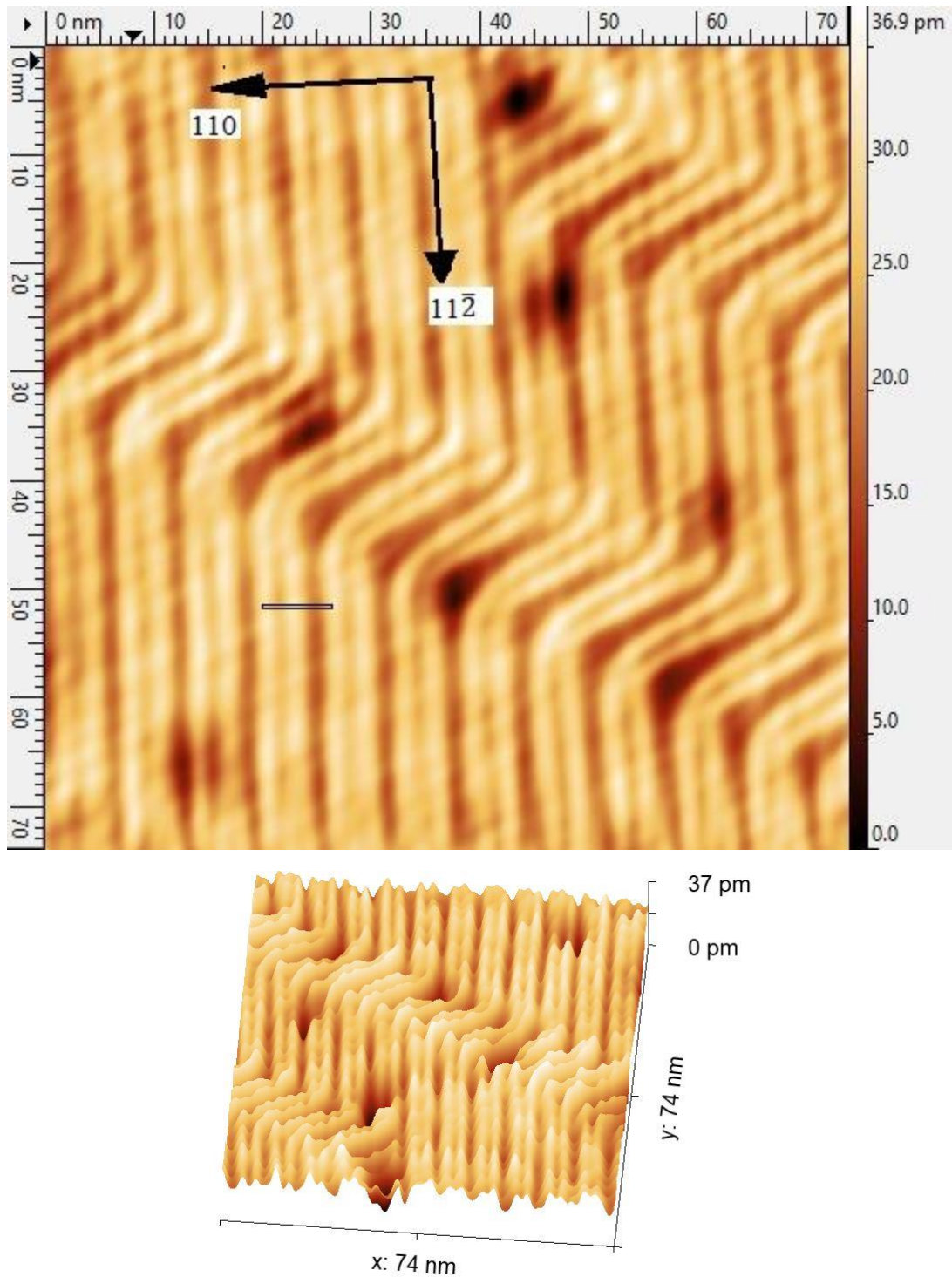


Fig 5.1. 2-D and 3-D of Au(111) and its reconstruction 3D view of Au(111). The small rectangular in 2D view is an unit cell of reconstructed Au(111) ($22 \times \sqrt{3}$). The 3D view is to show its 3-dimensional structures, however, since there is much noise and 3D image 3D image is not intuitive on a 2D screen, I will not exhibit 3D view for the following analysis.

5.2 Thiols on Au(111)

Since 1980s, self-assembled monolayers of thiols have attracted a lot of attentions, SAMs of thiols on metal surfaces offer the platform to study applications including corrosion inhibition, lithography, lubrication, catalysis, and molecular recognition^{[89][90]}.

The main reason to choose thiols on Au(111) is the interaction between S and Au which is of order 188 kJ/mol (1.9 eV)^[89], this is a rigid semicovalent bond, while C-C bond in organic is 347 kJ/mol (3.6 eV)^[90]. Such strong bond could diminish surface stress in Au(111) as mentioned in section 5.1, this leads to the disappearance of reconstruction of Au(111).

From another point of view. In the formation of SAM of thiols on Au(111), the S-C bond remains, and S-H bond is broken, H atom is diffused into the solution and is replaced with ‘half’ a gold atom to form RS-Au-SR staple^{[59][91]}. This consumes gold atoms, some of which are from gold atom released as the reconstruction is lifted. However, such amounts of gold atom is not enough for monolayer, it can be hence observed that gold atoms are extracted from the top layer of Au(111) and as a consequence the so called pits are formed. If sample is prepared in vacuum with slow exposure to thiol vapour, then extra atoms required to form RS-Au-SR staple can be supplied by atoms released from step edges, in other words, no pits.

Fig 5.2 illustrates my results. Image B to D are detected from the sample annealed at 50 °C, 70 °C and 90 °C for 1 hour respectively, and data are statistically displayed on image A. The results are in accordance with section 2.5 and Ref. 57 qualifiedly. The mean total area of pits is 3890 nm², while the number of pits decrease from 847 to 92. This significant decrease indicates that the structure of saturated decanethiols on Au(111) can be modified violently at higher temperature just below 90 °C. Higher than 90 °C, a little part of decanethiol has vaporized from the gold surface, and hence there are coexistence of some strip phases and closed packed decanethiols without pits.

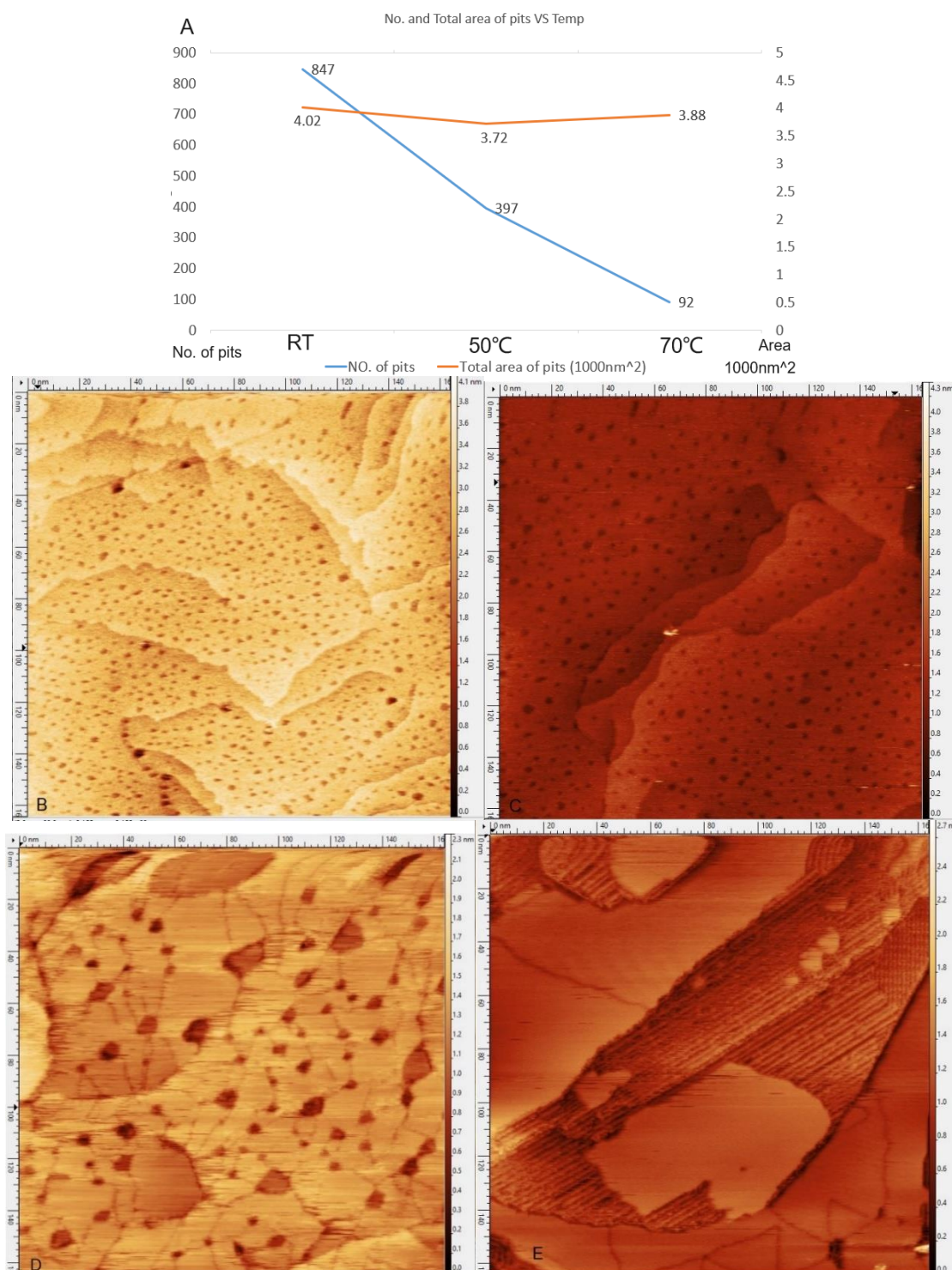


Fig 5.2. A. a statistic for No. and total area of pits versus temperature at room temperature (B), 50 °C (C) and 70 °C (D). E. The sample annealed at 90 °C.

For the chemical condition to lift the surface reconstruction. If electro-negative species are put onto Au(111), such that charge is transferred from the Au substrate, there is a

tendency that the reconstruction is lifted. On the contrary, if electro-positive species such as Na or K are put onto Au(111), the reconstruction becomes narrower, that is from $(22\times\sqrt{3})$ to $(P\times\sqrt{3})^{[101]}$. The lifting of the reconstruction indicates a relatively strong interaction between thiol and Au. The interaction is, however, not too strong, thus at the temperature lower than 130 °C, the RS-Au-SR staple has freedom to diffuse on Au(111) without leaving. This ability to diffuse is essential for the formation of mixed thiol- C_{60} layers.

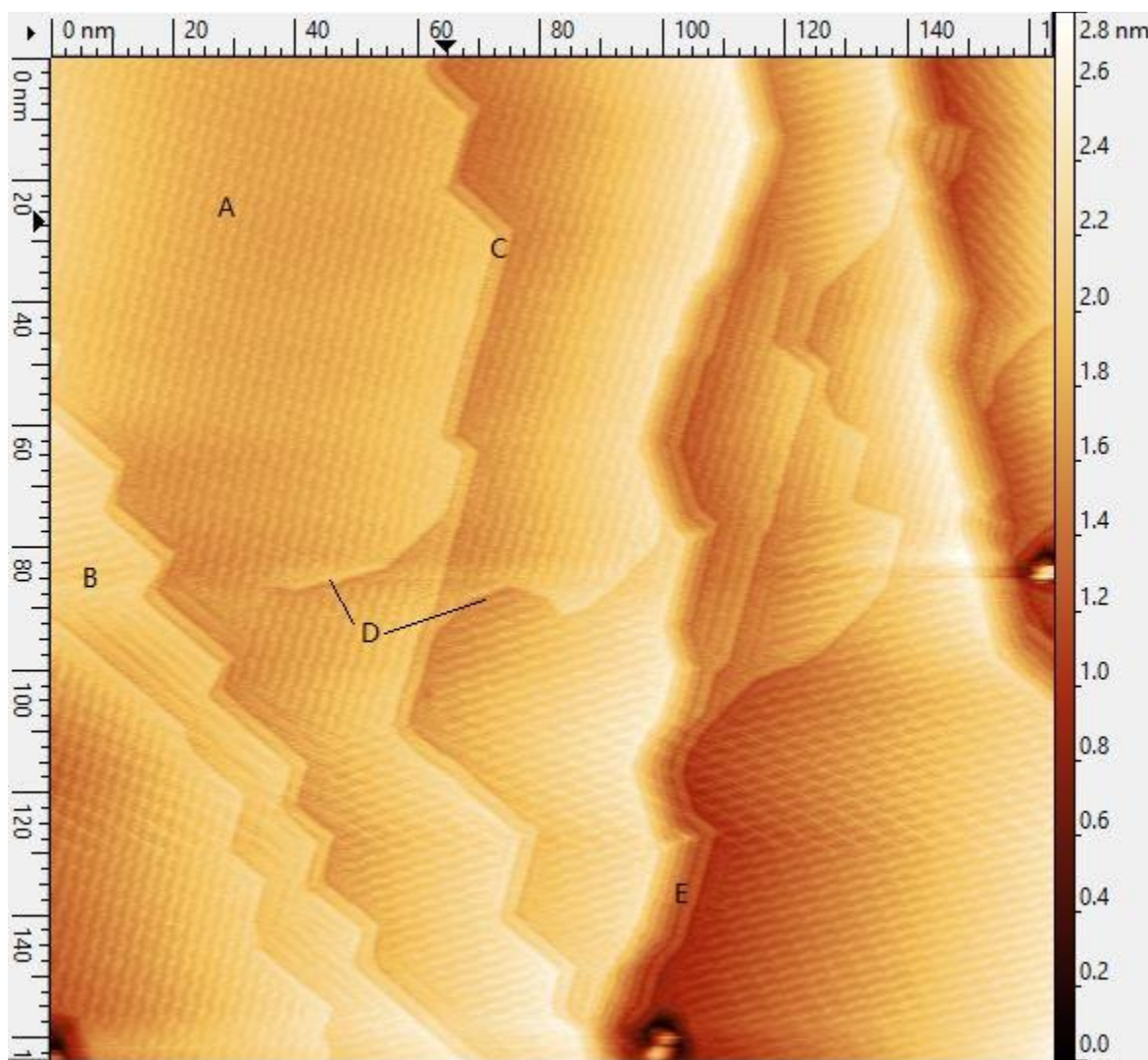


Fig 5.3. Decanethiol on Au(111) after annealed at 100°C for 5 mins.

Region A is the flat terrace of decanethiol, after annealed at 100°C for 5 mins, some decanethiol has left from the Au(111), there is enough space for decanethiol molecules to lay down on the Au(111). However, due to the strength of S-Au bond, the interaction is between physisorption and chemisorption. There are only 3 directions for aligned decanethiol molecules. All molecules on a terrace of a region A share the same direction $[1\bar{1}2]$ (Since Au(111) is 3-fold symmetry, the other 2 are $[1\bar{2}1]$ and $[\bar{2}11]$ which are exhibited on the terrace B)

Fig 5.4 exhibits some details of unsaturated thiols of region A. Measurement taken along line 1 shows the width of 15 strips is 32.4 nm, that is the distance of neighbouring strip is about $2.16 \text{ nm} = 7.5 a$ ($a = 2.88 \text{ \AA}$), this is accordance with previous research^{[59][60]}.

Line 2 is along one single strip, although it can't exhibit every single thiol molecule, previous studies has proved the distance of neighbouring thiols within one strip is $\sqrt{3}a$ ^{[59][60][63][110]}, as illustrated on the lower image of Fig 5.4, so an unit cell is $7.5 \times \sqrt{3} \text{ Rec}$ as rectangle denoted as '3'.

In addition, there are eight segments along line 2, each of which is similar to rectangle 4. The length of line 2 is 28.5 nm, each segment is $3.56 \text{ nm} = 7\sqrt{3}a$, i.e., each segment contains $7 \times 2 = 14$ thiols. The appearance of segments is attributed to the imperfect match between gold and decanethiol, although thiols assemble regularly, each molecule is under stress from gold atoms. Such stress would be accumulated gradually until beyond potential wells between gold atoms, in other words, there is a tiny transverse displacement on the 8th thiol molecule to release the stress and the next segment begins. The displacement is too small to drag the thiols from the strip, finally every strip appears to be segmented.

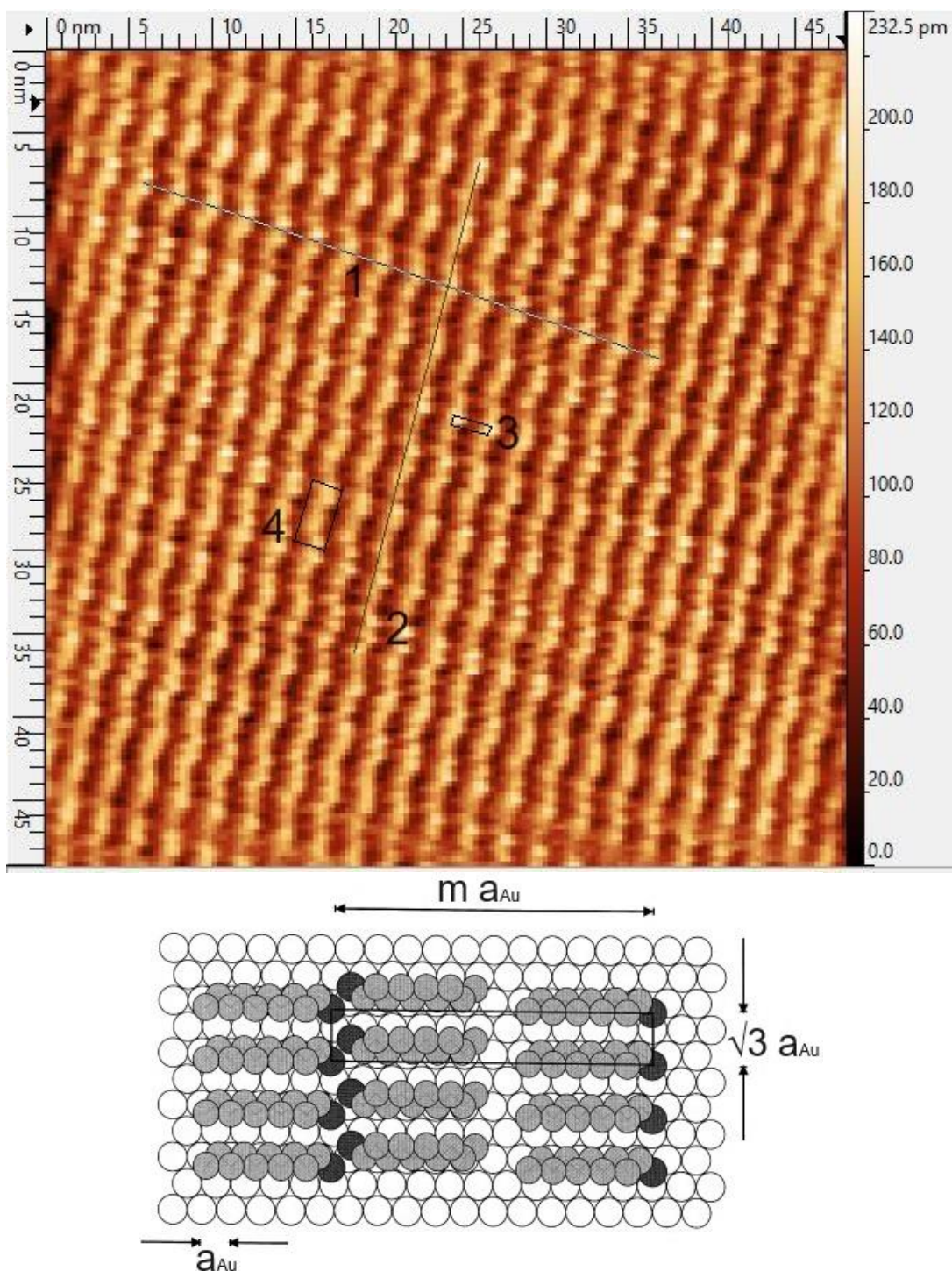


Fig 5.4. Top: A zoomed in image of region A on Fig 5.2. Line 1 measures the distance between ambient striped phases. Line 2 measures the distance of neighbouring thiols along one strip. Rectangle 3: A unit cell of decanethiol, $7.5 \times \sqrt{3}$ Rec. Rectangle 4: A segment of a strip phase. Down: A general model for lower coverage phase of thiols on Au(111)^[110].

