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**SURFACE ORGANISATION AND TRANSISTOR ACTION
IN NAPHTHALOCYANINE AND PORPHYRIN NANORING
THIN FILMS**

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Abstract

In this thesis, the growth of metal-free naphthalocyanine (Nc) and copper naphthalocyanine (CuNc) on both bare Si/SiO₂ and octadecyltrichlorosilane (OTS) modified Si/SiO₂ surface were studied. The effects of the substrate temperature on morphology and structure of Nc and CuNc thin film growth were presented. For these purposes thin films of Nc and CuNc prepared by thermal vacuum evaporation were studied using atomic force microscopy (AFM) and X-ray diffraction (XRD). We observed that the increase of substrate temperature during growth affects the morphology, preferential molecular orientation and degree of crystallinity of both Nc and CuNc thin film, which were used as active layers in organic field effect transistor (OFET) devices. Organic thin film transistors (OFETs) were fabricated using these molecules as the active layers and their electrical characteristics were measured under both vacuum and atmospheric conditions and they were found to exhibit p-type transistor action.

A series of samples of the Nc and CuNc thin films were grown on Si/SiO₂ and OTS-modified oxide surface at different substrate temperature but fixed equivalent deposited thickness. The growth conditions, particularly the substrate temperature strongly affect nucleation size and shape of the organic thin film. In general, the thin film morphology shows a near circular grain and elongated grain shape at low substrate temperature, while the thin Nc film shows small needle-like structure and extended needle-like crystalline structures with large gaps at high substrate temperature. The optimum substrate temperature during the growth of Nc on both surfaces is achieved at 200 °C, and this occurs for growth of CuNc at 180 °C and 160 °C on Si/SiO₂ and OTS surfaces, respectively, for which the naphthalocyanine thin film shows the best morphological and electrical properties.

We used Nc and CuNc thin films prepared at different substrate temperatures as active layers to fabricate bottom and top-contact organic field effect transistors. Their electrical characteristics were measured at room temperature in vacuum and air in the dark. We plotted the output characteristic and transfer characteristic of all OFET devices so that the effects of grain size and crystal structure on the

performance characteristic of Nc OFET device could be investigated. Then we studied the effects of hysteresis and charge traps on device performance when exposed to air. We found that the changes generated by exposure of the device to atmosphere may be reversed by annealing the thin film to ~ 100 °C in vacuum. We reported the highest mobility of $(5.16 \pm 0.23) \times 10^{-2} \text{ cm}^2/\text{Vs}$ for top-contact Nc device prepared at 200°C on SiO₂ after annealing in vacuum, and also we reported the highest mobility of $(3.56 \pm 0.14) \times 10^{-2} \text{ cm}^2/\text{Vs}$ for top-contact CuNc device prepared at 180°C on SiO₂ after annealing in vacuum. We found that the top-contact device always performs better than the bottom-contact device. We attributed this to the change of morphology of active layer in the interface between contact metal and SiO₂.

Solvent induced self-assembly, self-trapping, and self-organizing of c-P30 cyclic porphyrin polymers on the Au surface that are deposited from two solutions and various concentrations in ambient condition was also studied. This results in the arrangement of cyclic polymers in different configurations such as stacking columnar, supramolecular nesting and uniform height hexagonal close packed structure. These conformations are observed using scanning tunnelling microscopy. Highly covered surface stacking columnar like porous array is also observed. We show that toluene:methanol mixture can play a crucial role in self-assembly of supramolecular structure in two dimensions, π - π stacking conformation perpendicular over surface in three dimensions and single in double nested nanoring conformation. Cyclic porphyrin polymers deposited from toluene shows nested nanorings structure, such as single nanoring self-trapped inside a near-circular shape single ring on surface. Diluted solutions using a large volume of methanol relative to the toluene can suppress the adsorption of nanorings to the surface. Interestingly, adsorption of the cyclic polymer from toluene:methanol 3:5 can result in the formation of uniformly height hexagonal close packing on surface, where nanorings aggregate as columnar stacks in two layers, dependent on concentration. Our results show that the self-assembly of artificial cyclic polymers is dependent on solvent and concentration provides a significant step towards control of the three-dimensional arrangement of supramolecular conformation on surfaces using non-covalent interactions.

List of Publications

Kondratuk, Dmitry V., Luís MA Perdigão, Ayad MS Esmail, James N. O'Shea, Peter H. Beton, and Harry L. Anderson. "Supramolecular nesting of cyclic polymers." *Nature Chemistry* 7, no. 4 (2015): 317-322.

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Acronyms

AA	After annealed sample
AECNc	Copper naphthalocyanine sample
AENc	Napthalocyanine sample
AFM	Atomic force microscopy
Ar	Aryl groups
Au(111)	Gold on mica substrate
BA	Before annealing sample
C₆₀	Fullerene molecule
c-PN	Cyclic porphyrin polymer
CuNc	Copper naphthalocyanine
CuPc	Copper phthalocyanine
fcc	Face centered cubic
hcp	Hexagonal close packed
HOMO	Highest occupied molecular orbital
HOPG	Highly oriented pyrolytic graphite substrates
I(V)	Current voltage characteristic
K-cell	Knudsen cell
LDOS	Local density of states
LEDs	Light-emitting diodes
l-PN	Linear porphyrin oligomer
LUMO	Lowest unoccupied molecular orbital
MOSFET	Metal oxide-semiconductor field effect transistor
MPc	Metal phthalocyanine
Nc	Metal-free naphthalocyanine
OFETs	Organic field effect transistors
OTS	Octadecyltrichlorosilane
OVPD	Organic vapor phase deposition
Pc	Phthalocyanine
SAMs	Self-assembled monolayers
Si/SiO₂	Silicon/silicon dioxide substrate
STM	Scanning tunneling microscopy
T_s	Substrate temperature
XRD	X-ray diffraction
γ_f	Film surface energy
γ_i	Substrate and film interface energy
γ_s	Substrate surface energy

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Chapter 1

Introduction

Organic semiconductors are attractive materials for applications in organic field-effect transistors (OFETs), gas sensors, photovoltaic solar cells and light-emitting diodes (LEDs) due to their easy processability (low temperature evaporation and solution processing), low costs, tunable chemical structures, compatibility with flexible substrates, strong optical absorptivity and efficient light emission [1]. In particular, the small-molecule organic semiconductors such as porphyrins and phthalocyanines are interesting species that have been used as active layers in organic field effect transistors in which a thin film is formed by deposition of the organic semiconductor on a suitable substrate [2-4]. High performance organic field effect transistor (OFET) can be formed for thin films with a high degree of molecular order. Typically, the substrate temperature can be used to control ordering and orientation of the molecules [5].

1.1 Organic Molecular Structure

The building block of all matter is the atom. When two or more atoms are brought together, the interaction of their valence electrons can result in the combining of their atomic orbitals, thus giving rise to molecular orbitals which can be either bonding or antibonding.

Bonding molecular orbitals are generated from linear combinations of atomic orbitals that lead to lower energy than the original atomic orbitals. However, antibonding molecular orbitals lead to higher energy levels and are generally not stable. Therefore, the single energy levels of an atom combine to form two molecular energy, and their separation is related to the strength of the interaction of atomic orbitals. The ground state is the lowest energy orbitals that is filled by electrons. The highest occupied molecular orbital (HOMO) is the highest energy orbital, which is filled by electrons. The lowest unoccupied molecular orbital (LUMO) is the lowest energy orbital, which is not filled by electrons. A further classification is determined by the molecular-orbital symmetry, such as the σ

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(sigma) bond that is symmetrical with respect to rotation around the internuclear axis, and the π bond that is asymmetric. Generally, the σ bond is stronger than the π bond. Antibonding orbitals labelled σ^* and π^* are also formed but normally are unfilled.

The electronic ground state configuration of an isolated carbon atom is ($1s^2 2s^2 2p_x^1 2p_y^1$). This implies that it can only form two covalent bonds with other atoms. [6]. When other atoms are close to the carbon atom, one of the carbon 2s electrons will promote to the unoccupied 2p orbital, thus the carbon atom forms an excited state ($1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$), implying that the four valence electrons are available for bonding. If the 2s combines with one, two, or three of the 2p orbitals, this will lead to form hybridized atomic orbitals of two sp, three sp^2 , or four sp^3 , respectively. For example, CH_4 forms four sp^3 , both C_2H_4 and C_6H_6 form three sp^2 while the remaining electron in p-orbital ($2p_z$) leaves un-hybridized that is perpendicular to hybridized orbitals, overlapping p_z orbitals will lead to form π bond between carbons and result in delocalisation π electron (see figure 1.1.1) and also C_2H_2 form two sp molecular orbitals [7].

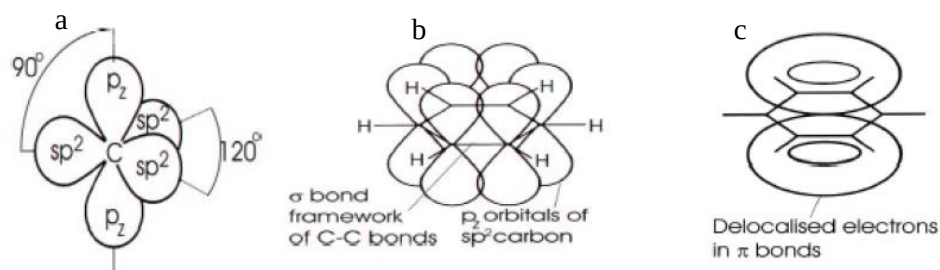


Figure 1.1.1: Orbitals of carbon atom: a) carbon atom with three sp^2 hybrid orbitals and one p_z un-hybridized orbital b) structure of benzene ring (C_6H_6) with σ bonds form by overlapping sp^2 orbitals between (C-C) and (C-H), and also p_z orbital exists in each carbon atoms with direction perpendicular to the sp^2 orbitals plane c) π bond form by overlapping p_z orbitals resulting in delocalisation π electron [7].

1.2 Basic properties of organic semiconductors

Organic materials behave like semiconductors because their molecules have a π -conjugated system in which carbon atoms are bonded by alternating single and double bonds. It is possible to use these materials to fabricate semiconductor

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devices, such as OFETs, solar cells and LEDs. Organic semiconductors can exist in two forms such as small molecule (copper phthalocyanine) and organic polymers like poly (benzimidazobenzophenanthroline) see Figure 1.2.1.

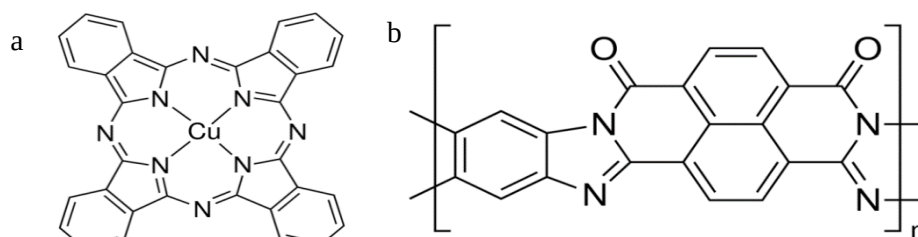


Figure 1.2.1: Organic semiconductors into two form such as a) small molecule (copper phthalocyanine) and b) organic polymer Poly (benzimidazobenzo-phenanthroline)

Figure 1.2.2 illustrates the energy level of a π -conjugated molecule. The bonding π -orbital has a low energy as compared to the anti-bonding π^* -orbital, there is a π - π^* band gap with a typical energy gap in the range 1.5-3 eV, which corresponds to a photon energy in the range of the visible spectrum. This energy gap makes it possible for organic materials to behave like semiconductors [8].

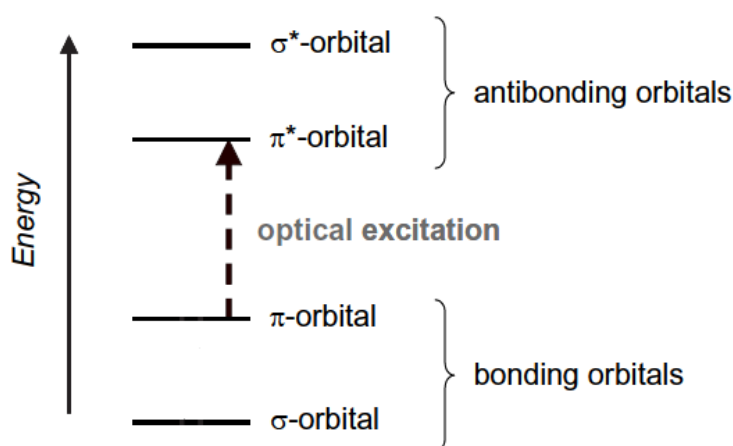


Figure 1.2.2: The energy levels of a π -conjugated molecule show the bonding π -orbital with low energy and the lowest electronic excitations is π - π^* band gap [8].

1.3 Porphyrins and phthalocyanines

The structure of porphyrin (Figure 1.3.1a) and phthalocyanine (Figure 1.3.1c) shows some similarity with the biological molecules chlorophyll and haemoglobin, and also their chemical and thermal stabilities make them interesting species to be studied for many applications in industry. The porphyrin is a macrocyclic planar aromatic compound, which has an extensive delocalized π -electron system, providing unique chemical and physical properties, and many researchers have studied their optical and electrical properties [9]. These molecules can also form a complex by coordination with a metal atom in the central cavity of the macrocycle with four pyrrole nitrogens (Figure 1.3.1b, d).

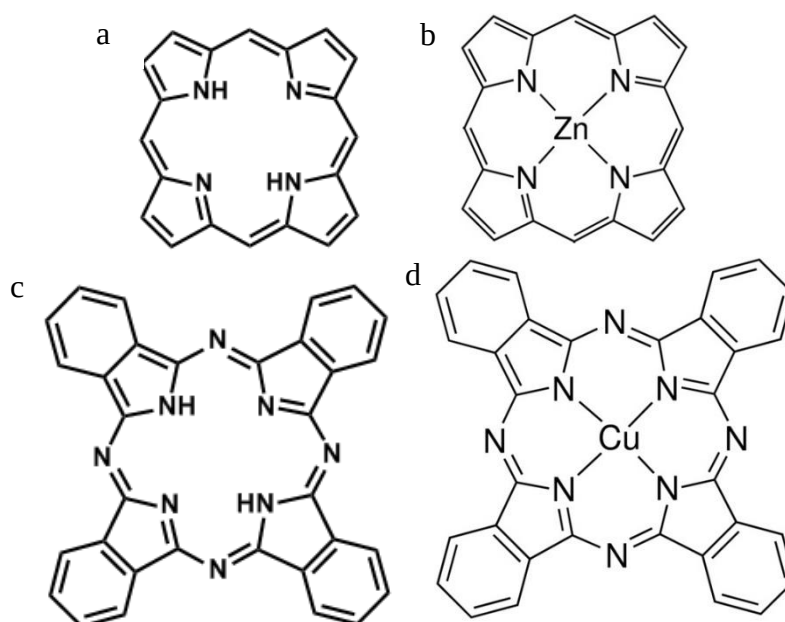


Figure 1.3.1: Molecular structures of metal-free porphyrin (a), zinc porphyrin b and metal-free phthalocyanine (c) and copper phthalocyanine (d)

Figure 1.3.2 show the highest occupied molecular orbital (HOMO) of isolated metal phthalocyanine. This corresponds to the valence band in inorganic semiconductors and its lowest unoccupied molecular orbital (LUMO) corresponds to the conduction band [10].

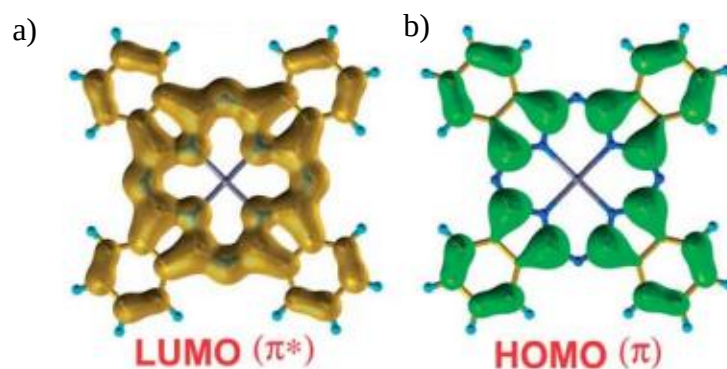


Figure 1.3.2: Schematic diagram of a) the lowest unoccupied molecular orbital π^* , b) the highest occupied molecular orbital π of an isolated metal phthalocyanine [10]

Figure 1.3.3 shows the energy-band diagrams of a phthalocyanine OFET in a p-channel mode of operation, including the highest occupied molecular orbital and the lowest unoccupied molecular orbital. The energy band diagram for zero gate voltage (V_g) is shown Figure 1.3.3 a. In the energy band diagram at negative applied gate voltage shown in Figure 1.3.3b, the bands are bent upwards and the HOMO approaches the fermi level, this leads to an accumulation of holes near the interface between SiO_2 and organic material [11]. Therefore, this active layer can be used as p-channel OFET device.

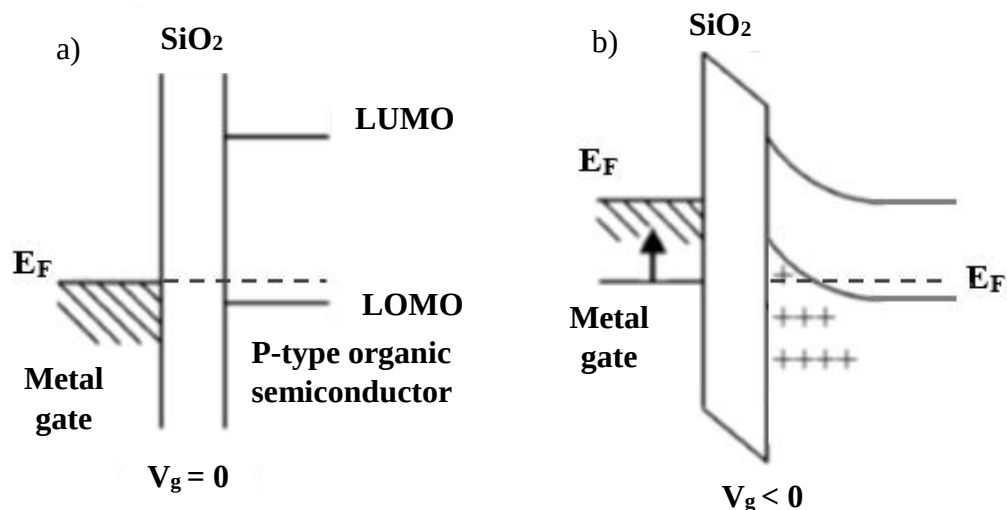


Figure 1.3.3: Schematic energy-band diagram shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for phthalocyanine OFET, which has structure of metal-oxide-(p-type) semiconductor. a) The OFET at no gate bias. b) The OFET at negative gate bias show the p-channel devices.

OTFTs have been widely fabricated using small molecules as active semiconducting layers. Many small molecule organic semiconductors have been used for fabricating OFETs such as rubrene [12] phthalocyanine [13] pentacene [14], porphyrazine [15], and thiophene [16] derivatives.

A great challenge for optimizing the performance of OFETs is to control the film morphology and orientation of organic semiconductor molecules. Improvements in charge mobility and charge injection across electrodes and organic semiconductor interface typically occur when molecules order in a π - π stacking configuration with an edge-on orientation [17]. Therefore, it is important to know how molecules interact with the substrate surface in order to make it possible to control the arrangement of molecules on a surface [18]. Since the intermolecular forces in organic films are weak, the molecule-substrate interaction will modify the arrangement and packing of molecules in different structures on a surface [19, 20]. Therefore, the type of substrate surface is an important parameters for controlling molecular ordering and orientation in the films. For example when metal phthalocyanine (MPc) is deposited on the most commonly used substrate (SiO_2 or indium-tin oxide (ITO)), at high substrate temperature the molecules stand edge-on orientation, due to the weak interaction at the surface-molecule interface [21]. The OFETs show the highest performance in this orientation [5].

Among different organic semiconductors, the most broadly studied small molecule organic semiconductors are phthalocyanine derivatives [11, 22-24]. In contrast, porphyrins, another species of tetrapyrrole derivatives, have been less investigated. There are limited reports of fabrication of OFET devices based on porphyrin compounds. For example in 2004, Aramaki et al. reported solution processed OFET device for planar structure tetrabenzoporphyrin compound [25], and also in 2003, Noh et al. reported sublimation deposition OFET device of 2,3,7,8,12,13,17,18-octaethyl-porphyrinato platinum [26]. In 2010, Ma et al. reported single crystals of metal-free 5,10,15,20-tetrakis(4-pentyloxyphenyl)porphyrin, which were used to fabricate OFET with relatively good performance [27].

Although the semiconductor properties of phthalocyanine molecules have been extensively investigated, the fabrication of OFETs from the larger analogue molecule naphthalocyanine (Nc) (Figure 1.3.4) has been limited to solution processed Nc derivatives with attached side groups in order to promote solubility [28]. The thin film properties of sublimed naphthalocyanine molecule have been rarely studied [29-31], although, several groups have sublimed monolayers of Nc molecules on surfaces [32-36].

In this thesis, we report the first demonstration of Nc OFETs under both vacuum and atmospheric conditions. These devices show p-type operation, and we also discuss Nc thin film growth by thermal evaporation on silicon oxide at various substrate temperatures as investigated using both atomic force microscopy (AFM) and X-ray diffraction (XRD).

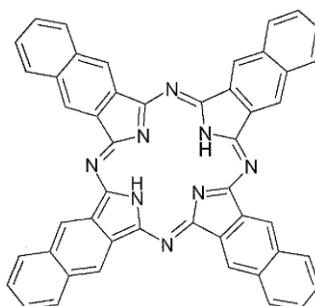


Figure 1.3.4: Molecular structures of naphthalocyanine

Also we have investigated the self-assembly of cyclic porphyrin polymers on Au(111) which result in a new mode of supramolecular organisation of nanorings when deposited from solution [37]. The porphyrin polymers show a disordered arrangement due to their flexibility [38]. These combine to give the cyclic polymers unique forms of surface organization such as stacking and nesting [37].

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Chapter 2

Organic field effect transistors and theory of thin film growth

In this chapter, we describe the organic semiconductor materials, and how they were used in organic field effect transistor (OFET), and the progress that has been made on this device, and also we describe the theory behind operation mode of the OFET system, the results give the current and mobility equation.

We describe the supramolecular organisation on surface using solution and evaporation methods. Finally, we explain theory of thin film growth.

2.1 Organic semiconductors

Organic semiconductors are π -conjugated molecules that contain carbon and hydrogen, as well as other elements, such as oxygen, sulfur and nitrogen. Organic semiconductors can be divided into two systems, small molecules and polymers. Examples of small molecule semiconductors are aromatic hydrocarbon compounds, such as pentacene, oligothiophenes and phthalocyanines. Thin films of small molecules can be thermally deposited and/or solution processed and can form highly ordered crystalline structures. Examples of polymer organic semiconductors are polyacetylene, polythiophenes and their derivatives. Polymeric materials are usually deposited from solution and form disordered structures on a surface.

There are important differences between organic and inorganic semiconductor materials. In conventional semiconductor or inorganic semiconductors such as Si and Ge atoms form covalent bonds which stabilise the crystal structure. However, molecular organic semiconductors bind through van der Waals interactions. Therefore, conventional semiconductors typically form a crystalline structure, but molecular organic semiconductors often form polycrystalline or amorphous films and have lower dielectric constant and a lower shielding of charges, which implies that the coulomb interaction between charge carriers is stronger than in conventional semiconductors [1]. Generally, inorganic semiconductors have high charge carrier mobility as compared to organic semiconductors. Therefore, it is difficult for transistors based on organic

thin films to compete with inorganic transistors in applications demanding high performance. Nevertheless, organic semiconductors are interesting materials for electronic devices because they can be deposited on different substrates with very low cost and cover large areas. Such substrates include polymers, glass and metal foils. In addition, organic compounds can easily be processed in solution or using vacuum deposition. Furthermore, organic polymer thin films are not only compatible with silicon substrates but also with flexible substrates [2]. Organic semiconductors have been used to fabricate many different electronic devices, for example, organic field effect transistors (OFETs), organic light-emitting diodes (OLEDs) and solar cells are the most advanced systems, which already have been produced and are available commercially including very bright, highly efficient colour displays [3]. There is also significant progress made in the fabrication of OFET [4, 5] and organic thin film photovoltaic cells for the generation of low cost solar energy [6]. The main disadvantage of organic semiconductors is their sensitivity to exposure to air. Organic electronic devices can be encapsulated in order to avoid film degradation resulting in extended life time [6].

In 1930 Lilienfeld, who first proposed the principle of the field-effect transistor (FET), described the operation of a FET device as a capacitor in which one plate, a semiconductor film, acts as a channel between two contacts. The accumulation of charge carriers in the channel can be tuned by changing the voltage across the capacitor; this is the gate voltage. Organic materials were known as a new type of semiconductor in the 1940s [7]. The first metal oxide-semiconductor field effect transistor (MOSFET) based on silicon was fabricated in 1960 [8]. In 1986, Tsumura and et al. first reported the fabrication of an organic field effect transistor based on polymeric organic semiconductors [9]. In 1989, Horowitz reported an organic field effect transistor based on a small conjugated molecule, a α -sexithienyl [10]. The OFETs based on small molecules showed high performance as compared to those with a polymer active layer. In 2003, Kelley et al. fabricated OFETs based on pentacene and reported a high mobility of 5 cm²/Vs. This is attributed to high ordering of molecules [11]. In 2002, Sandberg et al. reported that two orientations of poly(3-alkyl-thiophene) film are observed with the polymer chain either parallel or perpendicular to the surface. The

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highest mobility of $0.1 \text{ cm}^2/\text{Vs}$ was observed when polymer chains were in an edge-on orientation [12]. These were deposited by spin coating and the mobility could be increased up to $0.2 \text{ cm}^2/\text{Vs}$ when polymer was deposited by dip-coating [13].

2.2 Organic field effect transistor (OFET)

[8, 14, 15]

The basic structure of an organic field effect transistor consists of the following components: source and drain electrodes are in contact with an organic semiconductor thin film, which is insulated from the gate electrode by an oxide layer with thickness, t_{ox} , (see figure 2.2.1). The organic semiconductor is an active layer which allows a conducting channel to form between source drain electrodes. The channel has length L and width W .

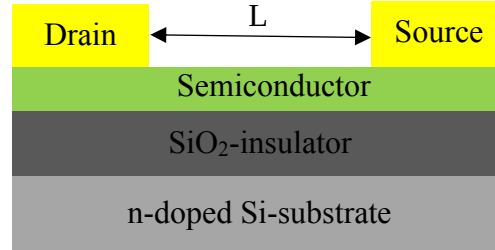


Figure 2.2.1: The basic structure of top- contact organic field effect transistor (OFET)

2.2.1 Device operation

An organic field effect transistor structure (as shown in previous section) is arranged as gate/oxide/organic semiconductor stack. This configuration is comparable to the planar capacitor that consists of parallel plates separated by dielectric, with a capacitance per unit area of oxide, C_{ox} ,

$$C_{ox} = \frac{\epsilon_{ox} \epsilon_o}{t_{ox}} \quad 2.2.1$$

ϵ_{ox} is the relative permittivity of the oxide, and ϵ_o is the vacuum permittivity.

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In order to take electrical measurements, two potentials are applied across the device, the gate voltage, V_g , and drain voltage, V_d , while the source electrode is earthed ($V_s = 0$) (see Figure 3.2.14 in chapter 3).

Generally, organic field effect transistors operate in the accumulation mode because charge carriers accumulate at the SiO_2 -semiconductor interface when a gate voltage are applied [11]. Accumulated charges are injected from the source electrode. The OFET may form either n-channel or p-channel depending on whether holes (positive charges) or electrons (negative charges) are accumulated in the organic semiconductor-oxide interface by applying gate voltage. For example, the channel is called p-channel if holes are accumulated at the interface due to applying a negative gate voltage while it is called n-channel if electrons accumulate due to applying a positive gate voltage.

The accumulated charge in the channel is equal to the gate voltage multiplied by the capacitance of the oxide. However, some of these charges will not contribute to current in the device because they are trapped at trap sites at the oxide/organic semiconductor interface. Therefore, the gate voltage should be higher than the minimum voltage that requires to fill these traps before the transistor channel is turned on. This is the threshold voltage, V_{th} . The charge trap density Q_t [16], is given by

$$Q_t = C_{ox} V_{th} \quad 2.2.2$$

Therefore, the effective gate voltage is $V_g - V_{th}$. The threshold voltage depends strongly on the organic semiconductor layer and oxide material in the transistor. The accumulated free charge carriers per unit area, or charge carrier density, Q_s , that is induced in the channel by applying a specific gate voltage ($V_g > V_{th}$) only, without applying drain voltage, can be determined by

$$Q_s = C_{ox} (V_g - V_{th}) \quad 2.2.3$$

From the above discussion, if gate voltage exceeds the threshold voltage, a uniform distribution of the charge carriers will be induced in the channel as shown in Figure (2.2.2a), but applying a drain voltage results in form a linear gradient of charge density in the channel from source to the drain electrode

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Figure (2.2.2b, c). Therefore, the potential within channel varies with channel position, x , from the source electrode ($x = 0, V(x) = 0$) to the drain electrode ($x = L, V(x) = V_d$). The charge carrier density that is induced in the channel depends on the position, x , along the channel, and can be determined by

$$Q_s = C_{ox} (V_g - V_{th} - V(x)) \quad 2.2.4$$

The resistance of the channel, R , of an elemental section dx is given by

$$dR = \frac{dx}{W Q_s(x) \mu} \quad 2.2.5$$

where μ is the field effect mobility of the semiconductor.

The potential drop, dV , across dx is given by

$$dV = I_d dR = \frac{I_d dx}{W Q_s(x) \mu} \quad 2.2.6$$

The drain current I_d can be obtained if we substitute $Q_s(x)$ from Equation 2.2.4 and then integrated both sides of the equation 2.2.6 from source ($x = 0, V(x) = 0$) to the drain ($x = L, V(x) = V_d$), assuming that μ is independent of the charge carrier density as follows

$$I_d \int_0^L dx = W C_{ox} \mu \int_0^{V_d} (V_g - V_{th} - V(x)) dV \quad 2.2.7$$

$$I_d L = W C_{ox} \mu \left(V_g - V_{th} - \frac{V_d}{2} \right) V_d \quad 2.2.8$$

Based on the I-V characteristics of an ideal OFET shown in Figure 2.2.2, [15] we now can simplify Equation 2.2.8 for the linear and saturation regions [8]. If we apply a small drain voltage, there will be a flow of current through the conducting channel between source and drain. The linear variation of drain current I_d with increasing drain voltage V_d , implies the channel can act as a resistor. This is called the linear region, as illustrated in Figure 2.2.2a [17]. In the linear region the drain voltage V_d is smaller than effective gate voltage $V_d \ll$

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$(V_g - V_{th})$, therefore the term $V_d^2/2$ can be neglected; the drain current equation can be simplified to

$$I_d = \frac{W}{L} C_{ox} \mu_{lin} (V_g - V_{th}) V_d \quad 2.2.9$$

The mobility of the OFET in the linear regime (μ_{lin}) can be calculated by differentiating Equation 2.2.9 with respect to V_g at constant V_d

$$\mu_{lin} = \frac{L}{WC_{ox}V_d} \left. \frac{\partial I_d}{\partial V_g} \right|_{V_d=\text{constant}} \quad 2.2.10$$

By increasing the drain voltage V_d until it reaches the effective gate voltage ($V_d = V_g - V_{th}$), at this point V_d is known as saturation drain voltage ($V_d = V_{Dsat}$) results in pinch-off the channel near to drain electrode. The pinch-off occurs because a charge-depleted region is induced next to the drain electrode. This leads to a saturation of the drain current, I_d^{sat} . The pinch off point indicates the beginning of the saturation regime (Figure 2.2.2b).

Further increases in the drain voltage V_d until it becomes larger than the effective gate voltage ($V_d > V_g - V_{th}$), leads to an expanded charge-depleted region while the drain current does not increase. Consequently, the pinch off point move toward the source electrode, this results in reduction in the channel length (L'), but the potential remains unchanged ($V(x) = V_g - V_{th}$) at the pinch-off points (Figure 2.2.2c). For this reason the drain current remains constant: this is known as the saturation drain current I_d^{sat} and called the saturation region.

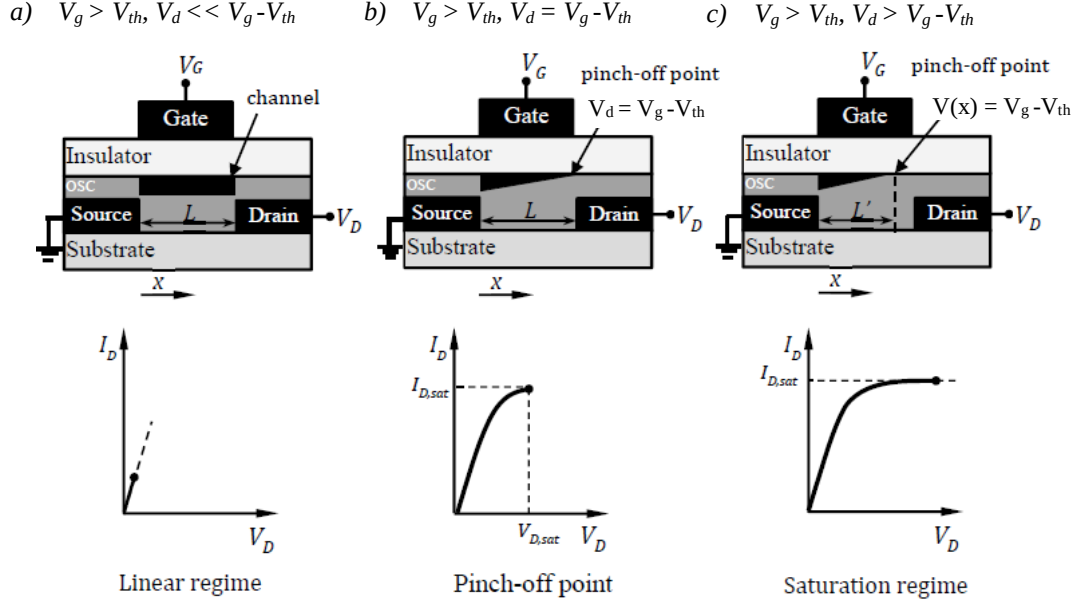


Figure 2.2.2: Schematic diagrams of the different operating regimes of an OFET and the corresponding I_d versus V_d curves a) the linear region ($V_d \ll V_g - V_{th}$) b) the beginning of the saturation regime at pinch-off point ($V_d = V_g - V_{th}$) c) saturation region ($V_d > V_g - V_{th}$) [17].

In the saturation region, at $V_d = (V_g - V_{th})$, the drain current I_d^{sat} is pinched off at accumulated regime and does not dependent on V_d , implying $\frac{dI_d}{dV_d} = 0$. Therefore, by neglecting channel shortening to L' , the saturation drain current I_d^{sat} is given by substituting $V_d = V_g - V_{th}$ into Equation (2.2.8) as follows

$$I_d^{sat} \simeq \frac{W\mu_n C_{ox}}{L} \frac{V_d}{2} V_d \quad 2.2.11$$

$$I_d^{sat} \simeq \frac{W\mu_n C_{ox}}{2L} (V_g - V_{th})^2 \quad 2.2.12$$

The mobility of an OFET device in the saturation regime μ_{sat} can be calculated by differentiating the square root of the saturated drain current I_d^{sat} in Equation (2.2.12) with respect to V_g

$$\sqrt{I_d^{sat}} \simeq \sqrt{\frac{W\mu_n C_{ox}}{2L}} (V_g - V_{th}) \quad 2.2.13$$

$$\frac{\partial \sqrt{I_d^{sat}}}{\partial V_g} \simeq \sqrt{\frac{W \mu_n C_{ox}}{2L}} \quad 2.2.14$$

$$\mu_n \simeq \frac{2L}{WC_{ox}} \left[\frac{\partial \sqrt{I_d^{sat}}}{\partial V_g} \right]^2 \quad 2.2.15$$

In this thesis, all mobilities for OFET devices are calculated from the saturation regime.

The Equations 2.2.8, 2.2.9, 2.2.11, 2.2.12 are based on ideal conditions, such as the insulator having no charges, the semiconductor-insulator interface having no charge traps, also assuming the work function of the metal and semiconductor are equal, the charge carriers in the channel have constant mobility, also neglects contact resistances, and the channel length must be larger than oxide thickness ($L \gg t_{ox}$) [18]. These equations are nevertheless used widely to calculate mobility in OFET devices.

2.3 Progress in performance n- and p-channel organic transistors

Both conventional inorganic and organic semiconductor materials can show either p-type or n-type characteristics. Pentacene is an example of a p-type organic semiconductor (see Figure 3.2.15). Pentacene is the most widely studied material for OFETs because this semiconductor shows high mobility that are stable in air [19]. On the other hand, C₆₀ illustrates n-type behaviour (see Figure 3.2.16), but n-type semiconductors usually are not suitable for practical application because their electrical characteristic are very sensitive to air [20, 21].

2.3.1 Progress in performance of p-type organic transistor

The first organic field effect transistors fabricated using a small organic molecule is Cu-phthalocyanine were fabricated using vacuum deposition system in 1964

[22]. Generally, there are two ways to improve OFET performance that can be described as follows. Optimising deposition parameters of thin films can be achieved in order to improve the morphology and structural order of the semiconductor layer. This gives rise to an enhancement of the OFET performance. Transistors configuration can also be improved by changing source and drain electrodes, gate electrode and dielectric layers in order to optimize OFETs performance [19].

After these early studies, the organic p-type semiconductors can be divided into three main groups in terms of the most widely used for fabricating OFETs; thiophene oligomers, polythiophenes (Figure 2.3.1) and pentacene. Thiophene oligomers represent a large class of organic materials with high mobility. The first study within this group was concentrated on α -sexithiophene. There was a significant improvement in the charge carrier mobility of α -sexithiophene OFET devices from $0.001 \text{ cm}^2/\text{Vs}$ in 1989 [10] to $3 \times 10^{-2} \text{ cm}^2/\text{Vs}$ in 1995 [23]. Another two organic semiconductors within this group have been investigated based on α - ω -dihexyl-sexithiophene with highest reported mobility $0.13 \text{ cm}^2/\text{Vs}$ in 1997 [24] and also α - ω -dihexyl-quanterthiophene with mobility reported $0.23 \text{ cm}^2/\text{Vs}$ in 1998 [25].

Polythiophenes are another group of p-type organic semiconductors that have been used in solution processed OFET devices with a mobility of $10^{-5} \text{ cm}^2/\text{Vs}$ [9] as reported in 1986. Poly(3-alkyl thiophene) was also used in OFET as a polymer semiconductor, which led to an increased carrier mobility to $10^{-3} \text{ cm}^2/\text{Vs}$ [26]. Another new polymer semiconductor in this group is poly(3-hexylthiophene) which is used to fabricate OFETs with a high mobility of $0.1 \text{ cm}^2/\text{Vs}$ reported in 1998 [27]. Pentacene is the most well know hole carrier group of small molecule semiconductors, because of its air stability and high charge carrier mobility. For the first time in 1992, Horowitz and co-workers used pentacene as the active layer in OFETs, and reported mobility of $2 \times 10^{-3} \text{ cm}^2/\text{Vs}$ [28]. Since then, many OFET devices based on pentacene p-type semiconductor have been fabricated, and the highest mobility of $2.4 \text{ cm}^2/\text{Vs}$ was reported in 2000 [29]. In addition, pentacene solution processed OFET devices have also been fabricated [30].

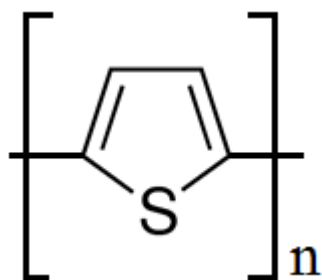


Figure 2.3.1: The structure of thiophene oligomer

2.3.2 Progress in performance of n-type organic semiconductor

High performance n-type organic semiconductors allow fabrication of heterostructure OFET devices and complementary logic circuits. p-type organic semiconductors have been the most widely investigated to date and have been disproportionally developed as compared to n-type OFETs because of the instability of n-type materials in air. This is attributed to the instability of organic anions, which react with water and oxygen. This gives rise to unstable devices. Most transistors with n-type organic semiconductor perform well in vacuum but not in air [31].

In 1990, Guillard and co-workers reported the first study on n-type OFET for both organic semiconductors lutetium bisphthalocyanine (Pc_2Lu) and thulium bisphthalocyanine (Pc_2Tm) [32]. The stability of the device is good under vacuum at room temperature. The mobility of n-type semiconductors Pc_2Lu and Pc_2Tm are measured in situ to be $2 \times 10^{-4} \text{ cm}^2/\text{Vs}$ and $1.4 \times 10^{-3} \text{ cm}^2/\text{Vs}$, respectively. Interestingly, on exposure of the device to air and re-acquisition of electrical measurements only a p-type transistor characteristic was observed. In 1994, Brown and co-workers used tetracyanquinodimethane (TCNQ) to fabricate n-type OFETs [33]. Gold electrodes were used as source and drain to make bottom-contact OFET configuration and the mobility of the device was $\sim 3 \times 10^{-5} \text{ cm}^2/\text{Vs}$.

In 1995 Haddon et al. used C_{60} to fabricate n-type OFET devices [34]. Deposition of C_{60} films were performed under ultrahigh vacuum (UHV) resulting in the formation of random polycrystalline grains. Gold and chromium were used as electrodes. If C_{60} films are deposited on pre-treated substrate with tetrakis(dimethylamino)ethylene (TDAE) this leads to an increase of the mobility of FET from

0.03 to 0.08 cm²/Vs. On exposure of C₆₀ OFETs to air the devices stop operating and the resistivity of the device increases by about 5 orders of magnitude. If the device is reheated at elevated temperature in a UHV chamber overnight, the operation of the device could be restored. This implies that the electron traps are formed by oxygen within the C₆₀ active layer. Performance of the device can also be affected by impurities in the molecular semiconductor film.

In 1996, Katz and co-workers reported many organic semiconductors based on the naphthalene structure [35, 36], which are used as active layer in OFET devices. The first material 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTCDA) was used in OFET device, and a mobility of around 3×10⁻³ cm²/Vs was measured when material was deposited at a substrate temperature 55 °C. However, mobility of 10⁻⁴ cm²/Vs was measured for a device that was prepared at 25 °C. The change of mobility is caused by change of thin film morphology. The mobility of the OFET device is reduced by 2 orders of magnitude when exposure device to air, and lower mobility was measured if device is exposed to moisture in atmosphere.

In 1996, Garnier and co-workers reported n-type organic semiconductor N,N' - diphenyl-3,4,9,10 perylenetetracarboxylic diimide (PTCDI-ph) (see Figure Figure 2.3.2) that was used to fabricate OFET device, and measured charge carrier mobility of 1.5×10⁻⁵ cm²/Vs [37]. A bottom-contact OFET configuration was used with both gold and aluminium as electrodes. They found a mobility is 3 times lower for aluminium electrodes. There is rapid degradation in field effect performance in air, the device do not operate after three days for gold contact, and deteriorate even quicker for a device with aluminium contacts. This is caused by oxidation of aluminium electrodes. Also both oxygen and/or moisture form charge traps in the film. In 1997, Ostrick and co-worker studied another n-type organic semiconductor 3,4,9,10-perylenetetracarboxylicdianhydride (PTCDA), and they used it as active layer in a OFET device. This material had poor charge carrier mobility of 10⁻⁴-10⁻⁵ cm²/Vs [38]. The variation of charge carrier mobility with increasing substrate temperature from 130k to 340k was also studied. This showed that charge carriers transport by hopping. It was found that OFET devices do not operate for temperatures lower than 130 Kelvin. In addition, these OFETs do not operate in moist air similar to most of the n-type

OFET devices. In 2002, Malenfant et al. studied the n-type organic semiconductor N,N'-dioctyl-3,4,9,10-perylene tetracarboxylic diimide (PTCDI-C₈H), and use it as active layer in OFET device [39]. This material was deposited onto a substrate at 50 °C substrate temperature under a vacuum pressure of 25-35 mTorr, and thickness of 50 to 100 nm. The electrical measurements show that the mobility of OFET devices was as high as 0.6 cm²/Vs. However, these OFET devices showed lower mobility in air.