Region C and D are a few steps between 2 terraces, the difference is their direction. Region C along the same direction of possible 3 directions of striped phases, while D is arbitrary. This can contribute to the formation of steps. C is formed by step-flow growth during annealing, when each molecule is gradually grown along the previous molecules, hence it duplicates the same pattern, or it will overcome much higher surface stress to construct along arbitrary directions. However, such surface stress can be reduced by defects as shown on region D, where is a growth of screw dislocation.

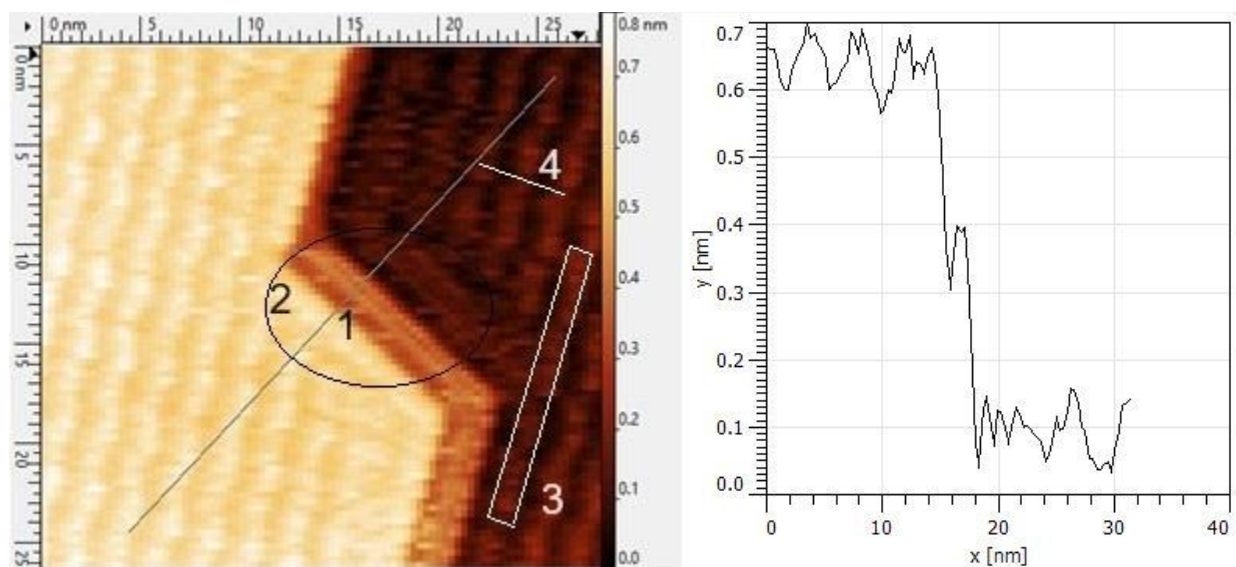


Fig 5.5. Some measurements on region C. Line 1 is to measure the steps, which is shown on the right. Ellipse 2 is the thiols near the steps. Rectangle 3 contains 4 segments parallel to a step. Line 4 is to measure the distance of neighbouring thiols.

From the right image on Fig 5.5, there are 2 steps on C, each of which decreases 0.28 nm ($1 a_{Au}$) in height. In the middle of the steps, there is a 0.1 nm increase in height, such value is also in the zigzag patterns on upper and lower steps. Comparing the atomic radii of gold ($1.4 \text{ \AA}$) and carbon ($0.7 \text{ \AA}$), it is more likely to be carbons, i.e., decanethiols. However, the structure of thiols in the steps is constrained to form a non-segmented strip. Additionally, the width of the central step is 1 nm, but it remains challenging to determine the number of thiols transversely from this STM image solely.

In ellipse 2, there is not segment like Fig 5.4 near the steps. In rectangle 3, there are 4 segments with total length 14 nm, hence each strip is still 3.5 nm. Line 4 has a length of 4.4 nm, that is the width of each strip is also 2.2 nm. Hence the structure of thiols parallel to a step is same as Fig 5.4. By comparing area 2 and 3, it can be concluded that a step parallel to a strip would not impact the structure of the strip phase while non-paralleled step would eliminate the segments.

There are 2 steps on region D, the curved step is formed from a defect. As a result, the height of the first step is 0.24 nm, and the second is 0.28 nm. Focus on the middle step, the height is about 1 nm. This is same as region C on Fig 5.5.

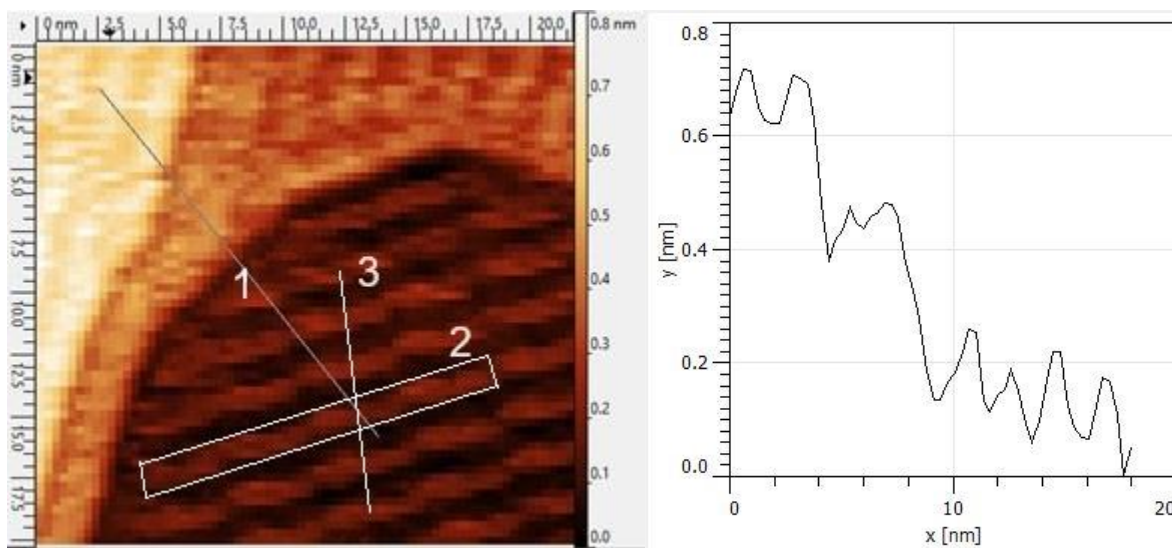


Fig 5.6. Some measurements on region D. Line 1 is to measure the steps, which is shown on the right. Rectangle 2 contains 4 segments. Line 3 is to measure the distance of neighbouring thiols.

Secondly, on rectangle 2, four segments are observed with combined length 14.7 nm, i.e., 3.7 nm each, considering the interference from nearby steps, the length of each segment of decanethiols remains consistent with that on Fig 5.4. However, the neighbouring distance is different, along line 3, there are 5 strips within a 9.2 nm, hence each occupies $1.84 \text{ nm} \approx 6.5 a_{Au}$. A unit cell in region D is $6.5 \times \sqrt{3} \text{ Rec}$.

Another situation to overcome stress surface is multi-steps as shown on region E, whose statistics are shown on Fig 5.7. Although the steps are exhibited clearly on Fig 5.3., it is hard to distinguish individual step on Fig 5.7. It appears that there are 6 steps with total decrease 1.5 nm in height. Hence each step decreases 0.25 nm average. However, the fifth step (indicated by an arrow) is different from others. Not only it is wider, but there is a bump with a height of approximately 1 nm. Same as region C and D, there are thiols on the fifth step. The first 4 steps are smoother with total width 6 nm. It is impossible to distinguish the surface particles are gold or thiols.

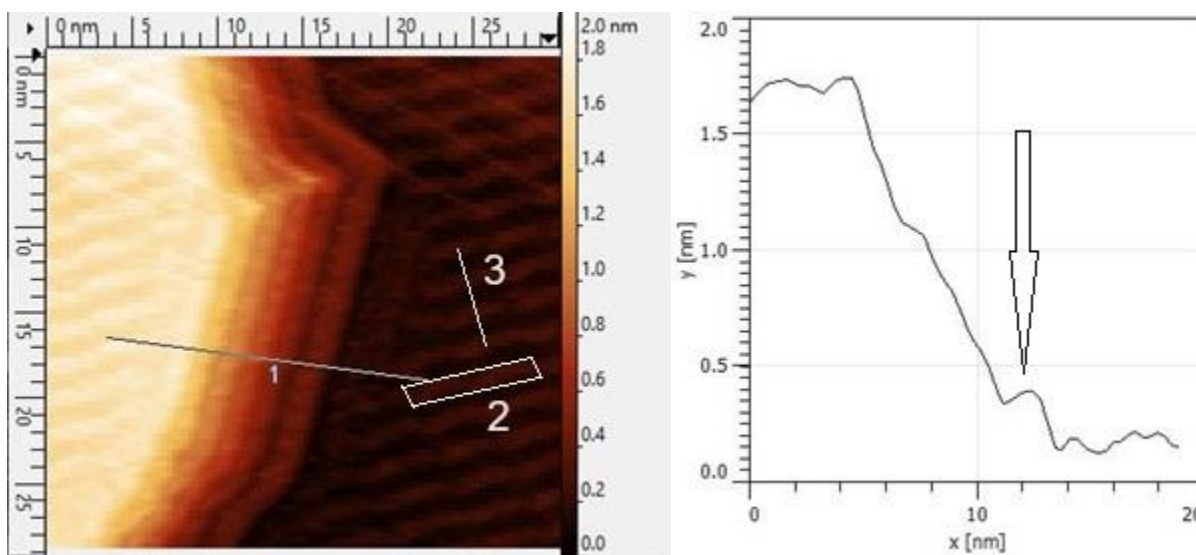


Fig 5.7. Some measurements on region E. Line 1 is to measure the steps, which is shown on the right. Rectangle 2 contains 2 segments. Line 3 is to measure the distance of neighbouring thiols.

Lastly, in rectangle 2, there are 2 segments with combined length 7.6 nm, i.e., 3.8 nm each, hence the segments are also similar to Fig 5.3. But the neighbouring distance is the third case: along line 3, there are 3 strips within 6.1 nm, hence each occupies $2.03 \text{ nm} \approx 7 a_{\text{Au}}$. A unit cell in region D is $7 \times \sqrt{3} \text{ Rec}$.

In summary, on a well-prepared surface of SAMs with lower coverage decanethiol on Au(111), there are still some steps, which divide the surface into different grains with various orientations and lattice constants.

6 Structure of C₆₀ and decanethiol on Au(111)

In this chapter, I will detailed discuss the structure of mixed C₆₀-decanethiol on Au(111). All image and data for such components were collected from my sample by STM. There are 5 types of regions on the sample: striped phase of decanethiol (without C₆₀), regular phase, heptamers of C₆₀, intermediate phase, disorder phase.

Striped phase has been discussed in Chapter 5; it can be used to direct the orientation for further analysis of structures.

Section 6.1: exhibition of irregular phase and corresponding statistics.

Section 6.2: regular phase is structure that C₆₀ are closely packed along one direction but are separated by decanethiol along other two directions, so, they look like rows of chains. The model can be constructed with the measurement.

Section 6.3: heptamers of C₆₀ are another uniform structure, where every seven C₆₀ molecules close-packed to a heptamer, each heptamer is separated by decanethiol. The model requires geometry analysis and calculations.

Section 6.4: intermediate phase, the measurements in this structure are slightly fluctuating around its mean value, but this is not enough to construct a model. However, I collected a series of imaged of the same region, this can exhibit the movement of C₆₀ and holes at room temperature.

6.1 Introduction to various structures of C_{60} and decanethiol on Au(111)

After the observation of striped phased decanethiols, C_{60} can be evaporated into the sample at vacuum until there are some areas of C_{60} on a STM image. The result image is Fig 6.1, which exhibits striped phase of decanethiols, irregular phase, regular phase, and the structures on stepped terraces.

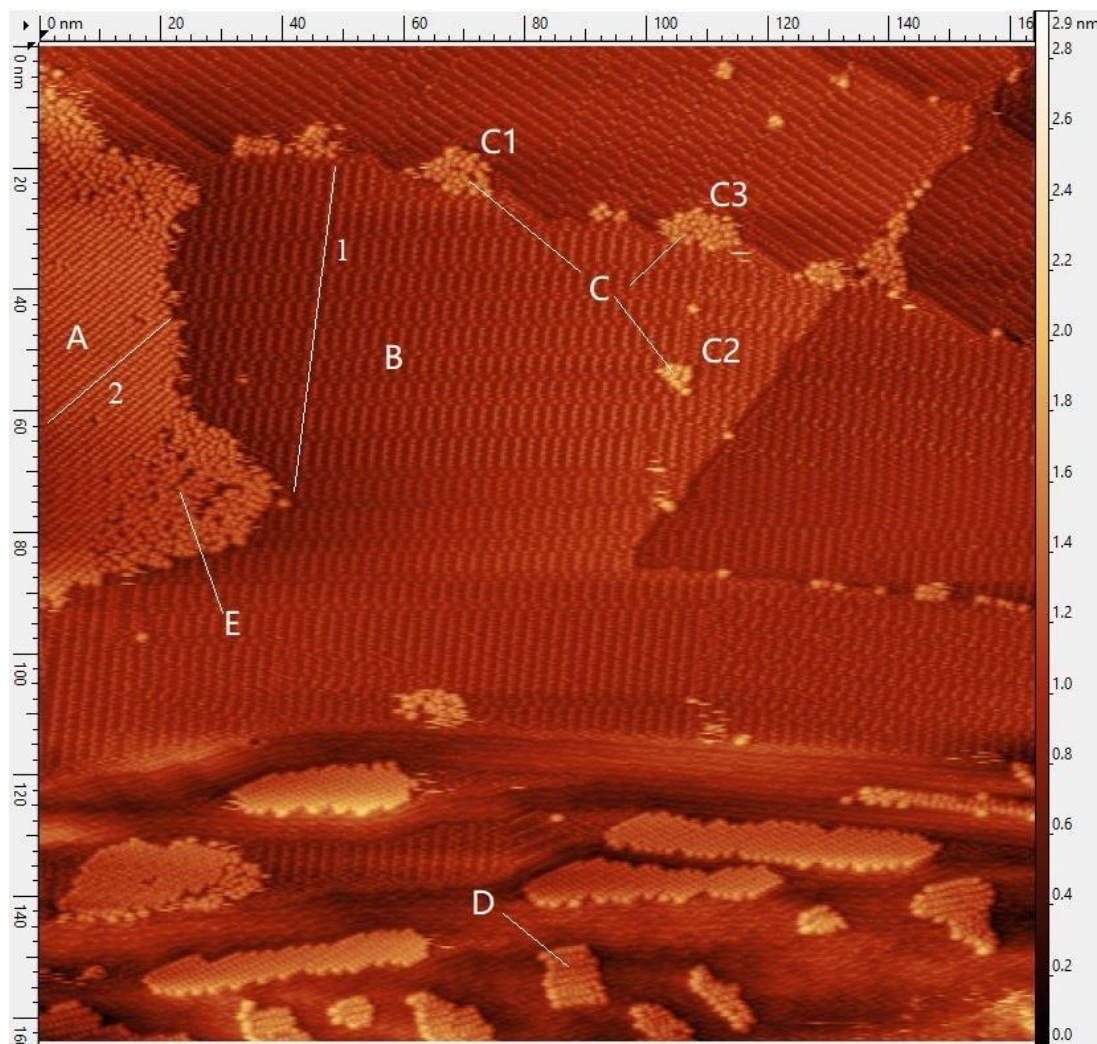


Fig 6.1. An image consisting of a number of structural phases on Au(111) with co-adsorbed decanethiols and C_{60} . Five typical regions are marked on the image. (A) Regular C_{60} rows. (B) Striped phase of pure decanethiols. (C) C_{60} and decanethiol mixture with no regular structure. (D) C_{60} on stepped terrace. (E) Irregular structure found at the edge of (A). Line 1 and 2 indicate the directions of striped phase of decanethiols and closed packed C_{60} molecules, respectively, the angle them is 43° .

The STM image suggests that C_{60} molecules are rather mobile after landing. The molecules seem to diffuse over the decanethiol layer for some distance before they are trapped. The trapping site is probably defect within the decanethiol layer. Defects are most abundant at boundaries between two different thiol domains. What is most interesting is that C_{60} and decanethiol can mix to form a uniform phase. In the following, I will describe each of the regions in Figure 6.1 in detail.

6.1.1 Dense thiol layer with few C_{60} molecules

Firstly, the structure in region B is clearly from the striped phases of decanethiols on Au(111) as shown on Fig 5.2. This region has captured few C_{60} molecules. It seems that the thiol layer in region A is dense enough to prevent C_{60} molecules dropping down to the Au substrate. C_{60} molecules cannot stay on top of the thiol layer at room temperature because the CH_3 end group of the thiol molecule has little affinity towards C_{60} . Region A shows the totally different structure from B, such uniform structure is shown on Fig 6.4.

6.1.2 Regular C_{60} rows

In region A, we see rows of C_{60} molecules. Along the row, molecules appear to be closed-packed. There is space between the C_{60} rows. We cannot see any distinct features. However, the space cannot be bare Au(111). Otherwise, C_{60} would condense into a two-dimensional closed packed layer. It can be deduced that the space is filled with decanethiol molecules. The reason of no decanethiol shown in regular C_{60} rows lies on the conductivity or band gap of C_{60} and decanethiol, C_{60} can be regarded as a semiconductor, while decanethiol has less conductivity. Hence, even though decanethiol is slightly longer than C_{60} , the electronic ‘length’ of C_{60} is longer than decanethiol. During STM scanning, this leads the structure same as shown on Fig 4.10, i.e., decanethiol becomes dead zone. The alkane chain is probably under constant motion: twisting, rocking, e.g. This is one of the reasons that the thiol molecules do not show in this part of the image. The other reason is that the thiol is less conductive and hence appear much lower. The C_{60} molecules in region A appear uniform in height not showing

the bright/dim contrast. This may be due to rapid flipping of the molecule at room temperature making all molecules appear equivalent. The direction of the C_{60} rows are 43° measured relative to $[11\bar{2}]$, and it is found that the row can take the following directions: C_{60} situated on the decanethiol on large terrace of Au (111), it can be observed there is not dim or disorder domain, the most important feature is C_{60} are not closed packed with different angles which are 40° , 70° , 70° , it is impossible that C_{60} molecules are on the Au (111), then they should be separated by striped phased decanethiol under C_{60} . Details are discussed later.

6.1.3 Irregular C_{60} /decanethiol mixture

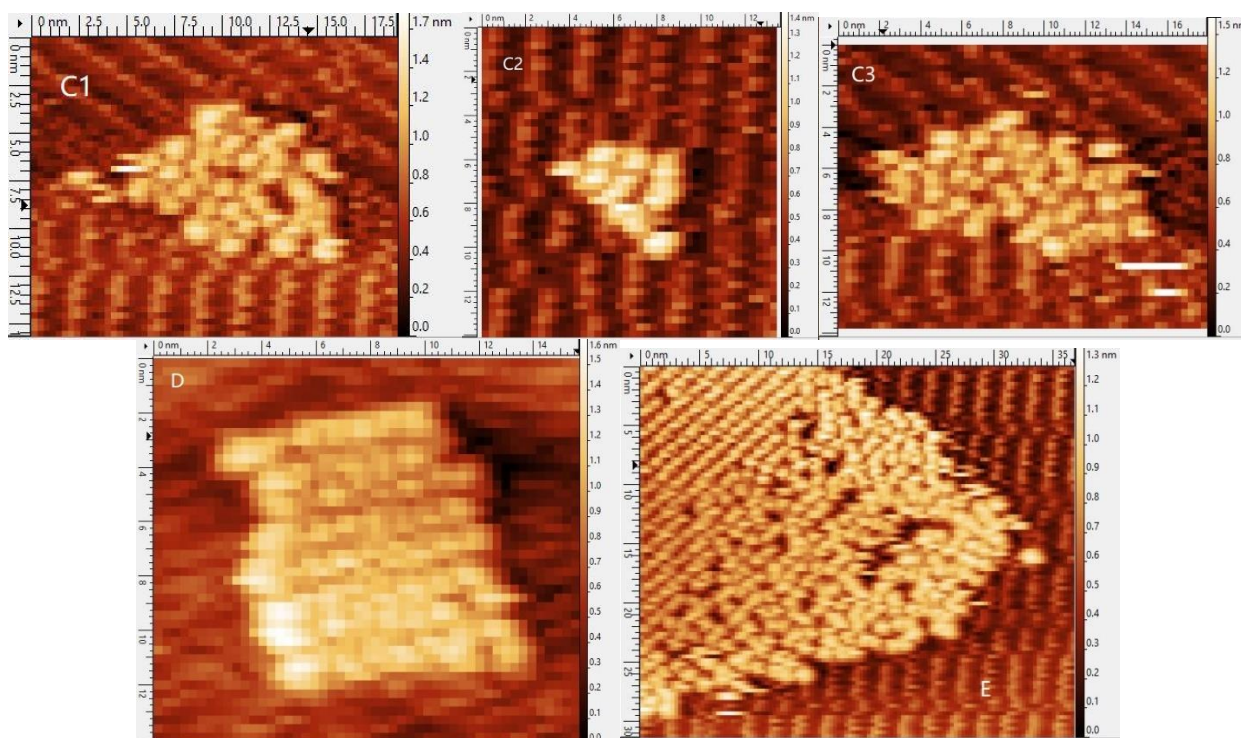


Fig 6.2. Zoomed in images of region C1, C2, C3, D and E. C1, C2, C3 and E are all the same type. D is a more regular structure on stepped terraces.

For regions without regular structure found, I did some statistical analysis and found the number of C_{60} molecules per unit area. This then allows me to estimate the C_{60} /thiol ratio for the different regions.

Table 6.1: Statistics for region C1 to E on Fig 6.1.

Region	Projected area (nm ²)	No. of C ₆₀	Mean area (nm ²)	Mean distance (nm)
C1	80	37	2.16	1.47
C2	28	10	2.8	1.67
C3	76	40	1.9	1.38
D	105	60	2.24	1.32
E	473	211	1.75	1.5

The relation between the distance of adjacent C₆₀ molecules and number of C₆₀ molecules are shown on Fig 6.3.

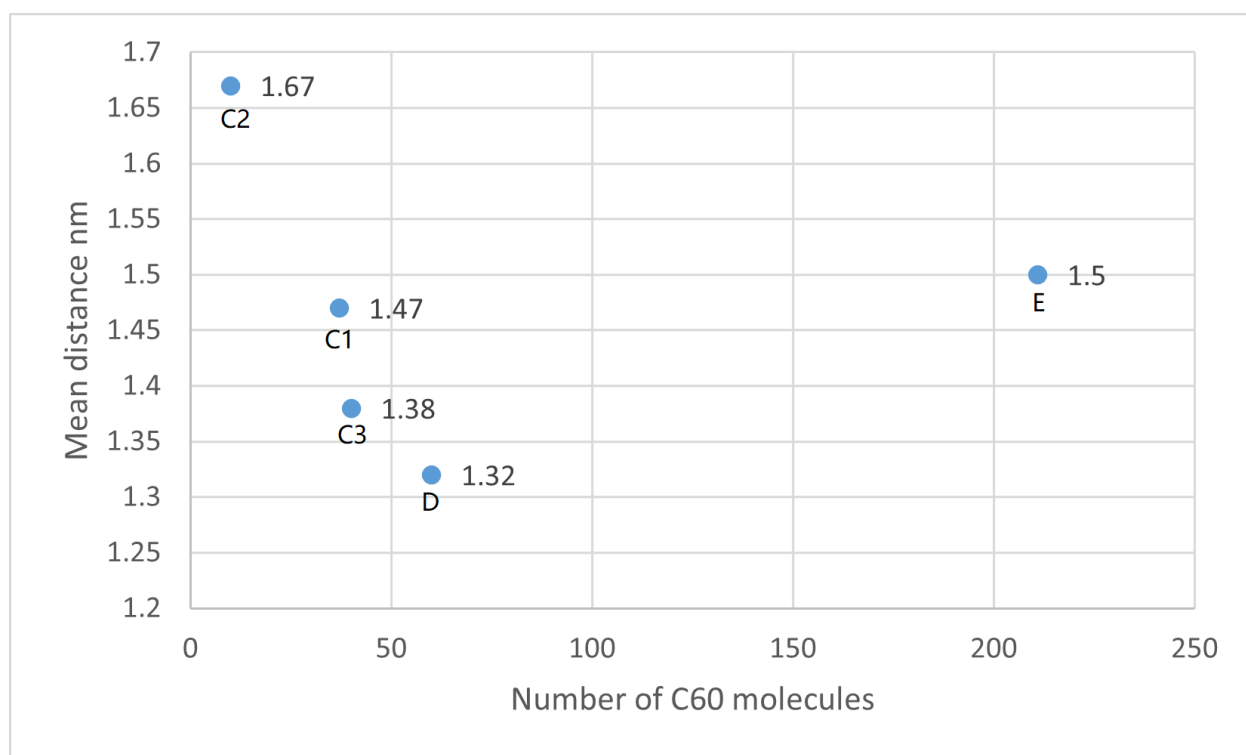


Fig 6.3. The relation between mean distance of adjacent C₆₀ molecules and number of molecules.

To estimate the mean distance of nearest neighbouring C₆₀ molecules, each molecule can be regarded as a congruent square in each region respectively. In addition, an STM image contains data on 3rd dimension, such statistics must use projected area rather than area.

From the statistics, mean projected areas and distance of adjacent molecules of each C_{60} molecule on the regions from C1 to E are listed in a table.

It is clear, from C1 to D, as the mean distances decrease with the increase in numbers of C_{60} group. This could be the first few steps in the formation of a large C_{60} group. Steps can release surface stress, this provides C_{60} molecules with positions and energy to nucleate. First, some individual C_{60} molecule hit on or mobile to such sites. This continuously remain lower surface stress relative to ambient uniformed striped phases of decanethiol. At such stage, although a few molecules are sited together, they are not interacted with each other, since the diameter of a C_{60} molecule is 0.7 nm. As the accumulation of C_{60} , they are condensed, so the distance decreases from 1.67 nm to 1.3 nm, this is close to that of on region A. And from Fig 6.1, it is clear the structure on region D is more uniform than C1 – C3.

However, although the group on E is much larger than C1 – D, the distance is higher. The reason should be that as the increasing of some groups of C_{60} molecules, they gradually close to each other, this reduces the gap (striped phases of decanethiol) between them i.e., some groups of irregular phases together look like one larger group. From Fig 6.1, some black gaps on region E could prove this.

As a large group like E continues to grow, now only does the distance decrease, but the structure becomes regular instead of uneven anymore.

6.2 Structures of uniform C_{60} and decanethiols

In this section, I will focus on regular structure of C_{60} -decanethiol on Au(111). Based on STM images, I will try to discuss why there is not decanethiol shown, the number ratio of C_{60} and decanethiol and the relationship between regular and irregular structures.

6.2.1 Description of image of regular C_{60} rows.

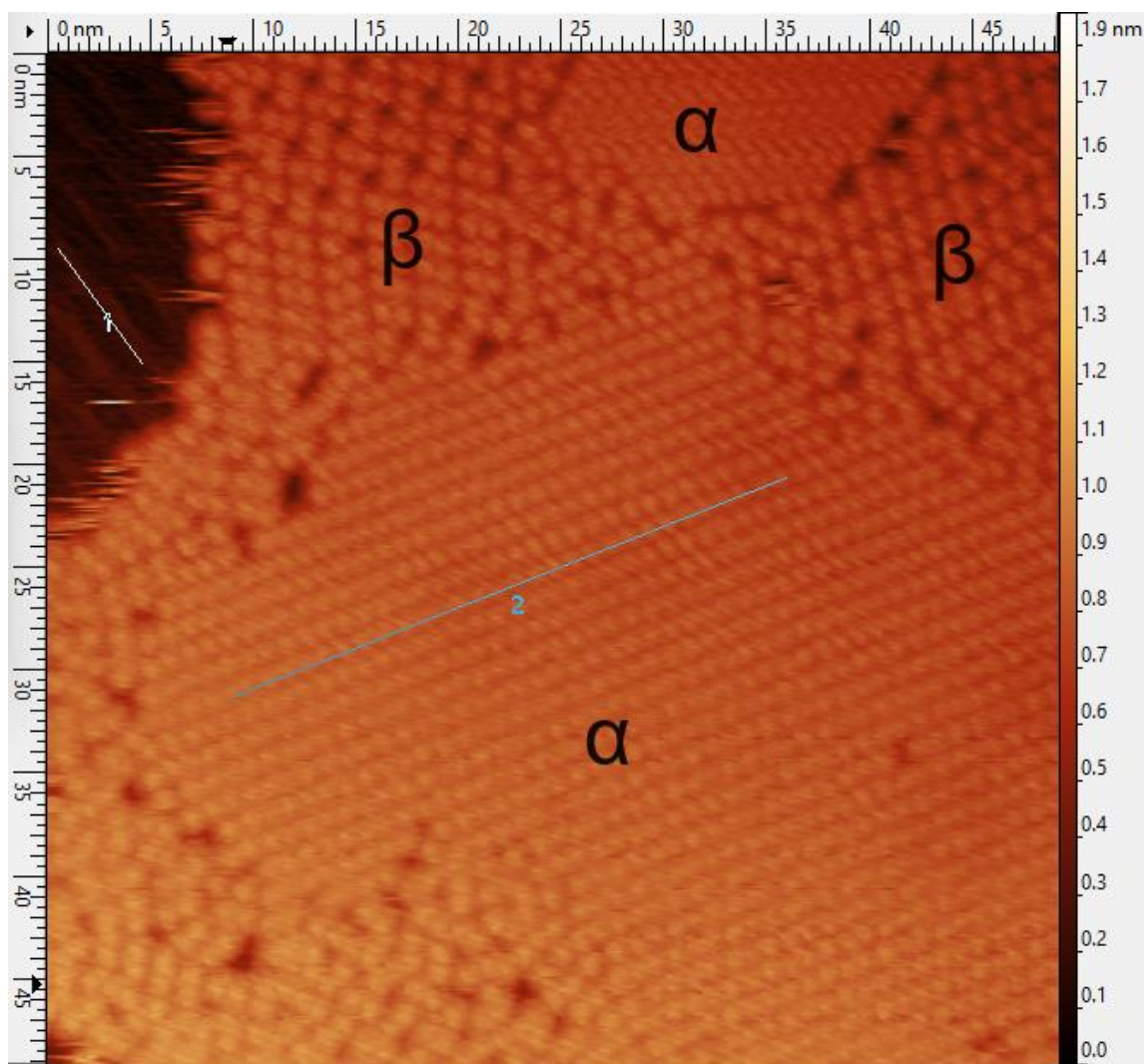


Fig 6.4. An STM image focuses on uniformly packed C_{60} . The angle between closed packed C_{60} and striped phase of decanethiols (line 1 and 2) is 76°.

Comparing β in Fig 6.4. and E in Fig 6.1. The structure in β is more uniform, every two C_{60} molecules become a unit and semi-uniform structure can be regarded as the repeat of

such unit. This could be an intermediate phase between uniform C_{60} like A and randomly distributed C_{60} like E in Fig. 6.1.

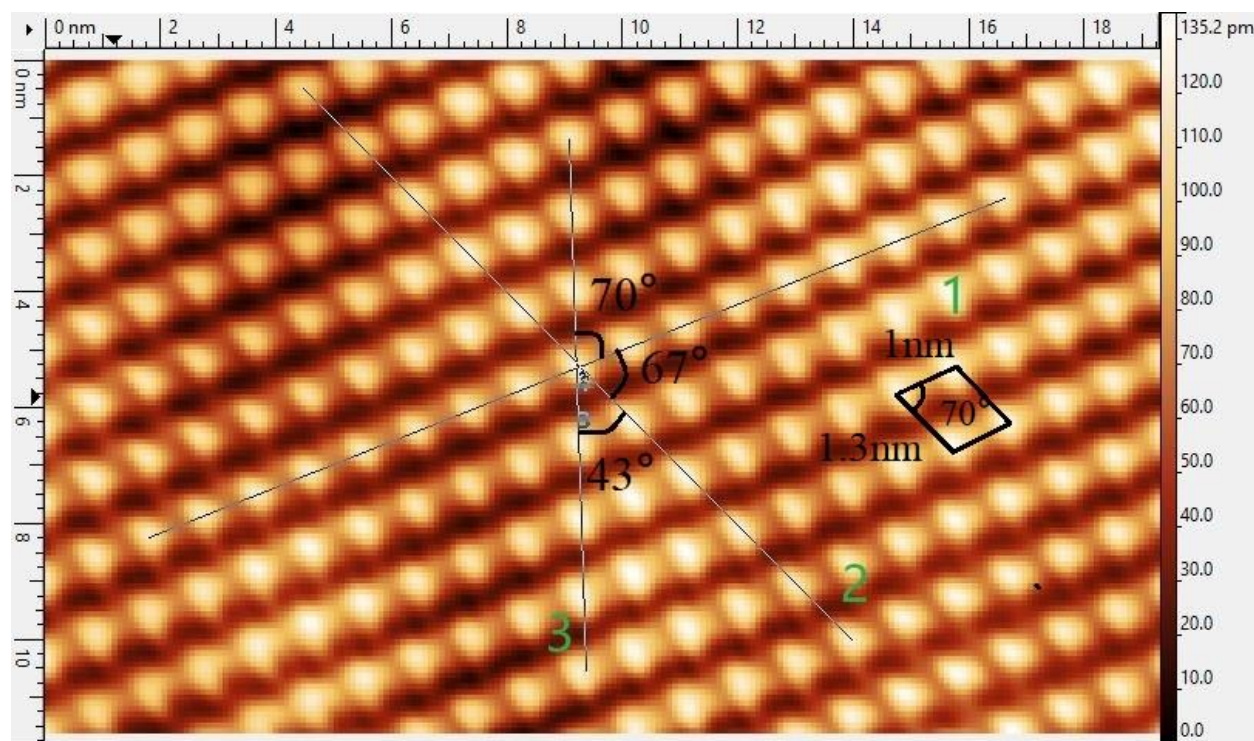


Fig 6.5. An image of crystal of C_{60} and decanethiol on Au(111). Line 1, 2 and 3 indicate 3 directions of aligned C_{60} . Along line 1, the distance is 0.99 nm, 2 is 1.34 nm, and 3 is 1.31 nm.

After Fourier Filtering for region α on Fig. 6.4. There are much periodic structures. Measuring 3 directions, the results are listed: line 1, 16 molecules with total length 15.93nm, the distance between nearest neighbouring C_{60} molecule is 0.99 nm. Line 2: 10 molecules, 13.44nm, 1.34 nm. Line 3: 7 molecules, 9.17nm, 1.31 nm. And the angels between them are $\angle 12 = 67^\circ$, $\angle 13 = 70.2^\circ$, $\angle 23 = 43^\circ$.

Since the distance along line 1 is same as that of closed packed C_{60} , C_{60} molecules are hence also closed packed along that direction. Along line 2 and 3 the structures are similar, the additional 0.3 nm due to a gap of one bar of decanethiol between 2 C_{60} molecules. The length of C-C covalent bond is 0.15 nm, 0.3 nm allows no more than two molecules can be side by side, since this distance must contain 2 carbons in 2 C_{60}

molecules respectively and a zig-zag course of a decanethiol molecule. Such data can be used to construct a ball model for detailed analysis in section 6.2.2.