Figure 2.3.2: The structure of PTCDI-ph molecule

In 1996, Bao and co-worker [40, 41] found that copper phthalocyanine (CuPc) is a p-type organic semiconductor [42, 43]. In 1998, they also reported copper hexadeca fluorophthalocyanine (F₁₆CuPc) as an active layer of an OFET, and found that it shows n-type characteristics [40]. F₁₆CuPc OFET device show an increase of mobility from 5×10^{-3} to 0.03 cm²/Vs if the substrate temperature is increased from 30 °C to 125 °C. They also found that F₁₆CuPc OFETs stable when exposed to air. This is attributed to fluorine atoms that provide a barrier to prevent moisture penetrating into the films.

2.4 Deposition of organic semiconductors

In general, organic semiconductor thin films are deposited using two techniques either from solution phase or vapor phase, depending on the solubility and vapor pressure of the semiconductor species.

2.4.1 Vacuum deposition

The deposition of organic semiconductor thin films from vacuum thermal evaporation is performed by heating the organic semiconductor under low pressure using a resistive heating source. This type of thin film growth is

performed in an ultra-high or a very high vacuum chamber. Polymers cannot be deposited by this technique because at high temperature they tend to decompose. The main advantage of this technique is that the thickness and purity of the film can be controlled. In addition, by controlling substrate temperature and deposition rate, highly ordered molecular films can be grown. The disadvantages of this technique is that it needs expensive equipment and consumes relatively large amounts of material.

The highest mobility for pentacene has been reported for vacuum deposited thin films [44, 45]. The vacuum deposition methods are organic molecular beam deposition (OMBD), organic vapor phase deposition (OVPD) and laser evaporation, which have been used to grow thin film for OFET fabrication. In this work, both thermally evaporated macromolecular organic semiconductors and solution deposition of cyclic porphyrin polymers have been studied.

In order to improve the performance of OFET devices, the surface treatment prior to deposition, and post-deposition annealing should also be considered. The deposition rate of organic semiconductors also affects their nucleation density on surface substrate. Generally, for growth at room substrate temperature, if deposition rate is increased, this will result in a reduction of the average grain size and increased nucleation density. This will help charge carriers to hop from one grain to another easily because larger grain size requires higher energy to avoid barrier between grains [46]. Furthermore, adsorption of oxygen, moisture and impurities from the air accumulates at the boundaries of grains. Therefore, thin films with interconnected grains can show higher mobility than grains with separate boundaries. In the last two decades, an investigation of the relationship between deposition rate and mobility of charge carrier for pentacene OFET has been reported [47]. Pentacene thin films were prepared with deposition rates of 1, 3, 5 and 7 nm/s at room temperature, and the field effect mobility was found to increase with deposition rate in spite of the lower crystallinity of the film. During the past few years many studies have been reported on the effects of deposition rate [48-50]. Another group reported an increase in the field effect mobility with increasing deposition rate, which is attributed to the higher ordering of molecules in the channel [5].

Substrate surface properties have a considerable effect on the orientation of molecules and the morphology of semiconductor thin films. It is found that the current flows in an OFET within the first layer of semiconductor [51]. In OFET devices both inorganic and organic dielectric materials have been used as insulator layer. There are many inorganic materials that have been used in OFETs as gate dielectric layers, such as SiO_2 , Si_3N_4 and Al_2O_3 [52-56]. These dielectric films are not compatible with a plastic substrate. A dielectric layer with high dielectric constant may be favourable because this leads to higher output current and higher charge carrier concentration for a given gate voltage [57]. Polymer dielectrics have been used as the insulator layer in OFETs [18, 58, 59] in spite of having low dielectric constants [60]. There are several advantages of polymer dielectrics: their insulating properties are good, and they have a high break-down voltage; they are flexible, and they can easily be prepared using a solution process. Investigation of polymer dielectric materials has been widely reported [59, 61, 62]. Some examples of dielectric polymers that have been used in OFETs are polyvinylphenol [30, 45], hexamethyldisilazane(HMDS) [63], polymethyl methacrylate (PMMA), and octadecyltrichlorosilane (OTS). They have been used in OFETs in order to reduce trapping sites (Si-OH) on a silicon oxide surface and improve the crystalline growth of organic semiconductor layers [44]. Pentacene OFETs on OTS-treated oxide layer have been reported, and their performance was better than devices without the OTS treatment [5]. Pentacene has been grown on a PMMA surface leading to growth of large single microcrystals, which are used in OFETs [64].

2.4.2 Solution deposition

Solution deposition has been used to deposit semiconductor polymer film by spin-coating. This technique is used to produce homogenous films, and precise control of film thickness over large areas. This technique can be used if the polymer has a good solubility in liquid. Unfortunately, many organic polymers are not soluble. Therefore, they are attached with side groups in order to promote solubility [65]. In this work, we used solution immersion to deposit cyclic polymers on a gold surface.

2.5 Supramolecular organization on gold and graphite surfaces

Complex supramolecular architectures are constructed using noncovalent bonds or weak interactions to combine molecules in ordered arrangements. The relevant intermolecular forces are, π - π stacking, hydrogen-bonding, π -donor- π -acceptor interactions, hydrophobic interactions, electrostatic forces, van der Waals interactions and metal-ligand coordination [66].

Historically, the biological species from nature such as the proteins tertiary and quaternary structure and the DNA double helix are known as supermolecules, which inspired researchers to construct supramolecular architectures [67, 68]. Since then, there has been a significant advance in supramolecular field with the development of new materials in chemistry including self-assembly, molecular machines and host guest chemistry. Supramolecular chemistry was described by J.M Lehn in 1978 as “chemistry beyond the molecule” [66]. Pioneers in the supramolecular field are Cram [69], Pedersen [70] and Lehn [71], they have been awarded with the 1987 Nobel prize in the area of host-guest chemistry for their work on cryptands and crown ethers. Also this year 2016, the Nobel prize in chemistry was awarded for the development of molecular machine [72].

Recently, there has been great interest in the formation of supramolecular structures from solution/thermal evaporation on gold and highly oriented pyrolytic graphite (HOPG) substrates because they are potentially suitable for applications in the fabrication of nano-devices. Extended supramolecular nanostructures have been organized in monolayer, bilayers and with their axes oriented perpendicular to surface. In this thesis, we have used self-assembly concepts to form 3 dimensional supramolecular structures, which are stabilised by based electrostatic and π - π interactions. Some examples of these different supramolecular configuration are depicted with their STM images and schematic diagrams as described below:

2.5.1 Limitation to monolayer

In this section, we have chosen four examples of molecules that can be deposited on surfaces as monolayers of supramolecular structures either by solution deposition or thermal deposition.

The self-assembly of 5,10,15,20-tetrakis(4-carboxylphenyl)porphyrin (TCPP) from solution forms supramolecular monolayer network on hexagonal boron nitride (hBN), where the molecules are stabilised by hydrogen bonding (see Figure 2.5.1) [73].

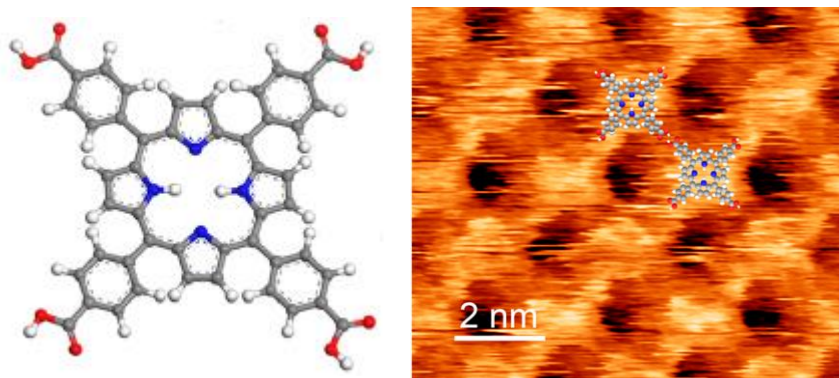


Figure 2.5.1: Structure of TCPP (left side), and STM image for supramolecular network of TCPP arrangement on Au(111) deposited by solution deposition (right side) [73]

In addition, the thermal evaporation of copper phthalocyanine [74], metal-free naphthalocyanine [75], under vacuum condition lead to form monolayer of supramolecular structure on Au(111) surface bonded by van der Waals force, with their molecular plane parallel to the substrate (see Figure 2.5.2).

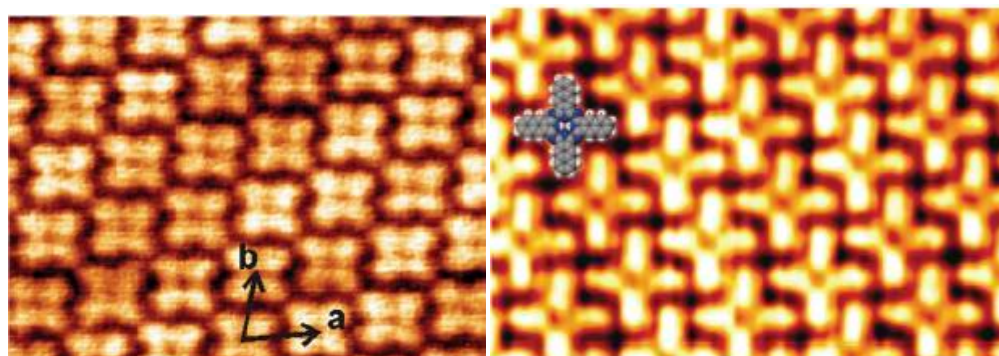


Figure 2.5.2: STM image for supramolecular network of phthalocyanine (left side) [74] and naphthalocyanine (right) [75] arrangement on Au(111) deposited by vacuum deposition

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Furthermore, the self-assembly of a mixture of perylene-3, 4, 9, 10-tetracarboxylic di-imide (PTCDI) and melamine molecules in dimethylformamide leads to the formation of monolayers of a supramolecular hexagonal network on gold. This arises from an interaction (three hydrogen bonds) between PTCDI and melamine [76]. This supramolecular network can be used as a host-guest template. The supramolecular network of PTCDI-melamine on gold was exposed to guest molecules by immersion in a solution of C_{60} in 1,3,5-trichlorobenzene. It was found that the C_{60} molecules were captured within the network pores in regular heptameric clusters [77] (see Figure 2.5.3).

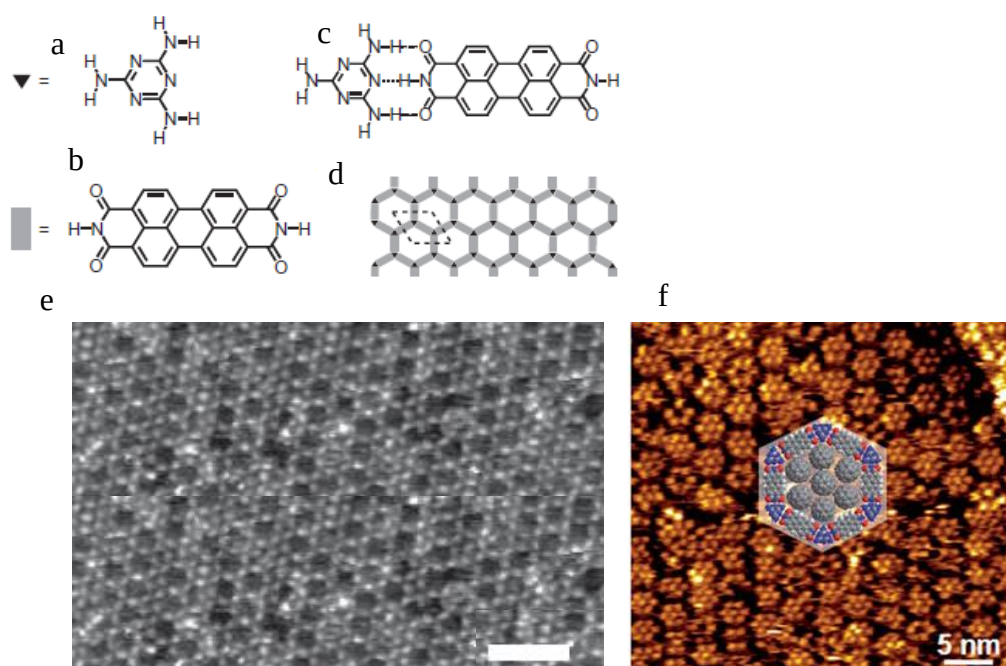


Figure 2.5.3: The self-assembly of PTCDI-melamine molecules on gold. a-d schematic diagram of a) melamine b) PTCDI c) hydrogen bonding of supramolecule d) supramolecular network. e, f STM image of supramolecular network (the scale bar 5 nm) [76] b) adsorption of C_{60} into network porous (the scale bar 5 nm) [77]

Also the monolayer supramolecular networks are shown on HOPG. The supramolecular PTCDI-melamine porous network can also be formed on HOPG when adsorbed from solution [78].

In another example the tetracarboxylic acids tectons are deposited from a nonanoic or heptanoic acid solution and form a two dimensional supramolecular network on HOPG. Coronene was added to the nonanoic acid solution of the

tetracarboxylic acids tectons that led to action as a guest molecule, transforming the supramolecular network configuration [79] (see Figure 2.5.4).

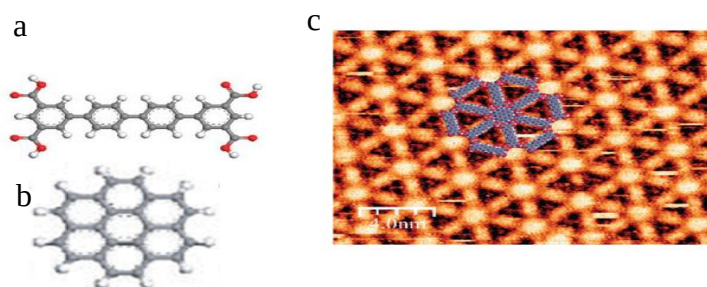


Figure 2.5.4: The self-assembly of supramolecular network of tetracarboxylic acids molecules on HOPG. a-b schematic diagram of a) tetracarboxylic acids b) coronene (guest molecule) . c) STM image of supramolecular network with adsorption of coronene into network porous (the scale bar 4 nm) [79].

2.5.2 Bilayer

Here, p-terphenyl-3, 5, 3'', 5''-tetracarboxylic acid (TPTC) molecule was chosen to show how it can be deposited on surface as double layer of supramolecular structures.

The self-assembly of TPTC in nonanoic acid on HOPG surface leads to an extended supramolecular monolayer network with pores. These pores are then used as a host template to accommodate guest molecules. A non-planar guest species fullerene (C_{60}) was added to nonanoic acid solution resulting in the growth of a bilayer supramolecular network with C_{60} trapping both the two layers. However, after a planar guest species (coronene) was added to nonanoic solution the C_{60} was displaced and the bilayer configuration destabilised. This gives rise to the reversion to a monolayer supramolecular TPTC network [80] (see Figure 2.5.5).

It is found that the most of molecules could be arrange as monolayer supramolecular structure more than the bilayer on surfaces.

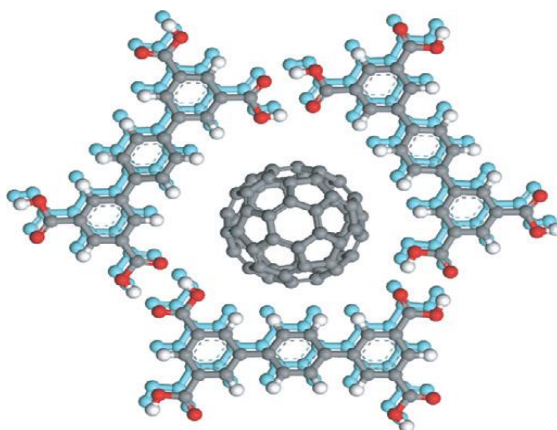


Figure 2.5.5: Schematic diagram of bilayer arrangement of supramolecular TPTC in pore structure with trapping C₆₀. The first layer pore structure (blue) and the second layer (grey) [80].

2.6 Theory of thin film growth

Thin film growth occurs through very complex non-equilibrium surface processes as illustrated in Figure 2.6.1 [81]. Atoms or molecules are deposited with deposition rate (R) (process (a) in Figure 2.6.1), and are incident on a surface substrate, where they are referred to as adatoms, and this process is known as adsorption. Then the adatoms diffuse on the surface with a diffusion constant (D) (b). Adatoms can form dimers, by joining other adatoms (c). In addition, adatoms may meet existing islands resulting in island growth by adsorption at the island edge (d). Attached adatoms can migrate from the edge of islands (e), or diffusion of an adatom may occur along the island edge (f). If adatoms are deposited on top of islands, the above surface processes may occur there as well (g), (h). Finally, adatoms may re-evaporate (i) [81-84], which is known as desorption. In this section, we describe some of these surface processes, which are important for studying organic thin film growth.

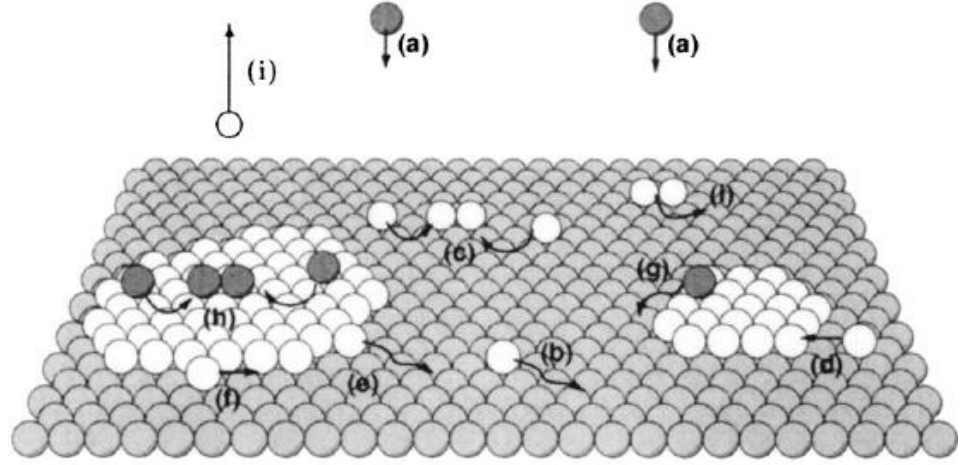


Figure 2.6.1: Typical surface processes during thin film growth [81]

2.6.1 Adsorption and desorption

When atoms or molecules evaporate, they will arrive at the substrate surface with deposition rate, R , which is given by [85],

$$R = \frac{P}{\sqrt{2\pi m k T}} \quad 2.6.1$$

Where, P , and m are the pressure and mass of atom or molecule, respectively. In addition, the temperature and Boltzman constant are denoted by, T , and k , respectively. When the molecules or atoms impinge onto surface, their probability of adsorption at the surface is equal to sticking coefficient S_v . The impinging particle is trapped or bound with atoms at the surface and loses its kinetic energy by transferring energy to the atoms at the surface. This binding may be due to physical adsorption (physisorption) or chemical adsorption (chemisorption) [86]. In physisorption, this bond is often due to van der Waals forces, a weak interaction force due to induced dipole-dipole interactions between adsorbed molecules and the surface. Transferring charge from molecule to substrate or vice versa does not occur in this type of bond. Notice that the van der Waals forces are the most relevant interaction between the molecules and surface which are studied in this thesis. A typical binding energy in physisorption

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is below 0.5 eV. Figure 2.6.2 show that the molecule arrives on the surface with kinetic energy E_k [86]. When the molecule impinges on the surface, it will lose its kinetic energy by exciting the atoms at the surface. This gives rise to trapping of the molecule within the potential well and adsorption on the surface. The adsorption energy, E_a , can be determined from the depth of the potential well. However, the molecule can regain energy by heating the surface. If the molecule has enough thermal energy to overcome the potential well E_a , the molecule will re-evaporate to leave the surface, this is called desorption.

The residence time of the adsorbate on the surface, τ_a , is given by

$$\tau_a = \tau_0 e^{\frac{E_a}{kT}} \quad 2.6.2$$

where τ_0 is of the order of 10^{-12} s, the adsorption energy E_a is typically 0.25eV or less, and the residence time τ_a is approximately 1.6×10^{-8} sec at room temperature. It is evident that the substrate temperature, T_s , can be used to control the molecular adsorption residence time τ_a according to equation 2.6.2. At low temperature, the adsorbate residence time on surface is relatively long, and the surface sticking coefficient is very high. However, at high temperature the adsorbate residence time on surface is very short because the molecule can re-evaporate. Therefore, the surface sticking coefficient for adsorbate is very low.

The other process of molecular adsorption is called chemisorption. In this case, a chemical bond forms between the adsorbed molecule and substrate. Which can be either covalent or ionic. The ionic bond will form if complete numbers of electrons are released from the adsorbed molecule and captured by the substrate or vice versa. However, a covalent bond arises from sharing electrons in binding orbitals between adsorbate and surface substrate atom. A typical binding energy in chemisorption is above 0.5eV.

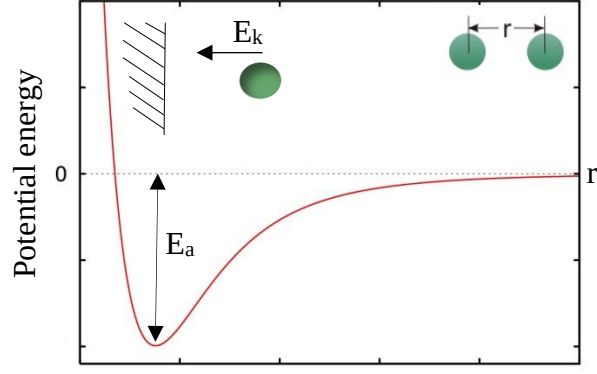


Figure 2.6.2: Schematic diagram of physisorption potential [86]

2.6.2 Diffusion

The adsorbed molecule may diffuse across the surface because thermal fluctuations allow the adsorbate to have sufficient energy to overcome a potential energy barrier and then transfer from the initial adsorption site to a neighbouring site. Figure 2.6.3 shows diffusion of an adsorbed atom from an initial adsorption site (x_1) with adsorption energy E_a to a neighbour site (x_2) with energy E_b . In order to transfer the adsorbate from position (x_1) into position (x_2), it has to overcome the energy barrier of transition state, E_d , between (x_1) and (x_2) state. τ_d is the hopping time, which is given by [87]

$$\tau_d = \tau_1 e^{\frac{E_d}{kT}} \quad 2.6.3$$

The diffusion energy barrier is denoted E_d , and $\tau_1 \sim \tau_0$, τ_0 is of the order of 10^{-12} sec.

The number of the hops, N , can be determined from the residence time of the molecule on the surface τ_a , N is given by

$$N = \frac{\tau_a}{\tau_d} = \frac{\tau_0}{\tau_1} e^{\frac{(E_a - E_d)}{kT}} \quad 2.6.4$$

The adsorbed molecule diffuses with average distance, L , before re-evaporation, L is given by

$$L = N^{\frac{1}{2}}a = a \left[\frac{\tau_0}{\tau_1} \right]^{\frac{1}{2}} e^{\frac{(E_a - E_d)}{2kT}} \quad 2.6.5$$

where, a , is the lattice constant.

The diffusion constant, D , for molecule that visited N sites can be given by

$$D \tau_a = Na^2 \quad 2.6.6$$

And the diffusion constant has $\frac{cm^2}{sec}$ unit. Where the D can be derived from equations 2.6.2 and 2.6.5,

$$D = \frac{L^2}{\tau_a} = \frac{a^2}{\tau_1} e^{\frac{-E_d}{kT}} \quad 2.6.7$$

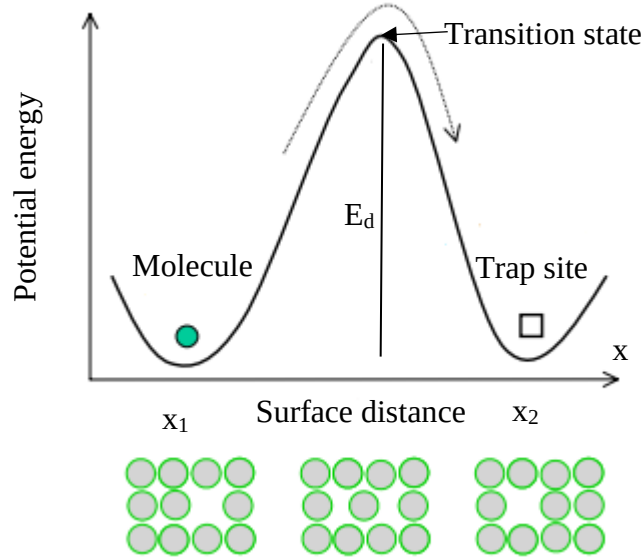


Figure 2.6.3: schematic diagram of molecular diffusion from initial position into a trap site [87]

From equation 2.6.3, at low temperature, the diffusion of the adsorbate on surface is suppressed because molecule has long hopping time τ_d . In this case the growth of film occurs by sticking molecule where they adsorb. However, at high temperature, the hopping time is short, and the residence time is also short. This implies that increasing the substrate temperature T_s will lead to a decrease in molecular diffusion length L , and also a reduction in both the sticking coefficient S_v and nucleation rate.

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Further deposition of molecules on the surface, gives rise nucleation and results in the formation of stable islands. After that the islands will grow not only by attachment of molecules diffusing on the substrate but also by molecular impingement directly on the island. If a molecule falls on top of an already formed island, the molecule may diffuse on the island and reach its edge, where the molecule will face a new potential energy barrier, called the Ehrlich-Schwoebel barrier. The molecule has to overcome this barrier so that it can jump to a lower terrace. Figure 2.6.4 shows a schematic diagram of molecular diffusion process on surface and surface potential energy [87].

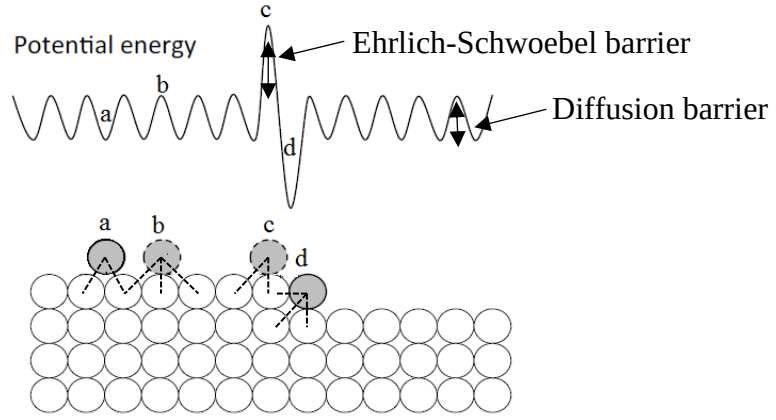


Figure 2.6.4: Schematic diagram of diffusion process and surface potential energy profile of atom [87]

2.6.3 Nucleation

The rate equation of the density of single molecules, n_1 , can be written as [84]

$$\frac{dn_1}{dt} = R - \frac{n_1}{\tau_a} \quad 2.6.8$$

From equation 2.6.8, the density of single molecule n_1 for $t \gg \tau_a$ can be written as follow

$$n_1 = R\tau_a \quad 2.6.9$$

where τ_a is the residence time.

In addition, D_s is the average distance between single molecules on the surface, which is given by

$$D_s = n_1^{-\frac{1}{2}} \quad 2.6.10$$

Therefore, the probability for one molecule to join another molecule and form a dimer will increase if $D_s < L$. From equations 2.6.2, 2.6.5, 2.6.9 and 2.6.10, the above condition for two molecules to meet can be rewritten as

$$R > \frac{\tau_1}{(a \tau_0)^2} e^{\frac{-(2E_a - E_d)}{kT}} \quad 2.6.11$$

From equation 2.6.11 the deposition rate required to nucleate molecule on surface depends on the substrate temperature. This implies that the probability of one molecule joining another can be increased if the deposition rate is increased.

τ_b is the time over which a pair of molecules is stable, Figure 2.6.2 shows the physisorption potential diagram, and τ_b is given by

$$\tau_b = \tau_2 e^{\frac{E_b}{kT}} \quad 2.6.12$$

The binding energy barrier is denoted by E_b .

A pair of molecules will separate if the time of a third molecule τ_2 to arrive is longer than τ_b , while if τ_b is longer than time of the arriving third molecule, then they will combine in order to form a larger cluster. Therefore, the stable nucleation will occur.

So far, two molecules binding to each other has been discussed above. Consider first the case when the island of two molecules is stable. After it nucleation, there will be an increase in the density of islands, n , and a decrease in the density of single molecules n_1 . Generally, the rate equation is given by

$$\frac{dn}{dt} = Dn_1^2 \quad 2.6.13$$

$$\frac{dn_1}{dt} = R - 2Dn_1^2 - Dnn_1 \quad 2.6.14$$

The diffusion constant is denoted by, D .

Equation 2.6.13 reveals that increasing the density of islands is due to the formation of new islands generated by the coalescence of single molecules. Therefore, the rate of growth is proportional to the probability of one molecule joining another. Equation 2.6.14 illustrates the dependence of the density of single molecules not only on deposition rate but also on the formation of two-molecule clusters. The decrease of n_1 is attributed to the formation of two-molecule clusters. The third term of this equation refers to the capture of single molecules by the islands.

2.6.4 Energetics of growth

The interaction between the substrate and adsorbate can result in growth thin film in different morphologies. The growth mode may be classified into three types (Figure 2.6.5), according to the surface energies can be used to distinguish between them [85]. The first mode is called the Frank-van der Merwe growth (or layer by layer growth), a monolayer forms on the surface from the adsorption of the first atoms or molecules. After that a second layer forms. The same behaviour occurs for the growth of subsequent layers (Figure 2.6.5a). Layer by layer growth occurs if the substrate surface has a larger energy (γ_s) than the over-layer film surface energy (γ_f).

Figure (2.6.5b) shows the second growth mode, which is called Volmer-Weber growth (or island growth) [84]. This mode occurs if $\gamma_f > \gamma_s$, and leads to form island directly on the substrate surface.

In addition, growth layers on the surface can lead to the formation of strain. Therefore, an effective interface energy between substrate and film (γ_i) is induced [83]. This energy increases with increasing layer thickness. Growth of further layers eventually leads to overgrowth of stable islands because $\gamma_f + \gamma_i > \gamma_s$. This growth mode is known as Stranski Krastanov growth or layer plus island growth (Figure 2.6.5c), and is observed in many crystal growth systems. In other words, the initial stage of growth is layer by layer growth, but when the thin film thickness reaches at a certain critical value, then islands will start to form on top of initial layer.

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Classification of the above growth mode is based on the assumption of limited effect of kinetic and chemical reaction in the interface between the film and substrate while without this assumption the growth process will be very complex.

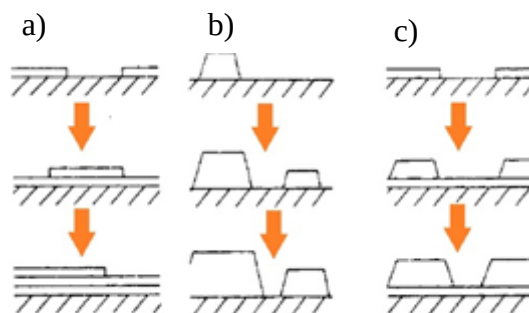


Figure 2.6.5: Schematic diagram of three types of film growth modes a) Frank-van der Merwe (or Layer by layer growth) b) Volmer-Weber (or island growth) c) Stranski Krastanov (or layer plus island growth) [84]

2.7 Summary

In this chapter, an overview of organic semiconductor, organic field effect transistors (OFET), and operation model of electrical characteristic of OFET are illustrated. The mobility of the OFET devices is derived from the $I(V)$ characteristics of an ideal OFET device. The literature review of progress in performance n- and p-channel organic transistors are shown. Solution and vacuum deposition of organic semiconductor thin films and supramolecular organization on surfaces are described.

The basics of organic thin film growth have been described through thermal and kinetic processes of molecules, such as deposition, diffusion and nucleation. The initial stages of crystal growth are described by thermal energy and rate equation, and also three basic growth modes are described through the energy between material and surface.

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Chapter 3

Instrumental Techniques

In this chapter, we describe the experimental process used to prepare sample of porphyrin cyclic polymers that were adsorbed on Au (111) from solution deposition under ambient condition. In addition, we describe the techniques used to fabricate organic thin film transistor such as, vacuum evaporation of organic thin film on Si/SiO₂ substrate, thermal evaporation of electrodes, octadecyltrichlorosilane (OTS) substrate modification and the acquisition of electrical characteristics of devices. Finally, we describe the instrumental techniques to image thin films for all samples.

3.1 Sample preparation in air

3.1.1 Au(111) surface preparation

Gold on mica is used as a substrate to investigate molecular self-assembly. Gold thin films with the thickness of 300 nm are bought commercially from Georg Albert Physical-Vapour Deposition; these films are oriented with the (111) direction normal to the surface. The Au(111) substrate is used because it can be prepared easily and is chemically inert and is also a good electrical conductor. The atomic arrangement on (111) surfaces for many fcc metals, such as Ag and Pt is a hexagonal close-packed structure, with no reconstruction. This is not the case for the Au(111) surface which forms a $22\times\sqrt{3}$ reconstruction in which 23 atoms of gold are incorporated within 22 lattice sites of bulk gold across the $\langle 110 \rangle$ direction resulting in an overall minimization of the energy of the surface layer [1]. The atoms within this ‘herringbone’ reconstruction on Au(111) surface are alternately positioned on face centered cubic (fcc) sites and hexagonal close packed (hcp) sites along the reconstructed unit cell, which has lattice constant 6.3 nm in the $\langle 110 \rangle$ direction [2]. The regions between fcc and hcp are separated by bright lines, which exhibit an out of plane corrugation of 0.02 nm. These lines are rotated around the (111) direction by 120° every 25 nm so that they follow different $\langle 112 \rangle$ directions to form the so called zigzag structure or herringbone reconstruction. The atomic arrangement of the herringbone reconstruction atoms

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of gold surface was first resolved by J. V. Barth and co-workers as illustrated in Figure 3.1.1.

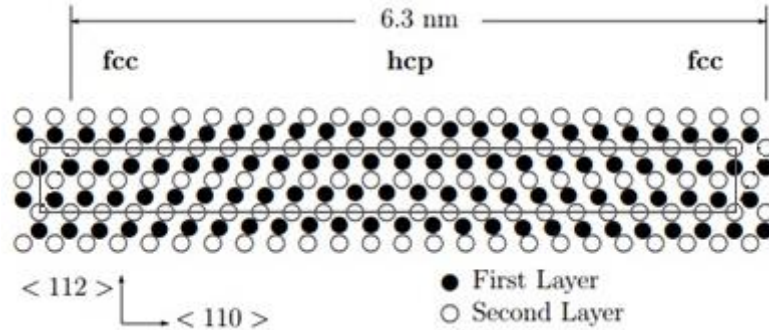


Figure 3.1.1: Schematic of $22 \times \sqrt{3}$ reconstruction of Au(111) illustrating how 23 surface atoms fit into 22 bulk sites. The sites of fcc and hcp atoms are shown

This reconstruction was experimentally investigated using STM. Figure 3.1.2 shows a topographic image of the Au(111) surface with clear terraces, step edges and the herringbone construction. To produce a flat and clean Au(111) surface the samples were annealed in a butane flame using butane gas prior to use.

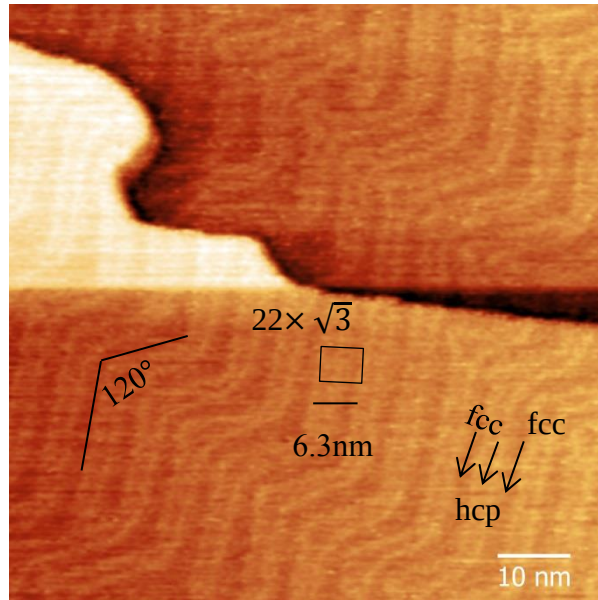


Figure 3.1.2: A topographic STM image of the herringbone-reconstructed Au(111) surface, forming a zig-zag structure, scanning parameters sample bias $V_s = 1$ V, tunnelling current $I_t = 0.03$ nA,

3.1.2 Solution deposition of molecules

In this thesis, the STM is used to image adsorbate molecules that self-assemble on the Au(111) surface and are deposited from solution under ambient conditions. To begin, the Au(111) samples were flame annealed as described above. After that the molecules are dissolved in an appropriate solvent. The substrate is then immersed in the solution for a fixed time, typically 10 min. Finally, the samples were blown dry using nitrogen. Images were then acquired using STM with all measurements carried out under ambient conditions. Another technique that can be used to deposit molecules on a surface is drop casting in which a 10 μ l droplet of the solution is placed on the surface. If the evaporation of the solvent is slow at room temperature, STM can be performed at the liquid-solid interface by immersing the tip in the solvent. However, many solvents evaporate quickly. As a consequence, the solution droplet on sample will evaporate completely, and the STM will scan the sample surface at the air-solid interface.

The selection of solvent depends on the following factors. Firstly, the target molecule must be soluble in the solvent. In addition, if the imaging is performed at the liquid-solid interface the solvent should be electrically non-conductive because the current will otherwise pass from the tip through the solvent to the sample surface, effectively shorting the tunnelling current. Typically, up to 1mg of material is dissolved in 10 ml of solvent. After that, the solution is transferred to an ultrasonic bath to ensure solution is effective.

In this work two different solvents have been used in order to deposit molecules on a surface, toluene, methanol and toluene/methanol mixtures. The effects of solvent on molecular self-assembly are studied, and it is found that different solvents can generate the arrangement of different molecular structures on a surface, such as stacked and nested supramolecular structures. These structures have been found to depend not only on the molecule-molecule and molecule-solvent interaction but also the interaction between the adsorbed species and the surface. In addition, it is found that self-assembly at high molecular concentration can result in a highly disordered and densely packed structure on

a surface, while molecular adsorption at low concentration can provide monolayer thickness adsorbate arrays.

3.2 Fabrication of organic field effect transistors

3.2.1 Structure of organic field effect transistors (OFET)

The structure of two types of OFET devices are shown in Figure 3.2.1, where source-drain electrodes may be evaporated after the semiconductor layer (top-contact OFET), or before (bottom-contact OFET). First, a top-contact device is illustrated in Figure 3.2.1a. The Si/SiO₂ substrate consists of a n-type silicon wafer on which a thermal oxide (thickness 200 – 300 nm) is grown. In some experiments a monolayer of octadecyltrichlorosilane OTS is evaporated on the oxide layer in order to passivate the substrate. A layer, with typical thickness 15 nm, of an organic semiconductor is sublimed on the dielectric substrate using a physical vapor deposition system. Two ohmic contacts, the source and drain, consisting of a 10/100 nm titanium/gold layer, are evaporated onto the organic semiconductor layer using vacuum thermal evaporator and shadow mask. The OFET channel length (L), which is the distance between two metallic contacts, is typically 25 μ m. The typical width (W) of the channel is 1.5 nm, which represents the length of the electrode.

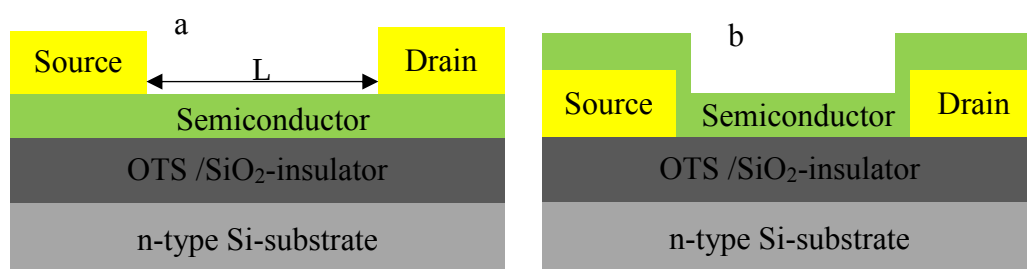


Figure 3.2.1: Schematic diagrams of two types of organic field effect transistor: a) top contact device, b) bottom contact device

Secondly, a bottom-contact configuration of an OFET device is illustrated in Figure 3.2.1b. In this case the organic semiconductor layer is deposited, following the evaporation of source and drain contacts. In our study of OFETs,

a naphthalocyanine thin film is grown as an active layer either before or after the deposition of the two contacts; therefore, not only top-contact but also bottom-contact OFET devices are studied.

3.2.2 Vacuum deposition of organic materials

A vacuum deposition system, which is necessary to fabricate organic FET devices, was constructed to enable both the growth of organic semiconductor thin films, and the acquisition of electrical measurements *in situ*. This system is shown schematically and in a photograph in Figure 3.2.2a,b. When the substrate is inserted into the vacuum deposition system, a scroll backing pump evacuates the chamber from atmospheric pressure down to $\sim 10^{-2}$ mbar. Then a turbo molecular pump is operated to reduce the pressure down to $\sim 1 \times 10^{-7}$ mbar, the base pressure of the system. The pressure can be monitored by a combined pirani and penning gauge.