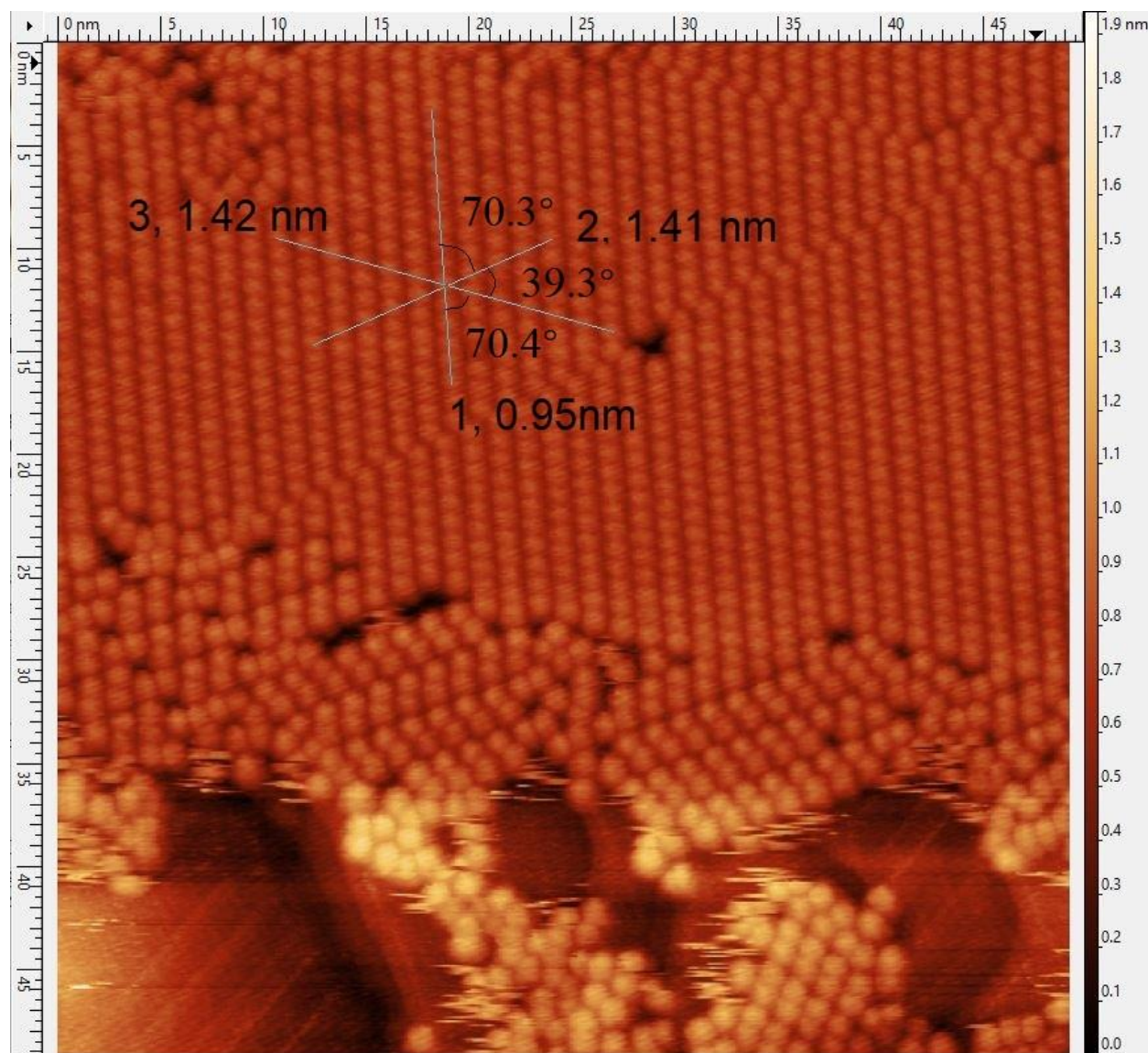


Fig 6.6. The structures uniform and intermediate phase of C₆₀. There are uniform C₆₀ group at the top, intermediate phase at middle and bottom. 1 – 3 are the line numbers, the lengths following indicate the mean distance of nearest C₆₀ molecules along corresponding directions.

Fig 6.6. is another image of C₆₀. 1-3 are at the uniform phase, comparing with Fig 6.4., the angles are more agreement than distance. It's most likely that the deviations on both figures differ from the ideal value in opposite directions. This leads to much difference between 2 figures.

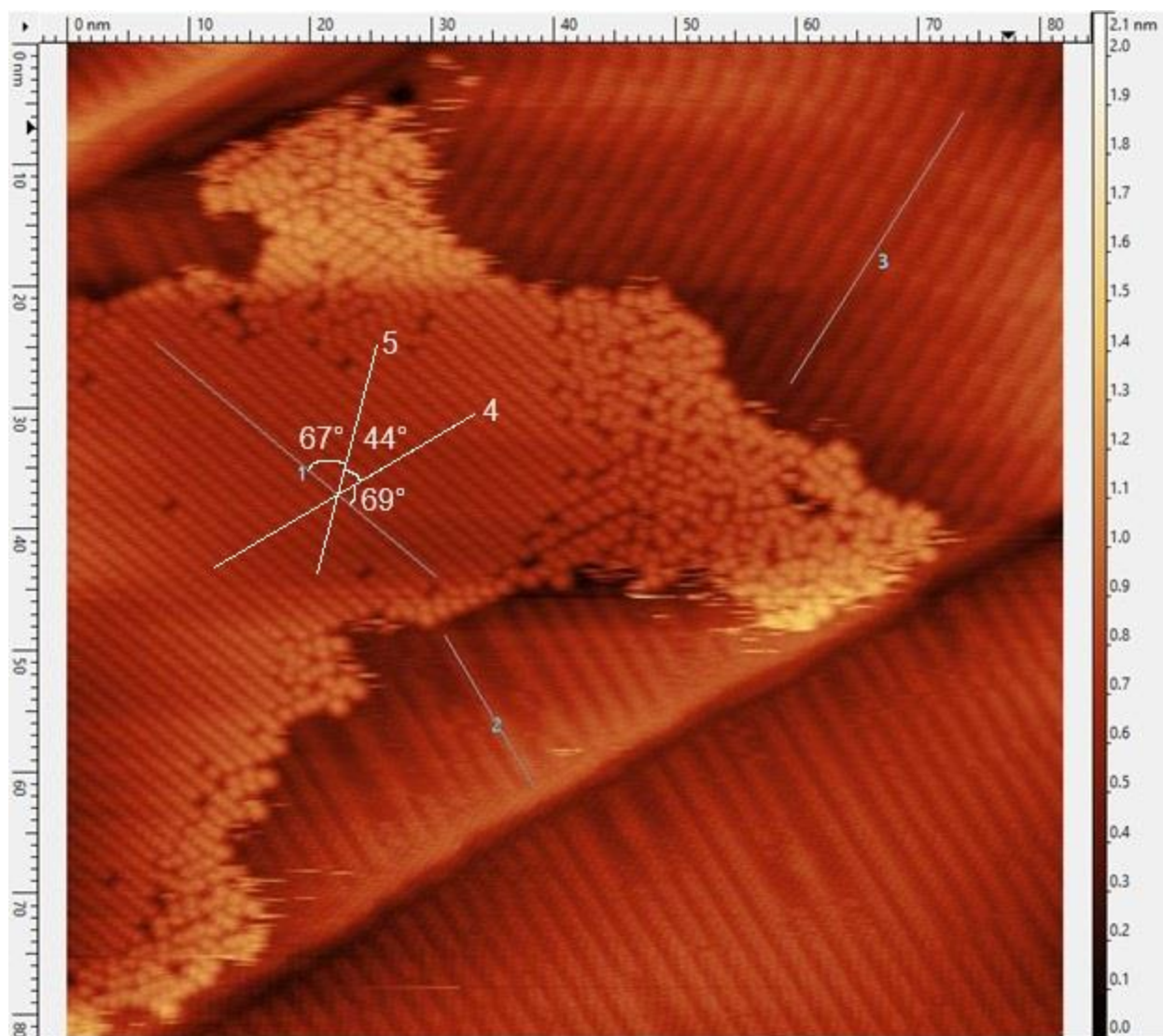


Fig 6.7. The third STM image of uniform phase. Line 1 indicates the direction of closely packed C_{60} , line 4 and 5 extend along other two directions, while line 2 and 3 are the striped phases of decanethiols.

Fig 6.7 is the third STM image, where distance of C_{60} along line 1 is also 0.97nm indicating closely packed C_{60} . The angles among 1, 4 and 5 are shown on the figure, they are consistent with previous results. The angle between line 2 and 3 is 62° , as well as segmented nature of line 3, indicating both molecules in line 2 and 3 are strip phases of decanethiol. The angle between 1 and 2 is 20° , this crucial angle will be explained in the next section.

However, due to the electrical properties of decanethiol, it is unobservable by STM. Before the evaporation of C_{60} , thiols were not closely packed, although they have covered the entire surface including regions with or without steps. It is reasonable to deduce that decanethiols are hidden in the dark tunnels among C_{60} molecules both in regular and irregular phase. It is a little possibility that C_{60} is located on the top of a decanethiol. Although a C_{60} molecule may be evaporated on a top, this situation is unstable, once the C_{60} falling down to Au(111), it is impossible to move back. Additionally, unsaturated thiols could remain some areas of defects and grain boundaries, serving for accumulating C_{60} , and decanethiols can even condense in an area and provide additional space for C_{60} , the dynamic of such process will be discussed in section 6.4.

6.2.2 Structural model of the regular C₆₀/decanethiol phase

Based on the STM images, I will now attempt to propose a structural model for the decanethiol stabilised C₆₀ rows. The development of the structural model follows the guidance of the experimental data: 1. C₆₀-C₆₀ distances along the close-packed row; 2. distance between neighbouring rows; 3. Angle of the C₆₀ row relative the major crystallographic axes of Au(111); 4. RS-Au-SR occupies the site with the Au adatom taking up the bridging site and the S atoms atop substrate Au atoms.

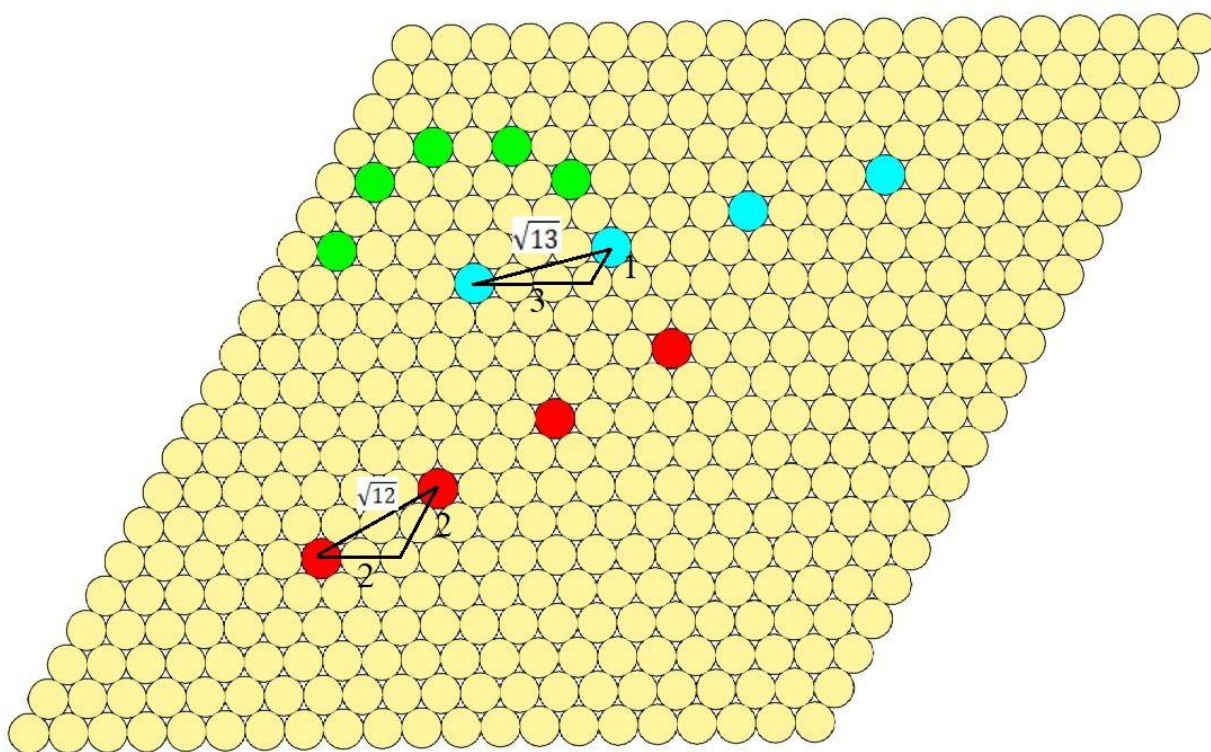


Fig 6.8. The two most possible directions of closed packed C₆₀. Yellow, red, green and blue circles all indicate substrate gold atoms, C₆₀ is not shown for clarity. A unit distance is 2.88 Å. Red circles are sites for C₆₀ locating with distance of $\sqrt{12}$ units, which is the long side of an obtuse triangle whose other 2 sides are 2 with angle 120°; blue are golds with distance $\sqrt{13}$ units, the corresponding triangle has two sides with lengths 1 and 3 and the included angle is also 120°. Green indicates other 5 possible direction for closed packed C₆₀ with distance $\sqrt{13}$ units.

First, considering the distance of nearest neighbouring C_{60} along the closed packed direction, that is about 10 Å. The distance of neighbouring gold atom on Au(111) is 2.88 Å, hence the distance of C_{60} is about 3.47 times of the Au-Au distance. This is nearly $\sqrt{12}$ (= 3.46) or $\sqrt{13}$ (= 3.61). In Fig 6.8, I have found surface sites separated by these distances. An unit cell of the structure may be extremely large such that neighbouring C_{60} molecules hold the distance but don't locate on the identical Au site. But such analysis requires more data, so I can start from the simplest model.

The next step is to consider the angle between the direction of closed packed C_{60} and striped phase of decanethiol outside. From Fig 6.1, 6.4 and 6.7, the angles between closed packed C_{60} and striped phase of decanethiol can be 43°, 76° and 20°. As mentioned in section 5.2, there are only 3 possible equivalent direction of striped phase namely $[11\bar{2}]$. If the distance of C_{60} is $\sqrt{12}$, then there are only 3 possible directions, each of which is 30° to one of the directions in the group of $[11\bar{2}]$. Those are not in agreement with measured angles. However, for $\sqrt{13}$, there are 5 more possible directions marked as green on Fig 6.8., as a result, the angle between such directions and $[11\bar{2}]$ can be 13.9°, 46.1° and 73.9°, they are more in agreement with measured values than that of $\sqrt{12}$. So, in terms of distance alone, $\sqrt{13}$ (that is 10.4 Å) is a bit longer for C_{60} , but it is very good match in terms of angles. The Van der Waals distance of C_{60} on Au(111) is about 10 Å, 10.4 Å may introduce some tensile stress on such structure, however, such stress could be reduced by the interaction between decanethiols and C_{60} . Needless to say, although there are 13.9°, 46.1° and 73.9° in Fig 6.8, those 3 angles can be $\pm 13.9^\circ$ to one of the directions in the group of $[11\bar{2}]$, since $46.1^\circ = 60^\circ - 13.9^\circ$, $73.9^\circ = 60^\circ + 13.9^\circ$.

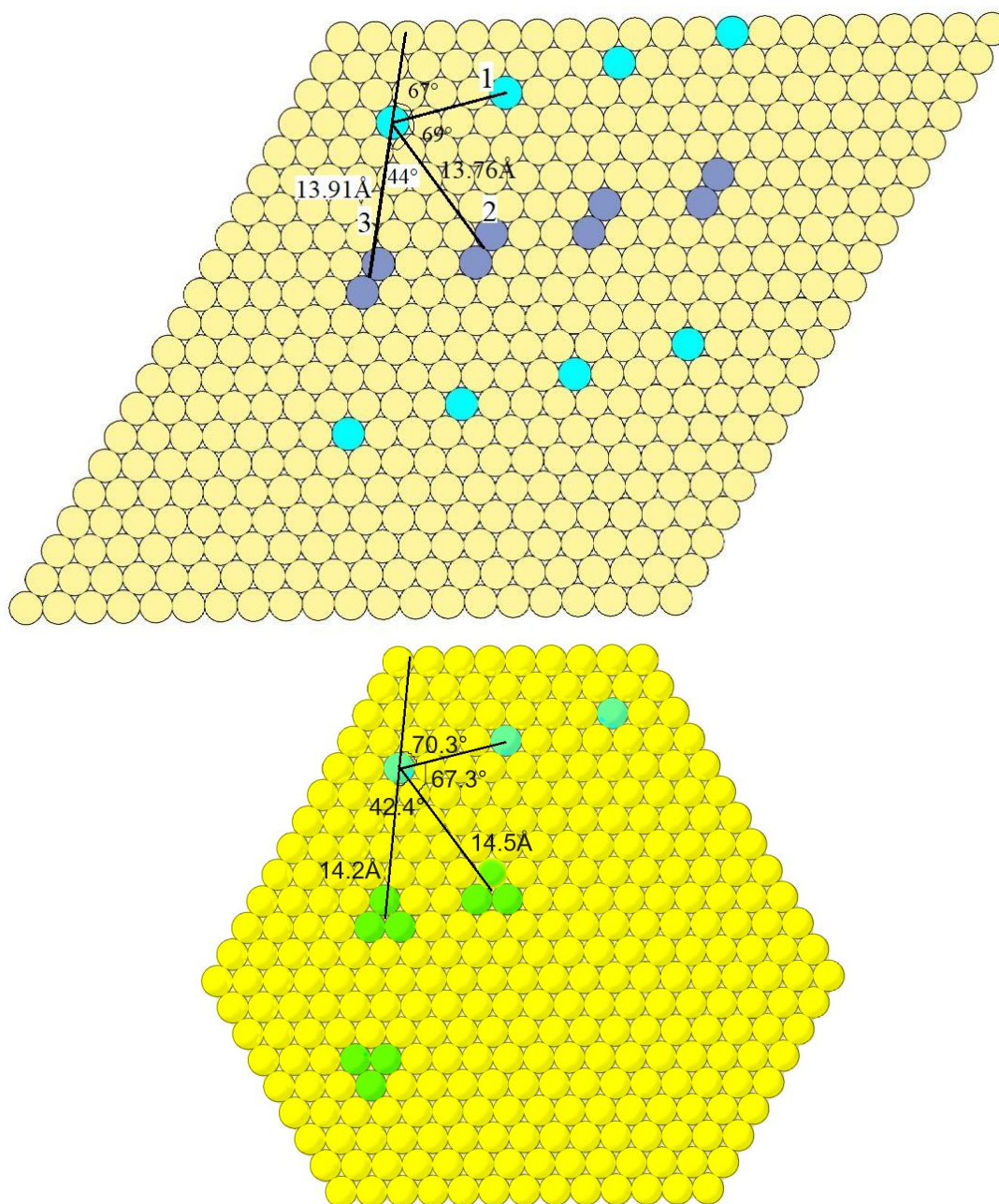


Fig. 6.9. Two possible ball models for the most possible structure of C₆₀ on Au(111). All coloured circles indicate gold atoms. Top: The first row (from top to down) of blue circles indicate the sites for C₆₀ molecule to locate. The third row of blue is for third row of C₆₀. The second row of C₆₀ molecules locate on bridges connecting 2 neighbouring grey circles (Au atoms). The line number, distance and angles are similar to marks on Fig 6.4. Down: the meaning of blue is same, however, the second row of C₆₀ molecules locate on HCP sites and the third row on FCC sites.

Now, we have the assumption that 10.4 Å is the distance of nearest neighbouring C₆₀, in other words, the closed packed row has been determined. The third step is to consider the other 2 directions. According to the values measured on Fig 6.4 and 6.6, the distances of nearest C₆₀ are 13 – 14 Å, the angles to closed packed direction are about 70 °, it is reasonable to predict those 2 directions are similar to each other. And the site for C₆₀ locating on another row cannot be arbitrary. In this case, there are 2 most possible sites for the next row of C₆₀ shown on Fig 6.9. For further discussion, there are three factors to be considered: length, angle, and energy.

In terms of lattice distance, the top situation is closer to Fig 6.5, because the measured distances and the distances calculated by the model are less than 1.4 nm. On the other hand, the lower situation is closer to Figure 6.6, because the distance is longer than 1.4 nm. In terms of angle, both models are closer to Fig 6.5. However, the lower case cannot align with either Fig 6.5 or Fig 6.6 in terms of lattice length and angles.

Yet, the lower case holds a slight advantage in energy, since the energy at sites of FCC or HCP are less than bridge. In summary, based on existing data, no one case can dominates. In addition, there is alternative rear case, that is both models are correct for the different grains of as shown on Fig 6.5 and 6.6, and it cannot ensure that the measured images are perfect. In such case, there should be a grain boundary between the grains on STM image. Such assumption also requires further experiments.

According to current data, the top case is slightly better, I choose it for further analysis. So, the unit cell of C₆₀ can be represented as 10.4 Å × 27.52 Å, 69° or 10.4 Å × 27.82 Å, 67°, the reason for double of 13.76 or 13.91 lays on that a unit cell is a repeating unit, corner atoms/molecules in a unit cell must be in identical places.

Under this structure, a unit cell of C₆₀ molecules with area 2.67 nm² contains 2 molecules, the estimation of mean distance of nearest C₆₀ molecule is 1.15 nm, which is larger than that of closed packed C₆₀ but smaller comparing with Table 6.1. In addition, in an area,

each C_{60} molecule can link exactly 1 gold bridge i.e., 2 decanethiols, hence the ratio of number of C_{60} to decanethiol is 1: 2.

For lower case, the unit cell, which can be represent $10.4 \text{ \AA} \times 43.5 \text{ \AA}$, 67° or $10.4 \text{ \AA} \times 42.6 \text{ \AA}$, 70° , has area 4.1 nm^2 , the mean distance of C_{60} is 1.17 nm . And the ratio of number of C_{60} to decanethiol is also 1:2.

The last step is to determine the possible location of decanethiols between 2 rows of C_{60} . It is known that the thiol takes the RS-Au-SR staple motif where Au is an adatom which occupies the bridging site on Au(111). In the following I use a single dot to represent RS-Au-SR for simplicity.

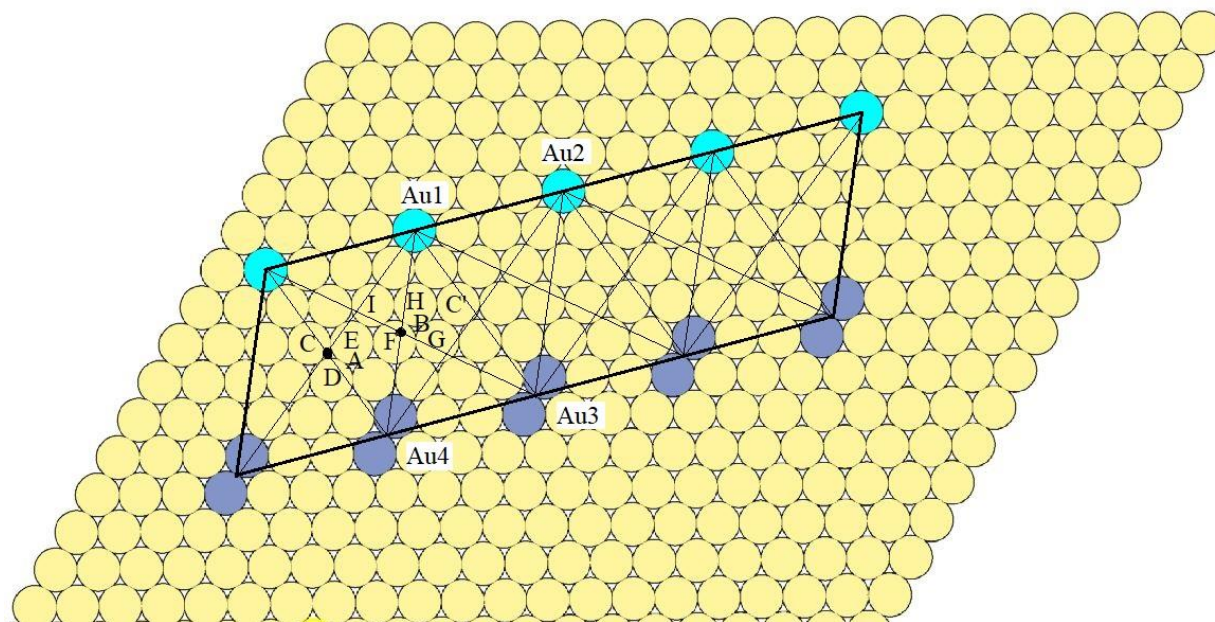


Fig 6.10. A ball model for finding the location of decanethiol, where the colour shares the same meaning as Fig 6.9. The bold parallelogram is a supercell containing 4 unit cells, thin line are either sides or diagonals of a unit cell. Points A and B are intersections of sides and diagonals. Points C – I and C' are all the gold atoms on Au(111), C – E are surrounding point A, C' is the point near A in the next unit cell, while F – I are surrounding point B.

The adjacent two rows of C_{60} are not congruent, since the C_{60} on the second row is not located on the centre of a gold atom, the RS-Au-SR is supposed to take the midpoint between two C_{60} such that it can interact with each row more or less equally.

There are two such midpoints, other midpoints can be obtained by translating A or B by the same parameters as an unit cell of C_{60} .

The distance between A and B is about 5.2 Å, considering 2 factors: 1. the previous structure of decanethiols shown on Fig 5.3. and 2. The size of decanethiol, in which the length of C – C is 1.54 Å, S – Au is 2.4 Å. There should not be 2 gold adatoms near A and B respectively.

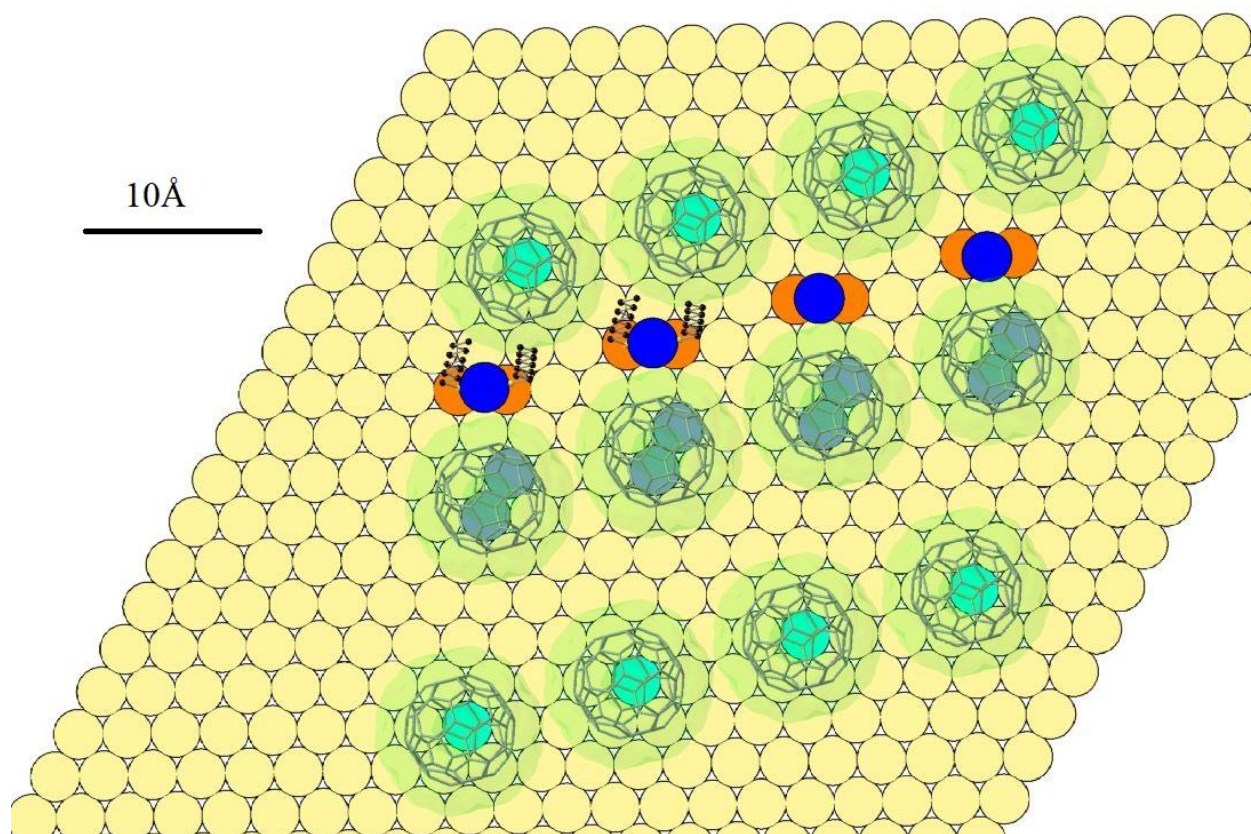


Fig 6.11. A ball model for whole structure of C_{60} and decanethiols on Au(111). Yellow circles are gold atoms of Au(111), light blue is the site for C_{60} on 1st or 3rd row to locate, while the C_{60} on 2nd row is sited on the bridge between 2 gold circles shaded grey. Blued gold adatoms bridge 2 orange gold atoms in Au(111), each of which connects 2 decanethiol molecules. Small yellow circles connecting gold adatoms are Sulphur atoms of decanethiol, and carbon atoms is presented as small black balls, hydrogen is not shown. The cage-like structure is the backbone of a C_{60} molecule, while light green shows its Van der Waals range.

So, there are 8 possible sites for gold adatom bridging 2 gold atoms on Au(111): between CD, CE, DE, FG, FH or FI, and 2 special cases where neither A nor B is gold atom but decanethiol, the gold adatom should be between A and B, in other words between EF or GC'. However, these 8 sites are much similar, it is impossible to distinguish them from STM image or geometry analysis. This requires further investigation by other devices in terms of energy or diffraction. Or it is possible that such geometry is co-existence on a large area but within different rows or areas of uniformly structured C₆₀. Despite this, it is necessary to pick up one to determine the 2 chains of decanethiols, which is shown on Fig 6.11. as an example for EF.

Fig 6.11 is just one possible structure. Apart from the location of gold atoms for decanethiol. There are 3 features requiring further research.

1. The angle of each decanethiol molecule since there is enough space for the carbon chain of decanethiol to twist or rotate. It is impossible to determine its right attitudes including azimuthal angle and polar angle by STM, since the moving tip with continuing electron would interrupt the structure and oscillation of each decanethiol molecule.
2. The direction of C₆₀. Although the position of each C₆₀ has determined, the attitudes of C₆₀ connecting to suited gold atom, for example, the gold atom could be near the centre of a pentagon or a hexagon or directly connect to a carbon of C₆₀ or a midpoint of a C – C bond.
3. The structure of defects. Such defects are shown on Fig 6.6 and 6.7. It requires further investigation that the change in structure due to different types of defects.
4. The gap between adjacent rows of decanethiol is about 1 nm. It is very possible that such value is not the distance between adjacent striped phased of decanethiol before evaporation of C₆₀. So, to form such structure, some decanethiols may be pushed away by moving C₆₀ molecules. As a result, some decanethiols should form more condensed phases. However, there is not such structures shown on Fig 6.4, 6.6 or 6.7. So, the reason

may be the pre-coverage of decanethiols of my sample is coincidence to be agreement to such ratio. This requires observation of sample with different coverage of thiols.

6.3 Heptamers of C_{60}

In this section, I will discuss another regular structure – heptamers of C_{60} . Based on the statistical data collected from the image, a geometric structure can be modelled to calculate idea structure and deduce the formation of heptamers.

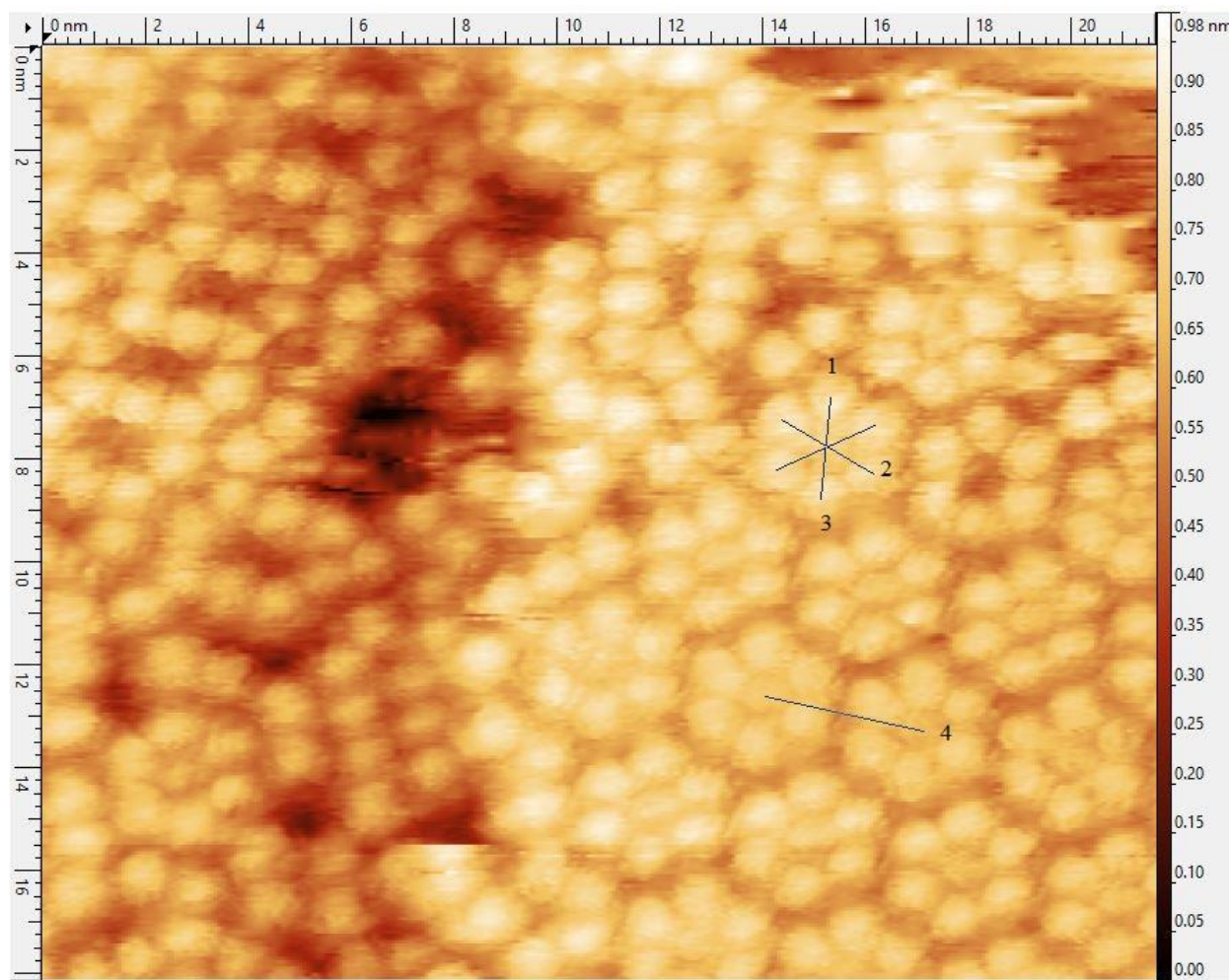


Fig 6.12. A STM image of flower-like structure of C_{60} and decanethiol on Au(111), there are 11 completed heptamers of C_{60} . Line 1-3 are for measuring the distance of nearest neighbouring C_{60} in a heptamer. Line 4 is for the distance of ambient heptamers. 1-4 are only for numbering in this image, more details are shown on Fig 6.13 and 6.14.

It is clear every seven C_{60} molecules form a heptamer, each of which is separated by decanethiol. Hence to measure the distance of nearest C_{60} molecule within a heptamer, we can measure neither a line through several heptamers nor a line just through two C_{60}

in a heptamer, but measure $3 \times 11 = 33$ lines, every three of which in a heptamer. For further discussion, there are only 3 shown on the image. The result is on Fig 6.13.