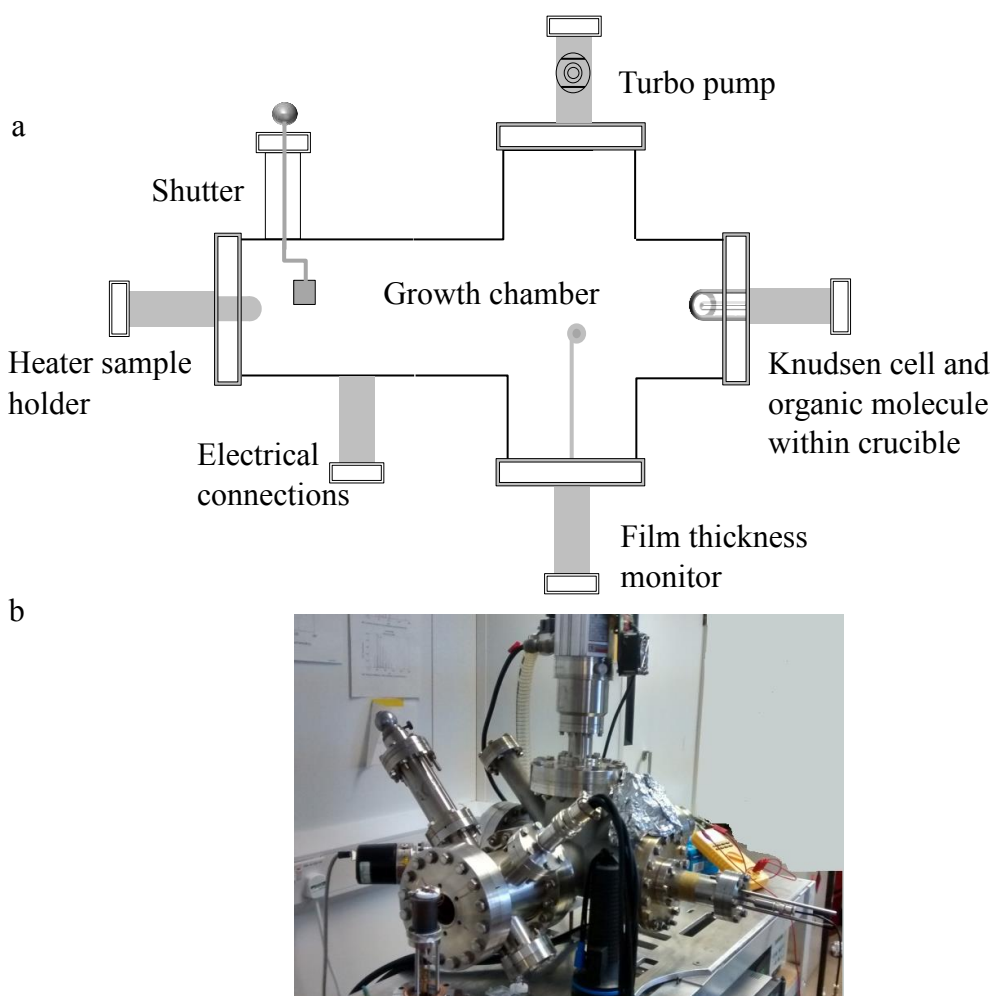


Figure 3.2.2: Both schematic diagram (a) and photograph of the vacuum deposition system (b)

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Knudsen cell (K-cell) consists of a heater and a crucible about 10 cm long, which is filled with 10-50 mg of organic semiconductor powder (see Figure 3.2.3). In order to heat the K-cell, current is passed through a resistive heater surrounding the crucible. Both the sample holder and K-cell are integrated into the vacuum system. An external power supply is used to pass the current through the crucible heater so that the K-cell temperature can be controlled. If thermal deposition of organic material occurs at a specific temperature, the sublimed molecules will cross the chamber in a molecular beam from the crucible onto the sample holder. There is a shutter between the K-cell and the sample holder. It protects the sample holder from being exposed to molecular adsorption before the deposition rate stabilises. The shutter is opened when the deposition rate stabilises at the required level which typically takes ~ 45 minutes. A quartz crystal thickness monitor enables both thin film thickness and deposition rate to be measured during sublimation.



Figure 3.2.3: Photograph of Knudsen cell and crucible that fills with source organic material.

Another important parameter for growing molecular films is the substrate temperature which can affect the morphology of the thin film significantly. There is a resistive heater connected to the sample holder and fixed underneath a ceramic insulator that supports the OFET sample. For taking electrical measurements *in situ*, contact probes are attached to source, drain and gate (see Figure 3.2.4a,b). Two insulated wires are used to connect both the resistive wire

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and power supply in order to provide current to the heater. A K-type thermocouple is used to monitor substrate temperature.

The use of this system is simple. The surface temperature is fixed for each experiment, and both the deposition rate and total dosage are kept constant. Note that for high substrate temperature the thickness and dosage are not equivalent due to a temperature-dependent sticking coefficient.

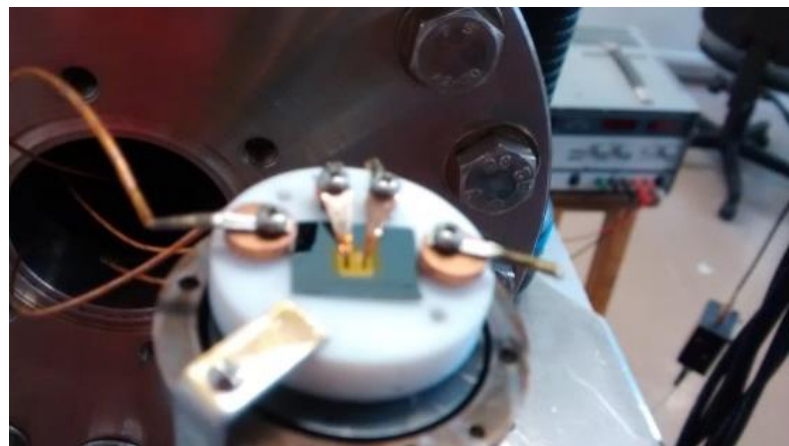
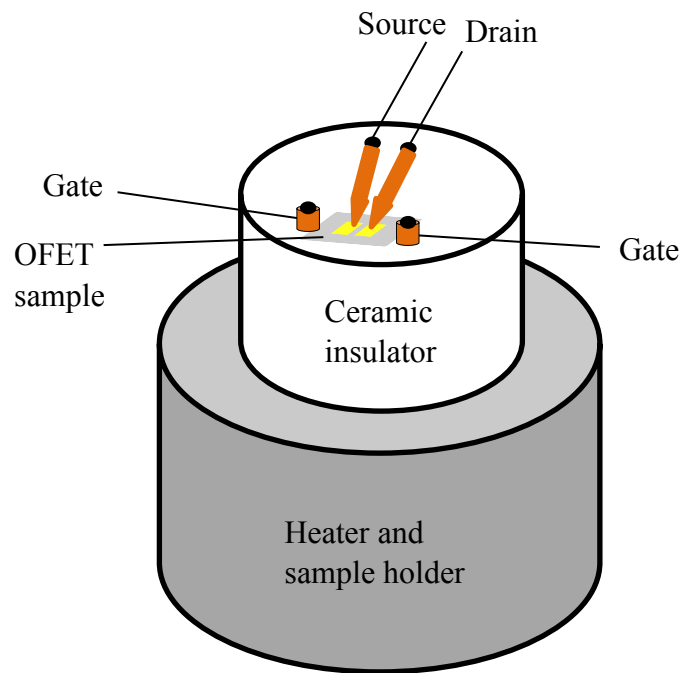


Figure 3.2.4: The schematic (a) and photograph (b) of the heater, sample holder and electrical connection for OFET sample

3.2.3 Thermal evaporation of gold contacts

A thermal evaporator is used to deposit metallic thin films under vacuum conditions (typical base pressure 10^{-7} mbar) (see Figure 3.2.5). This system consists of two tungsten boats and tungsten wire baskets which may be resistively heated, and also a sample holder (see Figure 3.2.6 a, b, c). When the temperature increases, materials such as gold in the tungsten boat will first melt then evaporate onto the substrate and form a thin film, while titanium is sublimed from a tungsten wire basket. In our experiments, titanium and gold were evaporated onto a Si/SiO₂ substrate through a shadow mask to form source and drain contacts with a channel gap of 25 μm . The thin film thickness of titanium and gold were 10 nm and 100 nm, respectively. In addition, the deposition rate for evaporation of titanium and gold were typically 0.2 nm/sec and 0.5 nm/sec, respectively.

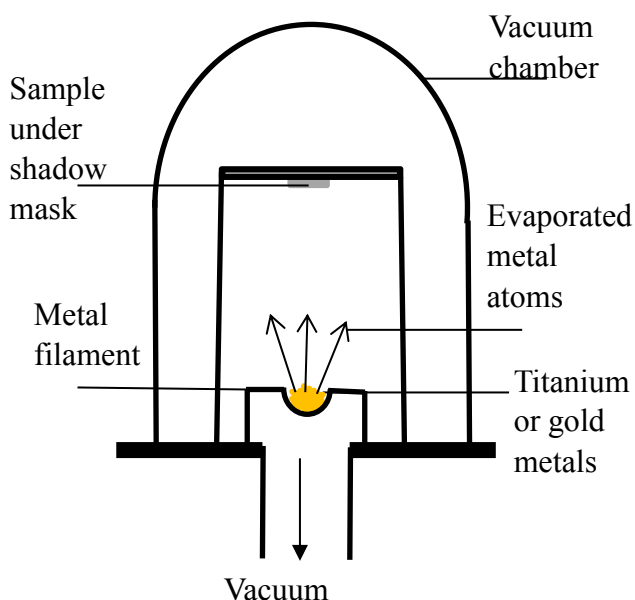


Figure 3.2.5: Schematic diagram (right) and photograph (left) of thermal evaporator

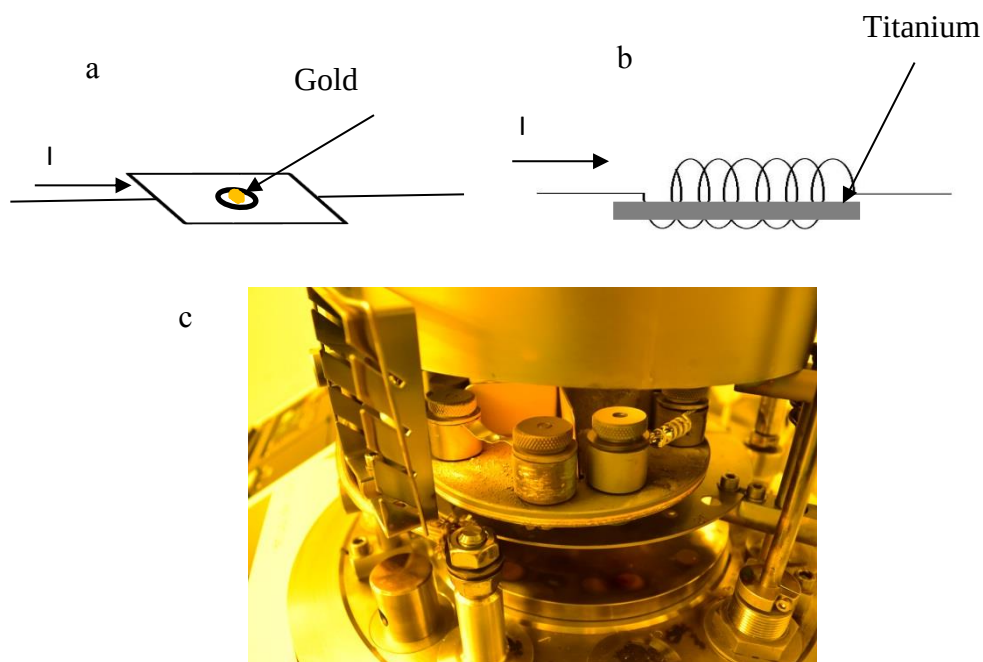


Figure 3.2.6: Schematic diagram of tungsten boat (a), tungsten wire basket (b) and their photograph inside thermal evaporator chamber (c).

An OFET device in the bottom or top-contact configuration can be fabricated by evaporating source and drain contacts either onto an organic semiconductor layer or onto the SiO_2 substrate using a shadow mask. Figure 3.2.7a, b show the shadow mask consisting of a plate, which has a pattern of three rectangular holes, and a tungsten wire which passes over the centre of the holes. This wire is necessary in order to generate a gap between source and drain and the wire width determines the OFET channel length, L .

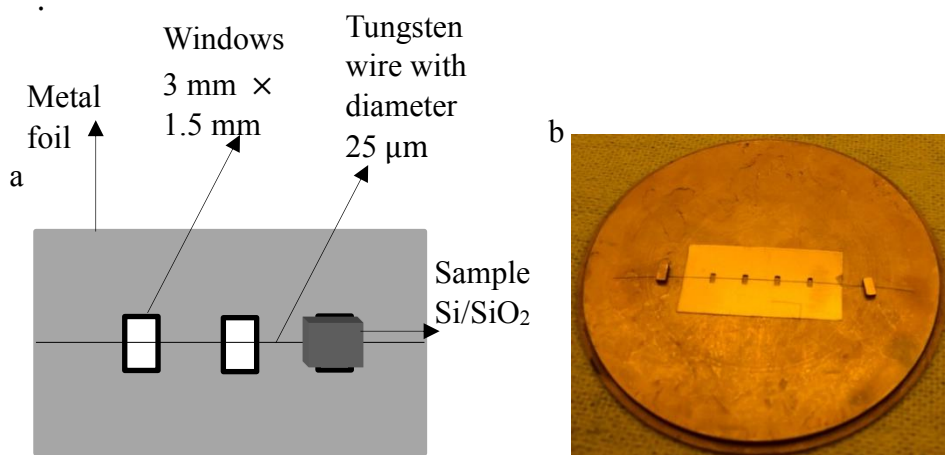


Figure 3.2.7: The schematic diagram of shadow mask structure (a) and Photograph of shadow mask setup on sample holder (b)

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In this work tungsten wire is used with a width, W , 25 μm , which is equivalent to the gap between source and drain. Photograph of bottom-contact organic field effect transistor that fabricated by evaporating C_{60} thin film on Si/SiO₂ substrate is shown in (Figure 3.2.8).



Figure 3.2.8: Photograph of organic field effect transistor of C_{60} thin film on Si/SiO₂ substrate

3.2.4 Self-assembled monolayer of octadecyltrichlorosilane (OTS)

Previous studies have shown that the electrical characteristics of organic field effect transistors can be improved by using OTS-modified silicon oxide substrate, which is formed before deposition of the semiconductor layer on the surface [3-5]. Treating the silicon oxide substrate with self-assembled monolayers (SAMs) of OTS not only improves the properties of the oxide substrate, but also will reduce the carrier trapping at the surface due to passivating OH bonds to the surface [6].

Self-assembled monolayers of organosilane OTS have attracted the attention of researchers because they form on Si/SiO₂ and glass surfaces and also since they can modify the chemical and physical properties of these surfaces. In order to make the bare Si/SiO₂ substrate more hydrophobic, the substrate was treated by octadecyltrichlorosilane (OTS). As a result, the contact angle of the substrate can be increased from 45° to 109° [7]. OTS consists of a polar headgroup (SiCl_3) and long hydrocarbon chains ($\text{C}_{18}\text{H}_{37}$), as illustrated in Figure 3.2.9.

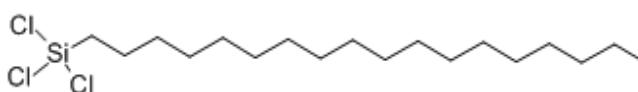


Figure 3.2.9: Chemical structure of octadecyl trichlorosilane (OTS)

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An OTS-modified Si/SiO₂ substrate is used in this thesis in order to obtain a substrate with passive organic termination, which can be used to control of growth morphology. The formation of OTS SAMs on hydroxylated silicon oxide surface can be explained through covalent linkage of polar headgroups (SiCl₃) to surface hydroxyl groups (OH). Also ordering and packing of OTS occurs due to attractive van der Waals interaction of the alkyl chains (see Figure 3.2.10) [8]. The self-assembly mechanism of OTS organosilane is that the polar headgroup reacting with hydroxylate surface resulting in a loss of Cl atoms. As a result two types of covalent bonds of siloxane (Si-O-Si) are formed, one between the OTS headgroup and Si-OH group of surface, another one between two adjacent OTS headgroups [9, 10].

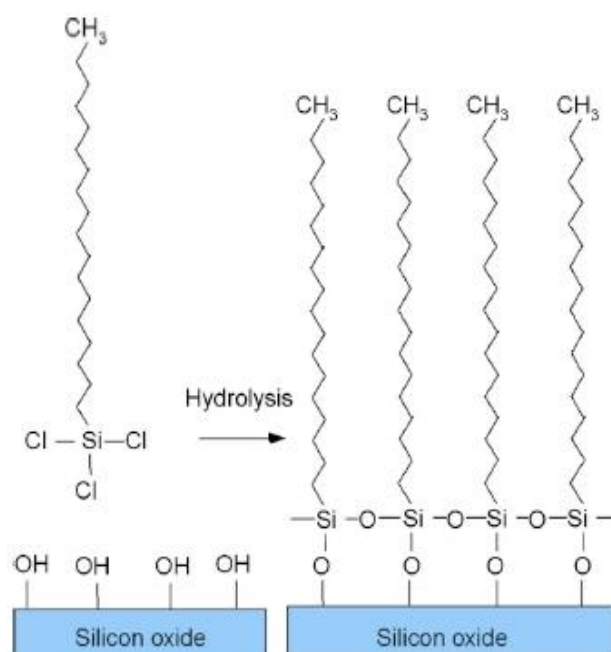


Figure 3.2.10: The self-assembly mechanism of OTS on SiO₂/Si surface

There are two methods to form SAMs of OTS on a silicon oxide substrate. They can be classified into liquid phase and vapour phase methods. In the case of the liquid phase deposition the SAMs of OTS were formed by immersing the substrate into a solution, which consists of OTS dissolved in a mixture of cyclohexane and chloroform, followed by rinsing. In the vapour phase deposition the OTS-based SAMs were formed on the silicon oxide substrate by evaporation of OTS [11].

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In this work, a furnace tube is used to adsorb monolayers of OTS onto a Si/SiO₂ substrate. The setup of the furnace tube for evaporation of OTS is shown in Figure 3.2.11. The Si/SiO₂ substrate and 40 μ l of OTS were inserted into the furnace tube and a constant rate flow of nitrogen gas 0.1L/min is then passed through the tube. The substrate and OTS inside the furnace tube is positioned at two different temperature points 65°C and 85°C, respectively. The substrate is placed into the higher temperature region so that the multilayer of OTS and contamination cannot be adsorbed onto substrate. The entire process of OTS evaporation onto a Si/SiO₂ substrate took around five hours.

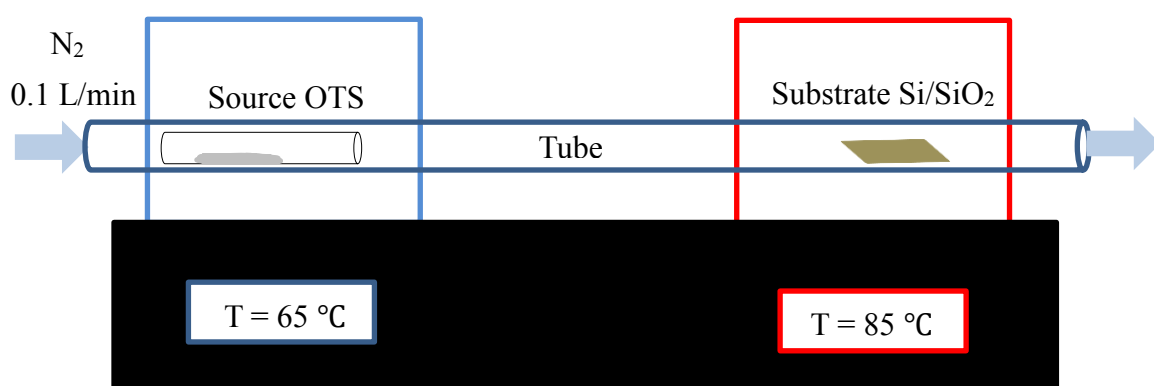


Figure 3.2.11: Setup of furnace tube for SAMs of OTS on Si/SiO₂ substrate

We have used two techniques to check the properties of OTS-treated substrates, AFM and contact angle measurements (taking a camera picture of water droplet on Si/SiO₂/OTS samples and measuring contact angle using computer software). The surface roughness of SAMs of OTS on a surface can be evaluated using AFM. In order to confirm the formation SAMs of OTS, the change of the contact angle is measured using a contact angle technique. Figure 3.2.12 [9] shows the contact angle both for the bare oxide surface and the OTS-treated oxide surface. The bare SiO₂ surface, which has a small contact angle around 60°, is a hydrophilic surface. The OTS-modified oxide substrate, which has a large contact angle between 80° and 95°, is a hydrophobic substrate. The OTS-modified oxide substrate makes it possible for surface to increase the contact angle to the highest value around 107°, which is related to the SAMs treatment condition.

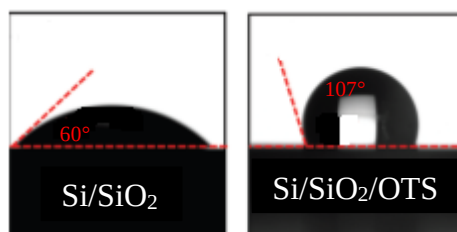


Figure 3.2.12: The contact angle of bare Si/SiO₂ and of OTS-modified Si/SiO₂ substrate [9]

The analyses of AFM images for the bare and OTS-modified substrates are shown in the Figure 3.2.13. To conclude, both analyses of AFM images and contact angle measurements are important data because the profile across the OTS-treated substrate are show low surface roughness (~ 0.7 nm) (Figure 3.2.13 c, d) similar to that of bare substrate (~ 0.7 nm) (Figure 3.2.13 a, b). In addition, the contact angle is consistent with the highest value stated in the literature. The results imply that the SAMs of OTS on Si/SiO₂ substrate can be successfully prepared.

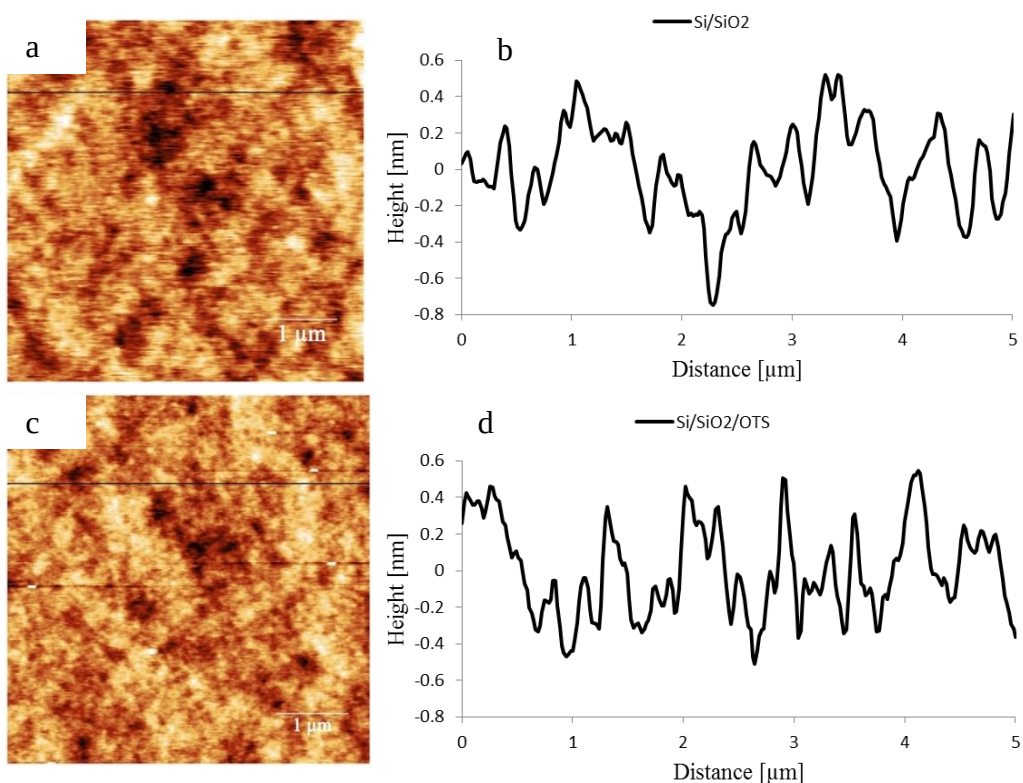


Figure 3.2.13: Both AFM image and height profile for bare substrate a, b and for OTS treated substrate c, d

3.2.5 $I(V)$ measurements

In this thesis, the $I(V)$ characteristics of naphthalocyanine (Nc) organic field effect transistors OFETs are extensively studied. $I(V)$ measurements were taken for both fabrication configurations of devices, bottom-contact OFETs and top-contact OFETs. A higher performance was obtained for top-contact OFETs than for bottom-contact OFETs. In addition, electrical measurements were taken under vacuum at room temperature and inside dark chamber directly after thin film deposition and also under ambient conditions. It is found that Nc OFETs exhibit transistor action even in air. Finally $I(V)$ measurements were taken in vacuum and atmosphere for devices with and without OTS-modification of the SiO_2 substrate. We use a probe station to take OFET characteristics measurements. Transistor performance improves for devices with OTS-treated oxide.

Figure 3.2.14 shows the setup of the OFET measurements circuit. The drain current, I_d , can be measured if the potential difference, V_R , across a series resistor, R , is determined (see Equation 3.2.1 and 3.2.2). Therefore, the $I(V)$ output characteristic and transfer characteristic of OFETs can be plotted. In order to obtain the $I(V)$ characteristic, a drain voltage, V_d , can be applied over a range -100 V to + 100V while the gate voltage, V_g , is kept constant and this measurement is taken for different gate voltages varying from -60V to +60 V (see Figures 3.2.19a, b). Alternatively, the $I(V)$ transfer characteristic can be obtained if V_d is kept at constant value while V_g is varied (see Figures 3.2.20a, b). The resistor, R , value for different OFET devices can be changed from 33 k Ω to 10 M Ω , depending on the channel or drain current across resistor. For high channel current, a small resistor is used for electrical measurements in order to avoid a high voltage drop across the resistor. However for low channel currents, a large resistor is used for improved current sensitivity. The potential difference between source and drain electrodes is denoted by V_{sd} , and the voltage drop across resistor is, V_R .

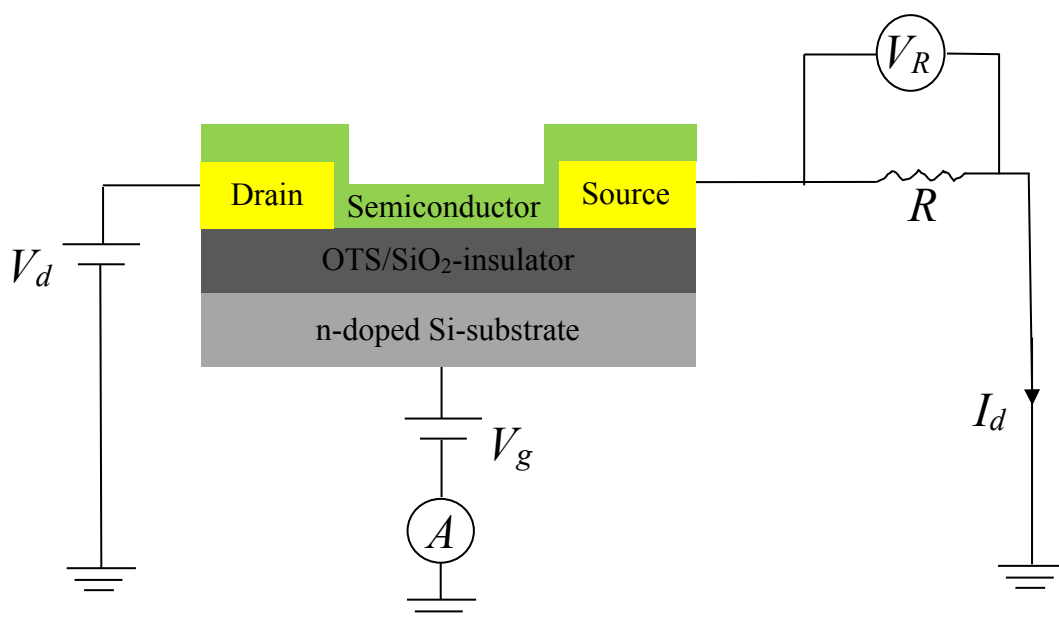


Figure 3.2.14: The setup of OFET electrical measurements circuit

$$I_d = \frac{V_R}{R} \quad 3.2.1$$

$$V_{sd} = V_d - V_R \quad 3.2.2$$

3.2.6 Fullerene and pentacene thin films organic field effect transistors as test systems

In this thesis organic semiconductors, such as fullerene C₆₀ and pentacene have been used to test the constructed experimental arrangement and device fabrication. The OFET devices were fabricated similar to those described in section 3.2.1. Figure 3.2.15 and Figure 3.2.16 show the structure of C₆₀ and pentacene, respectively.



Figure 3.2.15: Structure of fullerene C₆₀

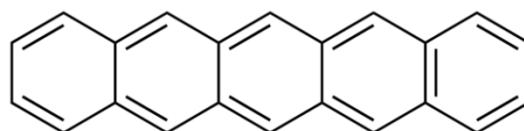


Figure 3.2.16: Structure of pentacene

C_{60} was grown on an n-type doped silicon wafer that has a silicon oxide SiO_2 thickness, t_{ox} , of 200 nm, while pentacene was grown onto p-type doped silicon wafer that has silicon oxide SiO_2 thickness of 300 nm. Only bottom-contact OFET devices with C_{60} active layer are fabricated because the fabrication process of top-contact configuration device requires exposure of C_{60} to air, but electrical characteristic of C_{60} is not stable under ambient condition resulting in a lower mobility. However, the fabrication of OFET device with a pentacene active layer is prepared in both bottom and top-contact configurations because pentacene thin film are not significantly changed if exposed to air. In order to metalize the Si/ SiO_2 surface with source (s) and drain (d) electrodes, metals were deposited using thermal evaporator system. Chromium (25 nm) and gold (40 nm) were evaporated to metalize C_{60} OFET devices. Titanium (10 nm) and gold (100 nm) were deposited to metalize pentacene OFET device. Both fullerene C_{60} thin film and pentacene thin film are grown under vacuum pressure of $\sim 10^{-6}$ mbar typically. This results in disordered polycrystalline grains of C_{60} with dimensions between 60-100 nm. The vacuum deposition of first layer of pentacene results in a terrace and step morphology. The vacuum deposition system used here is equipped with electrical connections to the OFET device so that the electrical measurements can be taken *in situ* prior to exposure to ambient conditions. The surface morphology of C_{60} thin film (see Figure 3.2.17 a) and pentacene thin film (see Figure 3.2.18 a) are studied using atomic force microscopy (AFM). In addition, the thin film height profiles of C_{60} are shown in Figure 3.2.17 b and that for pentacene are shown in Figure 3.2.18 b.

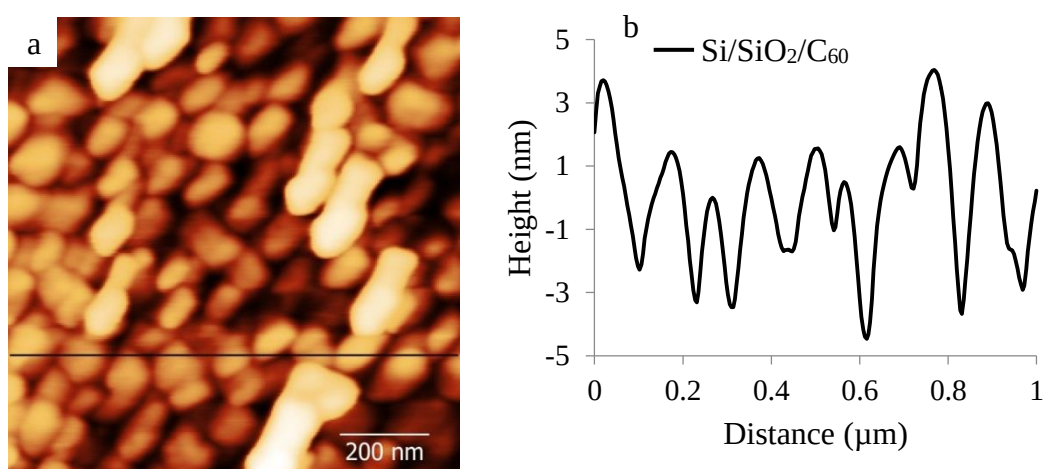


Figure 3.2.17: a: The surface morphology of a C_{60} thin film is imaged using atomic force microscopy (AFM). b: the height profile across a C_{60} thin films.

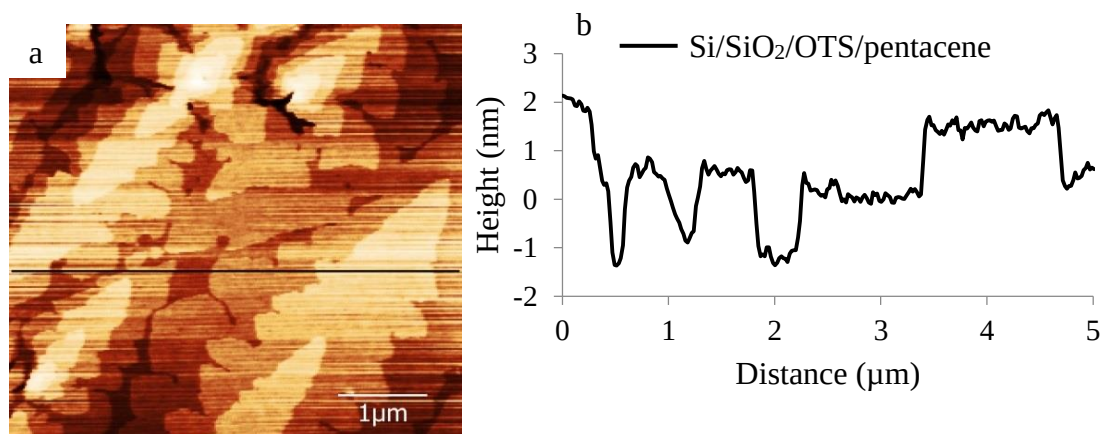


Figure 3.2.18: a: The surface morphology of a pentacene thin film is imaged using atomic force microscopy (AFM). b: the height profile across pentacene thin films.

The output characteristic of a C₆₀ OFET shows n-channel behaviour (see Figure 3.2.19 a), while pentacene is a p-channel transistor (see Figure 3.2.19 b). If the gate voltage V_g is applied to the the organic field effect transistor device, its channel will turn on and the drain current I_d will pass through channel between electrodes. In addition, the drain voltage V_d is applied to device (see Figure 3.2.14) so that the drain current can be increased linearly at low drain voltage V_d . However, for high drain voltage V_{sd} the drain current I_d will not depend on V_d ; as a result the current will level off to the saturation current I_d^{sat} . The output characteristic curve shows not only a linear region but also a saturation region clearly for both p-channel device and n-channel devices. The output characteristics for C₆₀ OFETs shows the threshold voltage V_{th} is about +30 V to turn on the n-channel, while it is found to be around -20 V to turn on a p-channel OFET.

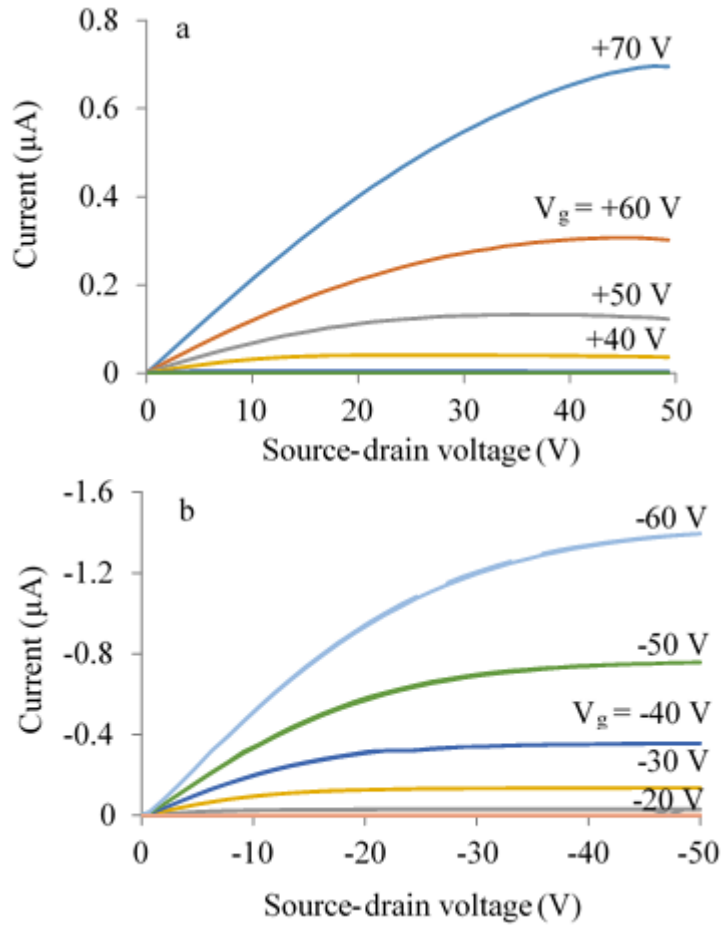


Figure 3.2.19: a: The output characteristic of n-channel transistor for a C_{60} thin film; b: The output characteristic of p-channel transistor for pentacene thin film.

The transfer characteristics for n-channel and p-channel transistors are shown in Figure 3.2.20a and Figure 3.2.20 b, respectively. A plot of drain current I_d versus gate voltage V_g with constant drain voltage 50 V, and a plot of $|I_d^{sat}|^{\frac{1}{2}}$ versus gate voltage V_g are drawn in order to determine the field effect mobility of the electrons μ_e and holes μ_h and also the threshold voltage V_{th} . The mobilities for OFET of C_{60} and pentacene thin films are found to be $(0.5 \pm 0.01) \times 10^{-3} \text{ cm}^2/\text{Vs}$ and $(3.4 \pm 0.8) \times 10^{-3} \text{ cm}^2/\text{Vs}$, respectively.

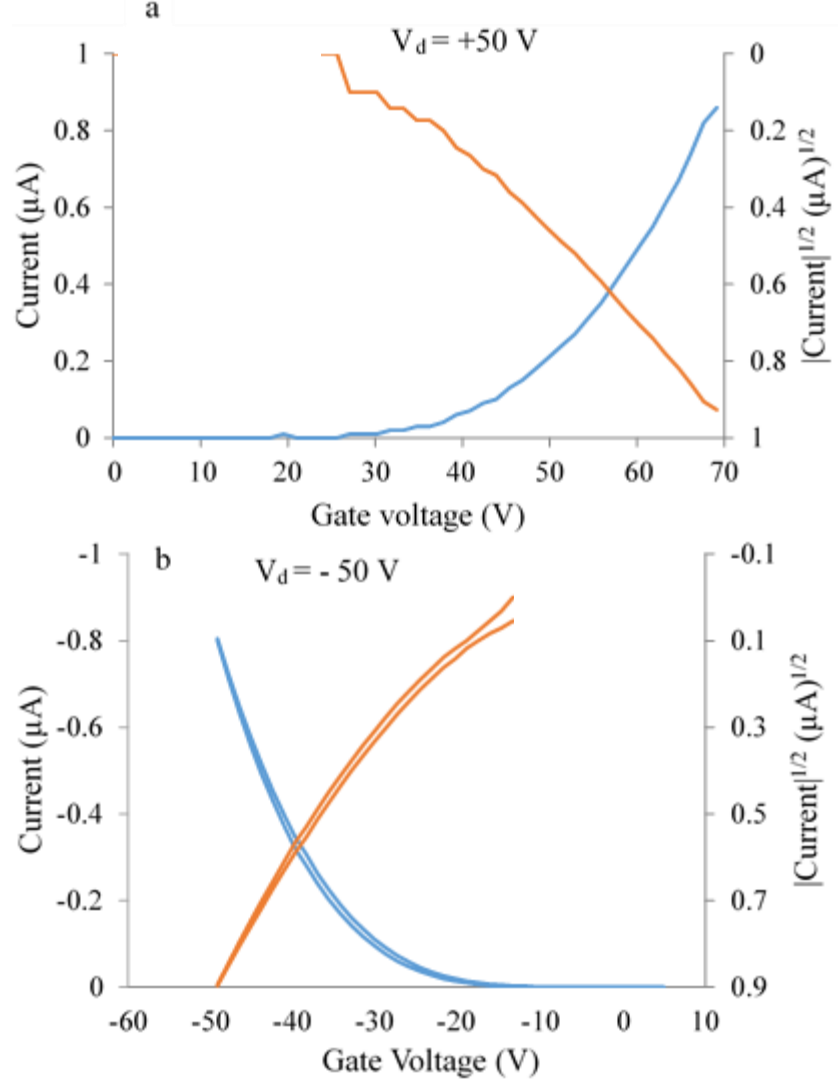


Figure 3.2.20: a: The transfer characteristics for an n-channel transistor of a C₆₀ thin film. b: The transfer characteristics for p-channel transistor of pentacene thin film.

The estimated drain current I_d across resistor and mobilities μ_n of OFET can be determined using Equation 2.2 .12 and Equation 2.2 .15, W is the width of OFET channel, L is the length of OFET channel, C_{ox} is the capacitance per unit area for SiO₂ substrate oxide. Those two equations are derived in section 2.2.1.

$$I_d^{sat} \simeq \frac{W\mu_n C_{ox}}{2L} (V_g - V_{th})^2$$

$$\mu_n \simeq \frac{2L}{WC_{ox}} \left[\frac{\partial \sqrt{I_d^{sat}}}{\partial V_g} \right]^2$$

3.3 Scanning probe microscopy

3.3.1 Scanning tunneling microscopy

Scanning tunneling microscopy (STM) was developed at IBM laboratories by Gerd Binnig and Heinrich Rohrer. STM is a technique that is capable of imaging in real space conductive surfaces with atomic scale resolution, and has become one of the most important tools in the field of nanoscience.

The basic principle behind scanning tunneling microscopy is the quantum mechanical tunnelling phenomenon [12-14]. In order to scan a surface by STM in an experiment, a metallic tip is positioned above a conducting or semiconducting surface. The tip is brought close to the surface, so that their separation is about several angstroms. If a small bias voltage is applied between tip and the surface, electrons can tunnel from the tip, passing through the potential barrier and into the sample surface (or vice versa) [15]. The direction of the tunnelling current can be controlled by bias voltage polarity. The magnitude of tunnelling current is extremely dependent on the tip-surface separation. The STM uses tunnelling current as a feedback parameter to control the tip-surface distance very precisely so that the topography of the surface can be imaged, while the tip is scanned across the surface [16].

3.3.1.1 Quantum mechanical tunnelling

STM imaging of the atomic arrangement of a surface is based on electron tunnelling through the vacuum gap between the metallic tip and the surface. However, describing the tunnel current of an STM experiment within an accurate theory is complicated because this requires precise information about the atomic structure of the tip and surface. Specifically, the exact termination of the metallic tip is often not known.