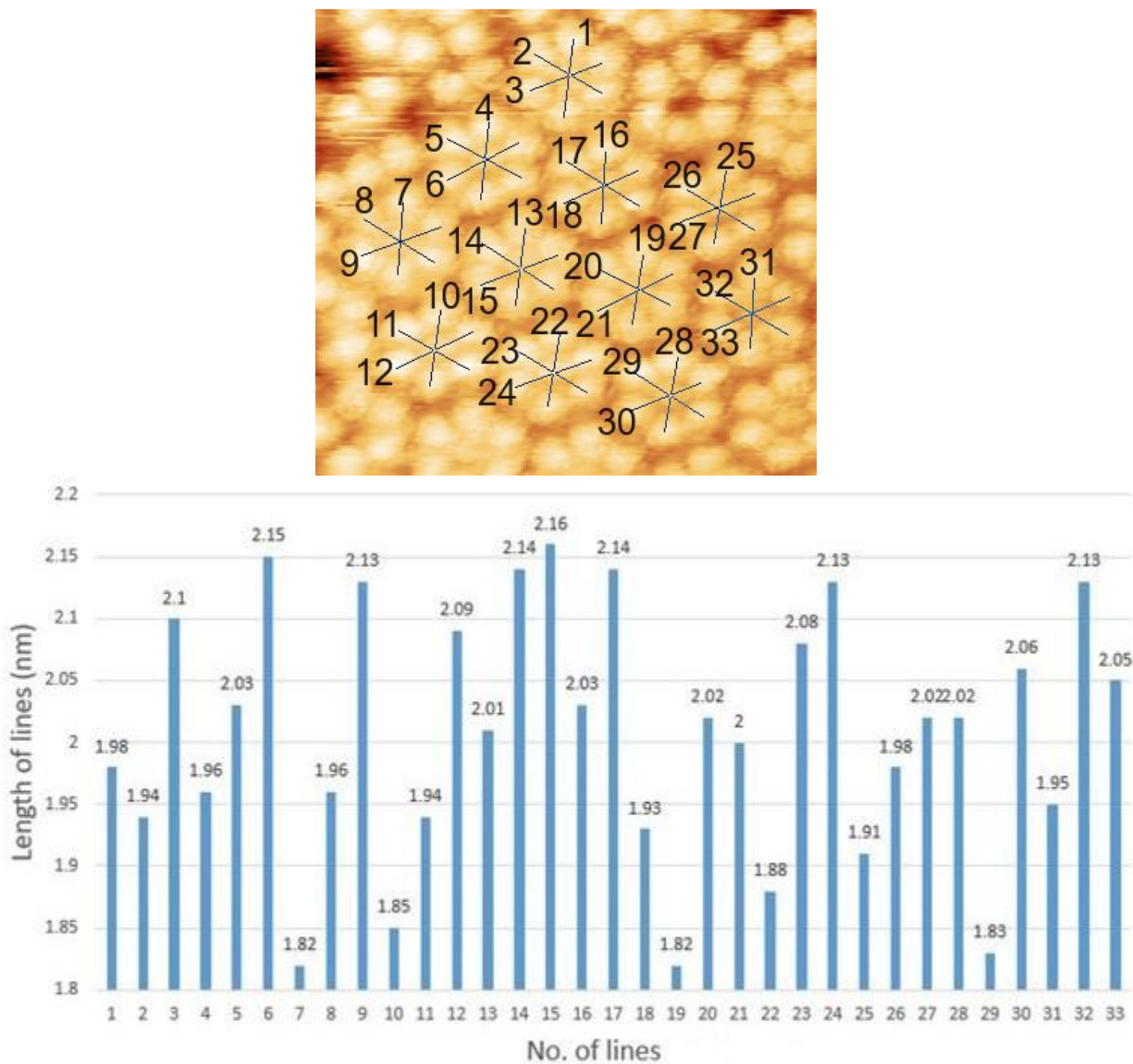


Fig 6.13. Statistics of length between two C₆₀ molecules.

The range of length is between 1.82 – 2.16 nm, the average value is 2 nm, which means the distance of nearest C₆₀ molecules in a heptamer is 1 nm. This is much close to the corresponding length measure in uniform structure of C₆₀ along closed packed direction. So, each heptamer is formed by seven closed packed C₆₀, i.e. no decanethiol in a heptamer.

It is reasonable to deduce that decanethiol is the gap between every two ambient heptamer, or each heptamer would have also closely packed with each other. Hence the next step is to measure the distance between centres of 2 ambient heptamers as line 4 on Fig 6.12. and calculate the gap size. With the same reason, such measurement requires many such distances and to average them. The length of line 4 is 3.13 nm and the statistic of total 18 measurements are shown on Fig 6.14.

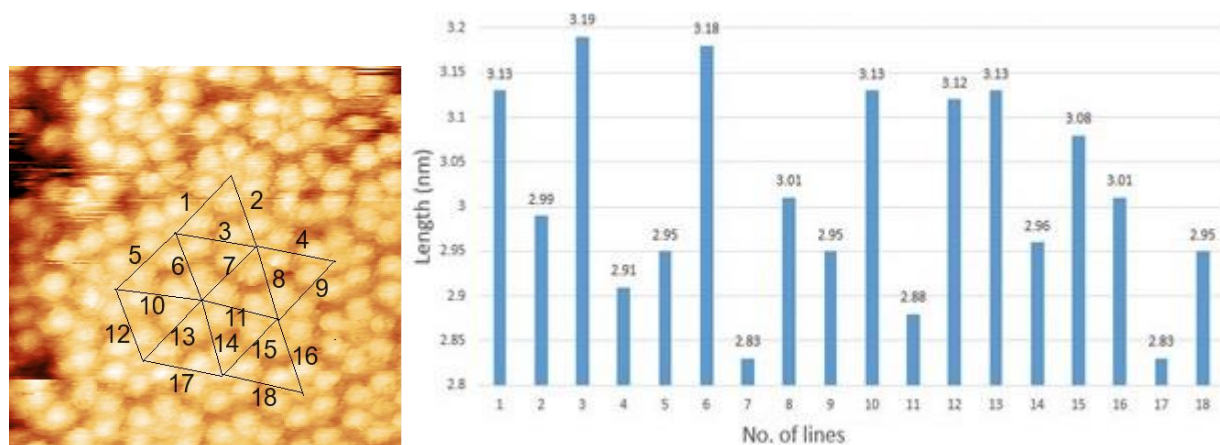


Fig 6.14. Statistics of 18 measurements of length of ambient clusters.

The average distance is 3.01 nm, to calculate the gap size, this requires geometry analysis. First is to measure closed packed heptamer, and then add a gap between them and calculate the distance due to the gap. As shown on Fig 6.15.

Since both statistics are based on some assumptions including identical heptamers, similar gaps, stabilization of manual selection and STM. So, such statistics are not accurate enough to be very carefully analysed but are used to provide some information to construct a frame for analysis.

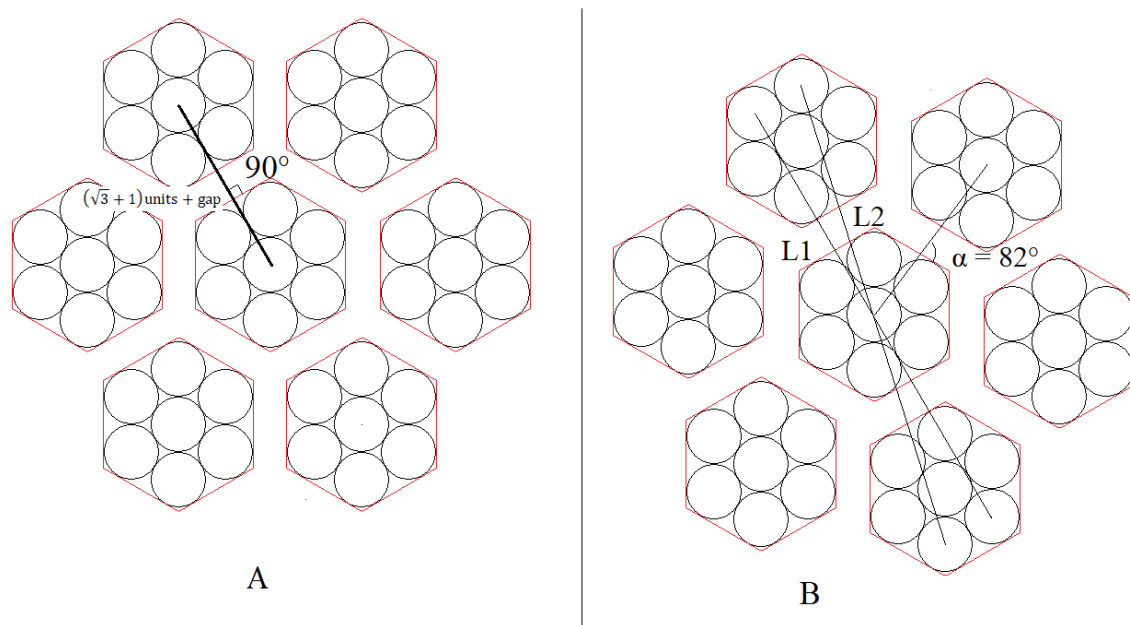


Fig 6.15. An image of simple model for measuring the gap. Each black circle indicates a C_{60} molecule, the diameter of a C_{60} is set as 1 unit. Red line is the boundary of each heptamer. Decanethiol is not shown for clarity.

Since the structures of C_{60} heptamer and decanethiol cannot be arbitrary, the gaps between different couples of adjacent C_{60} heptamer should not be varied too much. In a simple model, it is assumed each gap distance shares one value. However, in geometrical view only, there are infinite possible structure in large area. Fig 6.15 exhibits 2 examples. On image A, the line connecting 2 centres of ambient heptamers is perpendicular to the boundary, while on B, those 2 lines include a non-right angle set as α , which is 82° on B, and α can be varied from $60^\circ - 120^\circ$.

According to geometry model, the distance between 2 ambient heptamers L has the formula $L \times \sin(\alpha) = (\sqrt{3} + 1) \text{ units} + \text{gap}$ (L is also shown on Fig 6.16. D). From the value just measured, 1 unit = 1 nm, $L = 3.01 \text{ nm}$, hence

$$d_{\text{gap}} = 3.01 \text{ nm} \times \sin(\alpha) - 2.73 \text{ nm}.$$

Noted from measured value, $\sin(\alpha) \geq 2.73 / 3.01$, i.e., $\alpha \geq 65^\circ$

To measure α and reduce inaccuracy due to manual selections on image, we can measure the L1 and L2 which intersect at the centre of the whole structure as shown on B. The average value of L1 and L2 are 7.69 nm and 7.95 nm.

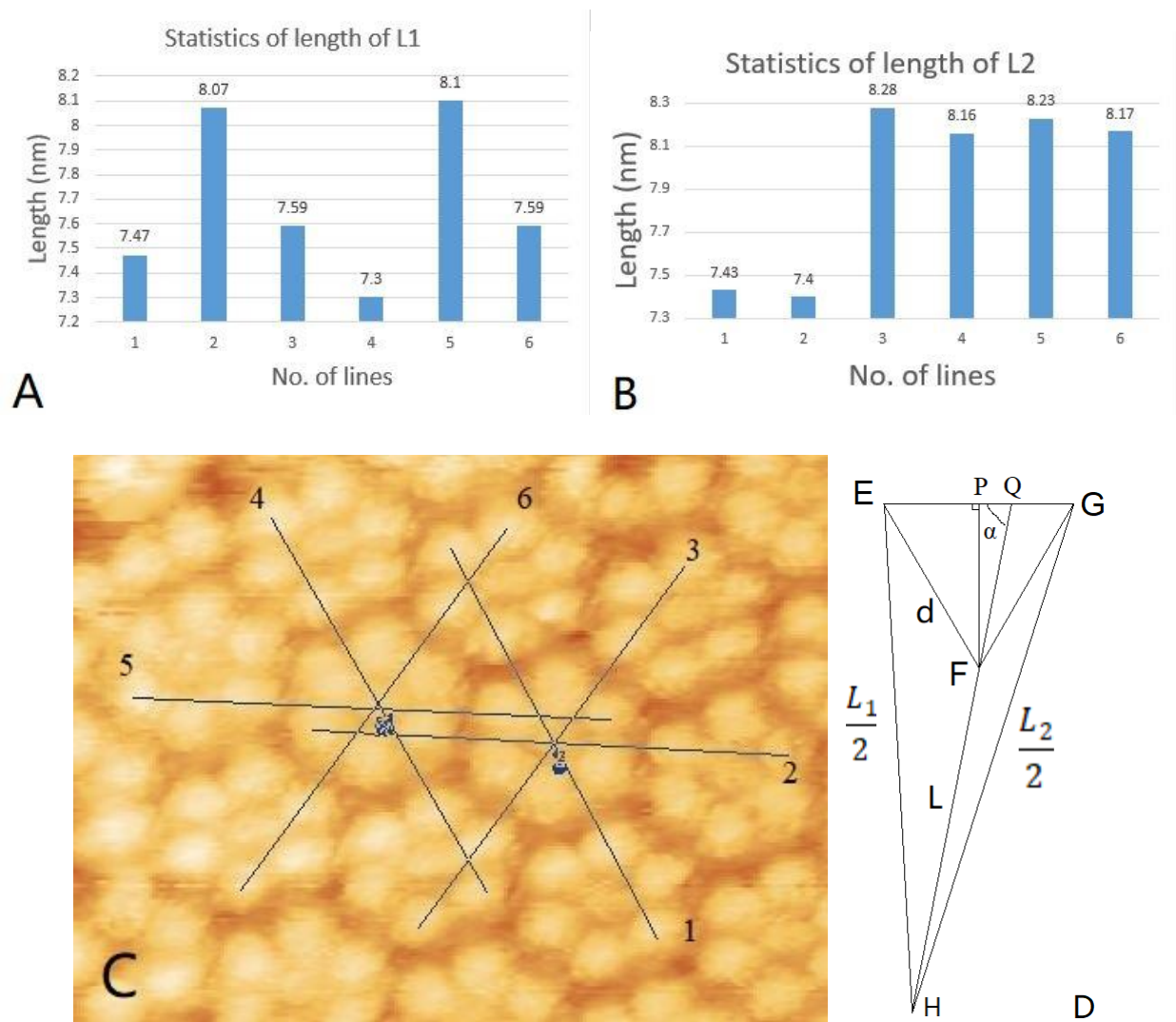


Fig 6.16. (A)(B) statistics of length of L1 and L2. (C) Selected L1 lines from Fig 6.12. The selection of L2 is similar, which is not shown for clarity. (D) The geometry structure for L1 and L2. H is the centre as the centre on Fig 6.15. B; E, F and G are centres of a circle of a C_{60} molecule, hence $EF = FG = EG = d$. The extension of L intersects EG at Q, $FP \perp EG$. Let $EQ = m$, $GQ = n$.

$$PQ = \frac{d}{2} - n = \frac{m+n}{2} - n = \frac{m-n}{2}, \quad FP = \frac{\sqrt{3}}{2}d = \frac{\sqrt{3}}{2}(m+n);$$

$$\tan \alpha = \frac{FP}{PQ} = \sqrt{3} \frac{m+n}{m-n} = \sqrt{3} \left(1 + \frac{2}{\frac{m}{n} - 1} \right)$$

$$\frac{S_{\Delta EHQ}}{S_{\Delta GHQ}} = \frac{m}{n} = \frac{S_{\Delta EFQ}}{S_{\Delta GFQ}},$$

$$\text{So, } \frac{m}{n} = \frac{S_{\Delta EHQ} - S_{\Delta EFQ}}{S_{\Delta GHQ} - S_{\Delta GFQ}} = \frac{S_{\Delta EHF}}{S_{\Delta GHF}} = \sqrt{\frac{p_1(p_1 - L_1/2)(p_1 - L)(p_1 - d)}{p_2(p_2 - L_2/2)(p_2 - L)(p_1 - d)}}$$

$$P_1 = \frac{1}{2}(L_1/2 + L + d) \text{ and } P_2 = \frac{1}{2}(L_2/2 + L + d). \text{ (Heron's formula)}$$

If the arithmetic mean values are taken into the above formulas, that are $L_1 = 7.69$ nm, $L_2 = 7.95$ nm, $L = 3.01$ nm, and $d = 1$ nm, then $\tan \alpha = 5.92$, $\alpha = 80.4^\circ$.

Noted under above notation, α is 79° for totally closed packed C_{60} (namely no decanethiol as shown on Fig 2.30.). It is reasonable that decanethiol just separate heptamers along the line connecting the centres of the heptamers. Such motion may minimize the energy to form such structure.

The distance $d_{\text{gap}} = 3.01 \text{ nm} \times \sin(\alpha) - 2.73 \text{ nm} = 0.24 \text{ nm}$. However, such value is the distance between boundaries, the distance between adjacent C_{60} on ambient heptamers is $\sqrt{0.5^2 + (1 + 0.24)^2} = 1.34 \text{ nm}$, the gap between them is 0.34 nm , which is slightly smaller than that in section 6.2. it fits into a decanethiol. According to the above values, as well as each gold adatom connects with 2 thiols, there are two possible ball models shown on Fig 6.17 and Fig 6.18.

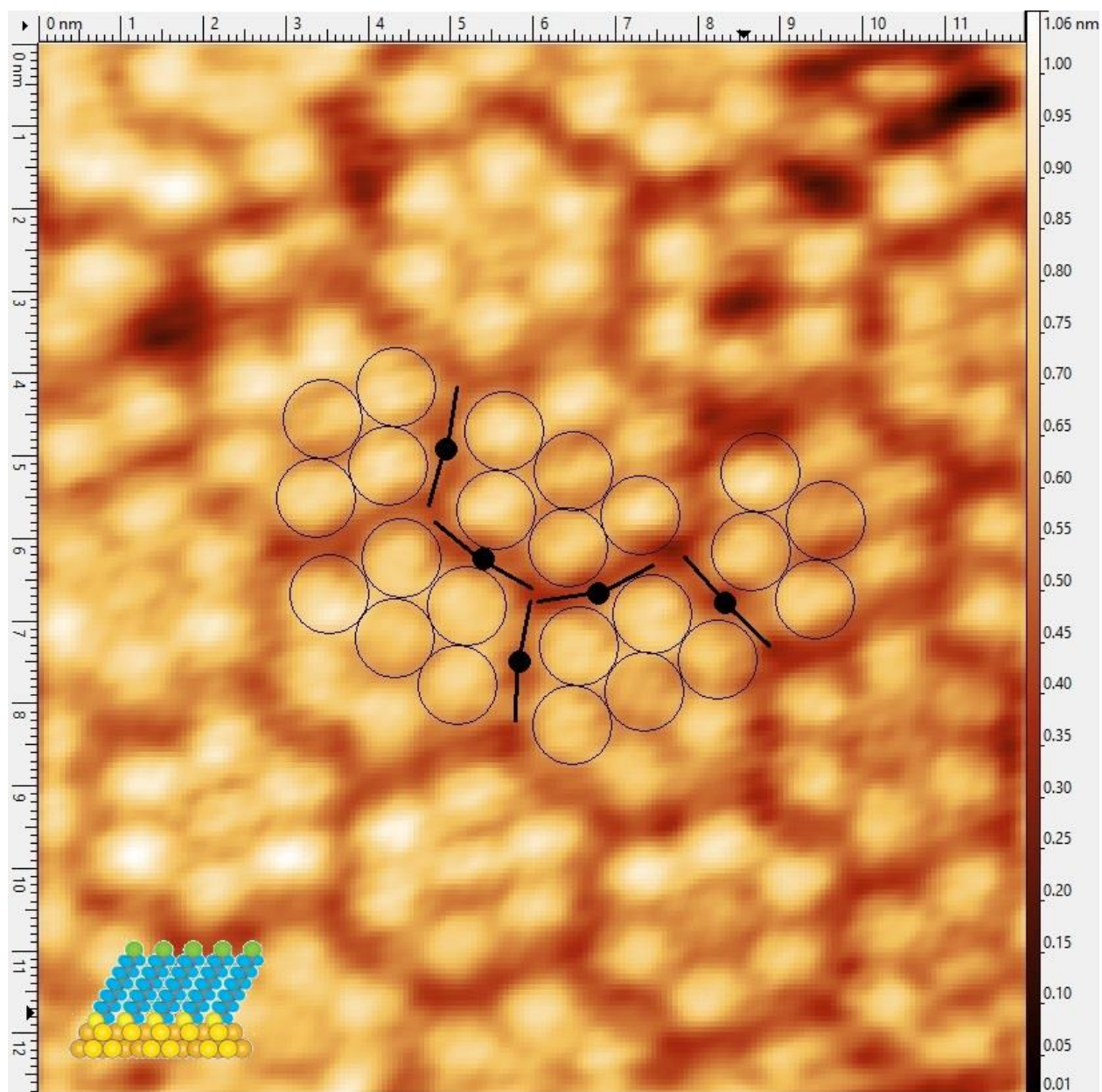


Fig 6.17. The first ball model for heptamers surrounded by thiols. A Hollow circle denotes a C_{60} molecule, a solid black circle represents a gold adatom, and a black line is a decanethiol molecule.

In this model, each decanethiol is positioned at a 60° to the Au(111) surface, as shown in the bottom left. Each heptamer of C_{60} is surrounded by 6 gold adatoms (12 decanethiols) each of which was shared by 2 neighbouring heptamers. So, the ratio of C_{60} : decanethiol is 7:6. And corresponding mean area of each C_{60} is 1.09 nm^2 and the mean distance is hence 1.04 nm. This is the smallest values comparing with regular phase and Table 6.1.

Such ratio is different from regular phase. And there are some dim sites at the left part of Fig 6.12. These may be condensed phase of decanethiols, which were displaced by C_{60} .

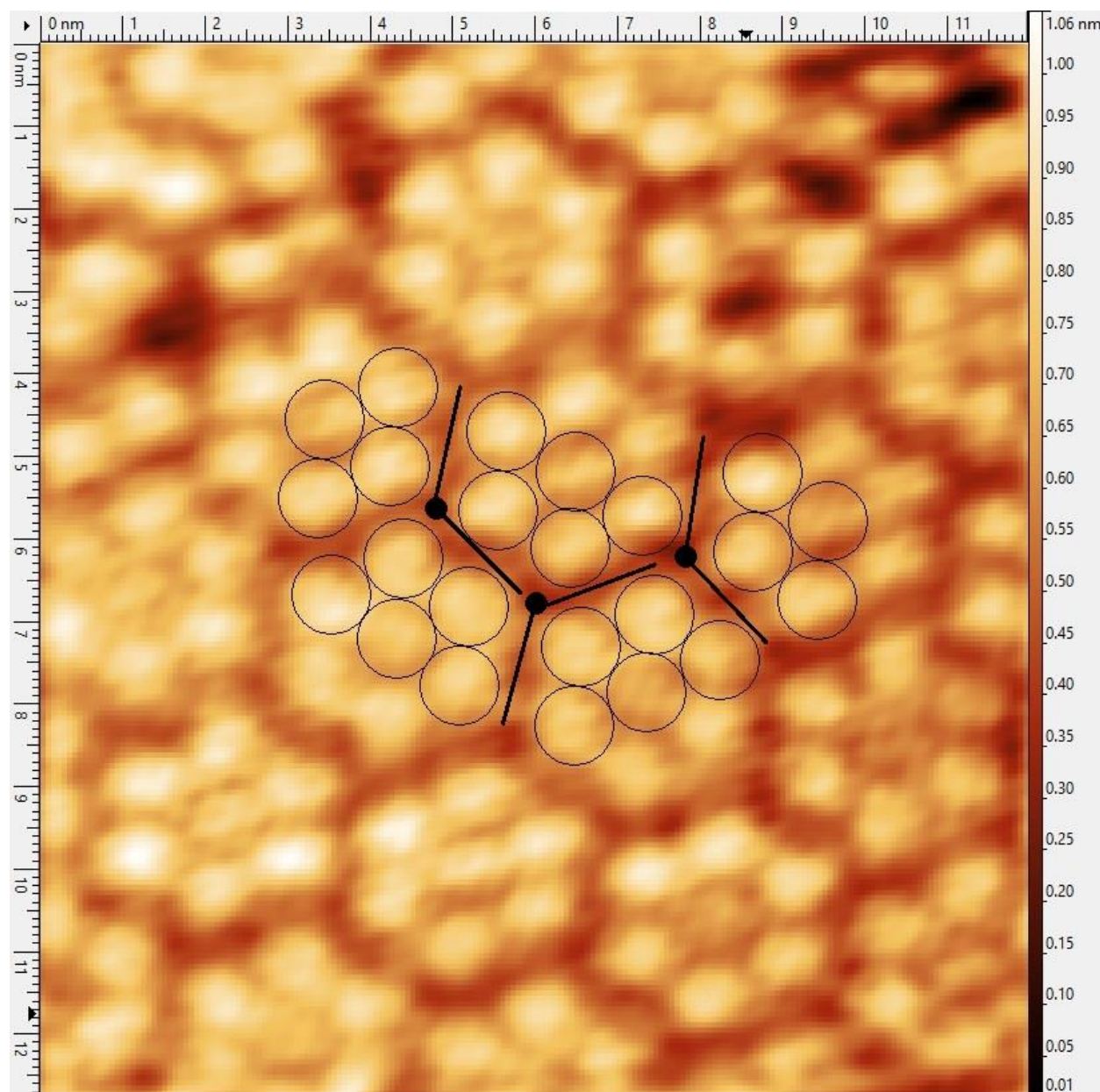


Fig 6.18. The second possible ball model, with the same legends as Fig 6.17.

Another model is different, where every thiol lay on Au(111) surface. In this case, each heptamer of C_{60} is surrounded by 6 thiols, resulting in a C_{60} to thiol ratio of 7:3, mean area, and mean distance of C_{60} are same as before.

Although from current images, it is impossible to distinguish the more appropriate one. I can list their features for further research and analysis.

Table 6.2: Comparison of balls model from Fig 6.17 and Fig 6.18

Features	Model in Fig 6.17	Model in Fig 6.18
Spatial arrangement of thiols	60° degree to the Au(111), creating hollow spaces beneath the inclined backbone of thiols	Decanethiol laying on Au(111), which is energetically favourable.
Arrangement of gold adatoms	Every gold adatom is positioned at the middle point of an edge of a hexagon	Gold adatoms occupy the centre of a triangle, whose vertices are from 3 adjacent hexagons.
Uniqueness of structure	The structure is unique as displayed on Fig 6.17.	Each gold adatom only connects two of the three nearest thiols, resulting in a non-unique structure
C ₆₀ to thiol ratios	7:6, this ratio is closer to the case in section 6.2.	7:3, this means that more decanethiols are displaced by C ₆₀ , in other words, it should be easier to find an area of denser thiols.

6.4 Intermediate structure and dynamic of C₆₀ and decanethiol

This section is to consider the intermediate phase. Although it shows some degrees of regularity, it cannot be quantitatively analysed for modelling. I will focus on qualitative analysis to exhibit the motion of C₆₀ and the growth of regular phase.

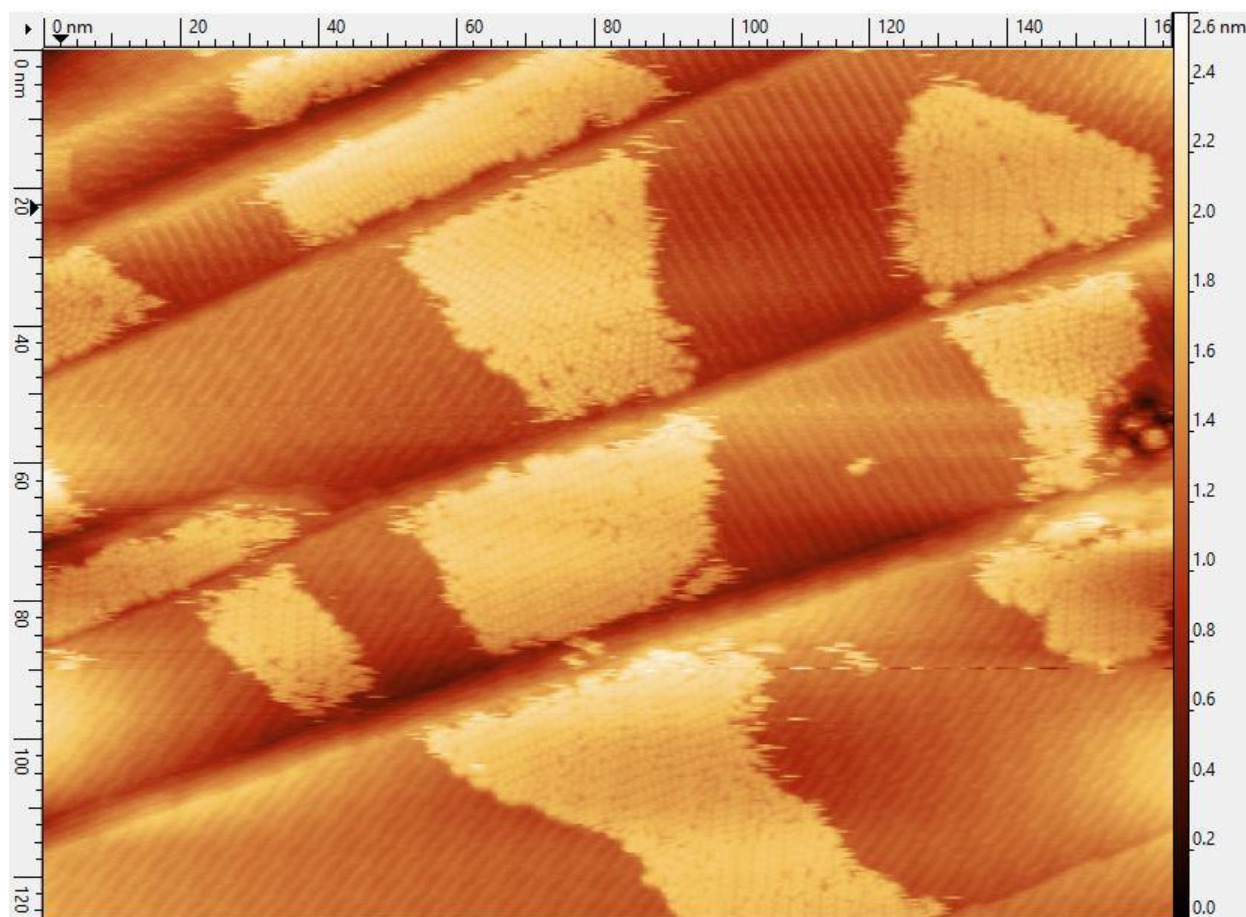


Fig 6.19. A STM image of many terraces and intermediate phase of C₆₀ molecules.

Firstly, referring the Fig 6.19. There are many terraces with striped phase of decanethiols and many regions constructed by intermediate phase of C₆₀. Although this image cannot be further analysed due to lower resolution, the intermediate phase is more common than uniform structures on narrow terraces.

Lower parts of Fig 6.6. is shown on Fig 6.20. line 1 may be inaccurate, since there is a gap between each group of two C₆₀ molecules, it is impossible to draw a long line to

measure the mean distance. However, the distance 1.1 nm indicate such two C_{60} has close touched. Along line 2, the mean distance and the angle between line 1 and 2 are close to that on uniform structure. This is the reason I named such phase as intermediate. Apart from they are not closed packed, some parameters are close to crystal. It can be predicted, if the groups of two C_{60} molecules can overcome the gap (decanethiol) between them, they can form uniform structure.

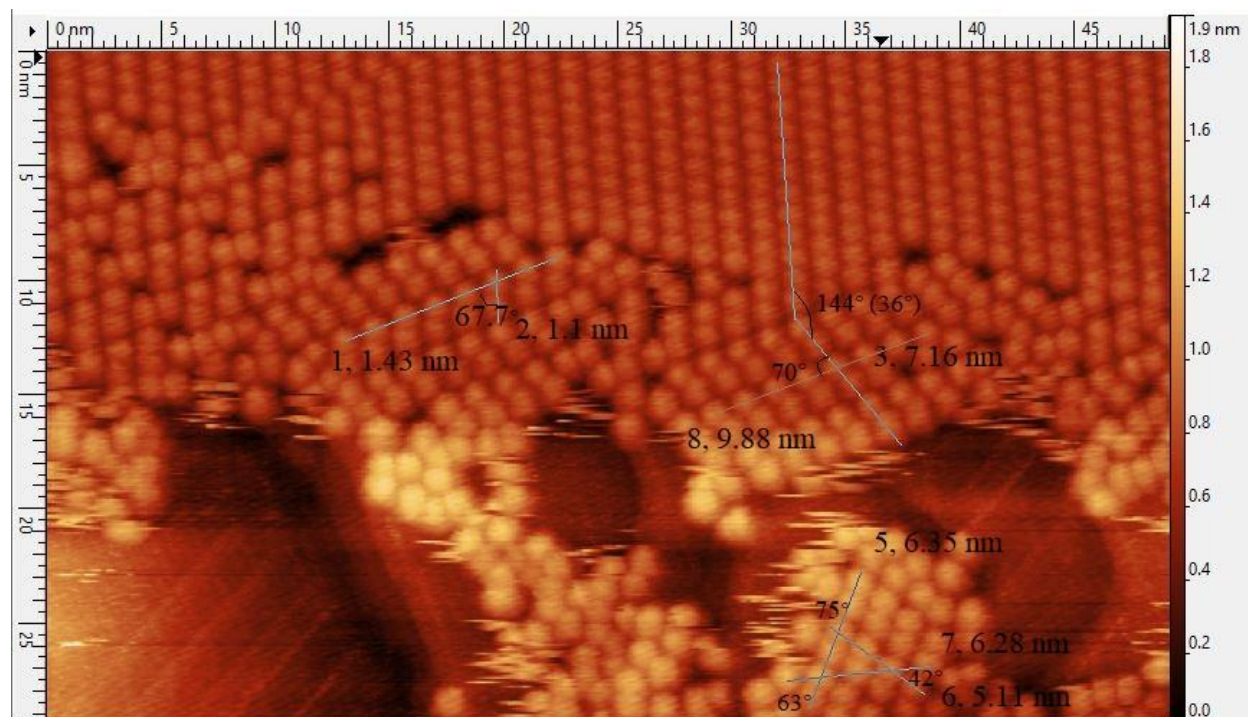


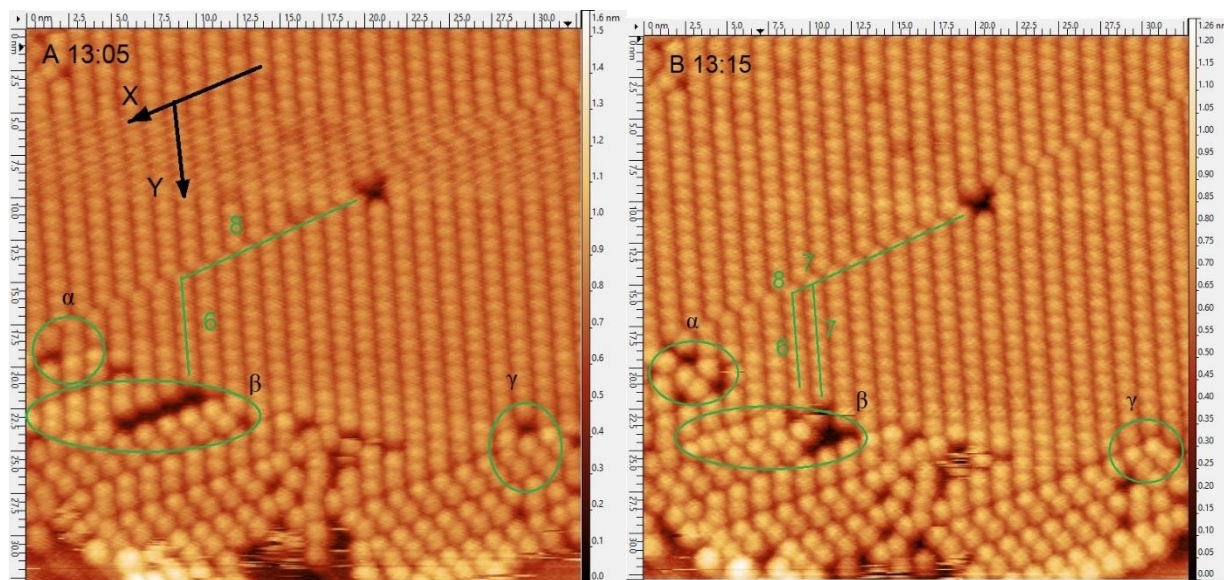
Fig 6.20. Lower parts of Fig 6.6. There are 8 featured lines 1- 8. Since Line 1 and 2 are uniform like in uniform structures, the length after line 1 or 2 is the distance of nearest C_{60} , while the last 6 distances are the total length of corresponding lines due to uneven distribution of C_{60} .