A simplified representation of the vacuum gap between tip and sample is a one dimensional rectangular potential barrier, as shown in Figure 3.3.1 [13]. The electron wave function, $\psi(x)$, satisfies the one dimensional time-independent Schrödinger equation.

$$\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + U(x)\psi(x) = E\psi(x) \quad 3.3.1$$

$$U(x) = \begin{cases} 0 & \text{for } x < 0 \\ U_0 & \text{for } 0 < x < a \\ 0 & \text{for } x > a \end{cases}$$

This equation describes an electron of mass, m , energy, E , incident on a finite potential barrier of height, U_0 , and width, a . The wave function of an electron, $\psi(x)$, outside and inside the potential barrier is given by,

$$\psi(x) = \begin{cases} Ae^{-ikx} + B e^{ikx} & x < 0 \\ Ce^{-\kappa x} + De^{\kappa x} & 0 \leq x \leq a \\ E e^{-ikx} & x > a \end{cases} \quad 3.3.2$$

where A, B, C, D, E are constants, κ is a decay constant $\kappa = \frac{\sqrt{2m(U_0-E)}}{\hbar}$, k is wave number of the incident electron $k = \frac{\sqrt{2mE}}{\hbar}$. The reflection and transmission coefficients, r , and, t , are defined

$$r = \frac{B}{A}, \quad t = \frac{E}{A}$$

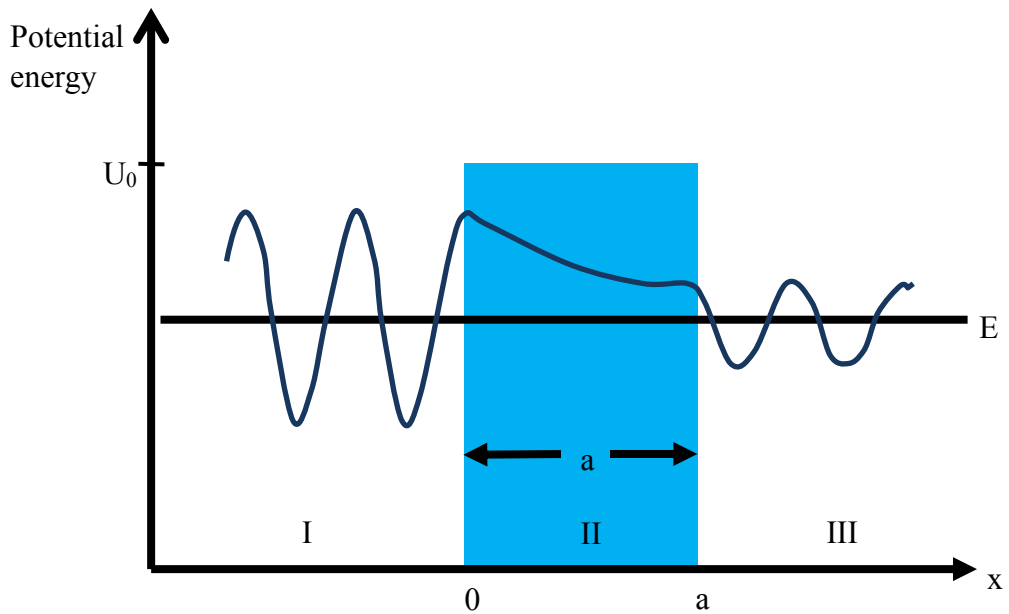


Figure 3.3.1: Quantum tunnelling through a one dimensional potential barrier. An electron impinges on the potential barrier from a metallic tip

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The square of the absolute value of transmitted amplitude t is equal to the transmission probability, T , for an electron to tunnel through the barrier.

$$T = |t|^2 \quad 3.3.3$$

The transmission coefficient can be calculated by solving Equations 3.3.2 assuming that the wave function $\psi(x)$ and its derivative are continuous across the boundaries at $x = 0$ and $x = a$. Therefore, the transmission probability is given by

$$T = \left[1 + \frac{\sinh^2(\kappa a)}{4(E/U_0)(1 - E/U_0)} \right]^{-1} \quad 3.3.4$$

For a thick barrier $\kappa a \gg 1$ the transmission probability of an electron passing through the potential barrier is, approximately, exponentially dependent on the barrier width, a , and square root of the barrier height ($U_0 - E$).

$$T \propto |\psi(a)|^2 \propto e^{-2\kappa a} \quad 3.3.5$$

Therefore, the tunnelling current decays exponentially with increasing barrier width a and can be written by the following expression [14]

$$I \propto T \propto e^{-2\kappa a} \quad 3.3.6$$

Figure 3.3.2 shows schematic diagrams of the Fermi levels of two metals for different separations and bias voltages. When the tip and surface are far and isolated from each other, their Fermi levels are different (see Figure 3.3.2a). As the separation between tip-substrate is brought into close proximity with a zero bias voltage applied, their Fermi levels are aligned and a contact potential between tip and surface is established as shown in Figure 3.3.2 b. However, if a bias voltage is applied between the tip and surface the Fermi level will shift by eV upward or downward depending on the polarity of bias voltage. In the case of applying a negative bias to the tip the Fermi level energy, E_F , will shift by eV upward then electrons with energy between E_F and $(E_F + eV)$ will tunnel from occupied states in tip to unoccupied states on the surface (see Figure 3.3.2 c).

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However, by applying a positive bias to the tip the Fermi level will shift by eV downward so that electrons with energy between E_F and $(E_F - eV)$ can tunnel across the barrier from occupied states in the substrate to unoccupied states in the tip (see Figure 3.3.2 d).

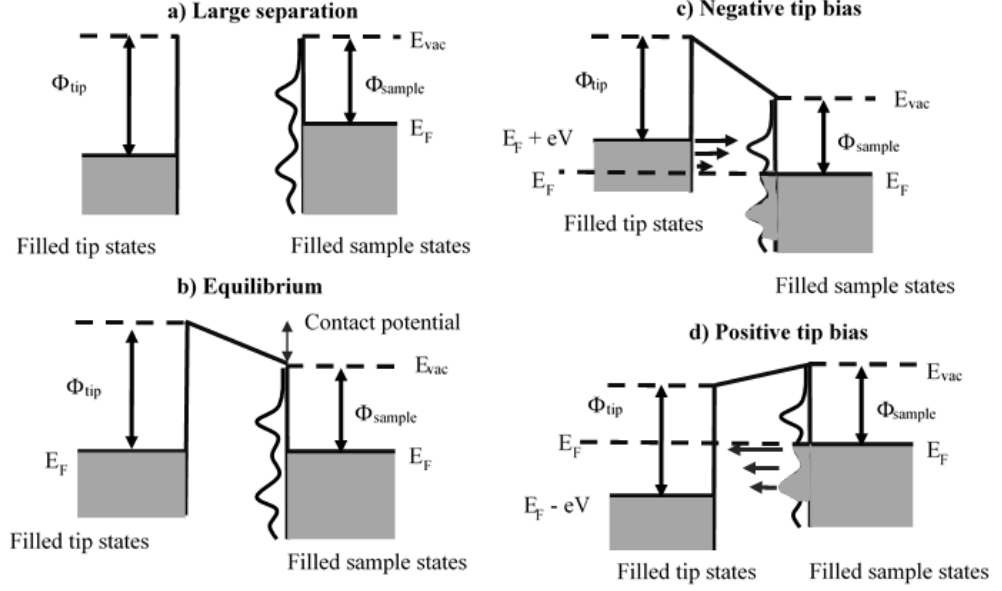


Figure 3.3.2: Schematic energy level diagram for different bias voltages in a metal tip/vacuum/metal junction; (a) if the two materials are far away; (b) if the two materials are close together; (c) a negative bias voltage is applied to the tip; (d) a positive bias voltage is applied to the tip

The tunnel current flowing for a small bias voltage is given approximately by,

$$I \sim e^{-2\kappa a} n(E_F) eV \quad 3.3.7$$

Where, $n(E_F)$, is the density of surfaces at the Fermi level. The tunnelling current is exponentially dependent on the distance between tip and surface, a , and the decay parameter, κ , which is determined by the work function, W ,

$$\kappa = \sqrt{2mW/\hbar^2} \quad 3.3.8$$

For STM experiments a typical work function is in the range 3-5 eV and the distance between tip and surface is about a few Å so that the change in the tunnelling current can be calculated and it is found to change by one order of

magnitude when a is increased by $1 \text{ \AA}$. This current sensitivity to distance enables the STM to resolve atomic arrangements on surfaces.

3.3.1.2 Bardeen formalism and Tersoff-Hamann theory

In the previous section the tunnelling current was calculated by effectively treating the sample and tip as parallel plates with an electron wave function satisfying the one dimensional time-independent Schrödinger equation.

In the Tersoff and Hamann theory for STM, which is based on Bardeen's perturbation theory [16], electronic states of tip and surface are considered as two independent systems which are close enough for their electron wave functions to overlap inside the barrier region, allowing electrons to tunnel. The tunnelling probability per unit time, p , for an electron to transfer from a tip state, ψ_μ , through the potential barrier into a surface state ψ_ν is given by formula,

$$p = \frac{2\pi}{\hbar} |M_{\mu\nu}|^2 \delta(E_\mu - E_\nu) \quad 3.3.9$$

where, $M_{\mu\nu}$, is the tunneling matrix element between the states μ of the tip and states ν of the surface. E_μ and E_ν are defined as the energy of states μ and ν respectively.

$M_{\mu\nu}$ is given by the overlap integral evaluated over a surface inside the potential barrier region [17].

$$M_{\mu\nu} = \frac{\hbar^2}{2m} \int (\psi_\mu^* \nabla \psi_\nu - \psi_\nu^* \nabla \psi_\mu) ds \quad 3.3.10$$

The Tersoff and Hamann formula, describing the tunnelling current evaluated when a small bias voltage is applied between tip and surface, can be written as,

$$I = \frac{2\pi e}{\hbar} \sum_{\mu,\nu} \{f(E_\mu)[1 - f(E_\nu)] - f(E_\nu)[1 - f(E_\mu)]\} |M_{\mu\nu}|^2 \delta(E_\nu - E_\mu + eV) \quad 3.3.11$$

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where $f(E_\mu)$ is the Fermi-Dirac function.

For simplification, at small bias voltage and low temperature, Equation 3.3.11 is given by [18].

$$I = \frac{2\pi}{\hbar} e^2 V \sum_{\mu, \nu} |M_{\mu\nu}|^2 \delta(E_\nu - E_F) \delta(E_\mu - E_F) \quad 3.3.12$$

Tersoff and Hamman developed this model for a tip with arbitrary shape. They further assumed that the tip was spherical with a radius of, R , and centred at the point, r_t . Also they model the tip as a spherical potential well with the separation, d , between the tip and the surface (see Figure 3.3.3) [18]. They showed that the tunneling matrix element for a tip and a surface with the same work function is given by

$$M_{\mu\nu} \propto k R e^{\kappa R} \psi_\nu(r_t) \quad 3.3.13$$

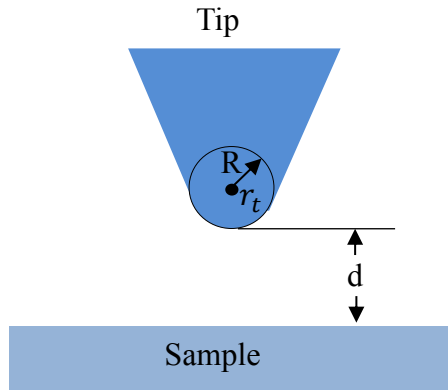


Figure 3.3.3: Schematic diagram of tunnelling geometry. The shape of the tip is assumed to be locally spherical

The tip wave function is taken to be the ground state of spherical potential well, an s-wave. When a small bias voltage is applied across the junction the tunneling current can be expressed as [19],

$$I \propto \sum_{\nu} |\psi_\nu(r_t)|^2 \delta(E_\nu - E_F) \equiv \rho(r_t, E_F) \quad 3.3.14$$

where $\rho(r_t, E_F)$ is local density of states, LDOS, of the surface at the Fermi level. This calculation shows that constant current STM images are equivalent to images of the LDOS, assuming the spherical one-atom tip. Therefore this theory is appropriate and widely used for describing the majority of STM images, and shows that images do not simply reproduce surface topography [20].

3.3.1.3 Voltage-dependent STM imaging

When a large voltage is applied, the tunnelling current may be approximated as follows,

$$I \sim \int_0^V \rho(r_t, E_F + eV) dV \quad 3.3.15$$

STM images show different features at different voltages; therefore, imaging the surface structure is voltage dependent.

Semiconductor surface images, obtained by STM are found to be dependent on the polarity and magnitude of the bias voltage. In the case of applying a negative bias to the tip the Fermi level energy E_F will shift by eV upward then electrons with energy between E_F and $(E_F + eV)$ will tunnel from occupied states in tip to unoccupied state on the in surface (see Figure 3.3.2c). Therefore, the STM images obtained at a negative tip bias are referred to as unoccupied state images. However, by applying a positive bias to the tip the Fermi level will shift by eV downward so that electrons with energy between E_F and $(E_F - eV)$ can tunnel across the barrier from occupied states in substrate to unoccupied states in the tip (see Figure 3.3.2d) [21]. Therefore the STM images obtained at a positive tip bias are referred to as occupied state images. For example (see Figure 3.3.4), the STM images of Si(001) reconstruction surface shows both filled state and empty state for negative and positive surface bias, respectively [22].

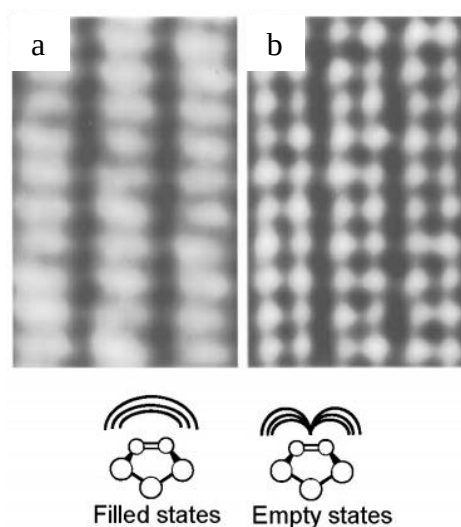


Figure 3.3.4: STM images of reconstructed Si(001) surface, (a) shows filled states at negative surface bias (b) shows empty states at positive surface bias. The schematics at the bottom show side view of dimer structure of the surface. Adopted from [22]

3.3.2 Scanning tunnelling microscopy set-up

The basic structure of an STM consists not only of mechanical elements such as a metallic tip and a piezoelectric tube, but also electronic elements including a feedback loop and amplifiers for current measurement, as illustrated in Figure 3.3.5. When an atomically sharp metallic tip is brought close to the surface with a separation between tip and surface of few angstroms, and a small bias voltage is applied to the tip, the electron may tunnel through the potential barrier to the surface [23]. The direction of the tunnelling current can be controlled by changing the polarity of the bias voltage. The piezoelectric tube is used to precisely control the vertical height and lateral coordinates of the tip within sub-angstrom precision. This is possible because piezoelectric materials have properties to deform their shape if a voltage is applied across them. Also these materials can generate voltage, if stress is applied on them. This makes it possible to scan the tip over a surface area using the lateral and vertical deformation of the piezoelectric tube [12].

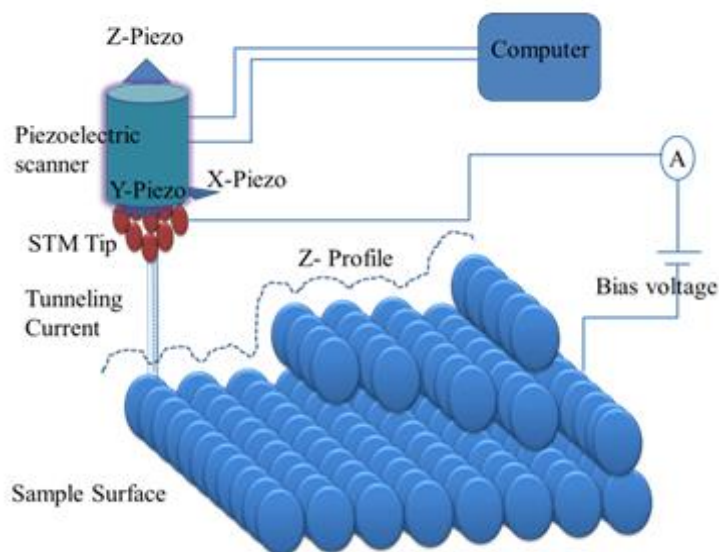


Figure 3.3.5: Basic structure of a STM system showing tip, surface, bias voltage between them, feedback and piezoelectric

The STM can be operated in two modes: in the constant current mode, the tip scans above the surface in the x, y-directions. A feedback loop maintains the tunnelling current at a constant value (see Figure 3.3.6 c) because the vertical position of tip is continuously adjusted using the z-piezo. For instance, if the feedback detects changes in tunnelling current due to higher or lower features on the substrate, the feedback will increase or decrease the z-piezo voltage to adjust the tip height. Thus the z-piezo retracts if current increases and expands if current decreases. The vertical height of the tip, z , as a function of the lateral position x , y is plotted and displayed by computer (see Figure 3.3.6 a). The advantage of this mode is that relatively rough surfaces can be imaged.

In constant height mode a tip is scanned quickly over the surface because the feedback is disabled, and the vertical position of the tip is fixed (see Figure 3.3.6 b). The tunnelling current varies as the tip moves across surface features and the variation of the tunnelling current as function of the lateral position is plotted and displayed by computer (see Figure 3.3.6 d). This mode works well for very flat surfaces, but the tip can easily crash into the surface or shift away from the surface due to misalignment so that tunnelling current cannot be measurable.

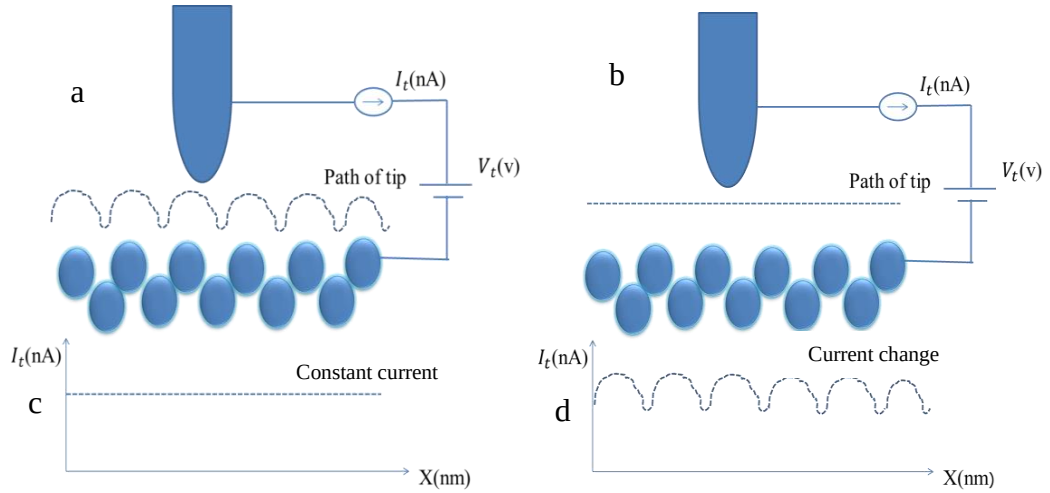


Figure 3.3.6: STM imaging surface topography (a) in constant current mode; (b) in constant height mode. Also, tip current I_t (nA) curve versus lateral positions x (nm) are shown for both mode (c, d).

3.3.3 Atomic force microscopy (AFM)

In the previous section the STM was introduced. This technique can be used to image surfaces but is only compatible with conducting and semiconductor substrates. To address this limitation of STM, Binnig, Quate and Gerber invented a new type of scanning probe microscope, the atomic force microscope AFM in 1986. The AFM is capable of imaging nonconductive surfaces with nanoscale resolution [24, 25]. The most important part of the AFM experimental set-up is a force sensor, usually a cantilever or quartz tuning fork. In this research cantilevers are used. Typically the cantilever-tip assembly is fabricated from silicon, or silicon nitride. These consist of a sharp probe mounted on a laser beam.

The cantilever or sample is mounted on a piezoelectric transducer to enable the accurate positioning of the tip relative to the sample at atomic dimensions. Using the piezoelectric transducer it is possible to control the sample motion in the x , y and z directions. The sample is positioned in close proximity to the tip using the z -piezo and raster scanned in the x, y directions. In order to monitor the cantilever deflection, a laser beam is focused onto the top surface of the tip and reflected onto the centre of photodiode detector, which consists of four separate

segments (see Figure 3.3.7). During scanning the cantilever will deflect in response to changes in surface topography. This leads to a deflection of the laser beam; as a result the laser spot will move away from centre of the photodiode and the intensity of the spot will change in each of photodiode quadrants producing an electrical signal, which is proportional to the vertical (up and down) tip motion. In addition the difference in intensity of right and left segments can be used to measure the twisting or lateral tip motion [26].

In the simplest mode of AFM operation, contact mode, the topography of the surface induces a deflection, Δz , of the cantilever due to the variation of the interaction force, F , between surface atoms and the probe. The bending of the cantilever can be determined by the deflection of the laser beam. The interaction force between tip and surface can be determined using Hooke's Law,

$$F = -k \Delta z \quad 3.3.16$$

where k is the spring constant of the cantilever, and Δz is the cantilever deflection.

In the contact mode, a feedback loop maintains a constant cantilever deflection at each scanning point. Feedback reduces the z-piezo voltage if the probe scans over a high feature on surface, so that the piezo will retract to adjust the deflection of cantilever. Alternatively, the z-piezo voltage is increased if the probe is above low feature on surface, so that the piezo will expand to maintain a constant deflection of cantilever. Finally the piezoelectric scanner displacements in three directions x, y and z will be recorded and displayed to generate a topographic image of the surface of sample.

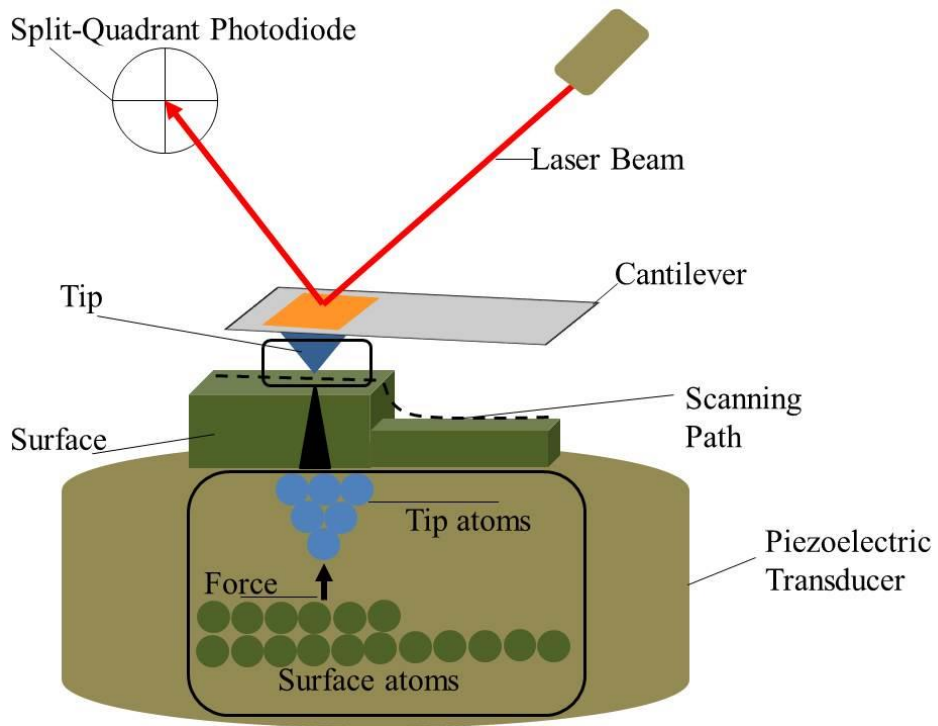


Figure 3.3.7: Atomic force microscope (AFM) set-up

Figure 3.3.8 shows the deflection of the cantilever as the tip and sample separation is varied. This variation is shown for both approach and retraction curves. The approach profile is started from position (*a*) where the tip is far away from surface so there is no interaction between them, and as a result no deflection is generated in the cantilever. At positions (*a* → *b*) there are very small interactions, but at position (*b*) the curve shows a sharp dip due to the tip jumping into contact with surface. This instability occurs when the surface gradient of the attractive force is greater than the spring constant of the cantilever. Further movement of the tip toward surface at positions (*b* → *c*) tip results in an upward cantilever deflection due to a rise of the repulsive force. The position (*c*) demonstrates the completion of an approach profile and the start of the retraction curve profile (*c* → *d* → *e* → *a*). At positions (*c* → *d*) during the retraction cycle, the adhesion force begins to act between tip and the surface as results the cantilever deflect downward maintaining contact with the surface. At position (*d* → *e*) the cantilever is deflected further until the elastic force for the cantilever overcomes the tip-surface adhesion force (F_{adh}), then a tip abruptly

retracts away from the surface at points (e). Further withdraw of the tip from the surface returns the cantilever back to the original point away from the surface ($e \rightarrow a$). Hooke's Law can be used to calculate the adhesion force (F_{adh}) from the displacement region (de). In addition the energy of the adhesion (E_{adh}) can be worked out from the area under the loop ($bb * de$) [27].

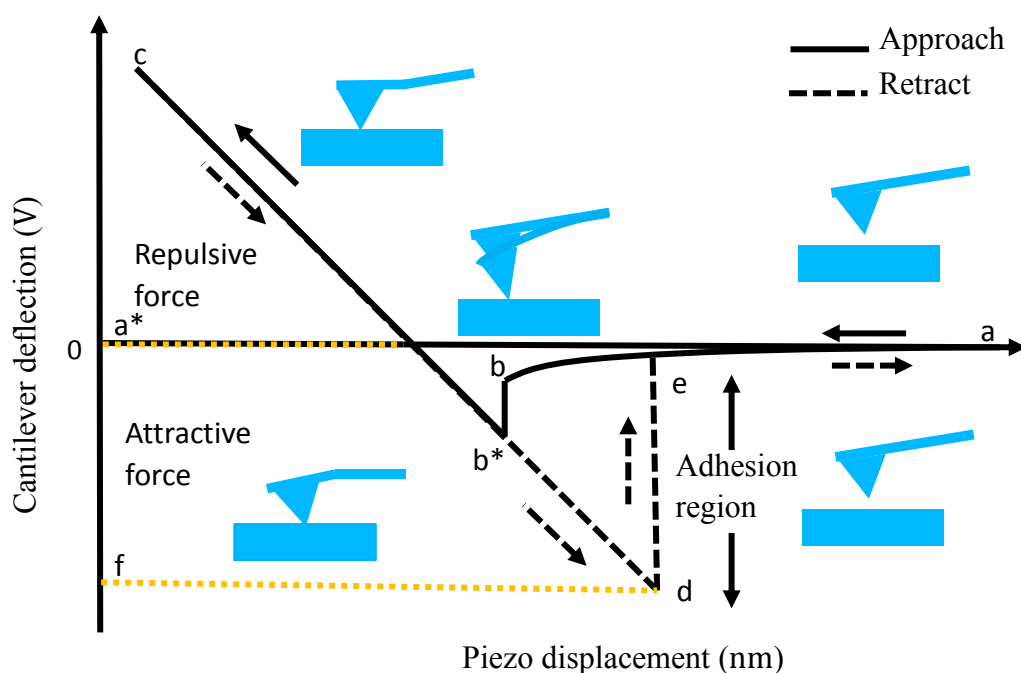


Figure 3.3.8: Schematic of force - distance curve for approaching and retracting the tip and to the surface.

3.3.3.1 Atomic force microscopy (AFM) modes

The AFM can be operated in three different modes to acquire images of a sample surface: contact mode, non-contact mode and tapping mode (see Figure 3.3.9). In these modes different regimes of interactions between the tip and surface are probed and the typical separation is different. In contact mode, the interaction between tip and surface is in the repulsive regime of force-distance curve. This force causes deflection of cantilever, as the tip is tracked over the surface topography. As discussed above, to keep the force constant the cantilever deflection is maintained at a constant value by adjusting the cantilever height using z-piezo voltage. In this mode it is possible to obtain high resolution images,

but the lateral force between sample and tip act on the sample so that the tip may damage soft material [28, 29].

In the non-contact mode, the cantilever is placed over the surface at a large separation about (1-10 nm). At this distance, the interaction force between tip and sample is small and is due to long range weak attractive forces, such as electrostatic, van der Waals or magnetic forces [30]. To operate this mode the cantilever is oscillated at a frequency close to its resonance frequency. In order to detect interaction forces between the tip and surface, changes in the frequency or amplitude of the oscillating cantilever are measured. The change in frequency is proportional to the force gradient, $\frac{dF}{dz}$. During scanning the frequency or amplitude is kept constant by adjusting the height of the cantilever using the z-piezo. The force gradient $\frac{dF}{dz}$ is kept constant and the z-height of the cantilever is used to generate surface image. Historically, the resolution in this mode is lower than that in contact mode because the interactions between tip and sample are weak, and their separation is large. Nowadays, this mode can be used to give high resolution images as well. However, this mode can be useful for scanning soft and fragile sample surfaces because the tip has weaker physical interactions with surface so there is less possibility to damage the surface [28, 31]. The tapping mode AFM was developed to enhance lateral resolution and reduce the effects of distortion and damage. In the tapping mode the tip intermittently taps or contacts the surface so that the separation between tip and sample varies by the oscillation amplitude 0.1-10 nm. To operate the tapping mode the cantilever oscillates close to its resonant frequency but is positioned closer to the surface or oscillated at higher amplitude, than in the non-contact mode. A feedback loop maintains constant oscillation amplitude, frequency or phase. To a first approximation this results in the force gradient between tip and sample remaining constant during imaging. By adjusting the height of the cantilever using the z-piezo, this height is used to generate the surface topography [27, 32-34]. However, detailed image interpretation is difficult in this mode; because forces are not uniform over the range of movement of the cantilever. Tapping mode was exclusively used in this thesis.

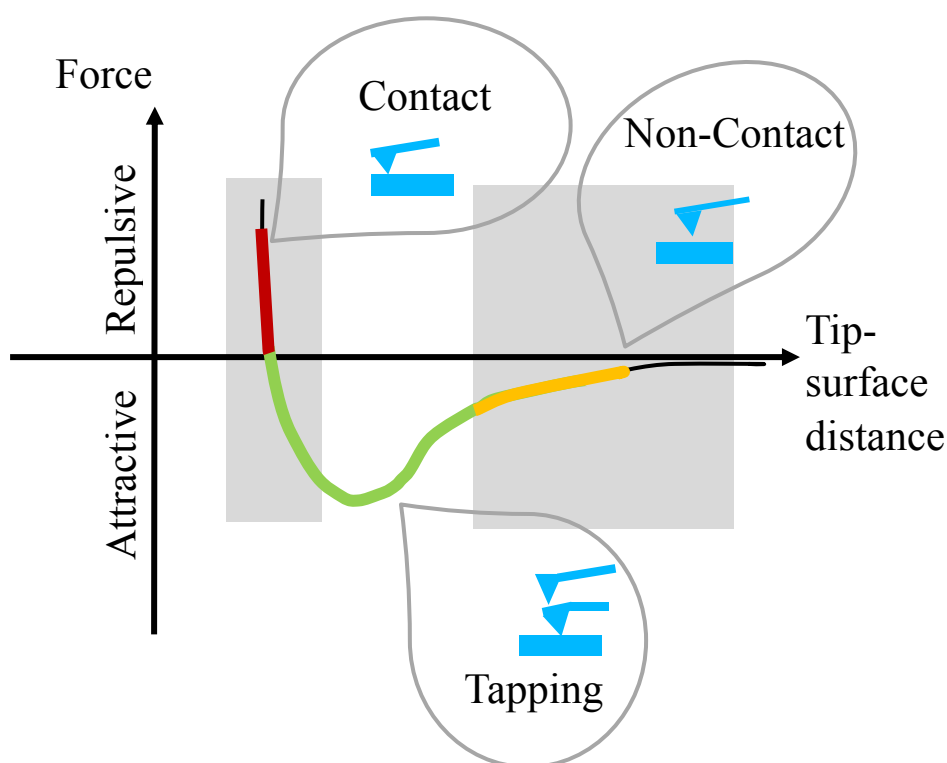


Figure 3.3.9: Force -distance curve highlighting the regime of operation for different modes of AFM

3.4 Summary

In this chapter, Au (111) surface preparation and solution deposition of cyclic polymers using immersion method have been introduced. The details of the experimental technique used for fabricating organic field effect transistors have been given. The structure of the OFET device and the comparison of the bottom and top-contact configuration have been discussed. The self-assembled monolayer of OTS on Si/SiO₂ has been confirmed, and leads to form hydrophobic oxide surface. The setup of OFET electrical measurements circuit are discussed, and applied to measure $I(V)$ characteristic of fullerene and pentacene OFETs *insitu* and ambient conditions to test the process of fabricating devices and the constructed experimental arrangement. The basic physics behind STM and AFM techniques and their structure have been explained.

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Chapter 4

Thin film growth

In this chapter, metal-free naphthalocyanine (Nc) and copper naphthalocyanine (CuNc) thin films were grown on both Si/SiO₂ and OTS-modified substrates using vacuum deposition. The effects of growth conditions on film morphology, the crystallinity and the preferential molecular orientation have been investigated using AFM and X-ray diffraction (XRD).

4.1 Growth of naphthalocyanine thin films

Naphthalocyanine (Nc) was purchased from Sigma-Aldrich. The Nc and CuNc molecular structures are shown in Figure 4.1.1a, b. Thin films of (Nc) on Si/SiO₂ were prepared by sublimation under vacuum at a typical pressure of 1×10^{-6} mbar. The naphthalocyanine source is heated to 450-500 °C resulting in a deposition rate of approximately 1nm/min. A quartz crystal microbalance was used to measure the thin film deposition rate and thickness, and the deposited thickness was calibrated by AFM. The substrate temperature was measured using a thermocouple. The Nc and CuNc source were heated to 500 °C and 560 °C, respectively for 10 hours before deposition to purify the source material.

In order to compare the thin film morphology at different substrate temperatures, the effective volume sticking coefficient, S_v , fractional coverage, Ω , and the ratio of the length to the width (L/W) of the thin film morphology were determined and plotted against substrate temperature (for example see Figure 4.1.6, 4.1.7, 4.1.8 and 4.1.9).

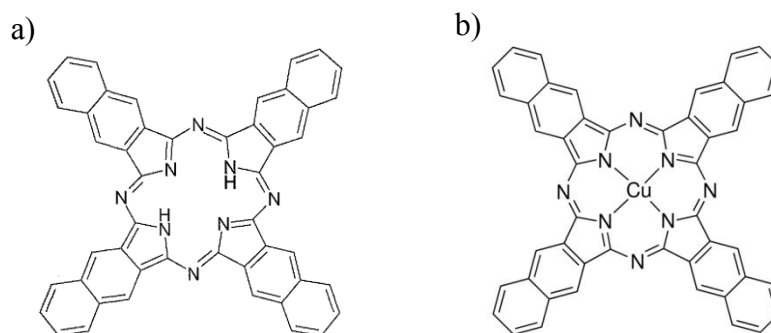


Figure 4.1.1: Molecular structures of Nc (a) and CuNc (b)

4.1.1 Growth of naphthalocyanine thin films on SiO₂

The study of the growth of naphthalocyanine thin films was performed in two stages. Firstly, a series of samples were grown with the same equivalent deposited thickness, D , but at different substrate temperatures, T_s . Secondly, a set of samples were grown with different deposition thicknesses but at the same substrate temperature. AFM images show that the thin film morphology of naphthalocyanine deposited at room temperature consisted of amorphous small grains. In addition, needle-like crystalline structures were formed when the naphthalocyanine film was grown at high substrate temperature. To analyse the growth of continuous thin films, such as grains and needle-like structure network we have plotted S_v , Ω and L/W against substrate temperature.

The effective volume sticking coefficient,

$$S_v = \frac{V_{ads}}{V_{evp}} \quad 4.1.1$$

is defined as the ratio of the volume of adsorbates, V_{ads} , on the substrate to the total volume of evaporated molecules, V_{evp} , which is incident on the surface as measured for room temperature deposition.

V_{ads} is determined from the AFM images. Each pixel of the AFM image has a measured height and a fixed area. The pixels with lowest height are assumed to be the substrate background while the pixels of adsorbed material are those with specific thickness. Then, the height of the pixel with material is multiplied by its unit area, giving the volume of material on each pixel. After that, the total

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volume of material V_{ads} on the surface is obtained by summing the volumes of each pixel. In addition, a thickness calibration is performed through the AFM height profile across an edge formed by scratching material (Figure 4.1.2).

The value of V_{evp} is determined from thickness of the deposited material (equivalent to D) at room temperature multiplied by the surface area (Equation 4.1.2). The thickness is determined using the calibrated deposition rate.

The total volume of evaporated material is,

$$V_{evp} = D \times A \quad 4.1.2$$

where A is the area of the AFM image being analysed.

To summarise, the effective volume sticking coefficient can be calculated from V_{ads} divided by V_{evp} . In particular, the volume sticking coefficient of naphthalocyanine is approximately equal to 1 for low substrate temperatures in the range from room temperature up to 170 °C but decreases dramatically for substrate temperature higher than 170 °C until it finally drops to zero at 246 °C (see Figure 4.1.6).

In addition, the fractional coverage, Ω , of material on the surface can be calculated from the area covered by the adsorbate divided by the AFM image area,

$$\Omega = \frac{\text{Adsorbate area } (\mu\text{m}^2)}{\text{AFM image area } (\mu\text{m}^2)} \quad 4.1.3$$

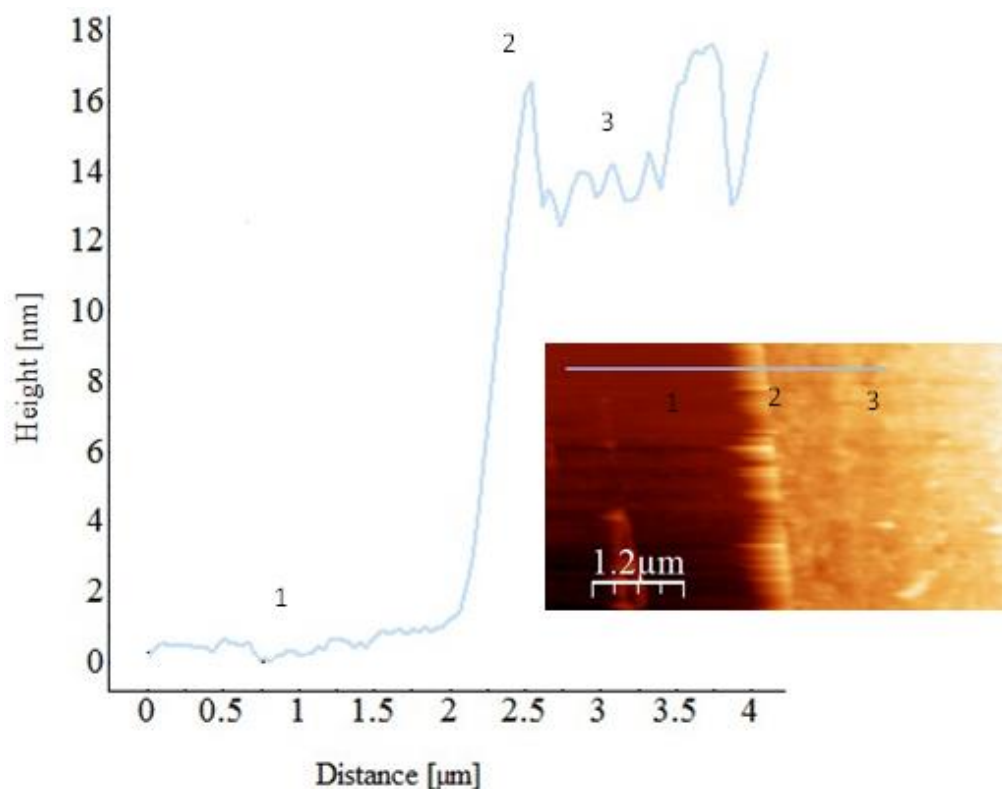


Figure 4.1.2: The line profile across a scratch in Nc on Si/SiO₂ revealed by an AFM image. The height marked by number 1 corresponds to the height of Si/SiO₂ substrate, while number 2 and 3 corresponds to the Nc

4.1.2 Substrate temperature dependence

Thin films were grown at substrate temperatures in the range 20-246 °C but fixed equivalent deposited thickness, D , of 15 nm. The growth conditions, particularly the substrate temperature strongly affect nucleation size and shape of the organic thin film. The surface roughness profile across all AFM images of Nc films grown on Si/SiO₂ substrate are plotted (Figure 4.1.3 and 4.1.4 right column).

Figure 4.1.3 shows AFM images of Nc thin films at different substrate temperatures in the range 21 – 130 °C for samples AENc18, 19, 30, 21. The thin Nc film grown at room temperature shows a dense circular grain structure with average size ≈ 40 nm that has surface roughness ≈ 2 nm (Figure 4.1.3a, b). The thin film morphology changes from a near circular grain to an elongated shape at substrate temperature 57 °C. In particular, we observed small elongated grains at 57 °C with average size along the major axis about 43 nm and surface roughness of 3 nm (Figure 4.1.3c,d). At substrate temperature 70 °C and 130 °C

the average size of the elongated grains increased to 80 nm and 140nm (Figure 4.1.3 e, g) and also the surface roughness increases from 2.2 nm to 8 nm (Figure 4.1.3 f,h).

We have observed that the thin film morphology changes from grain to a small needle-like structure at $T_s=170$ °C. Figure 4.1.4 displays the AFM images of Nc thin films grown at substrate temperatures in the range 200 – 230 °C for samples AENc22, 28, 31, 36. The optimum substrate temperature during growth is achieved at 200 °C, for which naphthalocyanine thin films show best morphological (Figure 4.1.4 a) and electrical properties (see chapter 6). At this temperature the thin film forms a well-connected needle-like crystalline structure with flat terraces and low surface roughness.

The thin Nc film changes from a small needle-like structure to extended needle-like crystalline structures at high substrate temperature, this mean that the growth occurs in face-face direction more than edges due to the higher binding energy on molecules faces than edges, this arises from π - π interaction between face-face of molecules. For example at 214 °C (Figure 4.1.4c), the crystals have widths of about 175 nm. The crystals become longer and more obvious in the films grown at 225-230 °C (Figure 4.1.4 e,g) with needles of lengths up to 1.2 μ m. Furthermore, the crystalline structures can be joined together as can be seen clearly in the inset Figure 4.1.4e and marked by a blue arrow, indicating that the crystals grow as islands initially then join together to form a crystalline network. The crystals have no preferable orientation leading to a disordered arrangement on the surface. The line profiles across AFM images of Nc films grown at substrate temperature in the range 200 – 230 °C (Figure 4.1.4 left column) show a height of $\simeq$ 17-25 nm. Note that the size of all AFM images is (1 μ m $\times$ 1 μ m).

To conclude, the Nc thin films at high substrate temperature grow as large and regular crystals. If the substrate temperature increases further, the Nc forms a discontinuous crystalline film with large gaps. This gives rise to a negative effect on the performance of OFETs. These results confirm that the grain shape, size and crystalline structure of film can be controlled by varying the substrate temperature.

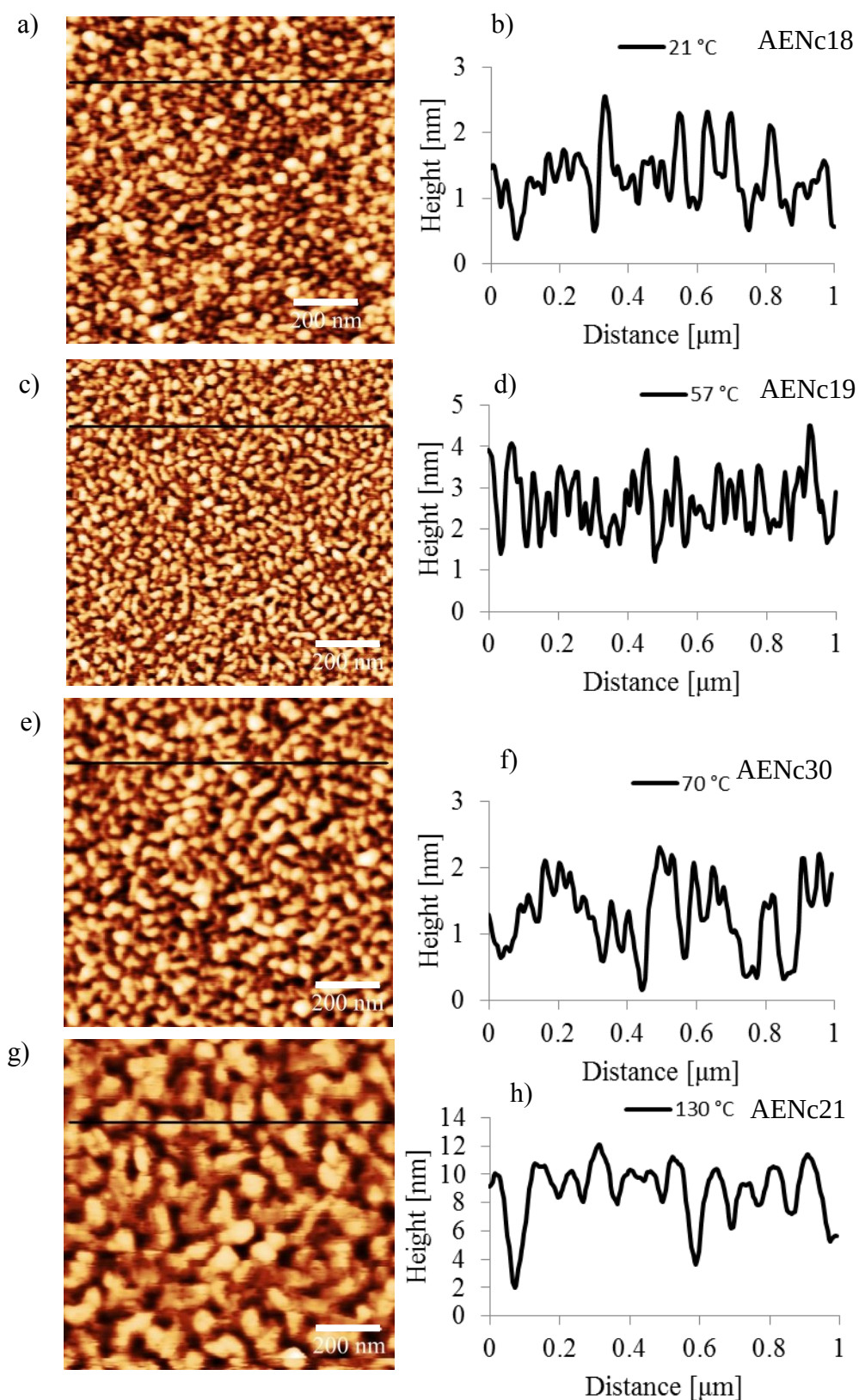


Figure 4.1.3: Topographic AFM images (left column) and surface roughness profile (right column) of grain structures of naphthalocyanine Nc thin films on Si/SiO₂ grown at deposition rate 1nm/min and different elevated substrate temperatures: (a, b) 21 °C, (c, d) 57 °C, (e, f) 70 °C, (g, h)130 °C.

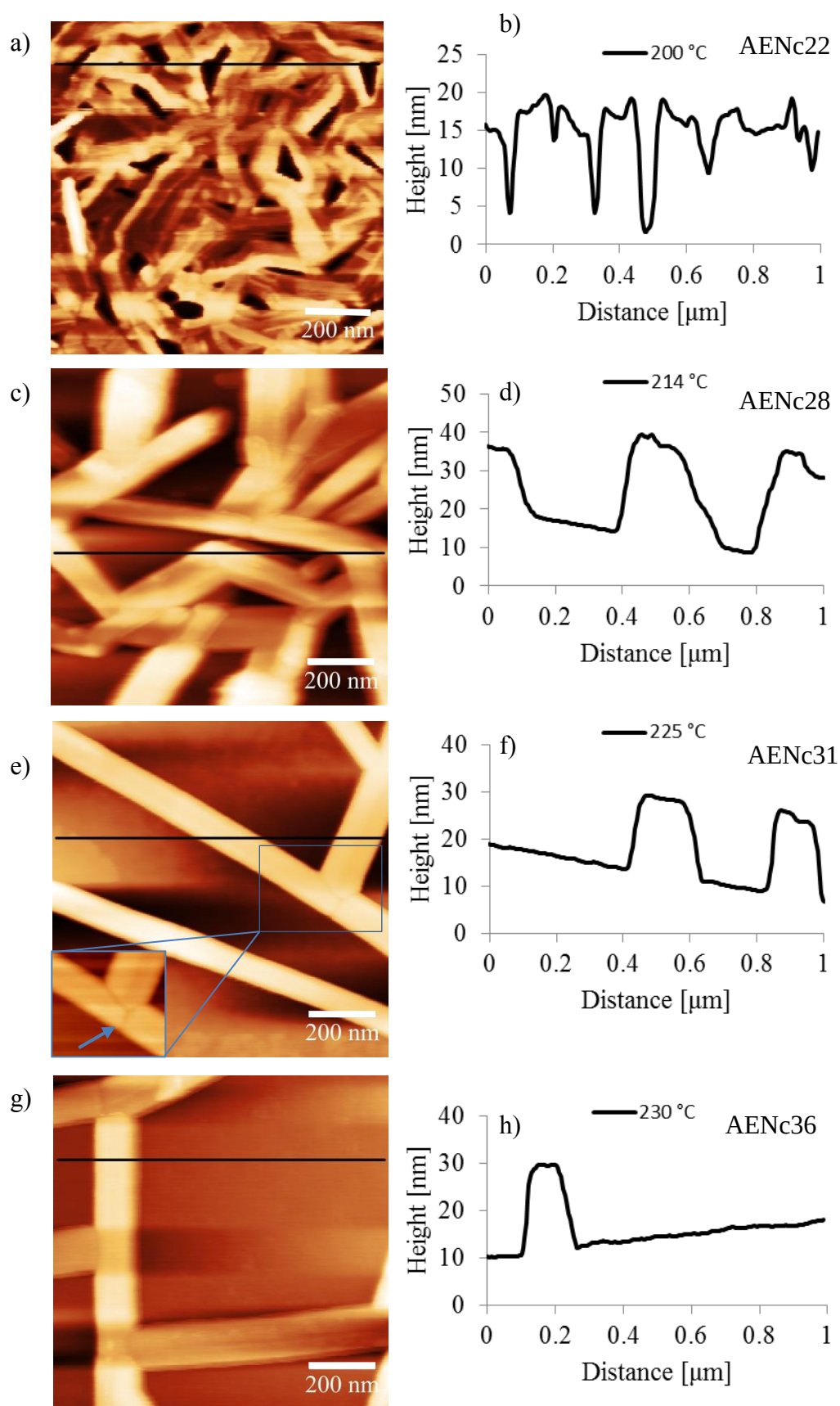


Figure 4.1.4: Topographic AFM images (left column) and height profiles (right column) of needle-like crystalline structures of naphthalocyanine Nc thin films on Si/SiO₂ grown at different elevated substrate temperatures: (a) 200 °C, (c) 214 °C, (e) 225 °C, (g) 230 °C.

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At substrate temperatures of greater than 240 °C, the deposition of Nc on Si/SiO₂ shows just bare oxide (sample AENc23), as shown by topographic AFM images (Figure 4.1.5a). Line profiles across this image show a low surface roughness of about 0.4 nm (Figure 4.1.5b), implying complete re-evaporation of impinging naphthalocyanine Nc at this temperature.

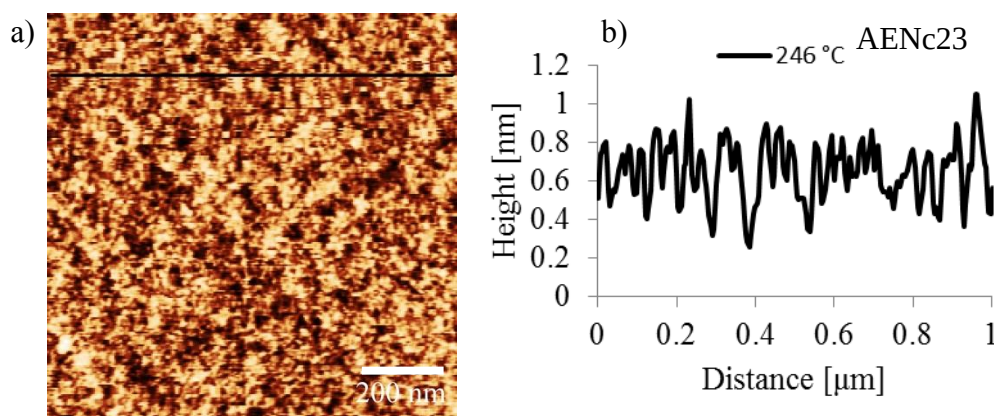


Figure 4.1.5: Topographic AFM images (left column) and surface roughness profile (right column) of bare Si/SiO₂ as a result of re-evaporation naphthalocyanine Nc when it is grown at substrate temperatures 246 °C.

Figure 4.1.6 shows the variation of the volume sticking coefficient of the Nc growth at equivalent thickness 15 nm as the substrate temperatures increases from room temperature up to 246 °C. There are no significant changes in the volume sticking coefficient of Nc on Si/SiO₂ at substrate temperature ranging from 25 °C to 170 °C but it drops rapidly at higher substrate temperatures until eventually no adsorption occurs at 246 °C. If the temperature of the substrate is increased, the molecules will have a higher thermal energy which leads to an increase not only of molecular diffusion but also the rate of desorption from the surface.

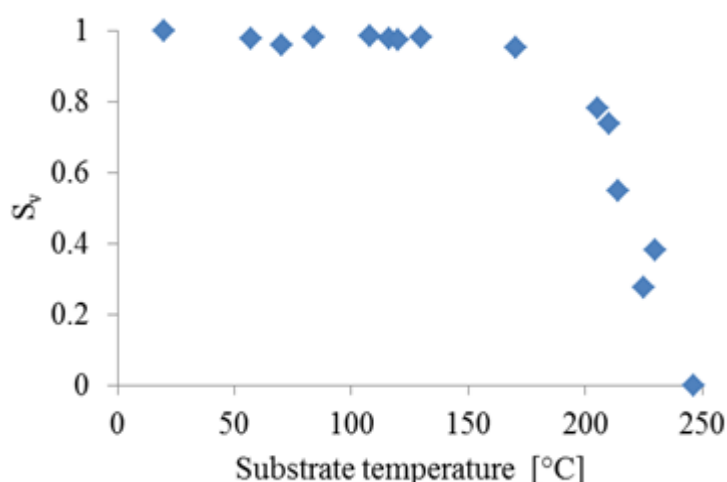


Figure 4.1.6: The volume sticking coefficient, S_v , of the Nc growth versus the substrate temperature for an equivalent thickness 15 nm.

At low substrate temperature the morphology of Nc thin films (see Figures 4.1.3 right) shows a densely packed grain structure. S_v remains constant at 1, indicating that desorption of molecules is very small. At high substrate temperatures ranging from 180 °C to 230 °C, the morphology shows the needle-like crystalline structure (see Figure 4.1.4 left column). In this range significant desorption occurs leading to large gaps on the substrate. Therefore, S_v drops dramatically from 0.79 at 214 °C to 0.38 at 230 °C.

The fractional coverage of Nc versus the substrate temperature is shown in Figure 4.1.7. At low substrate temperatures, from room temperature up to 200 °C, the adsorbed material is well connected (see Figures 4.1.3 and Figure 4.1.4a) so that the fractional coverage is approximately constant at 1. In contrast, at high substrate temperature ranging from 214 °C to 246 °C the surface is not completely covered and the size of gaps in the film increases with temperature (see Figure 4.1.4 left column) so that the fractional coverage drops.

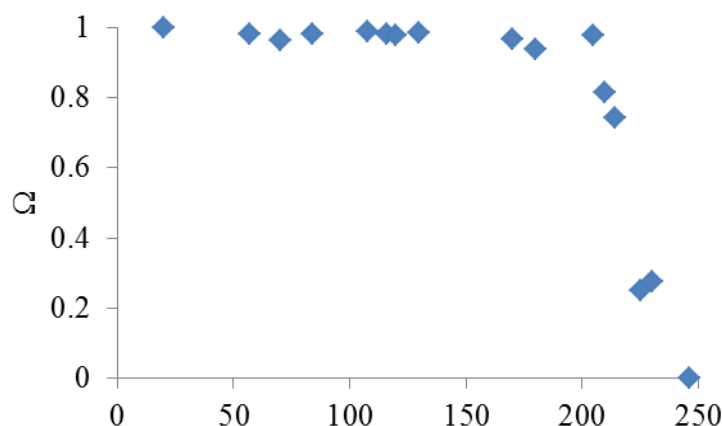


Figure 4.1.7: The fractional coverage, Ω , of Nc growth versus the substrate temperature for an equivalent thickness 15 nm

The average length of Nc islands shows a considerable rise as the substrate temperature increases. In addition, the average width of these islands increases slightly with substrate temperature up to a peak value of 180 nm at 214 °C but falls to 110 nm at 225 °C as shown in Figure 4.1.8. Furthermore, the ratio of length to width changes with different substrate temperature (Figure 4.1.9) because the growth structure changes from circular grains to extended needle-like structure at substrate temperature above 170 °C (Figure 4.1.3 and 4.1.4 left column). As discussed below it is likely that higher thermal energies allow the molecules to diffuse on the surface and then stack in an edge-on orientation in the large needle-like crystalline structure.

At room temperature the ratio of length to width is close to 1. For substrate temperatures up to 130 °C the AFM images show an elongated grain structure with an increase of the size, and a length to width ratio which is constant at approximately 2. The ratio of length to width shows a rapid increase at substrate temperature from 205 °C up to 230 °C, reflecting the growth of extended needle-like crystalline structures.

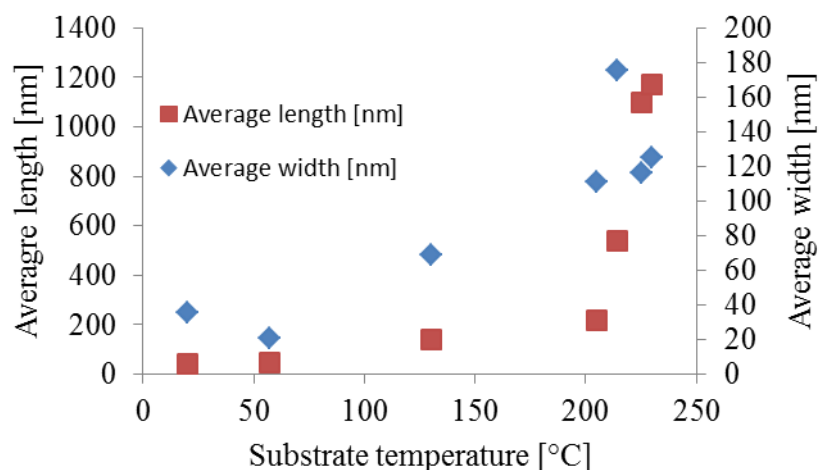


Figure 4.1.8: The average length and width of Nc grains versus substrate temperature

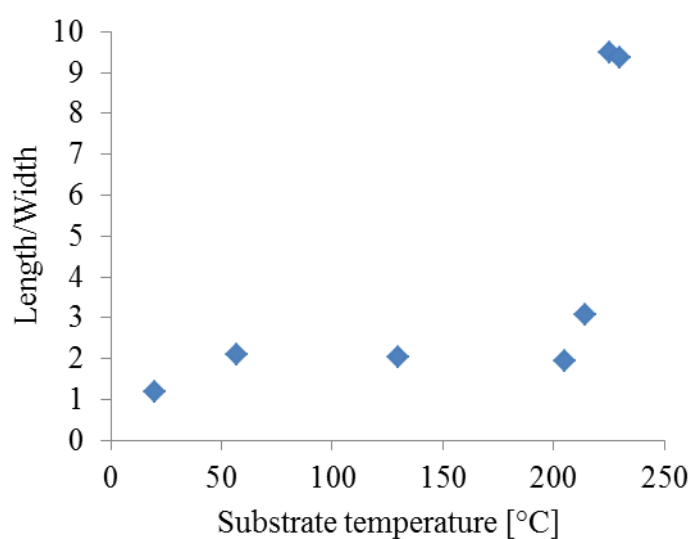


Figure 4.1.9: The ratio of length to width versus substrate temperature

4.1.3 X-ray diffraction study of thin films structure

The structure of Nc films with thicknesses D about 15 nm at different substrate temperatures (21, 120, 180) °C was investigated using X-ray diffraction (XRD) with Cu K α radiation ($\lambda = 1.54$ Å). We have plotted the XRD $\theta - 2\theta$ plots, for the sample prepared at room temperature (see Figure 4.1.10a). For this sample

we did not observe a sharp intense peak, indicating an amorphous thin film. However, samples prepared at 120 and 180 °C exhibit a clear peak located at $2\theta = 5.84 \pm 0.09^\circ$ corresponding to a plane spacing perpendicular to the surface of 1.51 ± 0.02 nm, and also higher order peaks with values 2θ of 11.6° and 17.5° implying crystalline thin films (see Figure 4.1.10b and 4.1.10c). In other words, the XRD data show that crystalline structure of thin films was enhanced as a result of increasing the substrate temperature during growth.

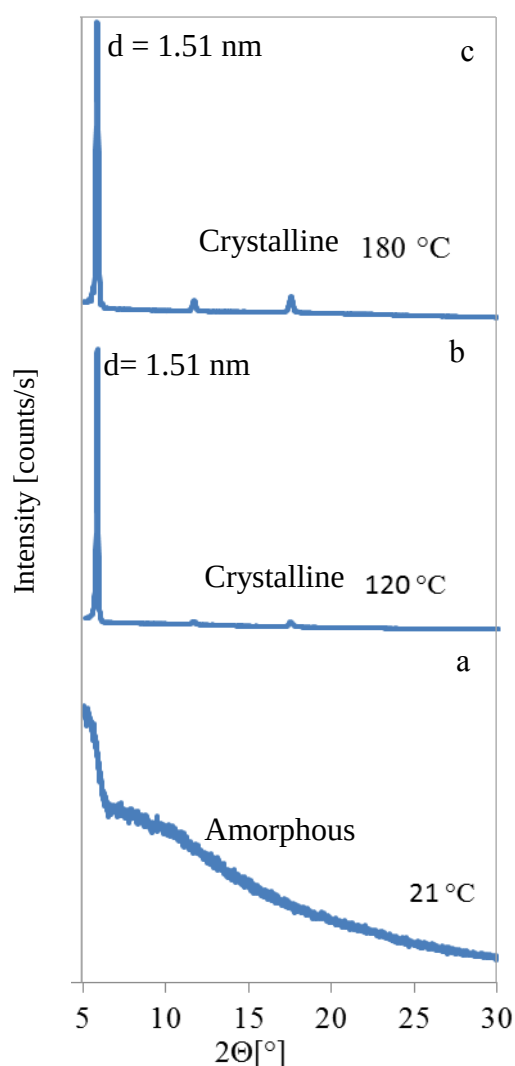


Figure 4.1.10: XRD data $\theta - 2\theta$ with x-ray intensity for the Nc amorphous and crystalline thin films prepared at different substrate temperatures during growth a) 21 °C b) 120 °C c) 180 °C

The crystal structure of a non-metallised Nc has not been published. In 1992, Yanagi et al. reported that the molecular bulk orientation of metal naphthalocyanine (ZnNc) prepared by vacuum deposition on glass shows a diffraction peak at $2\theta \approx 5.9^\circ$ which is close to our value [1]. On the basis of the above article this corresponds to inter-planar spacing $d = 1.51\text{nm}$, in which molecules prefer to stack as an edge-on arrangement with respect to a surface (Figure 4.1.11a). In addition, for molecules adsorbed on NaCl they observe another peak at $2\theta = 26.5^\circ$, which is not present in our data and corresponds to an inter-plane distance 0.33 nm , in which molecules prefer to stack as a face-on arrangement with respect to the surface (Figure 4.1.11b). From the above discussion we conclude that the Nc molecules prefer to stack as an edge-on arrangement with respect to SiO_2 at high substrate temperature similar to orientation of ZnNc on glass. The Bragg formula was used to calculate the distance between the reflecting planes, d , as follows:

$$n\lambda = 2d\sin\theta \quad 4.1.4$$

where, n , is the order of diffraction, λ , the X-ray wave length and, θ , the diffraction angle.

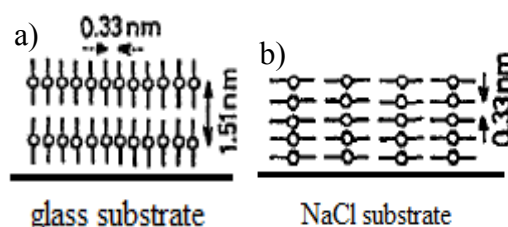


Figure 4.1.11: Schematic diagram of ZnNc film shows molecular stacking, in which molecules stood perpendicular to glass surface with inter-plane distance 1.51nm (a), and the molecules parallel to the NaCl surface with inter-plane distance 0.33nm (b) [1]

AFM and XRD show that the thin film growth changes from amorphous to crystalline structure with increasing substrate temperatures. Figure 4.1.12a shows amorphous growth at room temperature, while molecules stack edge-on to the substrate and form crystalline configuration (needle-like structure) at $T_s \geq$

120 °C (Figure 4.1.12b). The thin film growth mode at high substrate temperature can be explained as follows: the overall film is grown as islands initially then join together to form a crystalline network see (inset Figure 4.1.4e in blue arrow)

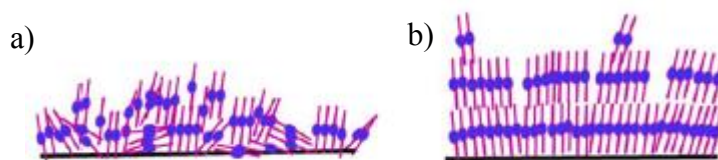


Figure 4.1.12: Schematic illustrates growth modes, molecular ordering and molecular packing of Nc molecules on SiO₂ surface deposited at (a) RT, (b) 120 °C

The growth morphology of Nc is very similar to that observed for phthalocyanine (Pc). Narayanan et al. reported an investigation of molecular ordering and packing of CuPc molecules using positron annihilation spectroscopic (PAS) and X-ray reflectivity (XRR) techniques. They observed a layer plus island formation with amorphous structure for film grown at room temperature (Figure 4.1.13 a), near layer by layer formation with crystalline structure of molecules stacking edge-on at $T_s = 100$ -150 °C (Figure 4.1.13 b), and island formation with large gaps between needle-like crystalline structures at $T_s = 225$ °C (Figure 4.1.13 c,d) [2].

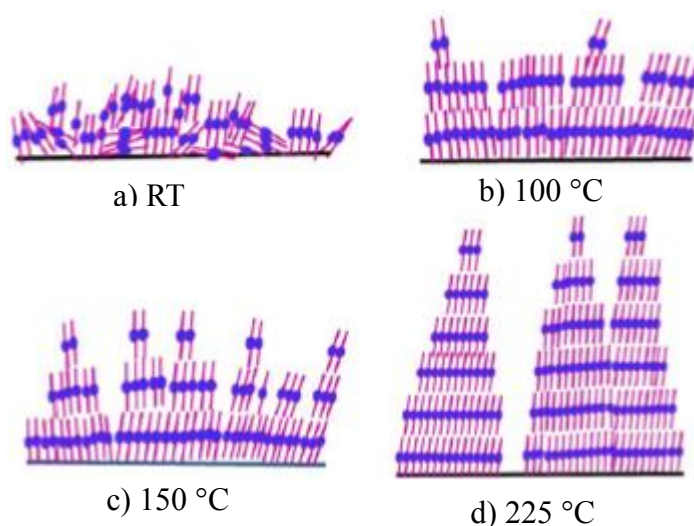


Figure 4.1.13: Schematic illustrates growth modes, molecular ordering and molecular packing of CuPc molecules on SiO₂ surface deposited at (a) RT, (b) 100, (c) 150, and (d) 225 °C [2]

In addition, in 2001, Hisatomo and co-worker reported vacuum deposition of oxotitanium phthalocyanine (TiOPc) thin film on OTS-modified Si/SiO₂, where TiOPc molecules preferentially nucleated in an edge-on orientation [3, 4]. The size of Pc grains increases if the substrate temperature is increased similar to our observation for Nc. In 2009, Gentry et al. reported asymmetric grain growth of phthalocyanine thin films when the deposited temperature was increased and found almost spherical grains with size 35 nm at 21 °C and elongated needle-like forms with size 200 nm at 260 °C. They also observed the optimum growth temperature for films grown at 200 °C. This is attributed to low surface roughness for elongated needle-like crystals [5]. Other groups have also reported the effect of deposition temperature on the grain size of the phthalocyanine thin films [6-8]. Several groups reported that the growth of thin films of organic molecules such as phthalocyanine and pentacene on graphene, where these molecules prefer stack in a face-on orientation on the substrate due to the favorable π - π interaction between the molecules and substrate [9]. This implies that both substrate temperatures and surface properties can be used to control of molecular orientation [10-13]. Finally, the diffraction peaks of Nc show differences, as expected, with these analogue molecules such as nickel phthalocyanine that show a strong peak at $2\theta = 7^\circ$ corresponding to stacking space at 1.25 nm [14].

4.1.4 Thickness dependence

Thin films of naphthalocyanine were grown on Si/SiO₂ in order to investigate the dependence of thin film growth on thickness at two substrate temperatures: room temperature and 180 °C.

4.1.4.1 Substrate at room temperature

We have grown a series of samples at room temperatures, AENc09, 18, 40, of naphthalocyanine thin films on Si/SiO₂ with thicknesses 5 nm, 20 nm, 105 nm, respectively in order to investigate the variation of thin film morphology with thickness. The analysis of grain size shows a typical dimension of 25 nm when the thickness of the material is 5 nm (Figure 4.1.14a). The grain size becomes larger with continued adsorption as follows: from 31 nm at deposition thickness 20 nm to larger grains of 85 nm at thickness 105 nm (Figure 4.1.14c, e). The line profile across AFM images of Nc films with various deposited thicknesses from 5 nm to 105 nm illustrated that the surface roughness increased from 1 nm to 8 nm (Figure 4.1.14b, d, f right column). It seems that the most significant difference in grain size is generated by varying growth temperature (see previous section 4.1.2) as compared to that by varying the sample thickness only. Many groups have also studied the thin film growth as a function of thickness. In 2011, Schünemann et al. reported thermal evaporation of ZnPc thin film on a Si/SiO₂ substrate at different thickness 5 nm, 10 nm, 25 nm, and 50 nm with different substrate temperature for each thickness. The thin film morphology shows that the grain size and surface roughness increases by increasing both thickness and substrate temperature. XRD data for ZnPc films show crystalline structure that is independent of thickness for a fixed substrate temperature [15].

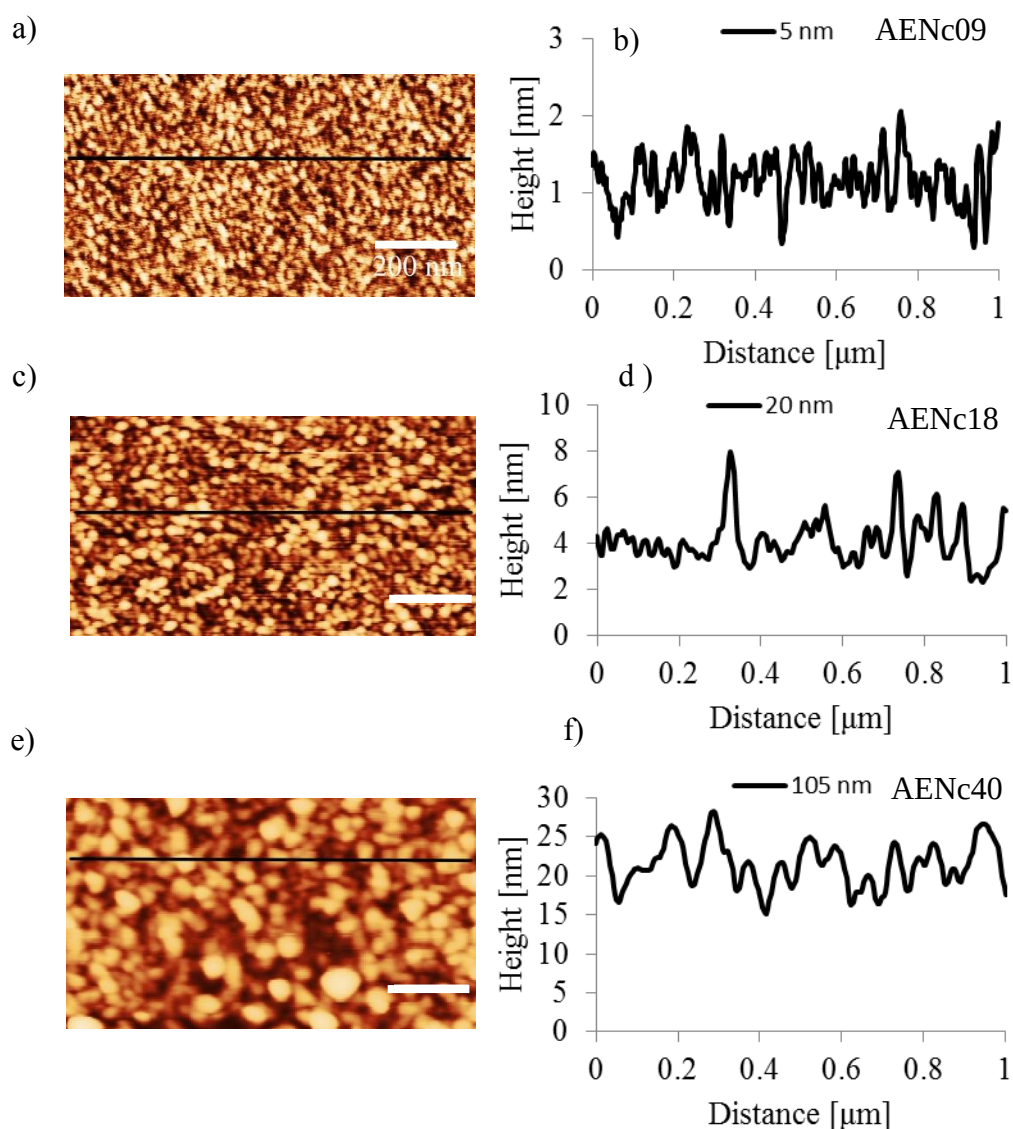


Figure 4.1.14: (left) AFM images and (right) the height profiles of naphthalocyanine Nc thin film growth as grain structure on Si/SiO₂ substrate at room temperature with various deposited thickness: (a) 5 nm, (c) 20 nm, (e) 105 nm while fixed deposition rate 1nm/min. Scale bar 200 nm

Table 4.1.1 illustrates the variation of the average length and width of grain growth with increasing deposited thickness at room temperature. There is a slight increase in average length from 25 nm to 85 nm and width from 23 nm to 60 nm of grains as the deposited thickness increases from 5 nm to 105 nm. The changes of grain size with increasing thickness are clearly observed from AFM images (Figure 4.1.14 left column).

Table 4.1.1: The variation of the average length and width of grain growth with increasing the deposited thickness on Si/SiO₂ at room temperature

Sample	Calibrated thickness [nm]	Grain average length [nm]	Grain average width [nm]
AENc09	5	25	23
AENc18	20	30	28
AENc40	105	85	60

4.1.4.2 Substrate temperature at 180 °C

In this section, the experiment discussed in previous section 4.1.4.1 was repeated, but here we have heated the substrate to a fixed temperature 180°C during thin film growth. We grew two samples named AENc42, 37 of naphthalocyanine thin films with thicknesses 13 nm and 80 nm, respectively. The thin film morphology shows an extended needle-like crystalline structure with free gaps, and as shown in Figure 4.2.15a, c, there is no preferable orientation of growing needles. The size of the crystalline structure of naphthalocyanine thin film and the gaps between them have been affected by increasing deposited thickness; increasing the thickness from 13 nm to 80 nm resulted in a significant increase in the average width of needle planar terrace from 81 nm to 190 nm. As a result, the thin film morphology changes from a network of crystalline structures at low thickness into a quasi-continuous film at higher thickness because gaps between crystalline structures are reduced. This may be due to the deposited molecules growing laterally rather than nucleating new islands on the Si/SiO₂ substrate. For this reason, the width of needle terrace increases. The line profiles across the thin films in AFM images show wider planar terraces for 180 nm films as compared to 13 nm films (Figure 4.2.15b, d).

Overall, it seems that the substrate temperature can control molecular ordering, while the dimensions of needle-like crystalline structure can be controlled by both substrate temperature and deposited thickness.

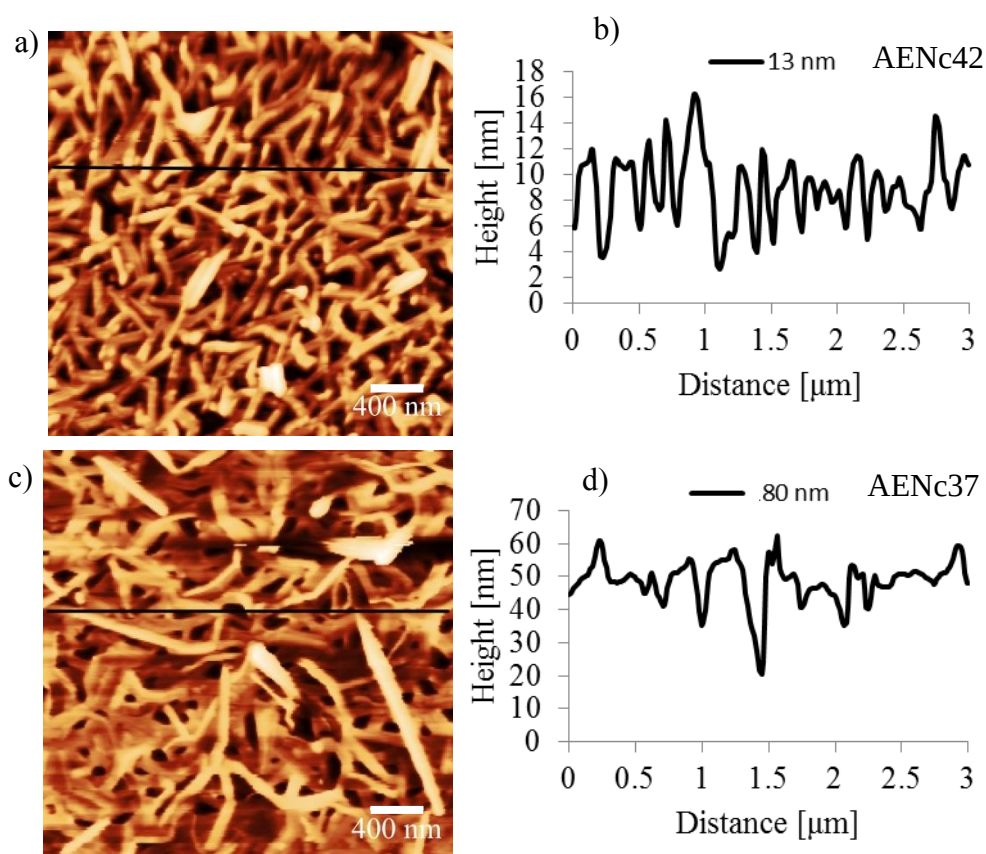


Figure 4.1.15: AFM images of naphthalocyanine Nc thin film on Si/SiO₂ with thicknesses 13 nm and 80 nm (left column) at substrate temperature 180 °C and the height profile across AFM image (left column)

4.1.5 Effect of OTS treated SiO₂ substrate

Another method to modify the molecular orientation on a surface is by silanization of the sample surface. In this work, the Si/SiO₂ substrate is treated with octadecyltrichlorosilane (OTS) as described in section 3.2.4, which results in a change of the chemical termination of the surface substrate. Forming a monolayer of OTS on SiO₂ surface passivates the surface, and makes it highly hydrophobic. The degree of hydrophobicity can be estimated by measuring the contact angle of a water droplet on the surface. In this work, a large contact angle of 107° was measured for the OTS-modified oxide substrate. Many groups have previously deposited different organic semiconductor layers on the OTS-modified oxide substrate and have found improved properties of OFETs. For example, in 2002, Shtein and co-worker reported that the grain size of pentacene thin-film was considerably smaller on OTS-treated SiO₂ as compared to that on

bare SiO₂ substrate. This was attributed to the greater adhesion interaction between pentacene and the OTS monolayer than that between pentacene and the SiO₂ [16]. In 2008, Li et al. reported that the OTS-modified substrate changes the thin film morphology of vanadyl phthalocyanine (VOPc), which leads to high performance electrical device OFETs [17].

In this work, we were interested to investigate the effect of OTS on Nc morphology and electrical properties of OFET devices. A series of Nc films, AENc56, 58, 72, 67, were grown on OTS-modified oxide at different substrate temperatures in the range (21°C - 214°C) with fixed deposited thickness (60) nm. AFM images of Nc film morphology and corresponding height profiles are shown in Figure 4.1.16. It was found that Nc film growth on both bare SiO₂ and OTS-modified substrates showed grains and elongated grains at low substrate temperature while at high substrate temperature it showed extended needle-like crystalline structure and elongated crystals.

At room temperature, films deposited on both untreated and OTS-treated substrates show circular grain structure (Figure 4.1.3a and 4.1.16a), which do not appear to be strongly dependent on chemical termination of the dielectric. The grains have a size ≈ 35 nm similar for that observed for bare SiO₂, and are densely packed on both substrates. At substrate temperature 120°C, we observe elongated grains, which have an elliptical shape with average length to width ratio 2.8 and show a disordered arrangement on the OTS similar to elongated grain structures we observed on the bare SiO₂ at 130°C (Figure 4.1.16c and 4.1.3g). The line profile across Nc film on OTS shows surface roughness about 4 nm at room temperature, but a higher value, 8 nm, at 120 °C (see Figure 4.1.16 b and d).

At high substrate temperature ranging from 160°C to 214°C (Figure 4.1.16e, g), we observe extended needle-like crystalline structures on the OTS-modified substrate and the elongated crystals become more obvious at 214°C. The average length of crystals increases from 290 nm at growth temperature 200°C to 680 nm at 214°C. However, the crystalline structures show a significant increase in width on the OTS-modified substrate increasing from 65 nm at growth temperature 200°C to 180 nm at 214°C. The thin film on the modified substrate shows many

overlapping and compact needle-like structures, as can be seen at 200°C (see Figure 4.1.16e). The overlapping of needle crystalline indicate that Nc molecules can grow perpendicular to the OTS-modified substrate. Interestingly, in 2002, Knipp reported that the pentacene molecules prefer to grow vertically on OTS treated substrates as compared to untreated oxide [18]. The line profile across AFM images shows that the height profile increases from 15 nm at 200°C to 60 nm at 214°C (Figure 4.1.16f, h).

For comparison, we observe extended needle-like crystalline structure on bare SiO₂ at $T_s \geq 170^\circ\text{C}$, the average length of crystallites are smaller than that on OTS-modified surface, while their average width are larger than that on OTS-modified surface. The thin film shows uniform crystalline structure on the unmodified substrate (see Figure 4.1.4a - g), while the thin film shows overlapping crystallites on the OTS-modified surface (see Figure 4.1.16e - g).

It is seems that the initial stage of growth needle crystalline structure is as an island then the islands join together to form a crystalline network since there are clear sites in which crystalline structures coalesce as marked by a blue arrow in Figure 4.1.16g (inset zoom in)

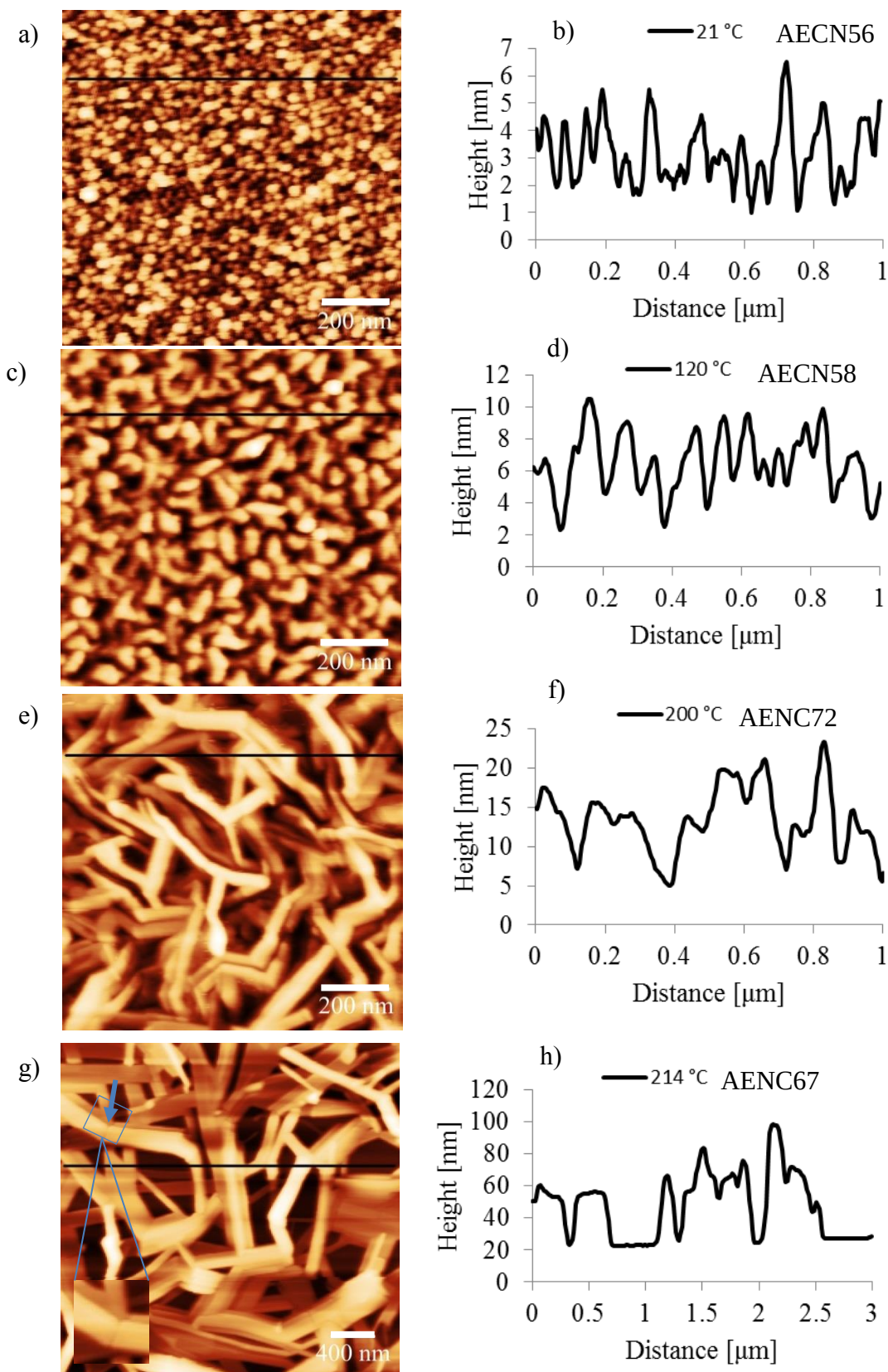


Figure 4.1.16: Topographic AFM images (left column) and height profiles (right column) of grain and needle-like crystalline structures of naphthalocyanine Nc thin films on OTS- modified Si/SiO₂ substrate grown at fixed thickness and different elevated substrate. Note scale bar for (g) is 400 nm.

The volume sticking coefficient S_v of Nc growth on OTS-modified substrate was measured for samples at different substrate temperature, and plotted in Figure 4.1.17. $S_v \approx 1$ for room temperature growth, and remains at this value up to 160 °C implying that molecular re-evaporation is small in this range. In contrast, there is a slight drop in S_v from 0.95 at 200 °C to 0.70 at 214 °C. At these temperatures the Nc morphology in exhibits extended needle-like crystalline structures (Figure 4.1.16e,g), but they do not completely cover the surface. This implies that the thermal energy results in a reduction of the nucleation density.

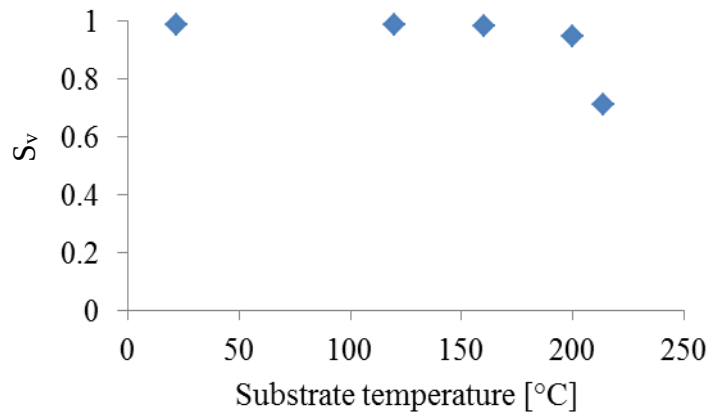


Figure 4.1.17: Volume sticking coefficient, S_v , of Nc growth on OTS-modified substrate at different substrate temperature and fixed thickness.