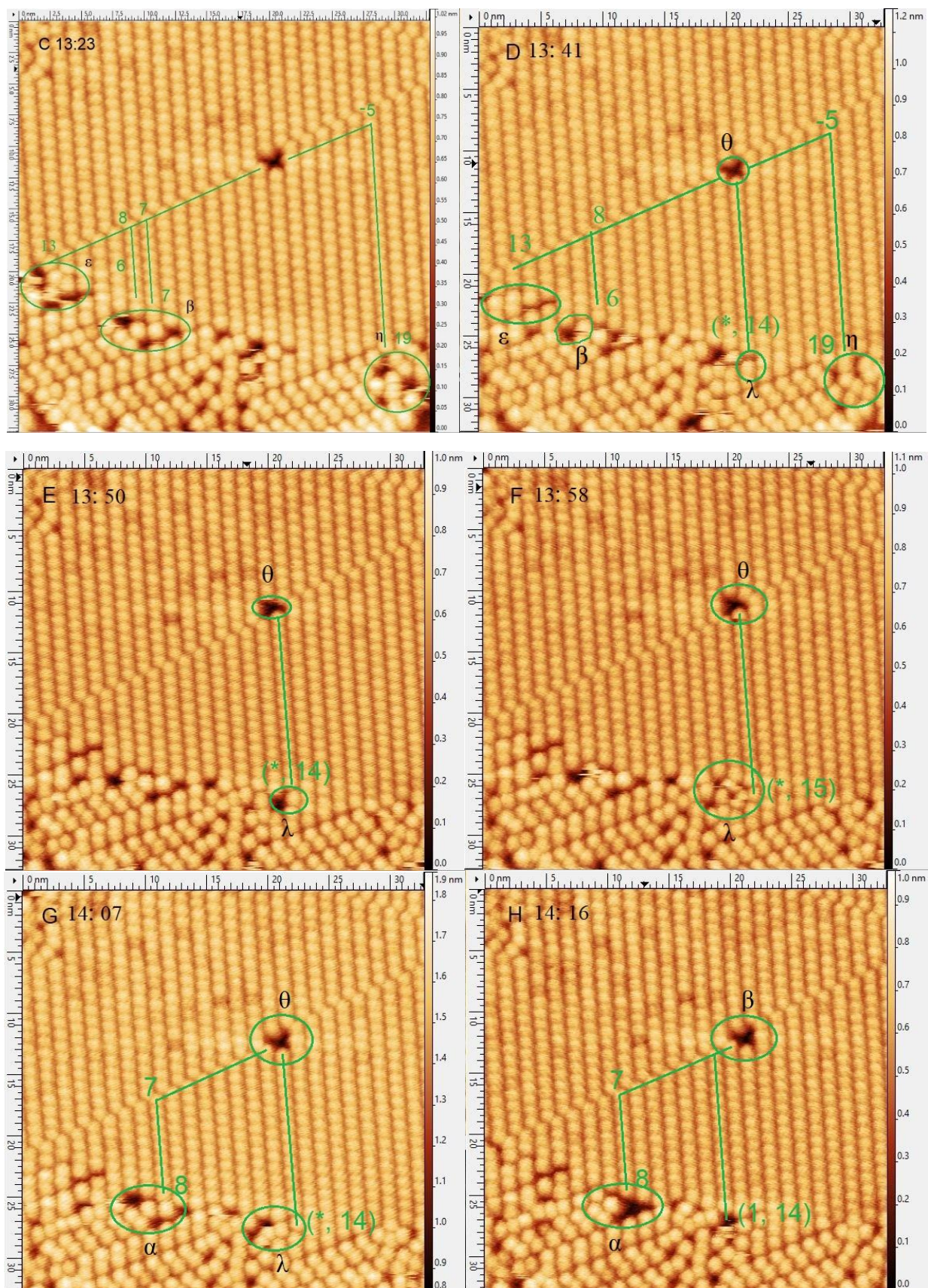
However, comparing the lengths, angles, and structures. There are not fixed structures of intermediates, but some features are interesting:

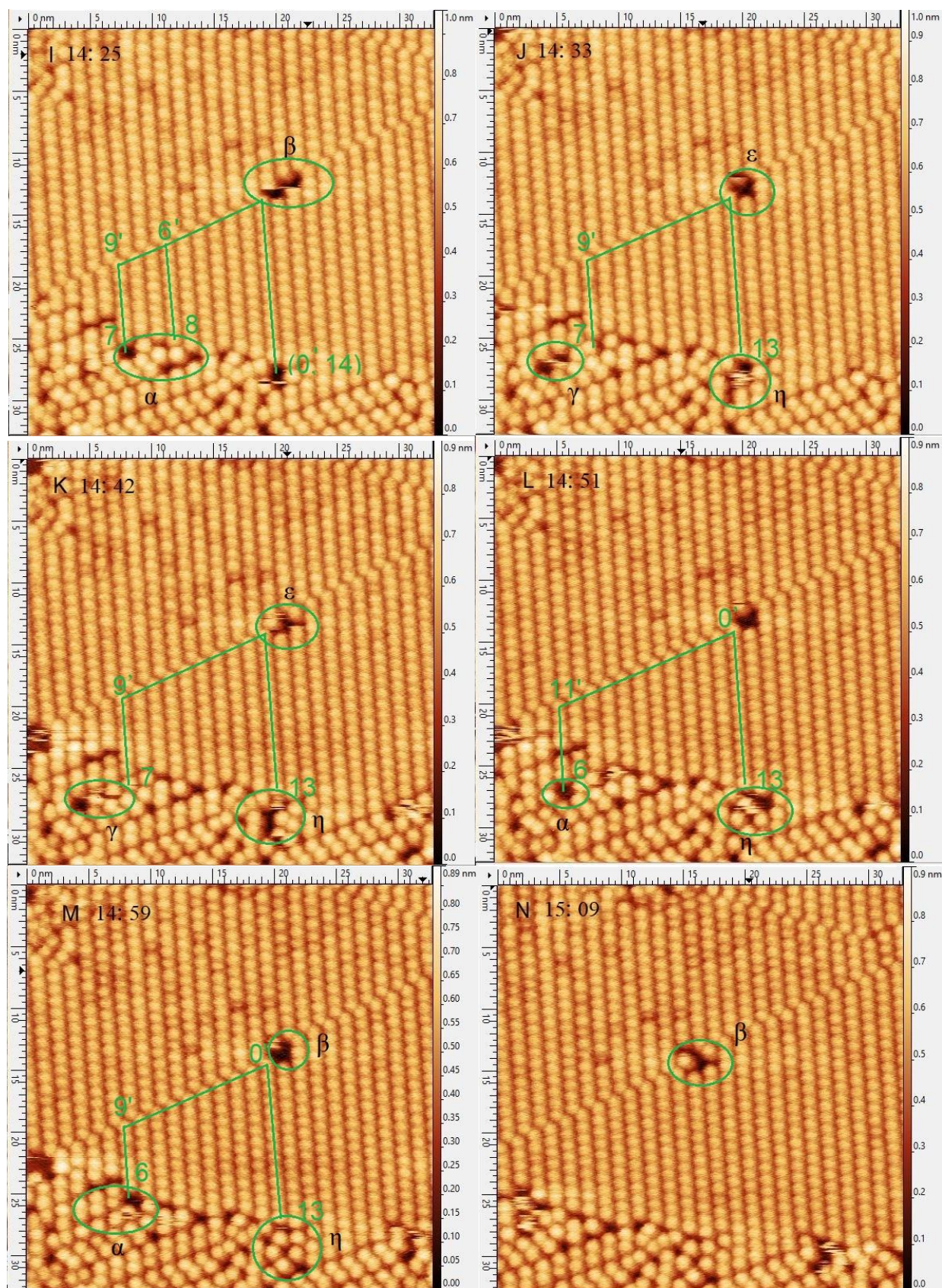
1. C_{60} molecules either come in pairs, or they (single or pairs) are separated by decanethiols. And there are only 1 pair of decanethiols between 2 units (single or pairs of C_{60} molecules).
2. The direction of such pairs is not random but have specific angles with decanethiols.

3. The distributions are the same along 2 non-closed packed direction.
4. The angle between two non-closed packed directions is approximately 40 degrees, while the angles between closed packed and either of non-closed packed are all around 70°.
5. The C₆₀ molecules on intermediate phase are more active. Comparing the upper and lower parts of Fig 6.20. There appear more ‘scratch lines’ in regions where molecules are not yet assembled into regular structures. According to the properties of STM, such scar may be either noise or moving molecules. However, the scars caused by noise should be extremely obvious periodicity along one direction. So, there are much more moving C₆₀ molecules than on uniform phase.

The formation of uniform phase is the competition among molecular thermal motion, their neighbouring stress and energy. The process of such formation at room temperature is exhibited on the following Fig 6.21.







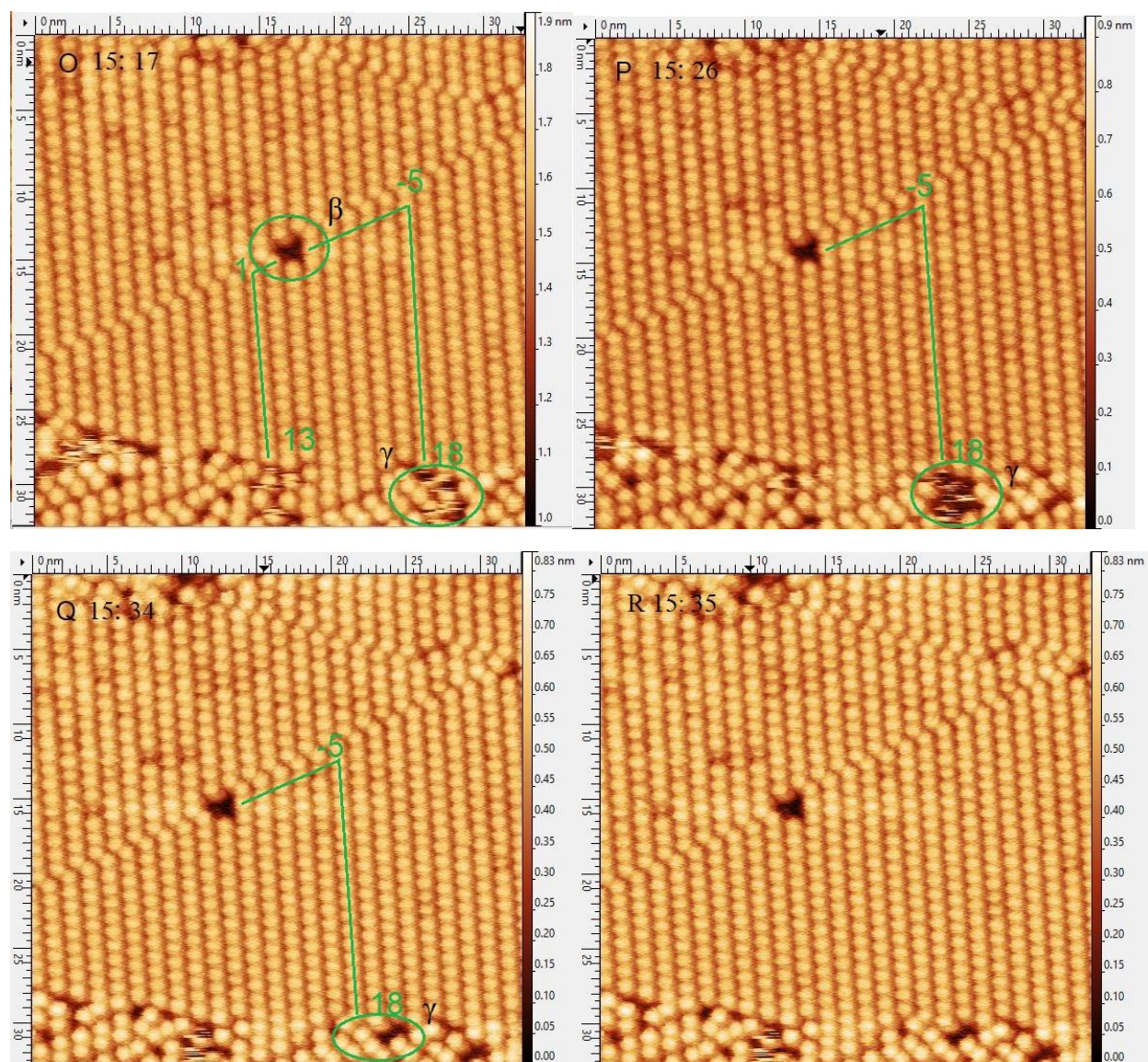


Fig 6.21. 18 images (A - R) to show the dynamic of formation of uniform C_{60} and decanethiols from intermediate phase at room temperature. The numbers on top left corner of each image indicate the time when the scanning is completed. The black hole as well as a line defect connecting it on each image can be used for positioning. In other word, the black hole is the origin of a XY coordinate system, X – axis along one non-closed packed direction and Y – axis along closed packed direction shown on A, some positions can be described in such coordinates. The circled regions on each image are the main change comparing with the previous or the next images.

Note:

1. Due to the irregular and changing shape of the black hole, the first molecules on the left and right sides of it are both marked as (0, 0), and its direct bottom is recorded as $X=*$.
2. Greek alphabet can only be used as marking to compare the same regions on adjacent images like A and B, or M and N, not for images that are too far away like C and O.

Table 6.2: Descriptions for changing between ambient images.

Comparison	Description
A, B	α : A complex motion leads to more defects. β : 4 C_{60} molecules push the elongated black region towards the right side, and one of molecules occupied (8,7). γ : 2 C_{60} molecules push the elongated black region towards the left side.
B, C	β : One C_{60} occupied (7, 8) and kept closed packed, split the hole into 3 small defects.
C, D	β : Substitution of C_{60} with defects. ε : A complex motion reduced the size of defects and extend uniform phase. η : One C_{60} occupied (-5, 20) and kept closed packed.
D, E	θ, λ : One C_{60} occupied (*, 15) and caused $X=*$ to move half a unit along (-Y) direction.
E, F	λ : A complex motion is shifting the defect near (*, 15).
F, G	θ, λ : The row $X = *$ moved half a unit along Y direction and make more organization around (*, 14).
G, H	α : 2 C_{60} molecules exchanged with a hole at top left and formed a larger hole near (7, 8)

H, I	β: C_{60} molecules around the black hole are moving to shift the position of the black hole along (+ X), this leads to the coordinate of the hole (1, 14) on H becoming (0', 14) on I. α: A motion of C_{60} leads to the formation of a hole at (9', 7), where 6' is 7 for previous black hole.
I, J	α, γ : C_{60} molecules pushed the hole at (9', 7) on I out of the uniform phase.
J, K	ϵ: Moving C_{60} is shifting the black hole. γ: Moving C_{60} is pushing a hole out of the uniform phase. η: A C_{60} is moving to (0, 14) in closed packed manner and pushing a hole out of the uniform phase.
K, L	The result of shifting black hole is no movement. η: A complex motion is shifting holes.
L, M	α: The hole at (11', 6) is moved back to (9', 6). η: A complex motion is splitting holes into smaller parts
M, N	β : The black hole is being moved.
N, O	Comparing the (0', 13) on M and (1, 13) on O, the black hole moved back to its initial position before H.
O, P	γ : A complex motion is expanding a hole.
P, Q	γ : A complex motion is reducing a hole.
Q, R	No obvious change due to one-min interval.

From the above description for dynamics, there are some conclusions listed below:

1. At room temperature, motion is not vigorous, some molecules may only move a few nanometres in several minutes.
2. The molecules on regions of mixed C_{60} , decanethiol and defects is much more active than molecules on uniform phase.

3. At regions of mixture of C_{60} , decanethiol and defects, a motion is random, i.e., the number and direction of moving molecules are both random.
4. A close-contacting pair of C_{60} can either move together or split away.
5. If a moving C_{60} is connecting to another C_{60} on uniform phase, the moving C_{60} tend to duplicate the pattern of uniform phase instead of occupying a random position. Then the C_{60} is less likely to move away.
6. According to 3 and 4, although the 'motion' of a hole is random, the probability of motion of a hole into uniform phase is less than moving away. As a result, the probability of expanding of uniform phase is greater than splitting. That is reason of stability SAMs.
7. A defects in uniform phase may increase the activity of C_{60} around, however, its motion towards any direction is random, it is less like to remove defects at room temperature.

7. Conclusions and Prospects

In the whole experiment, the sample of Au(111), decanethiol on Au(111) and C₆₀-decanethiol on Au(111) are investigated by the LT-STM. All scanning process is operated at ultra-high vacuum ($10^{-10} - 10^{-11}$ mbar), which ensures the stabilization of samples.

The investigation of Au shows herringbone reconstruction with low density of defects and steps. Such results are in agreement with previous work and hence the sample are of good quality for observing molecular adsorption with the STM.

After the immersion of decanethiols onto Au(111) at 4 °C for 24 hours, pits are observed on scanned images, indicating the formation of a saturated monolayer of decanethiol on Au(111). Such pits result from the extraction of Au atoms from the first layer and the extracted atoms are used to form RS-Au-SR. As the temperature increases from room temperature to just below 100°C, the pits undergo coalescence, i.e., the number of pits reduces with an increase in single pit area. Throughout the process, the whole area of pits remains constant. With a further increase in temperature, partial desorption of thiols occurs and the initial dense phase changes into a lower coverage stripped phase. On a surface of strip phase, all strips evenly segmented are along $[11\bar{2}]$, this is so called SAM.

Deposition of C₆₀ leads to the formation of 6 types of structures: striped phases of decanethiols with few C₆₀, islands of a few C₆₀ loosely distributed around defects, regular phase of mixed C₆₀/thiol, heptamers of C₆₀ surrounded by decanethiols, irregular mixture of C₆₀ and thiol, the last one can be used to observe dynamic in molecular exchange between different phases has also been observed.

The irregular phases are formed because of trapping of mobile C₆₀ molecules at defects or grain boundaries on the surface. Statistics of their mean areas and distances suggest that the mean values are negatively correlated with the size of irregular phases until some irregular phases merged together.

Regular phases provide enough information for modelling and a unit cell of the thiol/C₆₀ mixture is $10.4 \text{ \AA} \times 27.52 \text{ \AA} \ 69^\circ$, which contains two C₆₀ molecules. In this phase, C₆₀ are closed packed along one direction and are separated by one decanethiol along other two directions and the ratio of C₆₀: thiol is 1:2. The mean distance of nearest C₆₀ is 1.15nm, which is less than that in irregular phases.

Heptamers is another regular structure where every seven C₆₀ molecules closed packed and each heptamer is separated by one or two decanethiols. The corresponding model shows C₆₀ molecules within one heptamer are the densest in such phases in comparison with other structures. However, due to lack of key information, there are two possible models for heptamer. In the first model, each gold adatom is positioned at the middle point of a tunnel between two parallel edges of two heptamers of C₆₀ respectively, and every decanethiol is make 60° of elevation angle to Au(111), the density of thiol is closer to pure strip phase. The challenge lies in maintaining such an elevation angle. In the second model, each gold adatom is located at the centre of a triangle, whose vertices are 3 vertices of 3 adjacent hexagons respectively, and hence each decanethiol have enough space to lay down on Au(111), however the ratio of C₆₀ to thiol (7:3) raises a question regarding the location of the remaining decanethiol.

Intermediate phases exhibit semi-regularity with certain structures showing fluctuations around specific unknown values. A series of images taken at the same position on the sample provide insight into the semi-dynamic formation of the regular phases.

However, the formation of these structures contains many parameters, such as the chain length of alkanethiol, the coverage of striped phase of alkanethiol, and the amount of evaporated C₆₀. In addition, some processes are waiting for solution, like the transition from nucleation to intermediate phase, the thiol molecules squeezed together by C₆₀. Such problems require further investigation and analysis of using experimental and theoretical calculation.

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