Figure 4.1.18 shows changes in the fractional coverage Ω of a series of samples of Nc grown on OTS-modified SiO_2 substrates at different substrate temperatures. The fractional coverages remain close to one for substrate temperatures ranging from room temperature to 160 °C because there is a complete coverage of grain structures on OTS-modified substrate (Figures 4.1.16 a, c). However, the fractional coverages decrease slightly at high substrate temperature from 0.94 at 200 °C up to 0.85 at 214 °C because the needle-like crystalline structures form and these do not completely cover the OTS-modified substrate (Figure 4.1.16e, g).

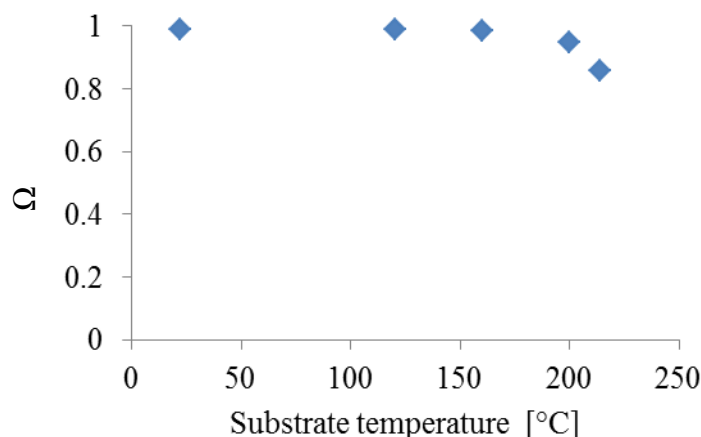


Figure 4.1.18: The fractional coverage, Ω , of serious samples with OTS-modified SiO₂ at different substrate temperatures and fixed thickness

The average length and width of Nc grown on OTS treated SiO₂ changes with increasing substrate temperature, as shown in Figure 4.1.19. The change from grain structure into needle-like crystalline structures, implies that the additional thermal energy makes it possible for molecules to stand and stack edge-on. At low substrate temperatures, the average length for grain structure start increasing slightly from 36 nm at 21 °C to 110 nm at 120 °C while the average width maintains stable around 40 nm. In contrast, at high substrate temperatures, the average length of crystallites increases from 290 nm at 200 °C to 680 nm at 214 °C, and the average width reach peaks 180 nm at 214 °C. There are clear increases in the size of grain and needle-like crystalline structures for a sequence of samples with different substrate temperatures (see Figure 4.1.16 left column).

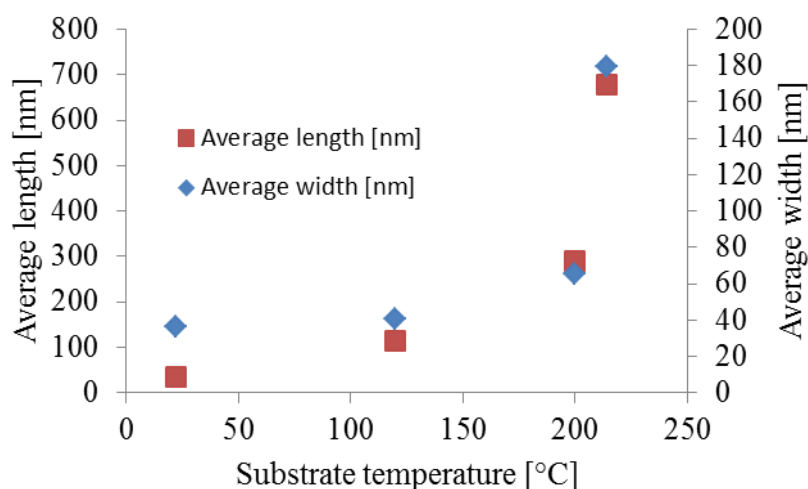


Figure 4.1.19: The average length and width of Nc islands on OTS treated SiO₂ substrate versus substrate temperature

Figure 4.1.20 confirms that the ratio of length to width of Nc grown on OTS-modified SiO_2 substrates varies with the substrate temperature. At room temperature, the length to width ratio is equal to 1, implying that the grains are approximately circular. However, at substrate temperatures above 120 °C the ratio of length to width increases substantially, indicating that needle-like crystalline structure grows longitudinally. At 214 °C the ratio of length to width drops, implying that needle-like crystalline structure undergo lateral growth.

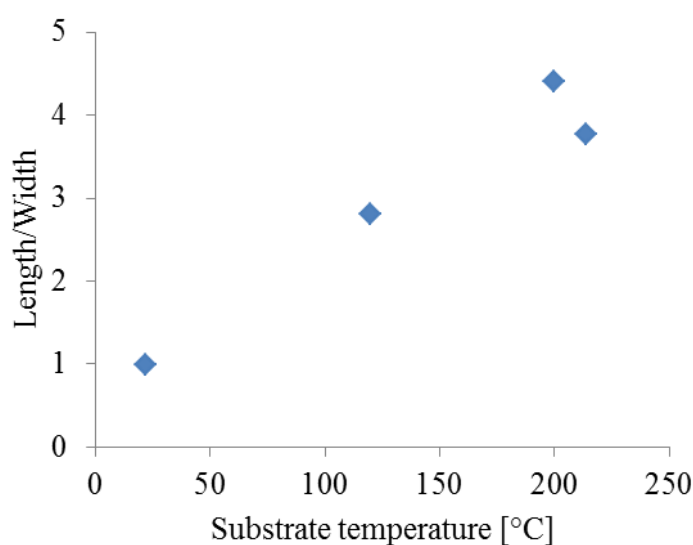


Figure 4.1.20: The ratio of length to the width of Nc on OTS-modified SiO_2 substrate plotted against substrate temperature

4.2 Growth of copper naphthalocyanine (CuNc) thin films on SiO_2 and OTS treated oxide

4.2.1 Substrate temperature dependence

In this section, we have chosen a closely related organic semiconductor to investigate, copper naphthalocyanine CuNc, so that the thin film morphology and electrical device performance can be compared for metal-free and metallized naphthalocyanine. The preparation conditions, such as substrate temperature during growth [19], deposited thickness [20], type of surface substrate [21, 22]

the chemical modification of the surface substrate by octadecyltrichlorosilane can affect the morphology of CuNc thin films with a behaviour which is similar to that observed for Nc. The CuNc source was heated to the higher degree (500 - 560) °C than that of Nc so that CuNc molecules can sublime on substrates.

A series of samples AECNc02, 03, 04, 10 were grown at different substrate temperatures in the range 21 °C – 340 °C but fixed equivalent deposited thickness of 30 nm. We found that the thin film morphology changes from grain to elongated grain at substrate temperature 140 °C and from grain to needle-like structure at 340 °C.

Figure 4.2.1 shows AFM images of the CuNc thin films grown at different substrate temperature and equivalent thickness. To begin, the CuNc thin film is grown at room temperature (see Figure 4.2.1a). The thin film has a surface roughness of about 7 nm (see Figure 4.2.1b) and reveals a high density of circular grains, which have sizes in the range of 30 - 40 nm. The thin film grown at substrate temperature 120 °C shows a slight increase of the size of grains to 82 nm (see Figure 4.2.1c), and has a surface roughness of about 4 nm (see Figure 4.2.1d). Furthermore, the thin film grown at 160 °C exhibits a small elongated grain structure and a disordered arrangement on the surface (see Figure 4.2.1e). The size of elongated grains shows a significant increase from 110 nm at 160°C to 210 nm at 220 °C. Finally, the CuNc thin film grown on Si/SiO₂ substrate exhibited extended needle-like crystalline structure at 340 °C (see Figure 4.2.1g). The stacking molecules stood on surface with an "edge-on" over large domains forming needles with planar terraces with a size about 300nm. The crystallites are in different orientations, and have highly faceted edges. The corresponding line profiles of each AFM image in Figure 4.2.1(right column) show that the surface roughness of thin films depends on the substrate temperature during growth. A similar effect of the substrate temperature during growth on film characteristics have been observed for copper phthalocyanine [2].

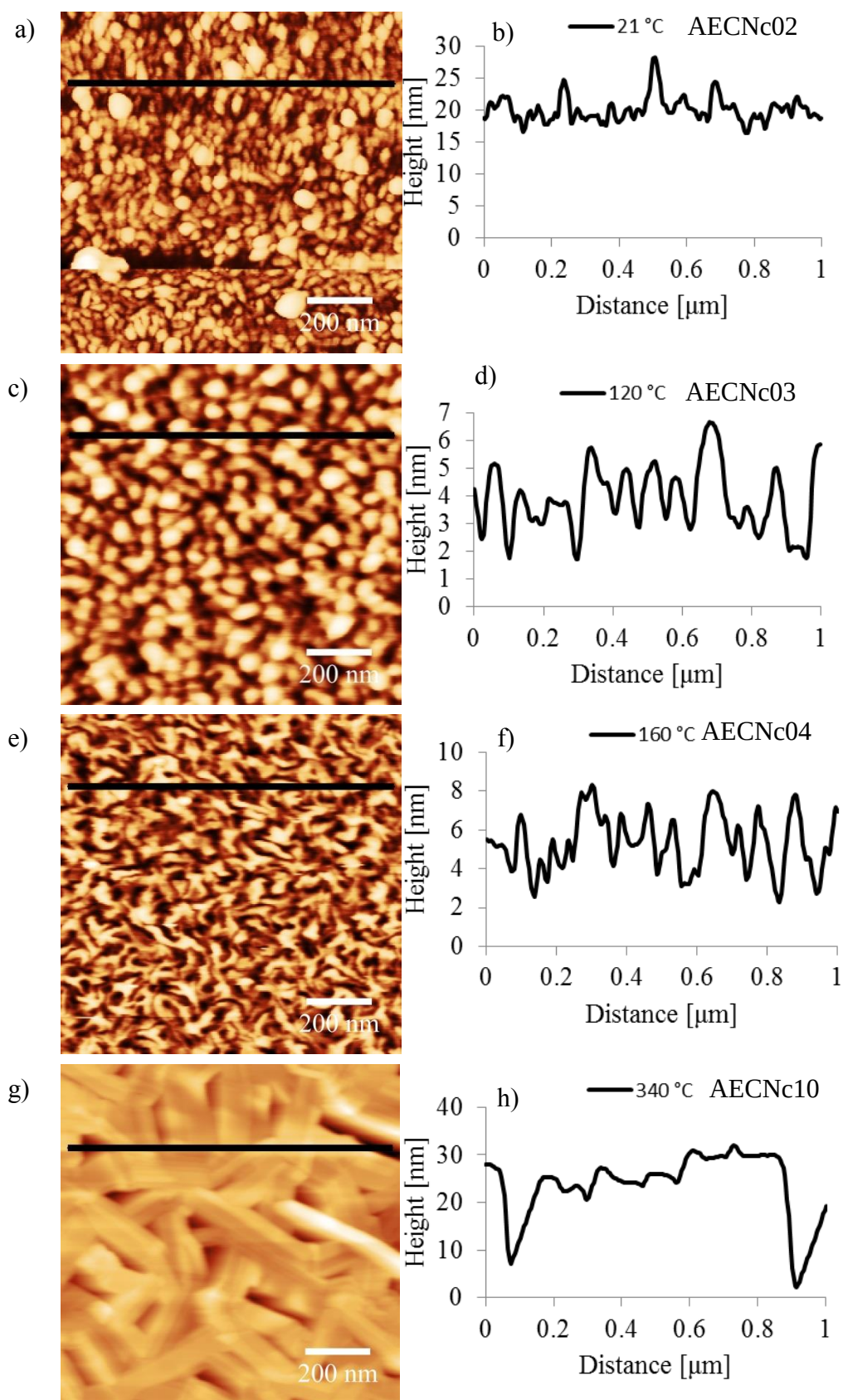


Figure 4.2.1: Topographic AFM images (left column) and height profiles (right column) of grains and extended crystalline structures of copper naphthalocyanine CuNc thin films on Si/SiO₂ substrate grown at different elevated substrate temperatures: (a) 21 °C, (b) 120 °C, (c) 160 °C, (d) 340 °C while fixed deposition rate 1nm/min.

Figure 4.2.2 shows the variation of the volume-sticking coefficient S_v as a function of the substrate temperature. At substrate temperatures ranging from 21°C to 220°C, the volume-sticking coefficient remains stable. This implies that desorption of molecules is small, and almost all impinging CuNc molecules remain on the surface. There is a slight decrease in S_v ($S_v < 1$) at 340°C because at this temperature the morphology of CuNc shows extended crystalline structures with small gaps (Figure 4.2.1g). This implies that the thermal energy makes it possible for molecules to diffuse and form crystalline structures or re-evaporate resulting in gaps on surface. However, the sticking coefficient is not reduced strongly in this temperature range as observed for Nc.

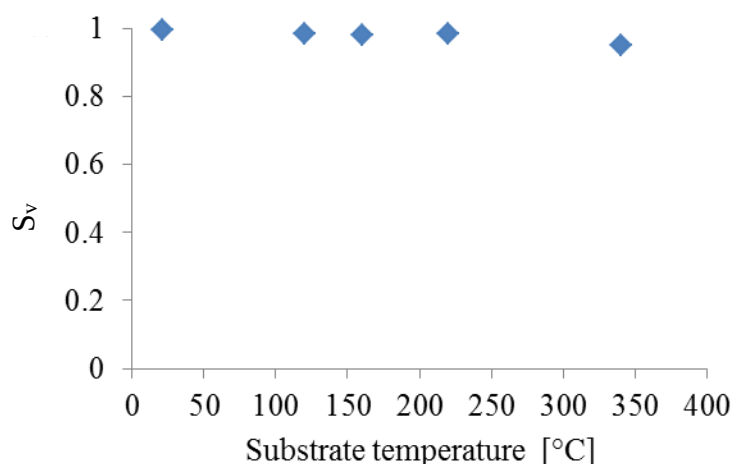


Figure 4.2.2: Volume sticking coefficient, S_v , of CuNc thin films grown on SiO₂ substrate at different substrate temperature and fixed thickness

For comparison, the variation of the volume-sticking coefficient S_v as a function of the substrate temperature for growth both Nc and CuNc thin films on SiO₂ are re-plotted in Figure 4.2.3. It seems that S_v of CuNc is higher than that of metal-free Nc. This implies that the adsorption energy of CuNc is higher than the Nc.

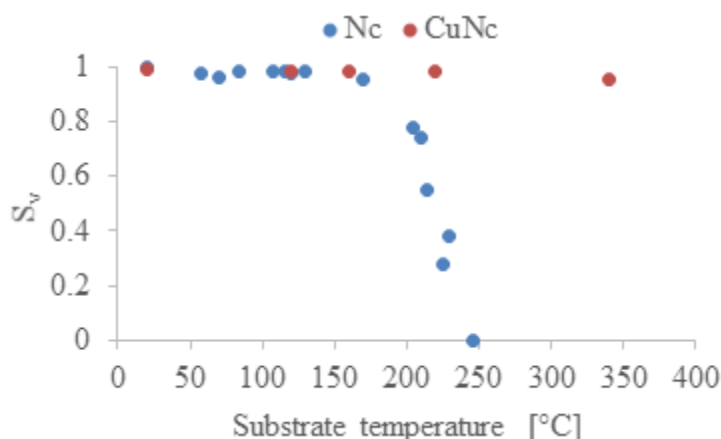


Figure 4.2.3: Volume sticking coefficient, S_v , of Nc and CuNc thin films grown on SiO_2 substrate at different substrate temperature

Figure 4.2.4 shows the variation of the fractional coverage Ω as a function of the substrate temperature for CuNc thin film growth on SiO_2 substrate. There is no significant change in the fractional coverage for a substrate temperature ranging from 21 °C to 220 °C, because at this range the CuNc morphology exhibits grain and small-elongated grain structures, which completely cover the surface. In contrast, Ω declines slightly at 340 °C because at this temperature the CuNc morphology adopts an extended needle-like crystalline structure with small gaps. This implies that the molecular density decreases as the thermal energy of CuNc molecules increases on the substrate, which results in re-evaporation of molecules and gaps between crystalline structures.

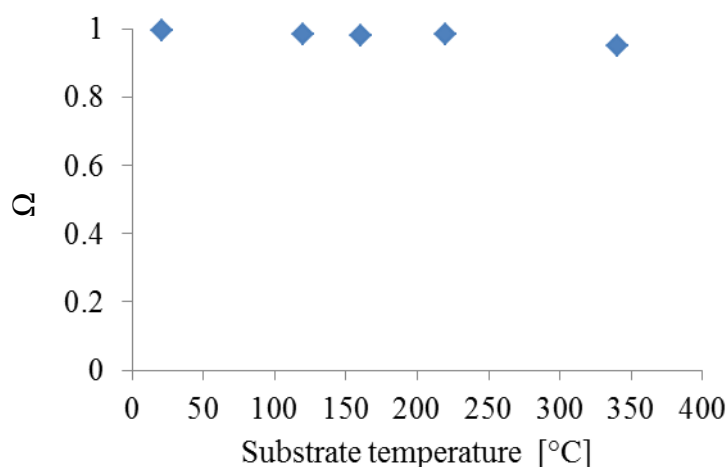


Figure 4.2.4: The fractional coverage, Ω , of CuNc thin film growth of serious samples on SiO_2 substrates at different substrate temperatures and fixed thickness

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Figure 4.2.5 shows the average length and width of CuNc islands versus substrate temperature T_s . There are three modes of growth of CuNc as follows: grain structure at $T_s < 140$ °C, small elongated grains structure for T_s ranging from 140 °C to 280 °C, and extended needle-like crystalline structure at $T_s \geq 340$. This implies that similar to metal-free Nc, the thermal energy makes it possible for molecules to diffuse and stack in an edge-on orientation in order to change from the amorphous grain structures to an extended needle-like crystalline structure. As a consequence, there is a slight increase in the average length of grains with increasing substrate temperature from 40 nm at 21 °C to 80 nm at 120 °C. Then the average length increases sharply for small-elongated grains structure from 110 nm at 160 °C to 210 nm at 220 °C up to a peak value at 300 nm for extended needle-like crystalline structure at 340 °C. In contrast, the average width remains approximately constant at 35 nm for a substrate temperatures ranging from 21 °C to 180 °C, and then significantly increases to 100 nm at 340 °C.

The ratio of the length to the width versus substrate temperature (T_s) for CuNc on SiO₂ is plotted in Figure 4.2.6. This ratio increases from 1.1 to 4.1 substrate temperatures ranging from 21 °C to 220 °C. However, it decreases to 3 nm at 340 °C. This implies that lateral growth of the extended needle-like structures occurs at high temperature.

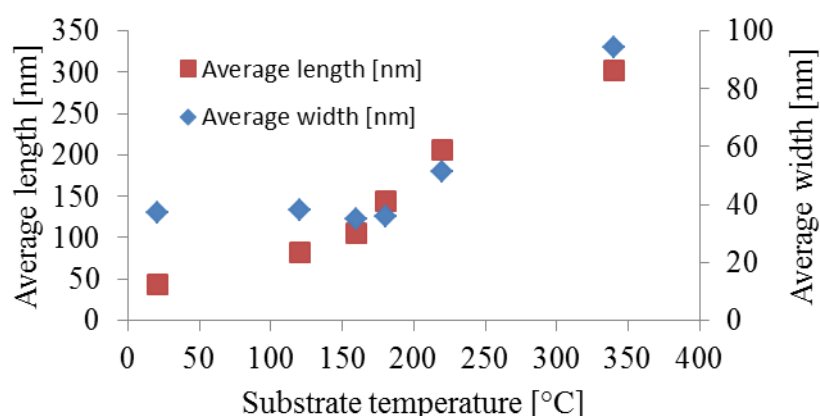


Figure 4.2.5: The average length and width of CuNc islands on SiO₂ versus substrate temperature at fixed thickness

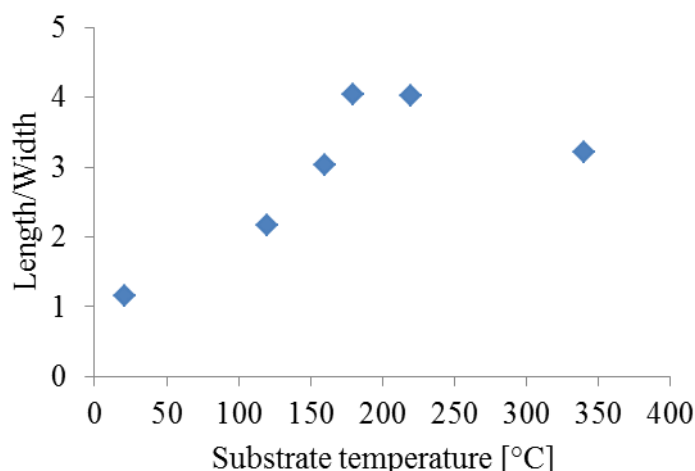


Figure 4.2.6: The ratio of length to the width of CuNc islands on SiO₂ plotted against substrate temperature at fixed thickness

4.2.2 Effect of OTS treated SiO₂ substrate

We also investigated the growth of copper naphthalocyanine (CuNc) thin film on the OTS-modified SiO₂. The thin film thickness was maintained at 30 nm. During the deposition of CuNc, the substrates were held at different temperatures 21 °C, 120 °C, 160 °C, 220 °C, 280 °C and 340 °C for samples named AENc11, 12, 13, 14, 15, 16, respectively. AFM images and corresponding line profiles reveal that the CuNc thin films morphology depend on both OTS-modified substrate and substrate temperature. In general, the passivation of SiO₂ has a similar effect on CuNc growth as previously described for metal-free Nc.

Figure 4.2.7a shows that CuNc thin films grow as circular grains on an OTS-modified SiO₂ substrate held at room temperature, and the size of grain is about 30 nm. Elongated grains are observed at $T_s = 120$ °C with a size about 100 nm (see Figure 4.2.7c,e). In contrast, CuNc thin films on bare SiO₂ at 120 °C grew as small grains (see Figure 4.2.1c), indicating the mobility of molecules on OTS-modified SiO₂ is higher, resulting in higher degree of crystallinity at lower substrate temperature. In Figure 4.2.7 (right column) the line profile reveals that the surface roughness is approximately 5 nm for CuNc growth at all substrate temperatures.

Figure 4.2.8a shows thin films of extended crystalline structures and well-connected crystallinity in films grown at $T_s = 220$ °C with the size of 280 nm, showing that the CuNc molecules preferentially order in an edge-on orientation

that has axes of stacking parallel to the surface. For $T_s = 280^\circ\text{C}$ and 340°C , extended crystalline structures are formed with the size of 400 nm and large gaps between them because re-evaporation of molecules starts to occur at these temperatures (see Figure 4.2.8c,e, note the scale bar are 400 nm). Needle crystallites with planar terrace are formed due to aggregation of crystallites in a locally parallel arrangement. Figure 4.2.8 (right column) the line profile for Nc growth reveals that the surface roughness increases with increasing substrate temperature from 6 nm at 220°C to 20 nm at both 280°C and 340°C .

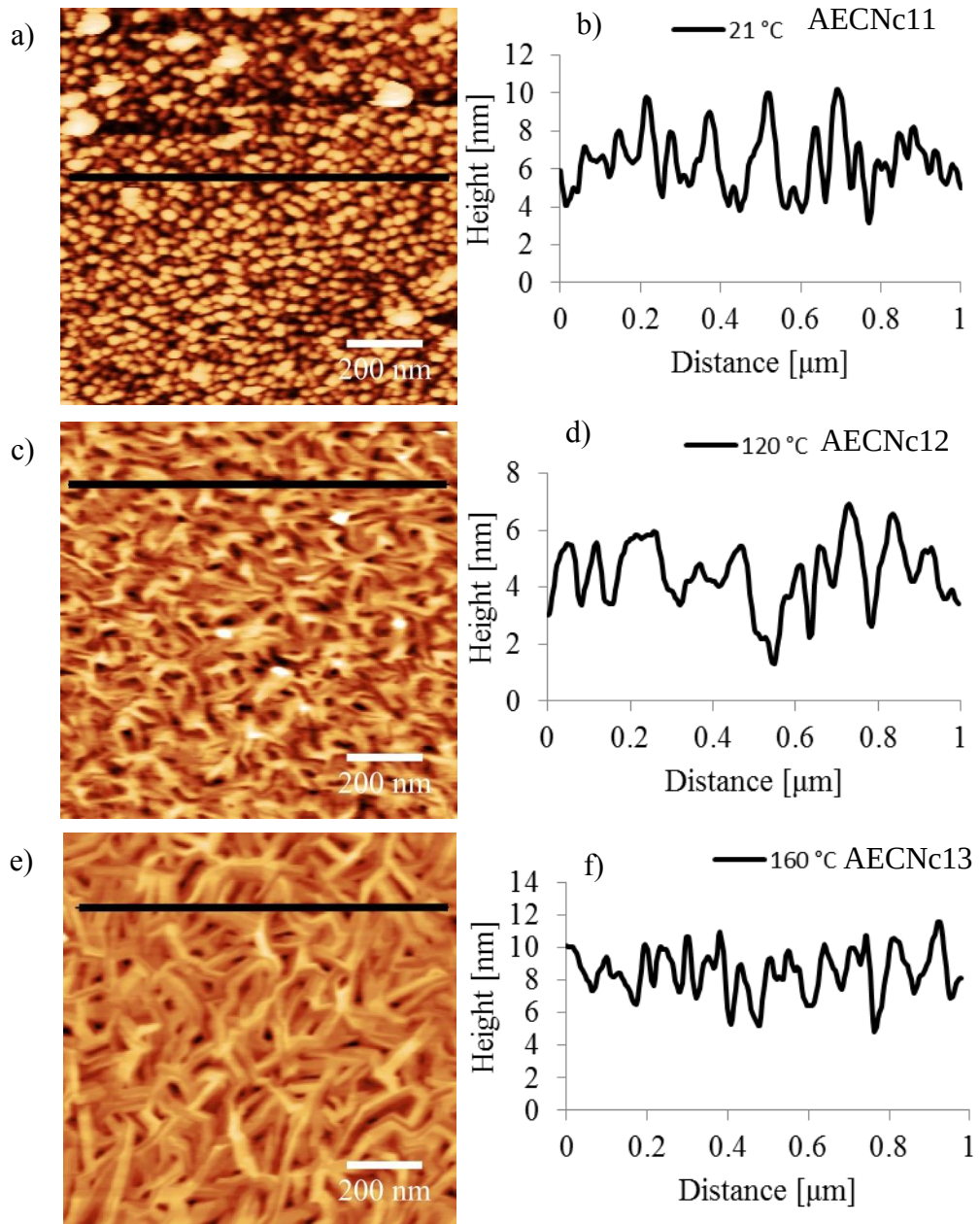


Figure 4.2.7: Topographic AFM images (left column) and surface roughness profile (right column) of grain and small elongated grain structures of CuNc thin films on OTS-modified Si/SiO₂ substrate grown at substrate temperatures: (a) 21°C , (c) 120°C , (e) 160°C while fixed deposition rate 1nm/min

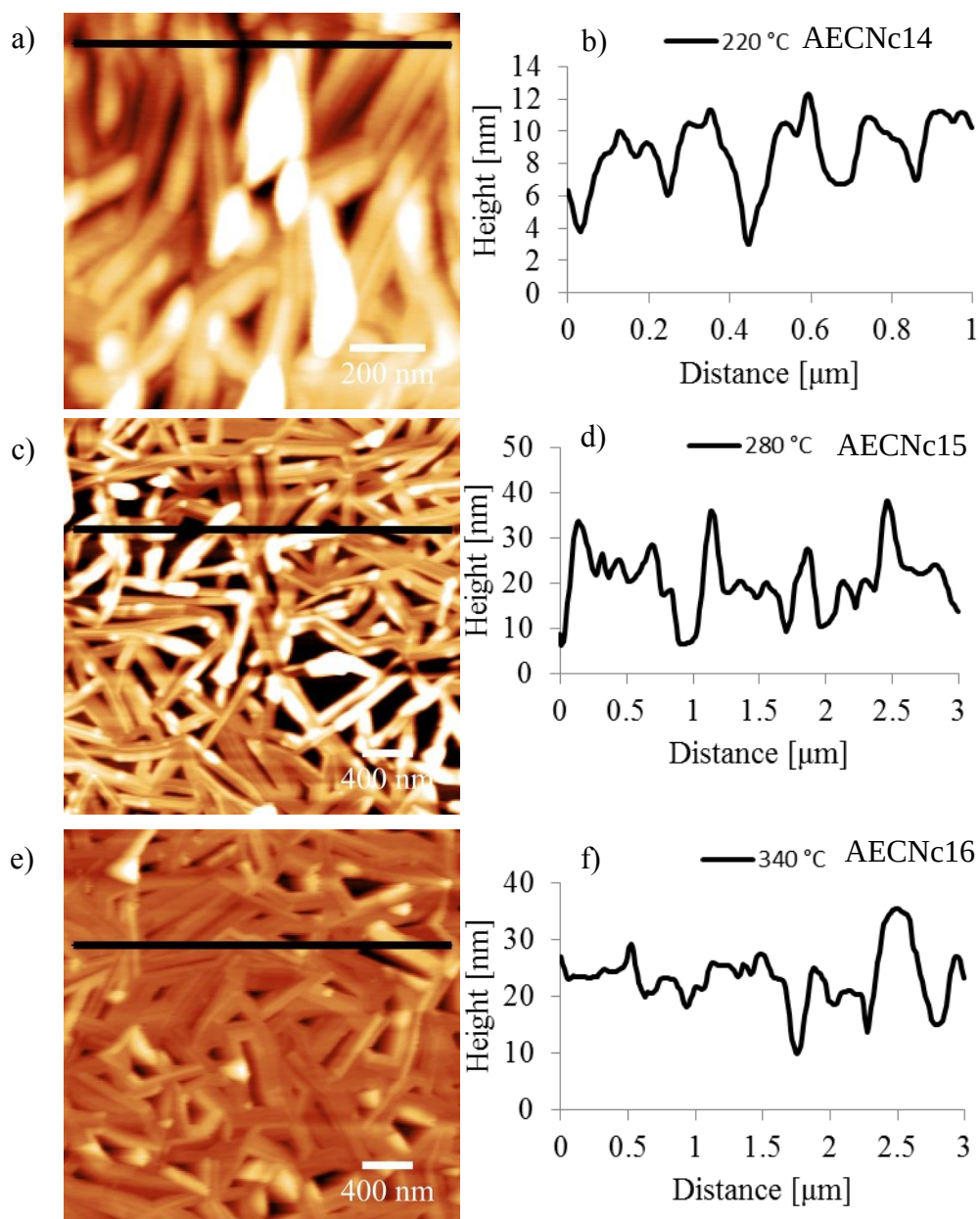


Figure 4.2.8: Topographic AFM images (left column) and height profiles (right column) of extended needle-like crystalline structure of CuNc thin films on OTS- modified Si/SiO₂ grown at substrate temperatures: (a) 220 °C, (c) 280 °C, (e) 340 °C while fixed deposition rate 1nm/min

The thin film morphology of CuNc on SiO₂ and OTS-modified substrates are compared to identify the difference in thin films properties as the surface substrate is modified. In the case of the CuNc film grown on bare SiO₂, the morphology show asymmetric grain structures at room temperature, with a size which increases with increasing surface temperature, and also elongated needle-

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like structures at substrate temperature $T_s > 340$ °C (Figure 4.2.1g). In contrast, the morphology of CuNc thin film on the OTS-modified substrate is more ordered at intermediate growth temperatures (≈ 120 °C), while the extended needle-like structure occurs at substrate temperature $T_s > 220$ °C. In addition, we observe elongated grain structure of CuNc on bare SiO₂ at $T_s \geq 160$ °C and on OTS at $T_s \geq 120$ °C.

Figure 4.2.9 shows the variation of the volume sticking coefficient S_v as a function of T_s .

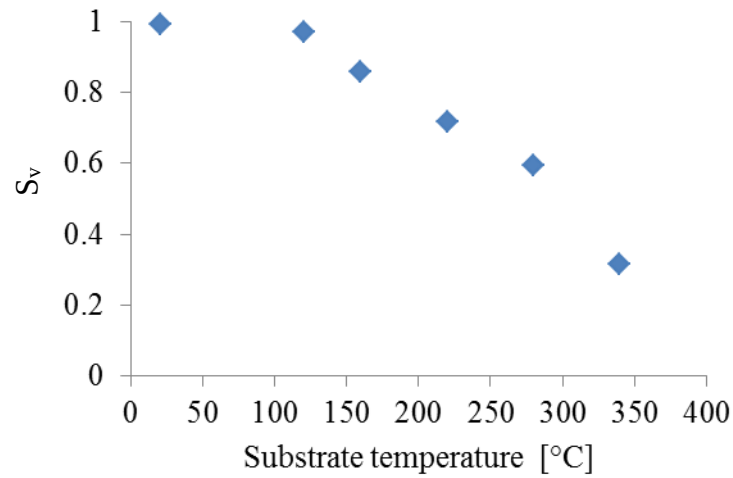


Figure 4.2.9: Volume sticking coefficient, S_v , of CuNc of series samples grown on OTS-modified SiO₂ substrate at different substrate temperature and fixed thickness.

Figure 4.2.10 and Figure 4.2.11 show the data of the average length (L), width (W) and length to the width ratio (L/W) for CuNc/OTS. The general trends are

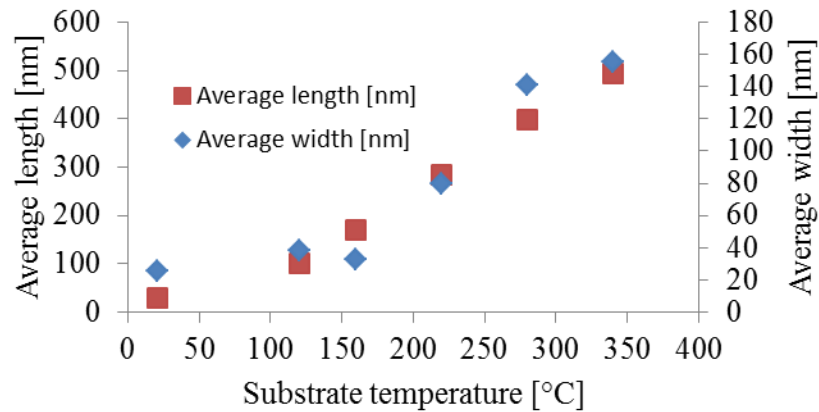


Figure 4.2.10: The average length and width of CuNc growth on OTS treated SiO₂ substrate versus substrate temperature at fixed thickness 30 nm

similar with that already observed for CuNc/SiO₂, Nc/SiO₂ and Nc/OTS. However, here for CuNc/OTS the L/W ratio decrease at T_s > 160 °C.

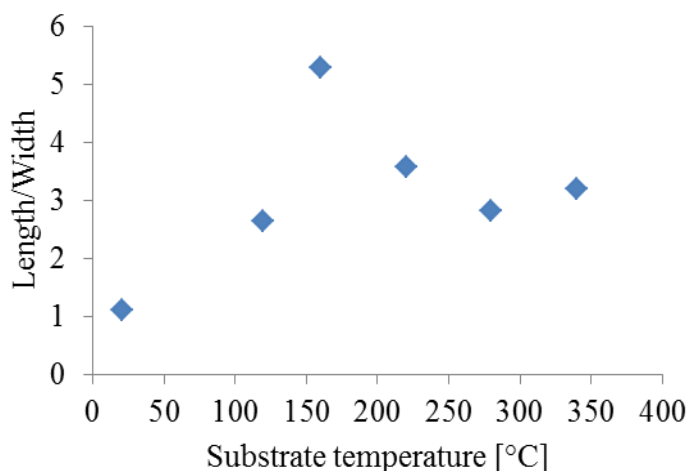


Figure 4.2.11: The ratio of length to the width of CuNc growth on OTS-modified SiO₂ substrate plotted against substrate temperature at fixed thickness 30 nm

The growth morphology of CuNc is very similar to that observed for metal phthalocyanine. For example, in 2003, Xiao et al. reported that the control of substrate temperature make it possible for them to control the orientation and morphology of copper phthalocyanine thin films [23]. In 2008, Liqiang reported thermal evaporation of vanadyl phthalocyanine on oxide and OTS-modified oxide substrates. The thin films on both substrates shows a grain structure, while the size and the shape of grain structure on OTS surface is slightly larger than that on SiO₂ surface [17]. In 2002, Hisatomo et al. reported that the molecular alignment of oxotitanium (IV) phthalocyanine can be controlled when this semiconductor was deposited using conventional vapor deposition on octadecanethiol modified surface substrates [3].

4.3 Summary

In this chapter, metal-free naphthalocyanine (Nc) and copper naphthalocyanine (CuNc) thin films were grown on both Si/SiO₂ and OTS-modified substrates using vacuum deposition. The effects of growth conditions, in particular

substrate temperature, on film morphology, the crystallinity and the preferential molecular orientation have been investigated using AFM and X-ray diffraction (XRD) were investigated.

We found that the optimum substrate temperature during growth is achieved at 200 °C, for which Nc thin films on SiO₂ and OTS show the best morphological and electrical properties (see chapter 6) because the thin film forms a well-connected needle-like crystalline structure with low surface roughness. However, the optimized growth temperature for CuNc thin films on SiO₂ and OTS substrates are determined to be (180) °C and (160) °C, respectively.

The XRD data show that crystalline structure and molecular orientation of thin film were enhanced as a result of increasing the substrate temperature, which also leads to changes in the surface morphology. The naphthalocyanine molecules prefer to nucleate either as amorphous arrangement (grain structure) at low surface temperature, or stood edge-on direction with stacking axes parallel to the substrate and form crystalline configuration (needle-like structure) at higher surface temperature. The direction of current flow is in direction of the π -stacking so that OFETs show high performance for films with needle-like crystallites. This improvement in performance of OFETs is discussed in the next chapter.

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Chapter 5

Naphthalocyanine organic field effect transistors

In this chapter we describes electrical measurements of metal-free naphthalocyanine and metallated naphthalocyanine organic field effect transistors (OFET) grown at different substrate temperatures as described in the previous chapter for both bottom-contact and top-contact configurations on bare Si/SiO₂ and OTS-modified oxide. We measured the output and transfer characteristics for all OFET devices in air and vacuum [1].

5.1 Organic field effect transistors and current voltage (I-V)

characteristics

The variation of drain current I_d^{sat} in the saturation region as a function of gate voltage, V_g , is given by [2],

$$I_d^{sat} \simeq \frac{W\mu_h C_{ox}}{2L} (V_g - V_{th})^2$$

The channel length, L , and width, W , in our devices are 25 μm and 3 mm, respectively. The capacitance, C_{ox} , per unit area of the 200 nm thick, t_{ox} , SiO₂ dielectric which we use is 17 nF/cm². The threshold voltage and the hole mobility are denoted by, V_{th} , and, μ_h , respectively. The mobility of the charge carriers in the saturation region may be related to the measured current as follows [3]

$$\mu_h \simeq \frac{2L}{WC_{ox}} \left[\frac{\partial \sqrt{I_d^{sat}}}{\partial V_g} \right]^2$$

the slope, $\frac{\partial \sqrt{I_d^{sat}}}{\partial V_g}$, can be calculated from the transfer characteristic by plotting

$|I_d^{sat}|^{\frac{1}{2}}$ versus V_g for fixed source-drain voltage, and the threshold voltage is obtained from the intercept with the gate voltage axis. The above two equations are derived at section 2.2.1 and re-written here for easy look at.

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From the output characteristic, the ON/OFF current ratio of OFETs can be obtained from the drain current in saturation region at maximum gate voltage divided by the minimum drain current at zero or positive gate bias. The ON/OFF current ratio is an important performance parameter that implies the ability of transistor to turn off.

The threshold voltage is the minimum gate voltage that is needed to generate a conducting channel between the source and drain electrodes. The application of a gate voltage leads to the accumulation of charge carriers at the insulator/semiconductor interface. These charges will first fill traps at the interface and then further induced charges will be introduced into the channel (see Figure 5.1.1).

Hysteresis phenomena often occur in OFET characteristics. This phenomenon results in a difference in the value of drain current during a ramp up and ramp down of the gate voltage [2]. In this study, and many previous papers on OFETs, hysteresis is observed when electrical measurements of devices were taken in ambient conditions [4, 5].

The effective charge trap density may be estimated from the threshold voltage as follows [2, 6],

$$N_t^{vac} = \frac{V_{th}^{vac} C_{ox}}{q} \quad 5.1.1$$

$$N_t^{air} = \frac{V_{th}^{air} C_{ox}}{q} \quad 5.1.2$$

If V_{th} or N_t is positive, this refers to the hole donors or electron trap and the transistor is normally on ($I_d \neq 0$ at $V_g = 0$). However, if V_{th} or N_t is negative, this refers to the hole trap and the transistor is normally off ($I_d = 0$ at $V_g = 0$).

$$\Delta N = N_t^{air} - N_t^{vac} \quad 5.1.3$$

$$\Delta V_{th} = V_{th}^{vac} - V_{th}^{air} \quad 5.1.4$$

$$\Delta N = \frac{\Delta V_{th} C_{ox}}{q} \quad 5.1.5$$

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The charge trap density is denoted by N_t . The charge trap density difference between that in vacuum N_t^{vac} and air N_t^{air} is denoted by the ΔN . The shift in threshold voltage between that in vacuum V_{th}^{vac} and V_{th}^{air} is denoted by ΔV_{th} .

From the above discussion, we conclude that if $\Delta V_{th} > 0$ or $\Delta N > 0$, this implies that the introduction of holes (electron traps = hole dopants). However, if $\Delta V_{th} < 0$ or $\Delta N < 0$ this implies that the hole traps.

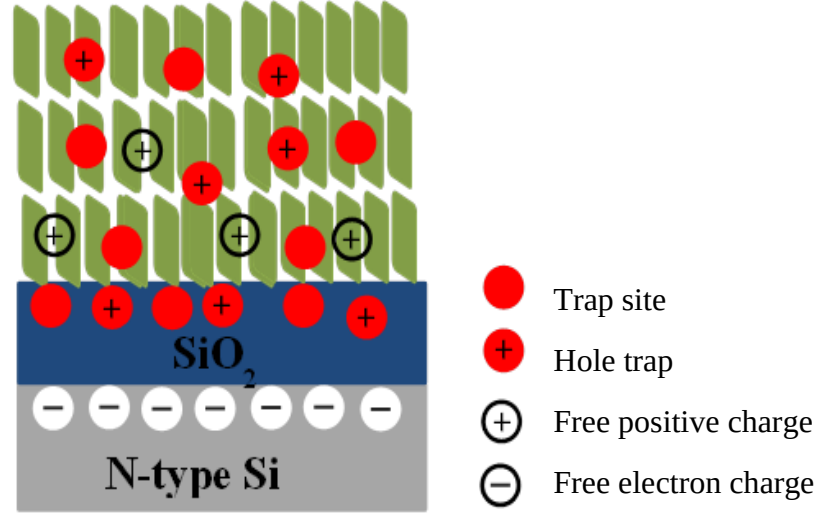


Figure 5.1.1: Schematic diagram of traps in OFETs: trapped holes in the semiconductor bulk and the insulator/semiconductor interface.

5.2 Performance of Naphthalocyanine Nc organic field effect transistor with bottom-contacts

5.2.1 Effect of substrate temperature on OFET characteristics in vacuum

In the previous chapter, we studied the effects of substrate temperature on the morphology and crystallinity of the Nc and CuNc films. It is evident from AFM images of Nc that the structure of films changes from amorphous to the extended needle-like crystalline as the substrate temperature is increased see Figure 4.1.3 and Figure 4.1.4. Here, we use these films as an active layer to fabricate bottom-contact Nc organic field effect transistors (Figure 5.2.1). The devices AENc54, 55, 61, 48 correspond to films prepared at $T_s = 21^\circ\text{C}$, 160°C , 200°C , 220°C , respectively. Their electrical characteristics were measured at room temperature in vacuum and the dark. We found that the performance of Nc OFET devices is

strongly dependent on the grain size and crystal structure of the semiconductor layer.

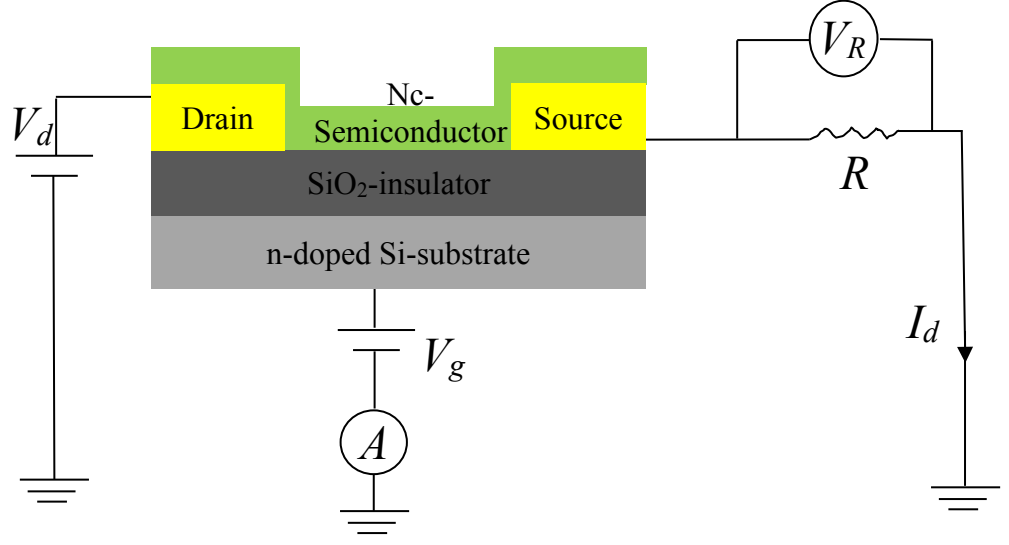


Figure 5.2.1: The setup of bottom-contact OFET on bare Si/SiO₂ with electrical measurements circuit

Figures 5.2.2 (a, c, e and g) shows the output characteristics of these devices. For each device, the dependence of drain current I_d on drain voltage is measured in bidirectional mode (sweeping both up and down) ($V_d = +5\text{V}$ to -70V) at discrete gate voltages ($V_g = -0\text{V}$ to -60V). The output characteristics show that the Nc film operates as an accumulation p-channel OFET device. Generally, there is a rapid increase in the saturation drain current I_d^{sat} as the applied gate voltage is increased. We observed a maximum saturation current ($I_{\text{max.sat}}$) of about $-0.02 \mu\text{A}$ at $V_g = -60 \text{ V}$ for the OFET grown at 21°C (Figure 5.2.2a), and an increase in the maximum saturation current with increasing substrate temperature. For example, the OFET grown at 160°C shows a maximum saturated current of $-0.7 \mu\text{A}$ at $V_g = -60 \text{ V}$ (Figure 5.2.2c). The highest saturation current of $-24 \mu\text{A}$ at $V_g = -60 \text{ V}$ (Figure 5.2.2e) is measured for the OFET prepared at 200°C . However, there is a significant decrease in the maximum saturation current to $-0.12 \mu\text{A}$ for $T_s = 220^\circ\text{C}$ (Figure 5.2.2g) [7].

Figures 5.2.2 (b, d, f and h) show the transfer characteristics of these OFETs in the saturation regime in a bidirectional mode with gate voltage varying from $+5\text{V}$ to -70V , and the drain voltage, V_d , fixed at -60V .

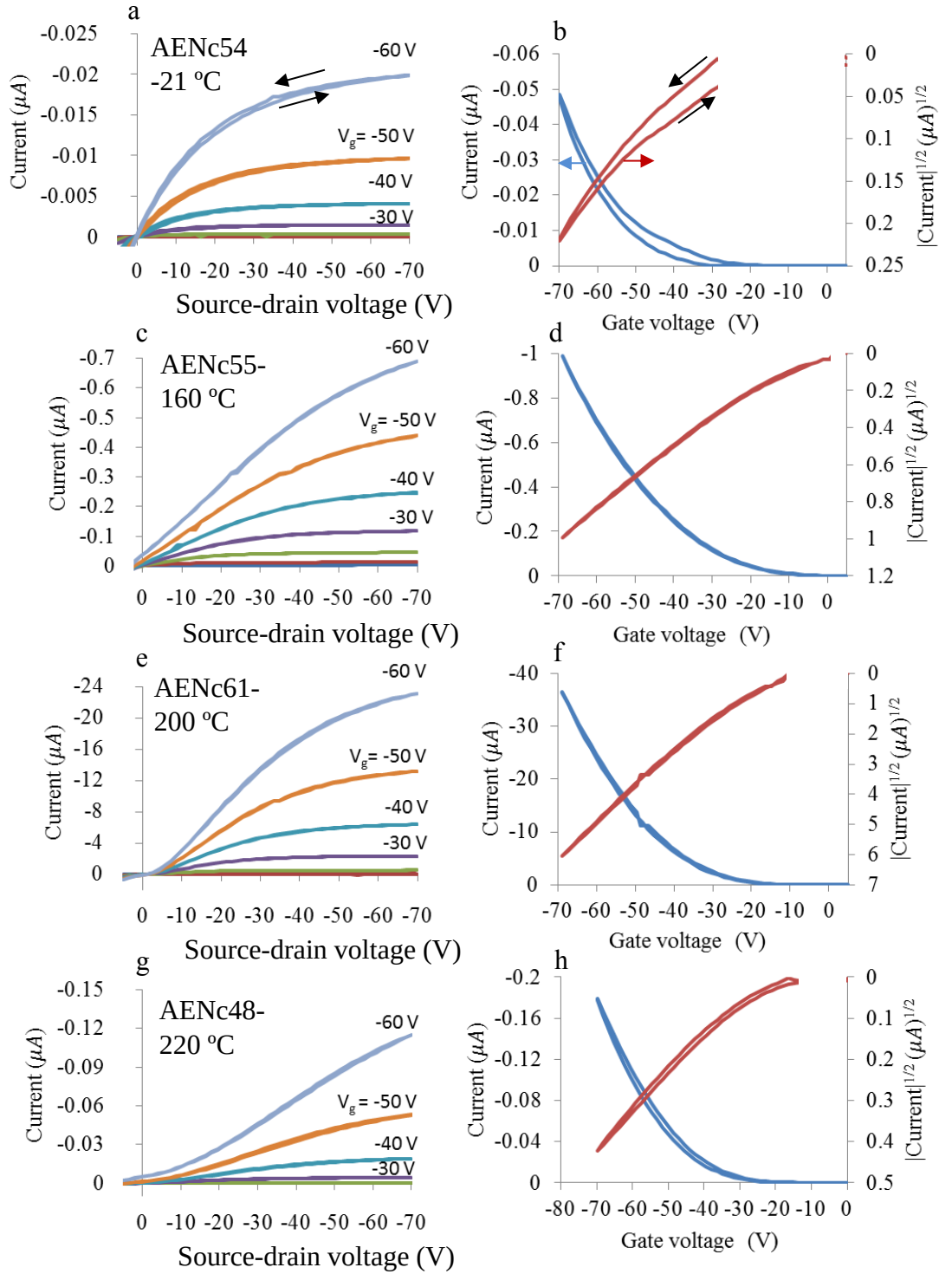


Figure 5.2.2: Output characteristics (a, c, e and g Left column) and transfer characteristics (b, d, f and h right column) of bottom-contact Nc OFETs on bare Si/SiO₂ prepared at different substrate temperatures (21 °C, 160 °C, 200 °C, and 220 °C, respectively) measured in vacuum and the dark.

Table 5.2.1 shows the effect of substrate temperature on OFET performance parameters. We obtained the highest mobility of $(1.4 \pm 0.05) \times 10^{-2} \text{ cm}^2/\text{Vs}$ for OFETs prepared at 200 °C while the OFET device prepared at 21 °C shows the

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lowest mobility of $(1.3 \pm 0.01) \times 10^{-5} \text{ cm}^2/\text{Vs}$. The threshold voltage V_{th} is the minimum gate voltage where the device transfers to the on state. A hysteresis is observed causing a shift of the threshold voltage from -16 V toward negative voltage -27 V for the device prepared at 21 °C. Interestingly, the threshold is lower for the devices prepared at 160 and 200 °C. We have measured the highest on/off drain current ratio of 10^5 for the OFET prepared at 200 °C. We have measured a lower value on/off ratio for device prepared at 160 °C. We find that the hole mobility and on/off current ratio increase with increasing substrate temperature from 21 °C up to 200 °C, but then these parameters decrease for 220 °C. In addition, the threshold voltage V_{th} has a lower value and no hysteresis is observed for OFETs prepared at 160 °C and 200°C as compared to OFETs prepared at 21 °C and 220 °C. The devices channel is normally off because threshold voltages for all devices are less than zero. According to these parameters, the performance of the OFETs grown at 200 °C is significantly better than those grown at other temperatures.

Table 5.2.1: Substrate temperature effect on performance parameters of bottom-contact OFET device: (a) sweep up, (b) sweep down. The electrical field was 2.4 MV/m

Device	Substrate temperature (°C)	Maximum saturated current (μA)	Threshold voltage (V)	OFETs mobility (cm^2/Vs)	On/Off drain current ratio
AENc54	21	-0.02	-16 ^a to -27 ^b	$(1.3 \pm 0.01) \times 10^{-5}$	10^3
AENc55	160	-0.7	-10	$(2.8 \pm 0.14) \times 10^{-4}$	10^2
AENc61	200	-24	-20	$(1.4 \pm 0.05) \times 10^{-2}$	10^5
AENc48	220	-0.12	-24 ^a to -27 ^b	$(3.0 \pm 0.06) \times 10^{-4}$	10^4

In 2008, Hirao reported the highest field-effect mobility of about $1.9 \times 10^{-2} \text{ cm}^2/\text{Vs}$ and the largest on/off ratio of about 10^4 for soluble naphthalocyanine [8], this mobility is similar to that observed for thermally evaporated Nc at $T_s = 200$ while the on/off ratio we measure is one order of magnitude larger than that of soluble naphthalocyanine device.

Study of CuPc deposited at different T_s is discussed here for comparison. In 2016, Narayanan et al. reported the vacuum thermal evaporation of CuPc thin films on to the SiO_2 surface with different substrate temperatures room temperature (RT), 100, 150, and 225 °C. The OFETs transfer characteristics show hysteresis that result in shifting threshold voltage for example at $T_s = 225$ °C the threshold voltage changes from 9 V to 14 V as gate voltage sweep up and sweep down [6]. In 2015, Maheshwari et al. reported that the estimated hole mobility value for CuPc OFET made on bare oxide at room temperature is $9 \times 10^{-4} \text{ cm}^2/\text{Vs}$, which is higher than mobility of Nc OFET on SiO_2 with same substrate temperature by the factor of 70 (see Table 5.2.1) [9].

To summarise, the mobility of the OFETs is highest for a substrate temperature of 200 °C. AFM images show that the morphology is also dependent on the substrate temperature, implying that the variation of the OFETs mobility is due to the change of thin film morphology and crystallinity, where the direction of current flow is in direction of the π -stacking of Nc. We have observed continuous highly crystalline films at 200 °C, the temperature for which we observe the highest charge carrier mobility. We attribute the significant decrease in the mobility for $T_s > 200$ °C to the discontinuities of the film and large gaps between needle-like crystals discussed in the previous chapter [10].

5.2.1.1 Effects of atmospheric exposure on OFET characteristics for device grown at 180 °C

In order to investigate the influence of exposure to ambient condition on the semiconductor active layer and OFET performance, a bottom-contact configuration Nc OFET (similar to Figure 5.2.1) was prepared at substrate temperature 180°C (AENc52). The electrical characteristics were measured as grown in vacuum then directly after exposure to ambient condition in the dark, and then under the same conditions 1 day later.

The output characteristics are shown in Figures 5.2.3 (a, c and e). There is a significant increase in the maximum saturated drain current at gate voltage ($V_g = -60V$) after exposure to air. The data are shown in Table 5.2.2. We also observe a small hysteresis in air, which may be due to impurity and trapped charge in the interface between semiconductor and SiO₂ dielectric. It can be clearly seen that the saturation regime shifts to higher source-drain voltage after 1 day exposure to air, in particular at high gate voltage (Figure 5.2.3c), and the channel is found to be off for $V_g = 0$ in vacuum (p-channel normally off) while this is not the case for the device after exposure to air. That is a positive gate voltage is required to turn the device off (p-channel normally on). Therefore, the highest on/off current ratio is about 10^5 for measurement in vacuum while this decreases by three orders of magnitude after 1 day in air.

The corresponding transfer characteristics are shown in Figures 5.2.3 (b, d and f). It is evident that the threshold voltage, V_{th} , decreases toward positive gate voltage with exposure time to ambient which may be due to increasing electron traps. Therefore, the density of air-induced traps was estimated from the shift of threshold voltage (ΔV_{th}) measured in vacuum and 1 day exposure to air (Figure 5.2.3 b and f). Applying Equations 5.1.5, gives a density of electron traps/hole donors $1.8 \times 10^{12} \text{ cm}^{-2}$. There is a considerable increase of the hole mobility in the saturation regime, and the highest value of $(8.3 \pm 0.34) \times 10^{-3} \text{ cm}^2/V$ is recorded after 1 day exposure (Table 5.2.2).

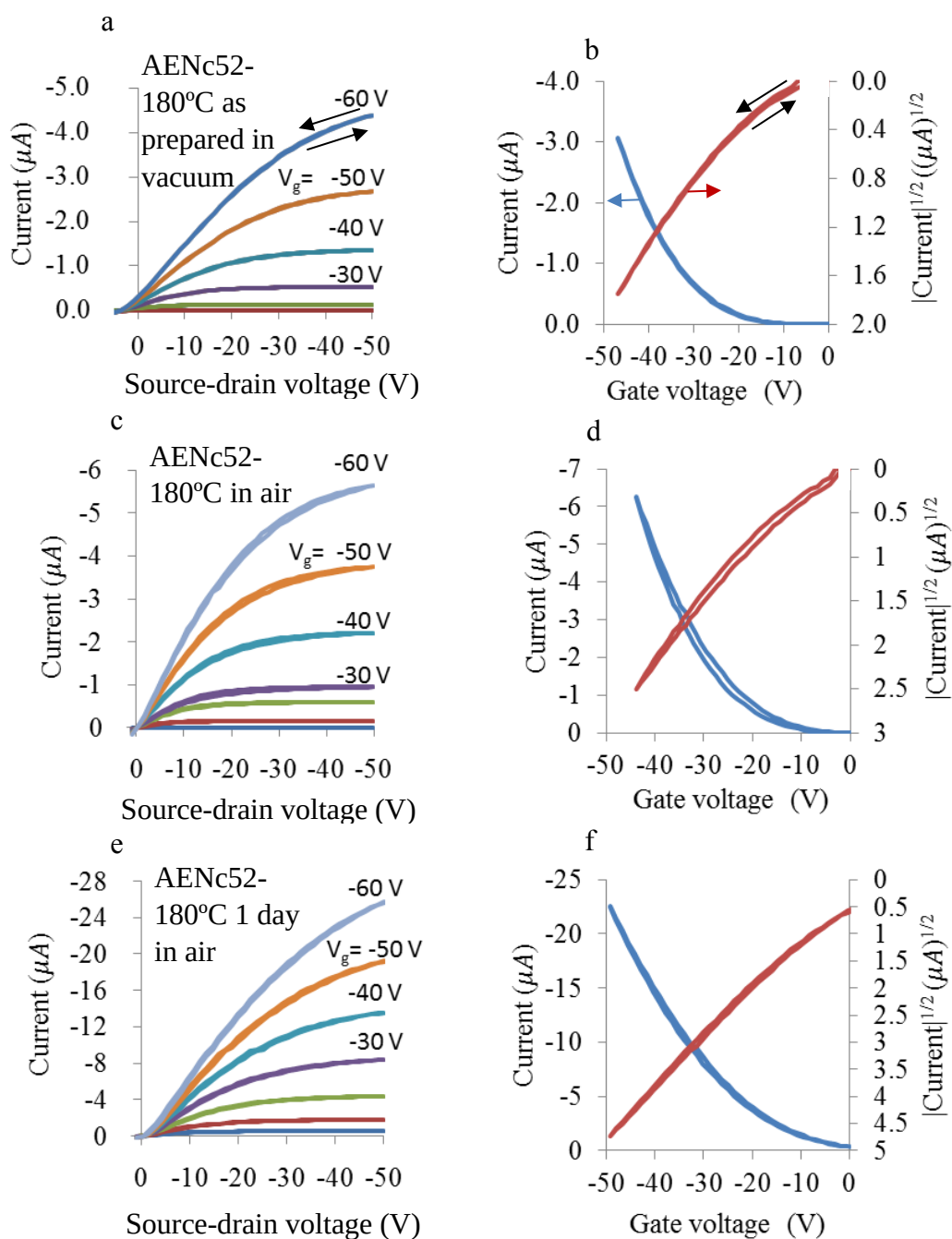


Figure 5.2.3: Output characteristics (a, c and e left column) corresponding to transfer characteristics (b, d, and f right column) of Nc OFET on bare Si/SiO₂ named AENc52 that prepared at 180°C and measured in vacuum, in air and 1 day in air, respectively.

Table 5.2.2: Effects of atmospheric exposure on performance parameters of bottom-contact OFET device as prepared at 180°C: (a) sweep up, (b) sweep down. The electrical field was 2 MV/m

Device	Measurement conditions	Maximum saturated current (μA)	Threshold voltage (V)	OFETs mobility (cm^2/Vs)	On/Off drain current ratio
AENc52	Vacuum	-4.3	-15	$(3.0 \pm 0.13) \times 10^{-3}$	10^5
AENc52	In air	-5.6	-8^a to -11^b	$(4.7 \pm 0.16) \times 10^{-3}$	10^3
AENc52	1 day in air	-26	+2	$(8.3 \pm 0.34) \times 10^{-3}$	10^2

Similar effects have been observed in studies of CuPc OFETs. In 2016, Narayanan et al. reported the fabrication of CuPc OFETs. The measurements of the electrical characteristics were performed in air at room temperature in the light. They studied the effect of thin film growth modes on hole and electron trap concentrations. The highest electron and hole traps concentrations observed are about 2.1×10^{12} and $8.9 \times 10^{11} \text{ cm}^{-2}$ for a film grown at 225 °C, which shows an island growth mode with large voids [6]. Also Padma et al. have reported an increase in mobility for CuPc based OFET if the device is exposure to air [2].

To summarise the drain current and mobility increased under ambient conditions, but there is a small hysteresis in the transfer characteristic for measurement in air, and the threshold voltages is shifted toward positive gate voltage for measurement after 1 day exposure to air. It is likely that the increase in electron traps/hole donors resulting in an increasing hole concentration is due to exposure to oxygen. Oxygen has been shown to act as a dopant in bulk CuPc films leading to reduced hole-trapping and higher hole doping in p-channel devices [2].

5.2.2 Effect of substrate temperature for OTS treated oxide on OFET characteristics in vacuum

In this section, we discuss the influence of OTS modification of the silicon oxide surface on the performance of OFETs. We fabricated four bottom-contact OFETs (AENc56, 60, 72, 73) in which Nc films are grown on OTS-modified oxide substrates $T_s = 21\text{ }^{\circ}\text{C}$, $180\text{ }^{\circ}\text{C}$, $200\text{ }^{\circ}\text{C}$, $220\text{ }^{\circ}\text{C}$, respectively. The output characteristics are shown in Figure 5.2.4 left column, and transfer characteristics in the right column. The details of OFET performance parameters are summarized in Table 5.2.3. The maximum saturated drain current $I_{\text{max.sat}}$ at gate voltage ($V_g = -60\text{ V}$) are increased significantly from $-1\text{ }\mu\text{A}$ to $-57\text{ }\mu\text{A}$ for substrate temperatures varying from 21°C up to 200°C , respectively, but then drop to $-0.85\text{ }\mu\text{A}$ at $220\text{ }^{\circ}\text{C}$. We attribute these changes in the current to the morphology change from grain to crystalline structure as previously discussed. In addition, we have observed that $I_{\text{max.sat}}$ for films grown on OTS is always higher than the value measured for films grown on bare silicon oxide (see section 5.2.1). This enhancement of the current for films on OTS might be due either to reducing the hydroxyl groups (OH) at the Nc/SiO₂ interface, (these groups act as trapping sites for charges because oxygen that are negatively charged may attract holes that are positively charged) or the higher crystallinity of the films on OTS surface at lower substrate temperature as compared to films on bare oxide (see Figure 4.1.3 and 4.1.16 in chapter 4). We have measured the highest value of on/off ratio 10^5 for a device prepared at $21\text{ }^{\circ}\text{C}$, but then it decreases by one order of magnitude for higher temperatures with small leakage current about 1 nA for devices prepared at $180\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$. It seems that the p-channel is normally off in vacuum for all devices on OTS similar to OFETs prepared on bare oxide (section 5.2.1).

Figure 5.2.4 (b, d, f and h) is transfer characteristics in the saturation region of the OFET devices.

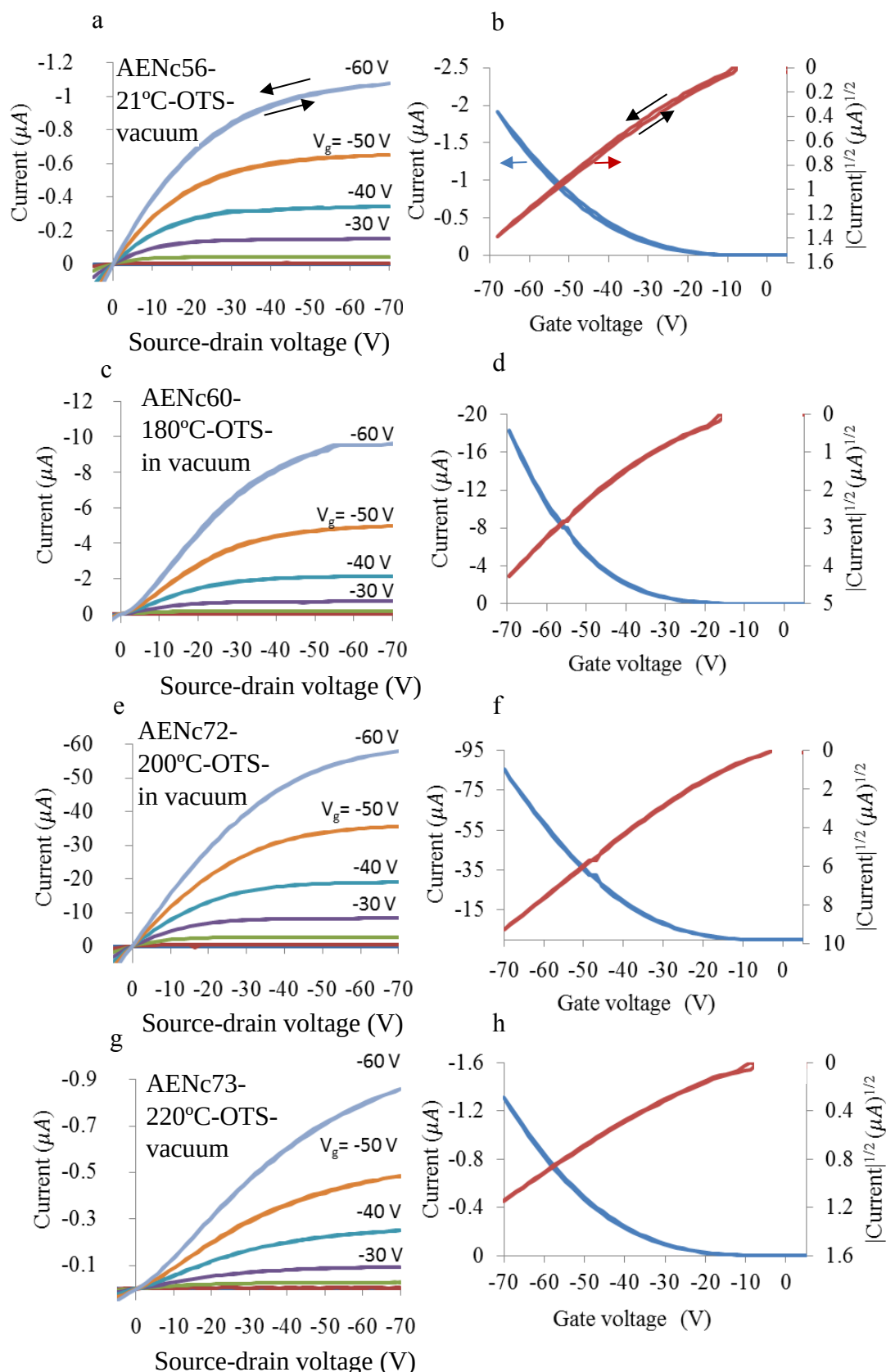


Figure 5.2.4: Output characteristics (a, c, e and g Left column) corresponding to transfer characteristics (b, d, f and h right column) of Nc OFETs on OTS-modified oxide named AENc56, 60, 72, 73 and prepared at different substrate temperatures (21 °C, 180 °C, 200 °C, and 220 °C, respectively) and measured in vacuum and dark.

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The details of device performance parameters are summarized in Table 5.2.3. It can be seen that hole mobility increases with increasing substrate temperature, and the highest value of $(2.3 \pm 0.10) \times 10^{-2} \text{ cm}^2/\text{Vs}$ is measured at 200 °C. Interestingly, we have found the lowest threshold voltage of -10 V for both devices prepared at room temperature and 200 °C while it occurs at more negative gate voltage for the other two devices.

Table 5.2.3: Effects of OTS-modified oxide and substrate temperature on performance parameters of bottom-contact OFETs. The electrical field was 2.4 MV/m

Device	Substrate temperature (°C)	Maximum saturated current (μA)	Threshold voltage (V)	OFETs mobility (cm^2/Vs)	On/Off drain current ratio
AENc56	21	-1	-10	$(6.3 \pm 0.20) \times 10^{-4}$	10^5
AENc60	180	-10	-24	$(1.0 \pm 0.03) \times 10^{-2}$	10^4
AENc72	200	-57	-10	$(2.3 \pm 0.10) \times 10^{-2}$	10^4
AENc73	220	-0.85	-18	$(8.8 \pm 0.50) \times 10^{-4}$	10^4

The performance parameters for the analogue molecule CuPc are discussed here. In 2005, Xiao et al. reported copper phthalocyanine thin film grows on bare Si/SiO₂ and OTS-modified SiO₂ substrates and also the performance parameters of the organic CuPc thin film transistors on both substrates. The field effect carrier mobility of about $4.3 \times 10^{-4} \text{ cm}^2/\text{Vs}$ for the device on the OTS-terminated the surface was about 1-2 orders of magnitude higher than that for a device grown on SiO₂. Also a lower threshold voltage and higher on/off ratio was observed for devices with an OTS-modified surface. This was attributed to the order and connectivity of thin films grown on the OTS-terminated surface, which

was confirmed by XRD and AFM [11]. The estimated hole mobility for Nc on OTS-modified oxide grown at room substrate temperature is higher than CuPc mobility on OTS by factor of 1.5. Similarly, a lower threshold voltage and higher on/off ratio for Nc OFET on OTS are observed as compared to that on bare oxide (also see Table 5.2.1).

To conclude, the optimum substrate temperature is at 200 °C because this device has the highest mobility and also lowest threshold voltage. The devices prepared with OTS-modified oxide always have higher mobility and reduced hysteresis as compared to the devices prepared on the bare silicon oxide. We have attributed this difference to the reduction of trap sites at the insulator/semiconductor interface by passivating with OTS and to an increase in the crystallinity of Nc films on OTS at lower substrate temperature as discussed previously. The threshold voltages are always negative for both OTS-modified oxide and bare SiO₂ devices. Finally, the mobility is enhanced by the factor of 1.7 for OTS-modified oxide devices as compared to device on SiO₂ both prepared at 200°C

5.2.2.1 Effects of atmospheric exposure on OFET characteristics for an OTS treated oxide device prepared at 120 °C

Here, we have studied effects of atmospheric exposure on a bottom-contact OFET (AENc58) grown on OTS-modified oxide at $T_s = 120$ °C. The electrical characteristics were measured as prepared in vacuum, in air and after 3 hours in air (Figure 5.2.5). The OFET performance parameters are listed in Table 5.2.4.

Figures 5.2.5 (a, c and e) show I_d versus V_{sd} at discrete gate voltage V_g ranging from -10V to -60V. There is an increase in the maximum saturated drain current $I_{max,sat}$ at gate voltage ($V_g = -60$ V) after exposure to air with a higher current of -1.5 μ A measured after 3 hours exposure to air. In addition, there is an increase in the on/off current ratio of about one order of magnitude. We attribute the increase in the drain current to the oxygen which might act as a dopant to increase the hole concentration in the bulk Nc film as discussed previously. The

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transfer characteristics of this device in saturation region are measured in different conditions and plotted in Figures 5.2.5 (b, d and f).

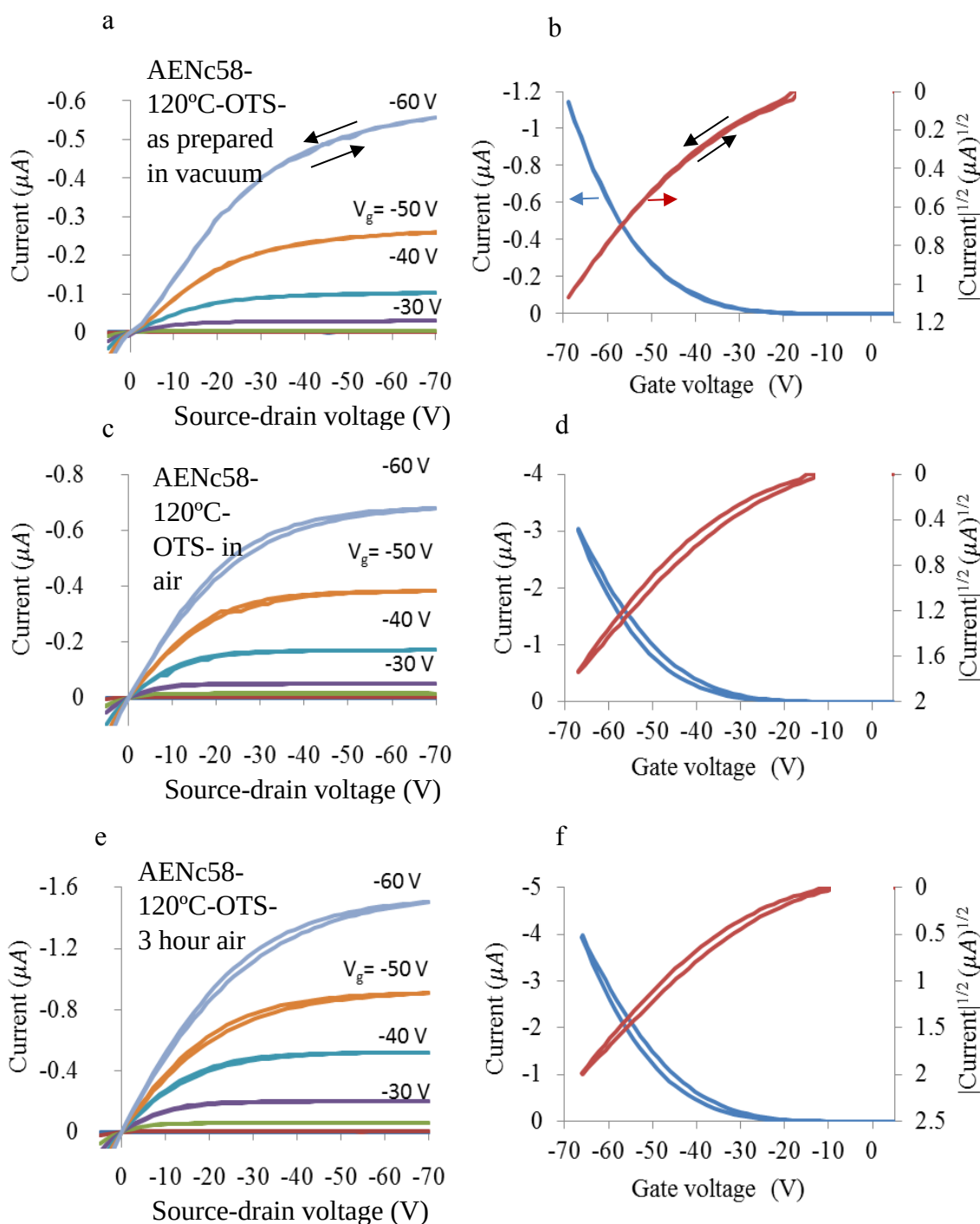


Figure 5.2.5: Output characteristics (a, c and e left column) corresponding to transfer characteristics (b, d, and f right column) of an Nc OFET on OTS named AENc58 prepared at 120°C and measured in vacuum, in air and after 3 hours in air, respectively.

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It is clear from Table 5.2.4 that the mobility increases by a factor of about 3 after 3 hours in air. There is a small hysteresis in the transfer characteristic for both measurements in air. The threshold voltage for measurements in vacuum and air are approximately the same which may be due to a suppression of the effect of hole trapping at the SiO₂/semiconductor interface by passivation with OTS. In contrast, the threshold voltage for the device prepared on bare SiO₂ shows a shift toward positive gate voltage for measurements in air (section 5.2.1.1) [12]

Table 5.2.4: Effects of atmospheric exposure and time dependent on performance parameters for OTS treated oxide bottom-contact OFET device as prepared at 120°C: (a) sweep up, (b) sweep down. The electrical field was 2.4 MV/m

Device	Measurement conditions	Maximum saturated current (μA)	Threshold voltage (V)	OFETs mobility (cm^2/Vs)	On/Off drain current ratio
AENc58	Vacuum	-0.55	-30	$(6.6 \pm 0.39) \times 10^{-4}$	10^4
AENc58	In air	-0.68	-27 ^a to -30 ^b	$(1.7 \pm 0.10) \times 10^{-3}$	10^4
AENc58	3 hours in air	-1.5	-22 ^a to -28 ^b	$(2.1 \pm 0.01) \times 10^{-3}$	10^5

5.2.3 Mobility versus substrate temperature for bottom-contact naphthalocyanine OFET

The hole mobility of bottom-contact Nc OFET devices that are prepared at different substrate temperatures ranging from 21 °C to 220 °C on both bare SiO₂ and OTS-modified oxide surface, and measured in different conditions (vacuum, in air) are summarised in Figure 5.2.6 and the corresponding Table 5.2.5. The mobility shows the same trend and increases with increasing substrate temperature up to 200°C then drops for further substrate temperature. This decrease in mobility was attributed to the discontinuities of films or forms the large gaps between crystal structures at high T_s. There is an increase in the mobility values if device is stored 1 day in air. The mobility of the OTS pre-treated surface is higher than that for bare SiO₂ at each substrate temperature.

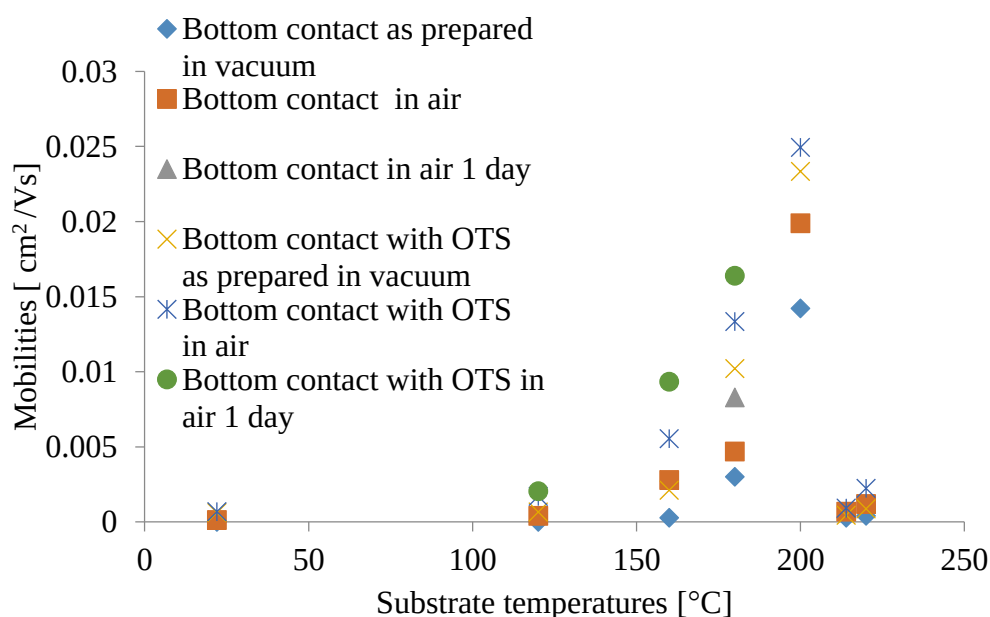


Figure 5.2.6: Mobility versus substrate temperature of bottom-contact Nc OFETs on bare SiO₂ and OTS-modified oxide

able 5.2.5: Mobility (cm^2/Vs) versus substrate temperature ($^{\circ}\text{C}$) of bottom-contact Nc OFETs on bare SiO_2 and OTS-modified oxide

Substrate temperature	Bottom contact as prepared in vacuum	Bottom contact in air	Bottom contact in air 1 day	Bottom contact with OTS as prepared in vacuum	Bottom contact with OTS in air	Bottom contact with OTS in air 1 day
22	1.3×10^{-5}	1.4×10^{-4}		6.3×10^{-4}	6.8×10^{-4}	
120	4.7×10^{-6}	4.1×10^{-4}		6.6×10^{-4}	1.7×10^{-3}	2.1×10^{-3}
160	2.8×10^{-4}	2.8×10^{-3}		2.1×10^{-3}	5.6×10^{-3}	9.3×10^{-3}
180	3.0×10^{-3}	4.7×10^{-3}	8.3×10^{-3}	1.0×10^{-2}	1.4×10^{-2}	1.6×10^{-2}
200	1.4×10^{-2}	2.0×10^{-2}		2.3×10^{-2}	2.5×10^{-2}	
214	3.0×10^{-4}	6.8×10^{-4}		4.6×10^{-4}	9.3×10^{-4}	
220	4.2×10^{-4}	1.2×10^{-3}		8.8×10^{-4}	2.3×10^{-3}	

5.3 Naphthalocyanine Nc organic field effect transistor with top-contacts

5.3.1 Effect of substrate temperature on OFET characteristics in vacuum

In the previous section, we have investigated the electrical characteristics of bottom-contact OFET device. In order to study the influences of contacts and growth temperature on the performance of OFET, we have fabricated top-contact OFET devices in which Nc films are grown at different substrate temperatures under vacuum, but then transferred through air to deposit metal contacts. The devices were annealed after returning to vacuum for 3 hours at $100\text{--}120^{\circ}\text{C}$. After that electrical measurements were taken in vacuum at room temperature under dark conditions. The OFET devices are labelled as AENc65, 68, 62, 66, which correspond to the Nc films prepared at 21°C , 160°C , 200°C ,

and 214 ° C. Their electrical characteristics are plotted in Figure 5.3.1, and the details of their performance parameters are summarized in Table 5.3.1.

The output characteristics of OFET devices are shown in Figures 5.3.1 (a, c, e and g left column). As before, I_d is measured versus V_{sd} at discrete gate voltage V_g ranging from -10V to -60V. The maximum saturated drain current $I_{max.sat}$ at gate voltage ($V_g = -60$ V) increased from - 0.28 μ A to -186 μ A as the substrate temperature is increased from 21 °C to 200 °C but then dropped for 214 °C due to the change in film morphology as previously discussed. The highest on/off current ratio of 10^4 is measured for a device prepared at 21 °C that is in the off state at $V_g = 0$ V. It is important to clarify that this transistor was in an on state (channel normally on) before annealing in vacuum. However, the on/off current ratio is lower by two orders of magnitude for devices prepared at 200 °C and 214 °C, and these devices have p-channel normally on even for positive gate voltage. We attribute this to atmospheric adsorption that leads to increase in hole concentration while the channel can be turned off at $V_g = 0$ V if the devices are annealed in vacuum for longer time. In addition, the saturation region for the device prepared at room temperature can clearly be seen while it became less obvious at higher substrate temperature.

The transfer characteristics in the saturation region are also plotted (Figures 5.3.1 b, d, f and h). Note that for the following measurements: symbols AA refers to after annealed sample, and BA refers to before annealing sample.

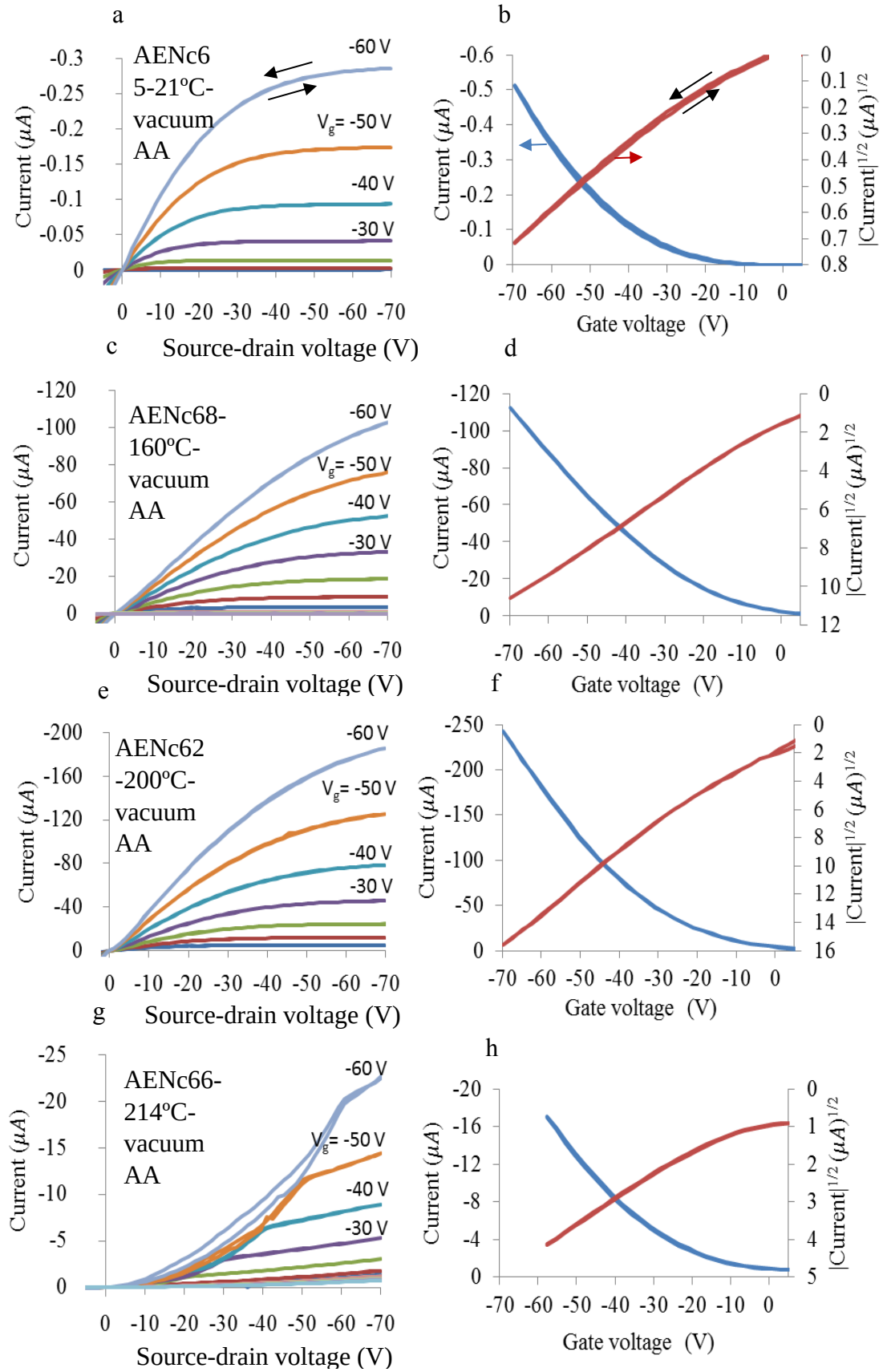


Figure 5.3.1: Output characteristics (a, c, e and g) and transfer characteristics (b, d, f and h right column) of top contact Nc OFETs on bare Si/SiO₂ named AENc65, 68, 62, 66 and prepared at different substrate temperatures (21 °C, 160 °C, 200 °C, and 214 °C, respectively) measured after annealing in vacuum and dark.

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It can be seen clearly from Table 5.3.1 that the mobility increases by two orders of magnitude as the substrate temperature increases from room temperature to 200 °C, but then the mobility decreases at higher substrate temperature. The threshold voltage V_{th} is negative for the device prepared at 21 °C while it is positive for the device prepared at 200 °C and 214 °C, implying transistor channel is normally off at 21 °C.

Table 5.3.1: Substrate temperature effect on performance parameters of top-contact OFET device. The electrical field was 2.4 MV/m

Device	Substrate temperature (°C)	Maximum saturated current (μA)	Threshold voltage (V)	OFETs mobility (cm ² /Vs)	On/Off drain current ratio
AENc65	21	-0.28	-13	(3.07 ± 0.12) × 10 ⁻⁴	10 ⁴
AENc68	160	-102	+10	(3.22 ± 0.10) × 10 ⁻²	10 ³
AENc62	200	-186	0	(5.16 ± 0.23) × 10 ⁻²	10 ²
AENc66	214	-22	+5	(8.91 ± 0.38) × 10 ⁻³	10 ²

To conclude the transport properties and the performance of OFET devices fabricated with top-contact at different substrate temperature show always better hole mobility than the bottom-contact OFET devices whose films prepared at the same substrate temperature. This is probably due to differences in thin film morphologies at the electrode/semiconductor interface for top-contact and bottom-contact devices see Figure 5.3.2, where the grain size on SiO₂ in area (C) are larger than that on gold electrode (A), (B). However, the on/off ratio for the top-contact transistor is lower than that for a bottom-contact device, and the top-contact OFETs are mostly normally on. This might be due to the exposure of devices to air prior to metal evaporation on active layer.

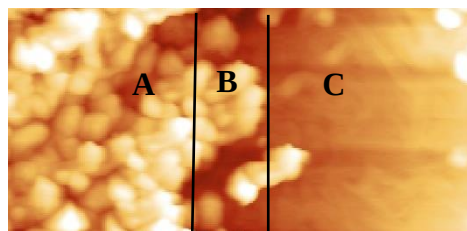


Figure 5.3.2: AFM image of naphthalocyanine thin film deposited on Au electrode and SiO₂ surface. Area (A): naphthalocyanine film deposited on Au electrode. B: naphthalocyanine film deposited on the interface between Au and SiO₂ surface. C: naphthalocyanine film deposited on SiO₂ surface away from the edge of electrode.

5.3.2 Effect of annealing sample and atmospheric exposure on OFET

characteristics for samples grown at 120 °C

In this section, we describe the influence of annealing Nc films in vacuum and the time dependence of atmospheric exposure on the performance top-contact OFETs, grown at substrate temperature 120 °C. We measured electrical characteristics of OFET devices as follows: as prepared in air, after annealing at 100 °C -120 °C for 3 hours in vacuum, after exposure to air directly and then for 1 day in air (Figure 5.3.3). The OFET device is labelled as AENc64. The output and transfer characteristic are analysed to obtain the performance parameters listed in Table 5.3.2.

The output characteristic of OFET devices is shown in Figure 5.3.3 (a, b, e and g) in which I_d versus V_{sd} curve is plotted for discrete gate voltage V_g ranging from -10V to -60V. The maximum saturated drain current $I_{max.sat}$ at gate voltage ($V_g = -60$ V) for device that measured: as prepared under ambient condition, and later after 1 day exposure air are higher than those measured for the annealed device in vacuum and then directly after exposure to air. In addition, a clear saturation region is not observed after long exposure to atmosphere. However, the saturation region for the annealed devices, immediately after exposure to air can be clearly observed. In addition, the on/off current ratio after annealing in vacuum is increased by two orders of magnitude. This device in all measurement conditions shows p-channel normally on, and it can be difficult to turn the channel off even for very high positive gate voltage, in particular when measuring in air. We attribute this decrease in drain current and increase in on/off ratio for the device in vacuum after annealing either to degassing of adsorbed oxygen leading to a decrease in hole concentration, or reduction in the contact resistance after annealing device.

The transfer characteristics in the saturation region are also plotted for different measurement conditions (Figures 5.3.3 b, d, f and h).

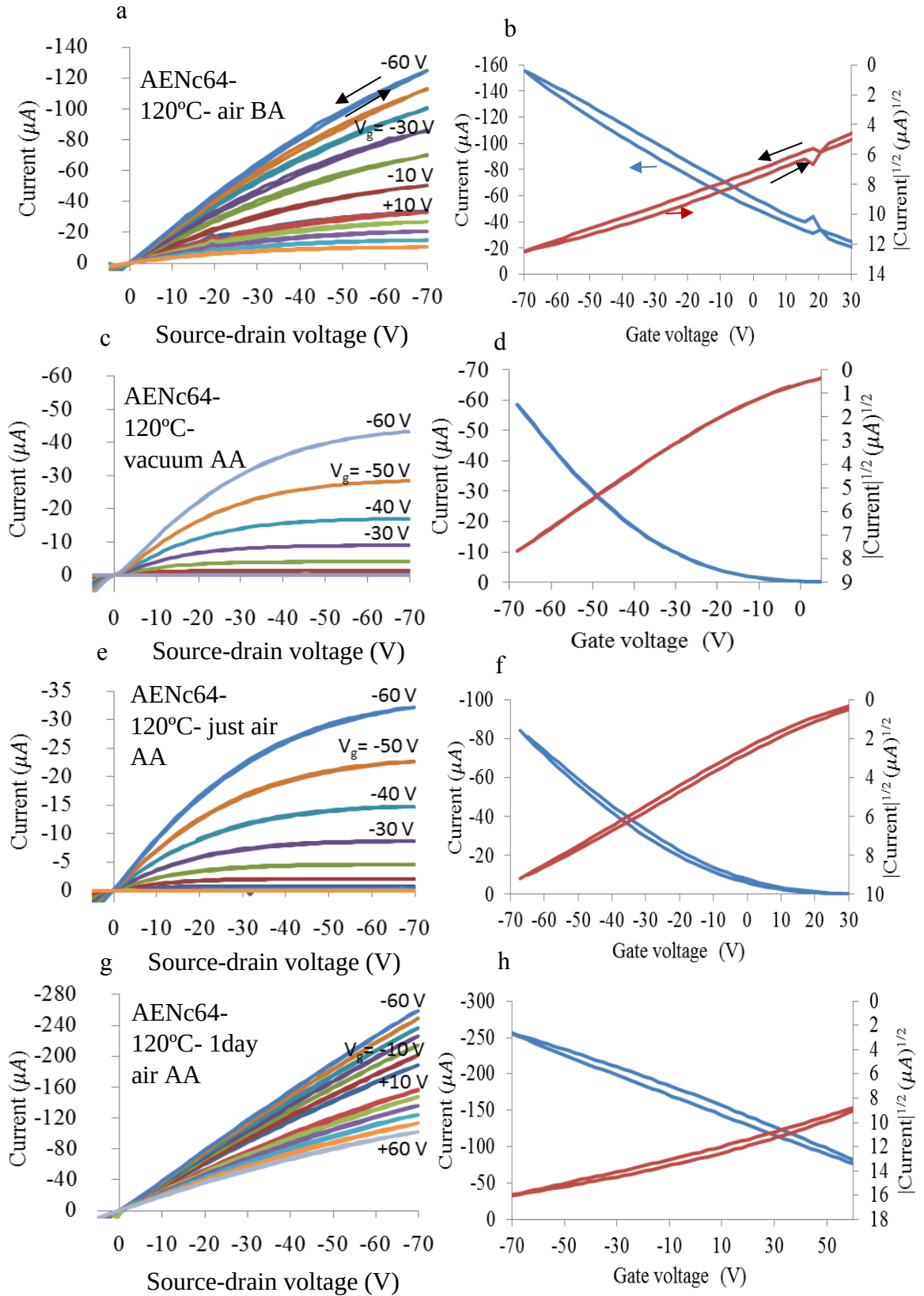


Figure 5.3.3: Output characteristics (a, c, e and g left column) corresponding to transfer characteristics (b, d, f and h right column) of top contact Nc OFET on bare Si/SiO₂ named AENc64 that prepared at 120 °C and measured in air as prepared, annealed in vacuum , in air and 1 day in air, respectively.

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It can be seen clearly from Table 5.3.2 that the mobility increases by one order of magnitude if the device annealed in vacuum, while it subsequently decreases if the device is re-exposed to air for 1 day. Interestingly, the transfer characteristics show hysteresis only if the device is exposed to air. In addition, the threshold voltage is almost zero for the device annealed in vacuum, while it is shifted toward positive gate voltage with time if device is exposed to air. Therefore, the change of trap density could be obtained by comparing shift of threshold voltage ΔV_{th} in transfer characteristic for both measurement conditions: annealed in vacuum and directly expose to air ($\Delta V_{th} = -35V$) according to Equation 5.1.5. This is found to be $3.7 \times 10^{12} \text{ cm}^{-2}$.

Table 5.3.2: Effect of annealing and atmospheric exposure on performance parameters of top-contact OFET device prepared at 120°C. The electrical field was 2.4 MV/m

Device	Measurement conditions	Maximum saturated current (μA)	Threshold voltage (V)	OFETs mobility (cm^2/Vs)	On/Off drain current ratio
AENc64	As prepared	-125	+70	$(8.6 \pm 0.27) \times 10^{-3}$	10^1
AENc64	Annealed in vacuum	-43	-5	$(2.9 \pm 0.12) \times 10^{-2}$	10^6
AENc64	In air	-32	+30	$(1.8 \pm 0.05) \times 10^{-2}$	10^4
AENc64	1 day in air	-259	+150	$(3.1 \pm 0.10) \times 10^{-3}$	10^1

In 2014, Tsegie et al. reported the effect of annealing thin films of zinc phthalocyanine derivatives on organic OFET performance. The thin film was heated to 70 °C under vacuum, and the electrical measurements were performed as deposited and after annealing under ambient conditions. They found that the mobility improved, and contact resistance reduced after annealing. This was attributed to interchain aggregation and crystallization of thin film layers. In addition, the hysteresis and threshold voltage after annealing show lower values than measured for the as-deposited film [13].

To summarise, the Nc OFET device shows high performance in vacuum condition after annealing when the device has higher hole mobility, lower threshold voltage and higher on/off ratio than when measured in air.

5.3.3 Mobility versus substrate temperature for top-contact

naphthalocyanine OFET: summary

The electrical measurement (hole mobility) for top-contact OFETs at different temperature (21-220) °C and in different conditions: as prepared in air, annealed in vacuum for (100-150) °C, directly after exposure to air and 1 day left in air are summarised in Figure 5.3.4 and Table 5.3.3. Similar to bottom-contact devices, there is an increase in the mobility as the substrate temperature increases reaching a peak at 200 °C, but then decreasing for higher substrate temperatures. The mobility after annealing devices in vacuum is always higher than that measured as prepared in air. This result is consistent with solution processed Nc derivative OFETs that reported an increase in mobility by a factor of 18 after annealing [14]. The mobility is significantly decreased when the device is re-exposed to air, in contrast to the previous measurements for bottom-contact Nc OFETs (see section 5.2.3). This decrease in mobility might be due to effect of oxygen adsorbed the metal/semiconductor interface that acts as a site for trapping holes, or increase in the contact resistance for top-contact configuration.

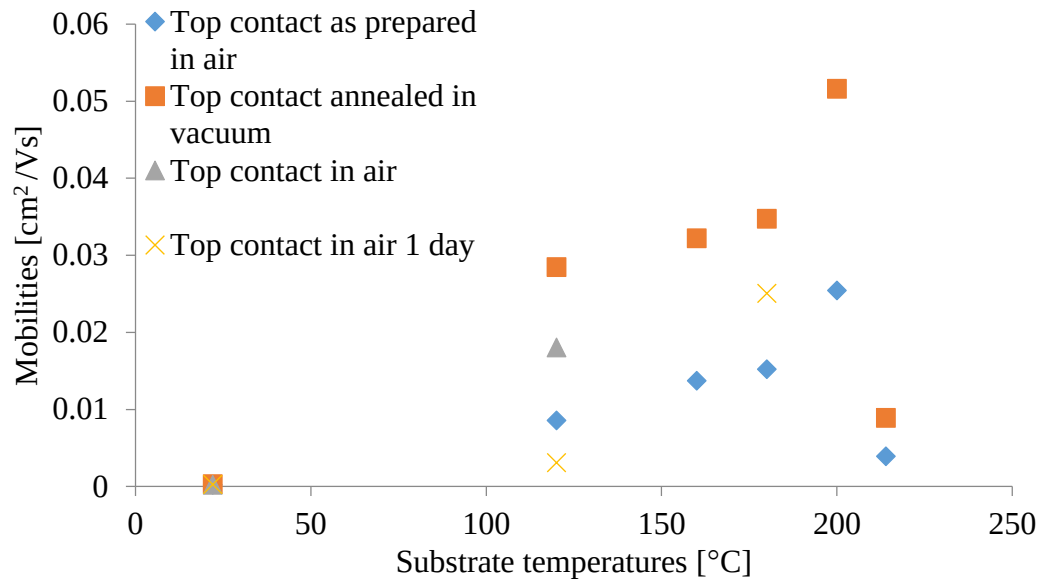


Figure 5.3.4: Mobility versus substrate temperature of top contact Nc OFETs on bare SiO₂

Table 5.3.3: Mobility (cm²/Vs) versus substrate temperature (°C) of top-contact Nc OFETs on bare SiO₂

Substrate temperature	Top contact as prepared in air	Top contact annealed in vacuum	Top contact in air	Top contact in air 1 day
22	2.1×10^{-04}	3.0×10^{-04}	2.2×10^{-04}	2.7×10^{-04}
120	8.6×10^{-03}	2.9×10^{-02}	1.8×10^{-02}	3.1×10^{-03}
160	1.4×10^{-02}	3.2×10^{-02}		
180	1.5×10^{-02}	3.5×10^{-02}		2.5×10^{-02}
200	2.5×10^{-02}	5.2×10^{-02}		
214	4.0×10^{-03}	9.0×10^{-03}		

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Overall the results for top-contact devices show better performance than bottom-contact Nc OFET devices at the same substrate temperatures and measured under the same conditions (see Figure 5.3.5).

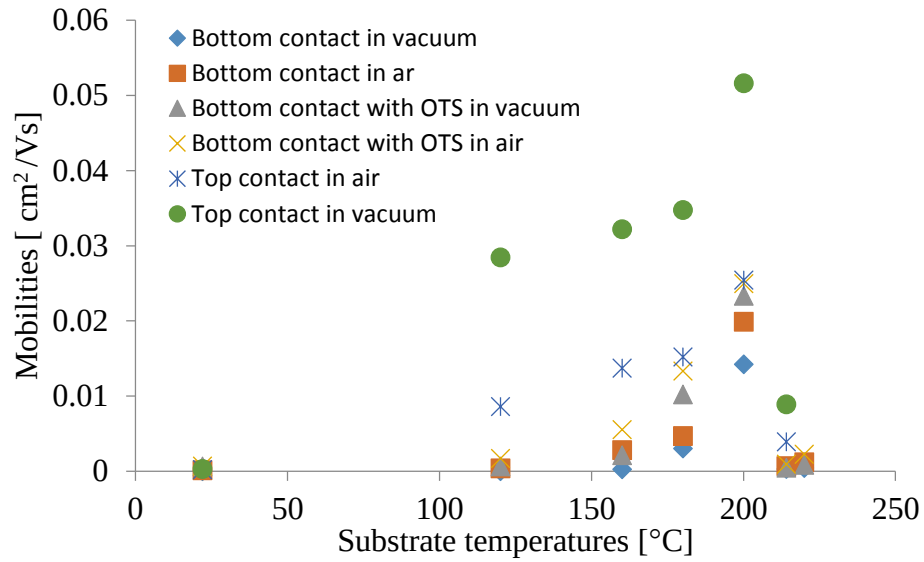


Figure 5.3.5: Mobility versus substrate temperature of top-contact and bottom-contact Nc OFETs on bare SiO₂ and OTS-modified oxide

5.4 Copper naphthalocyanine CuNc organic field effect transistors

5.4.1 Effect of substrate temperature on bottom-contacts OFET characteristics in vacuum

In the previous chapter, we studied the influence of copper naphthalocyanine (CuNc) on the film morphology and crystalline structure, and compared it with metal-free naphthalocyanine film. In this section, we will investigate metallated naphthalocyanine OFETs. We have fabricated bottom-contact CuNc OFET devices grown at different substrate temperatures. The OFET devices are labelled as AECNc02, 03, 05, 06 corresponding to films prepared at 21°C, 120°C, 180°C, and 220°C, respectively. The electrical characteristics were measured in vacuum and plotted in Figure 5.4.1. These characteristics were analysed in order to obtain details of performance parameters, which are listed in Table 5.4.1.

Figure 5.4.1 (a, c, e and g) shows the output characteristic of OFET devices. There is a significant increase in the maximum saturated current $I_{max. sat}$ from -0.15 μA to -72 μA as the substrate temperature increases from 21 °C to 180 °C, respectively, but then it drops to -12 μA at 220 °C. The on/off current ratios are around 10^2 - 10^6 for these devices, which show p-channel normally on behaviour. The device prepared at 180 °C has the highest value of $I_{max. sat}$ due to a change of film morphology and the formation of a highly crystalline structure.

Figure 5.4.1 (b, d, f and h) show the transfer characteristic in the saturation region for OFET devices prepared at different substrate temperatures.

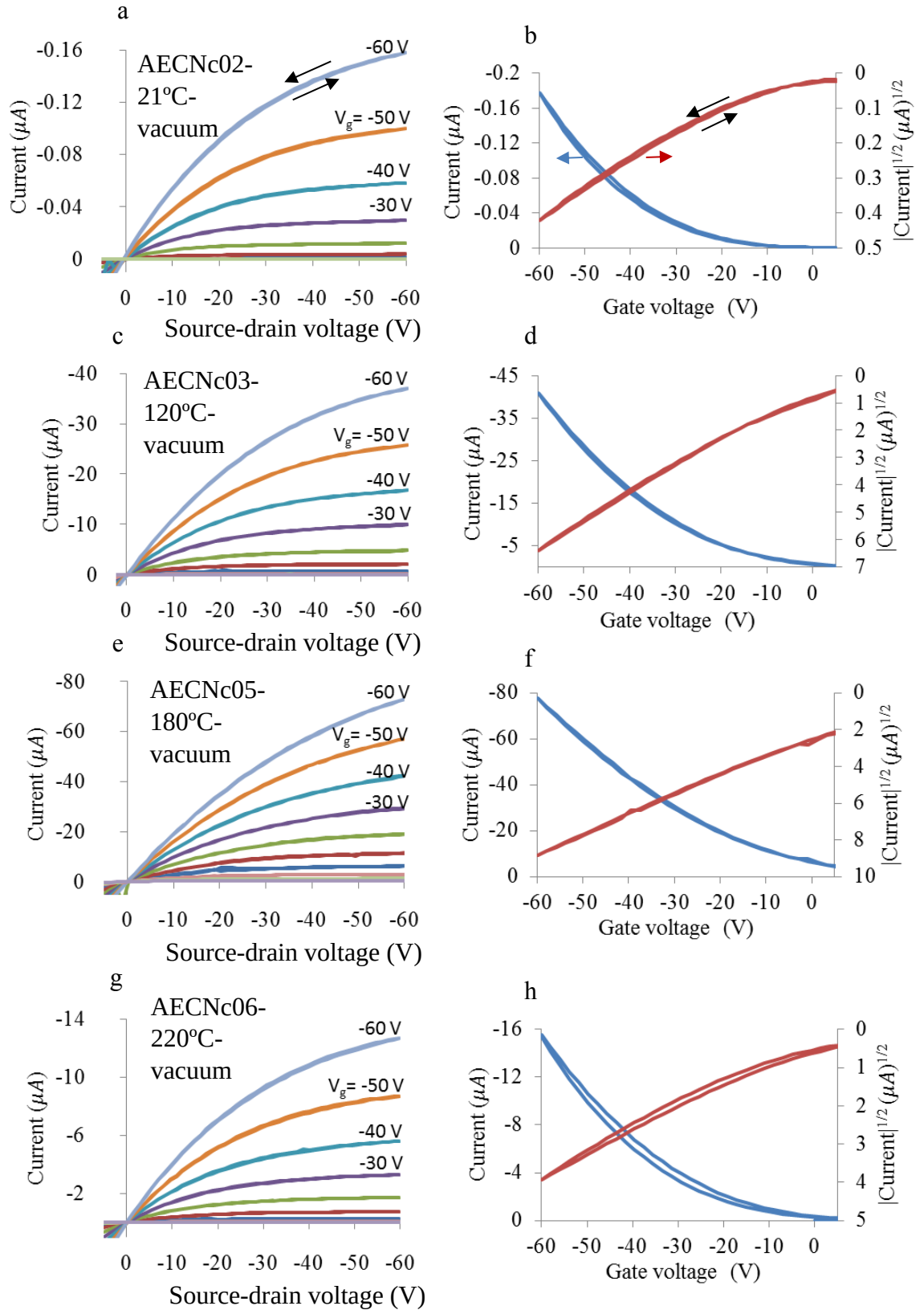


Figure 5.4.1: Output characteristics (a, c, e and g Left column) corresponding to transfer characteristics (b, d, f and h right column) of CuNc OFETs on SiO₂ named AECNc02, 03, 05, 06 and prepared at different substrate temperatures (21 °C, 120 °C, 180 °C, and 220 °C, respectively) measured in vacuum and dark.

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It can clearly be seen from Table 5.4.1 that the mobility increases from $(1.3 \pm 0.04) \times 10^{-4} \text{ cm}^2/\text{Vs}$ to $(1.8 \pm 0.06) \times 10^{-2} \text{ cm}^2/\text{Vs}$ as the substrate temperature increases from room temperature to 180 °C, but then decreases for higher substrate temperatures. As for the increase in saturation current, we attribute this increase to changes the crystalline structure.

Table 5.4.1: Substrate temperature effect on performance parameters of bottom-contact OFET device. The electrical field was 2.4 MV/m

Device	Substrate temperature (°C)	Maximum saturated current (μA)	Threshold voltage (V)	OFETs mobility ($\text{cm}^2/\text{V s}$)	On/Off drain current ratio
AECNc02	21	-0.15	-10	$(1.3 \pm 0.04) \times 10^{-4}$	10^4
AECNc03	120	-37	0	$(1.1 \pm 0.04) \times 10^{-2}$	10^6
AECNc05	180	-72	+20	$(1.8 \pm 0.06) \times 10^{-2}$	10^2
AECNc06	220	-12	0	$(6.0 \pm 0.28) \times 10^{-3}$	10^3

A study of lead phthalocyanine (PbPc) deposited at different T_s is discussed here for comparison. In 2015, Yao Li et al. reported thin films of lead phthalocyanine (PbPc) deposited using vacuum thermal evaporation on Si/SiO₂ substrate at different substrate temperatures 60, 100, 140 and 180°C. The optimal performance of organic field-effect transistors was observed for thin films grown at 140 °C because it provides the highest mobility of $3.2 \times 10^{-4} \text{ cm}^2/\text{Vs}$ and maximum drain current [15]. However, we observe the optimum performance of CuNc OFETs at $T_s = 180 \text{ °C}$ with mobility two orders of magnitude higher than that of PbPc.

To summarise, the optimum temperature to grow CuNc film for OFET devices is 180 °C.

5.4.2 Mobility versus substrate temperature for both bottom-contact and top-contact copper naphthalocyanine OFET

We have fabricated additional devices CuNc to investigate the effect of OTS-termination, exposure to air and a comparison between bottom-contact and top-contact devices. The electrical measurements were taken using a similar approach as for metal-free naphthalocyanine and summarised in (Figure 5.4.2 and corresponding Table 5.4.2). Their output and transfer characteristics are shown in Appendix A.

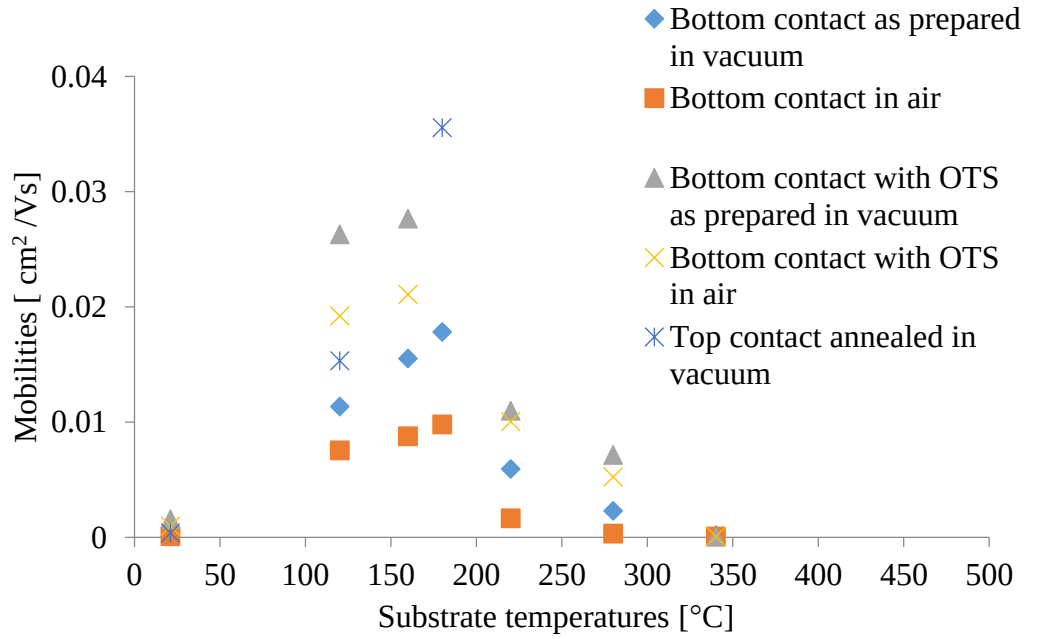


Figure 5.4.2: Mobility versus substrate temperature of bottom-contact CuNc OFETs on bare SiO₂

For bottom-contact CuNc OFET on SiO₂ substrate, we have measured the mobility as prepared in vacuum. The results show that the mobility increases from $(1.3 \pm 0.04) \times 10^{-4}$ to $(1.6 \pm 0.05) \times 10^{-2}$ cm²/Vs as temperature increases from 21°C to 160°C, and the highest mobility of $(1.8 \pm 0.06) \times 10^{-2}$ cm²/Vs was measured at 180 °C. However, there was a significant decrease in mobility to $(2.1 \pm 0.1) \times 10^{-4}$ cm²/Vs for the substrate temperature at 340°C. In addition, we

have repeated the electrical measurements for same devices at each temperature after exposure to air. The results show a decrease in mobility at each temperature; in contrast to bottom-contact Nc OFETs in air (see section 5.2.3). Also Braga and Horowitz reported that the mobility decrease if OFET is exposure to oxygen. They attributed this either to increase of the trap density or increase of the contact resistance [16].

Furthermore, for bottom-contact CuNc OFET on OTS-modified SiO₂, the electrical measurements show higher mobility for each substrate temperature as compared to mobility of OFETs on bare oxide, but we have repeated the electrical measurements for the same devices at each substrate temperature in air, and we have observed a decrease in mobility, which is again inconsistent with bottom-contact measurements in air for Nc OFETs. This may be due to increase in resistance on exposure to air for CuNc while increasing hole dopants associated with oxygen adsorption for metal-free Nc. The similar gas sensitivity behaviour have been observed for Pc and NiPc [17].

For top-contact CuNc OFETs on oxide substrate at growth temperature 21°C, 120°C and 180°C, we have measured the mobility after annealed device for (100-150)°C in vacuum. The results show an increase of mobility as compared to bottom-contact OFETs at same growth temperatures. We attributed this increase in mobility to the change of morphology in the metal/semiconductor interface for the top-contact device see Figure 5.3.2.

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Table 5.4.2: Mobility (cm^2/Vs) versus substrate temperature ($^{\circ}\text{C}$) of bottom-contact and top contact CuNc OFETs on bare SiO_2

Substrate temperature	Bottom-contact as prepared in vacuum	Bottom-contact in air	Bottom-contact with OTS as prepared in vacuum	Bottom-contact with OTS in air	Top-contact annealed in vacuum
21	1.3×10^{-4}	1.2×10^{-4}	1.6×10^{-3}	9.9×10^{-4}	4.0×10^{-4}
120	1.2×10^{-2}	7.6×10^{-3}	2.6×10^{-2}	2.0×10^{-2}	1.5×10^{-2}
160	1.6×10^{-2}	8.8×10^{-3}	2.8×10^{-2}	2.1×10^{-2}	
180	1.8×10^{-2}	9.8×10^{-3}			3.6×10^{-2}
220	6.0×10^{-3}	1.7×10^{-3}	1.1×10^{-2}	1.0×10^{-2}	
280	2.4×10^{-3}	3.5×10^{-4}	7.2×10^{-3}	5.3×10^{-3}	
340	2.1×10^{-4}	9.2×10^{-5}	9.2×10^{-5}	9.0×10^{-5}	

To conclude, the performance of CuNc OFETs shows higher mobility than the Nc OFETs at same growth temperature, growth condition and measurement conditions

5.5 Summary

In this chapter, Nc and CuNc OFETs were fabricated, and their electrical characteristics were measured in vacuum and air. We found that the device parameters were affected by preparation conditions such as substrate temperature and OTS-modification of the substrate, and also measurement conditions such as exposure to ambient conditions and post annealing.

The OFETs charge carrier transport is enhanced at high substrate temperatures because the degree of crystallinity of Nc and CuNc films is increased with molecules in an edge-on orientation, with the stacking axis parallel to the substrate and the direction of flow of charge carriers. This corresponds to molecules standing perpendicular to the substrate in the needle-like crystalline structure. We found that the optimum substrate temperature during growth is achieved at 200°C , for which Nc thin film on SiO_2 and OTS shows the best electrical properties. In addition, the optimized growth temperature for CuNc

thin films on SiO₂ and OTS-terminated substrates was determined to be 180 °C and 160 °C, respectively.

The chemical modification of SiO₂ with a self-assembled monolayer of OTS was performed and followed by the growth Nc and CuNc thin films. AFM images show that the interactions between the OTS and both the Nc and CuNc films produced a needle-like structure at lower temperature with a smaller size as compared to that on bare SiO₂. The changes of surface morphology and the reduction of surface traps caused by the surface treatment improved the field-effect mobility and reduced hysteresis.

The effect of exposure of Nc or CuNc OFET devices to atmosphere on carrier transport, hysteresis and threshold voltage stability has been studied. The changes in hysteresis threshold voltage and mobility of charge carriers in OFETs following exposure to air is likely due to the introduction of excess holes and filling of hole traps. The mobility decrease for CuNc when exposed to air which is attributed to the metal Cu may lead to increase in resistance on exposure to air. We have found that the density of charge carrier trap is about $1.8 \times 10^{12} \text{ cm}^{-2}$ for bottom-contact OFET device and about $3.7 \times 10^{12} \text{ cm}^{-2}$ for top-contact OFET devices.

The thin films of metallated and non-metallated naphthalocyanine molecules in top-contact OFETs configuration are annealed at 100°C-150°C for 3 hours in vacuum, that lead to improve performance of devices. The transfer characteristics show lower hysteresis and threshold voltage of the post-annealed devices in vacuum as compared for the same device as deposited films in the air. The improvement in mobility in the annealed device is possibly due either to degassing of oxygen from semiconductor layer during annealing in vacuum that lead to decrease hole concentration in semiconductor, or reduction in the contact resistance after annealing device.

The top-contact OFET devices always show higher mobility as compared to that of bottom-contact OFET devices possibly due to different film morphology at the interface between metal and SiO₂ surface for top and bottom-contact configuration see Figure 5.3.2.

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Chapter 6

Supramolecular structures of porphyrin nanorings

We have studied c-P30 the cyclic polymer (nanoring) with 30 porphyrin units. The nanorings are adsorbed on Au(111) from solution by immersion in different solvents at various concentrations. Scanning tunneling microscopy (STM) and AFM are used to image the nanorings on the substrate. This approach results in self-assembly of single layer nanorings and supramolecular structures such as stacked and nested nanorings, which are similar to those formed using electrospray deposition from solution onto a surface held under vacuum conditions [1]. For our experiments the c-P30 nanorings are dissolved in toluene. Then this solution is diluted further either by toluene, methanol or a toluene/methanol mixture (3:5 by volume), to investigate whether the adsorbate shape and configuration is solvent and/or concentration dependent. Our experiments were performed at room temperature under ambient conditions.

6.1 Porphyrin monomer

Porphyrin molecules have attracted scientific and technological attention because of their potential application in sensor, photovoltaics, medical and optoelectronic devices [2-5], and their π -conjugated electrons are delocalised as observed in biological derivatives. This allows two important processes to occur which are mediated by these molecules; oxygen transport and light harvesting. Porphyrin molecules may be synthesised with different side groups and central metal atoms in order to obtain different structures, and to control optical and electronic properties [6].

Porphyrin is a macrocyclic organic compound, consisting of four pyrrole rings joined by four methine bridges ($=CH-$) (Figure 6.1.1). The porphyrin can accommodate guest species in the centre of cavity typically a metal ion (Co, Zn, Cu) through deprotonation of nitrogen atoms. This leads to changes in optical and electronic properties (Figure 6.1.2).

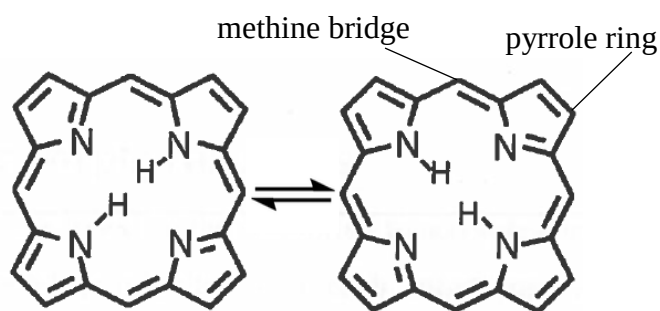


Figure 6.1.1: porphyrin structure and exchange of proton H bond between nitrogen atoms N

Another factor making porphyrin an interesting molecule is the aromaticity of its π electron system. The molecular aromaticity can be verified by Huckel's rule: $(4n+2)$ is equal to the number of π electrons in the molecule, where n is a zero or positive integer number. For example there are 22 π electrons in porphyrin, so it satisfies Huckel's rule with $n=5$. Above all, aromatic polymers and organic semiconductors have attractive electronic properties because the HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are analogous to the valence and conduction bands of a semiconductor. As a result, aromatic systems are good candidates for making organic electronic devices. In addition, porphyrin has high thermal stability. Moreover, the electronic and optical properties in porphyrin system are strongly dependent on substituents and coordinated metal-atoms.

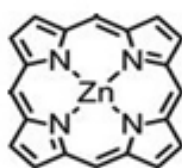


Figure 6.1.2: Porphyrin bonded to a central metal atom

There are two significant positions of a porphyrin structure, the β and meso points, where chemical groups such as an aryl group (Figure 6.1.3) may be substituted for hydrogen atoms in order to functionalise the porphyrin. Functional groups, that have only C, H and O atoms in their structure, are substituted at different positions in different molecules. For example, haemoglobin and chlorophyll are naturally occurring molecules, which are

substituted at the β - position while many synthesised porphyrin derivatives are substituted at the meso position.

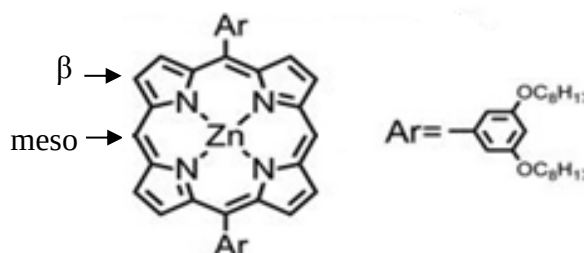


Figure 6.1.3: Porphyrin structure with aryl group substitution and a central metal atom

6.1.1 Butadiyne linked porphyrin oligomer

Porphyrin macrocycles have been joined together in various ways. The photophysics of porphyrin oligomers is considerably changed when they are linked by different types of bridging groups and using different attachment positions. In 1990, Therien used two types of bridge, ethynyl and butadiynyl, to link porphyrins. This gives rise to the strongest electronic coupling of porphyrins if they are connected through meso-meso positions, followed by β -meso and a much weaker effect for β - β links [7]. Lindsey observed a weak interaction of porphyrins when they were linked by a diphenylethyne bridge [8]. Kim and Osuka reported two porphyrins linked through three attachment positions, meso-meso and two β - β [9]. In addition, zinc porphyrin macrocycles can be linked together by a butadiyne bridge at meso-meso positions in order to form porphyrin oligomers, which leads to an enhancement of the electron conjugation system (Figure 6.1.4) [10]. Porphyrin oligomers have a flexible conformation which can influence their organisation on a surface substrate. Porphyrins linked by butadiyne bridge to form porphyrin oligomer and porphyrin nanoring are studied in this thesis. They were synthesised by the Anderson group at the University of Oxford.

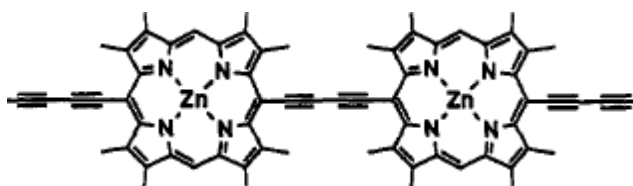


Figure 6.1.4: Zn-porphyrin oligomer linked by butadiyne bridge

6.1.2 Linear porphyrin oligomers

As discussed in the previous section porphyrin molecules can be covalently bonded together by appropriate functional groups to form a linear porphyrin oligomer. In this section, the synthesis of a linear porphyrin oligomer from butadiyne-linked porphyrin monomers by using template strategy [11] is described.

Figure 6.1.5 illustrates this strategy, in which three porphyrin units are assembled at three binding sites of template by a metal coordination bond between Zn and template (see section 6.1.3 for more details about the template work). Then the covalent coupling occurs between porphyrin monomers by butadiyne bridge, followed by removal of the template using pyridine. Porphyrin units and molecular templates are shown in red and blue, respectively. For example, a linear porphyrin oligomer with 3 monomers could be formed from three porphyrin groups with a linear template of 3 binding sites. This implies that the number of porphyrin units in the product is equal to the number of binding sites of the template.

Varieties of linker groups have been used by many researchers to create covalently coupled porphyrin oligomers as described in the previous section while a conjugated linker group is favoured in order to allow electron delocalisation occurs across the whole molecule. A conjugated butadiyne link groups is used within the oligomers that are presented in this work.

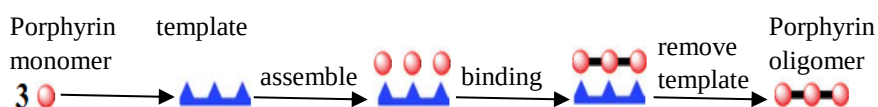


Figure 6.1.5: Template strategy to synthesis linear porphyrin oligomers that consisted of three monomers.

6.1.3 Vernier templating and cyclic polymer

Long chain porphyrin oligomers were synthesised from butadiyne-linked short linear porphyrin oligomers using a template directed strategy. In this method, the length of porphyrin oligomer can be determined from the number of building blocks (porphyrin units) (n) multiplied by the length of a porphyrin group ($a = 1.33\text{nm}$). In the Vernier approach a template molecule defined by the number of binding sites (m), leads to an oligomer, with a number of porphyrin groups equal to the lowest common multiple of n and m . For example, if we have ($n = 3$) and ($m = 2$); the length of the resulting oligomer will be equal to ($6 \times a$), see Figure 6.1.6a [12]. The long oligomer is generated by covalently bonding adjacent porphyrin groups of short oligomers. Finally, the molecular template is removed.

A cyclic polymer nanoring is a novel type of porphyrin-derived nanostructure, which has recently been synthesised [12, 13]. The Vernier template strategy has been used to synthesize cyclic polymer nanorings through a circular template (Figure 6.1.6b). The number of porphyrin groups in a cyclic polymer depends on the length of the initial porphyrin chains and the size of the template. Synthesised nanorings with the following numbers of porphyrin units, 6, 8, 12, 16, 18, 24, 30, 40 and 50 have been produced [1, 14]. The nanoring c-P12 has been synthesised using porphyrin 4-oligomers and circular molecular templates with 6 binding sites [12].

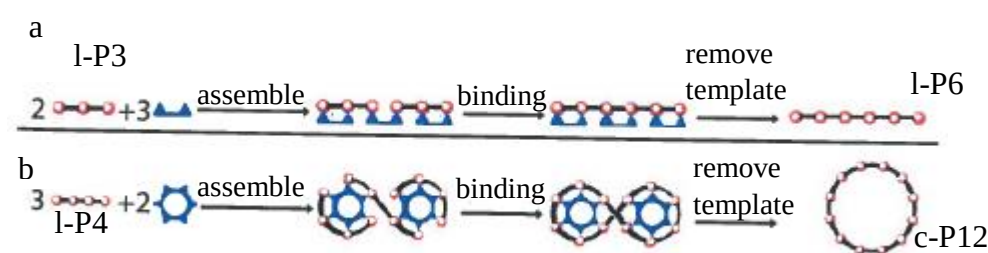


Figure 6.1.6: Synthesising porphyrin oligomers using a template-directed strategy. Porphyrin units and molecular templates are shown in red and blue, respectively. Short chain porphyrin oligomer assembles using a molecular template. A chemical reaction occurs that leads to the formation of covalent bonding between initial short oligomers to produce a long porphyrin oligomer, and finally the molecular template is removed. a) A linear porphyrin oligomer with 6 monomers is formed from short oligomers of 3 porphyrin groups with a linear template of 2 binding sites. b) A cyclic porphyrin polymer with 12 monomers is formed from a linear porphyrin oligomer of 4 porphyrin units and a circular molecular template of 6 binding sites [12].

Chapter 6

In order to give details about the work of template, Vernier-templated synthesis of c-P12 using template T6 are shown in Figure 6.1.7. The linear zinc-porphyrin tetramer l-P4 reacts with the hexapyridyl template T6 by metal coordination between (Zn) porphyrin-(N) template, then coupling of l-P4 by covalent bond butadiyne occurs. These reactions lead to nanoring-template complexes c-P12 ·(T6)₂. Addition of pyridine can be used to remove the template from the nanoring c-P12 [12].

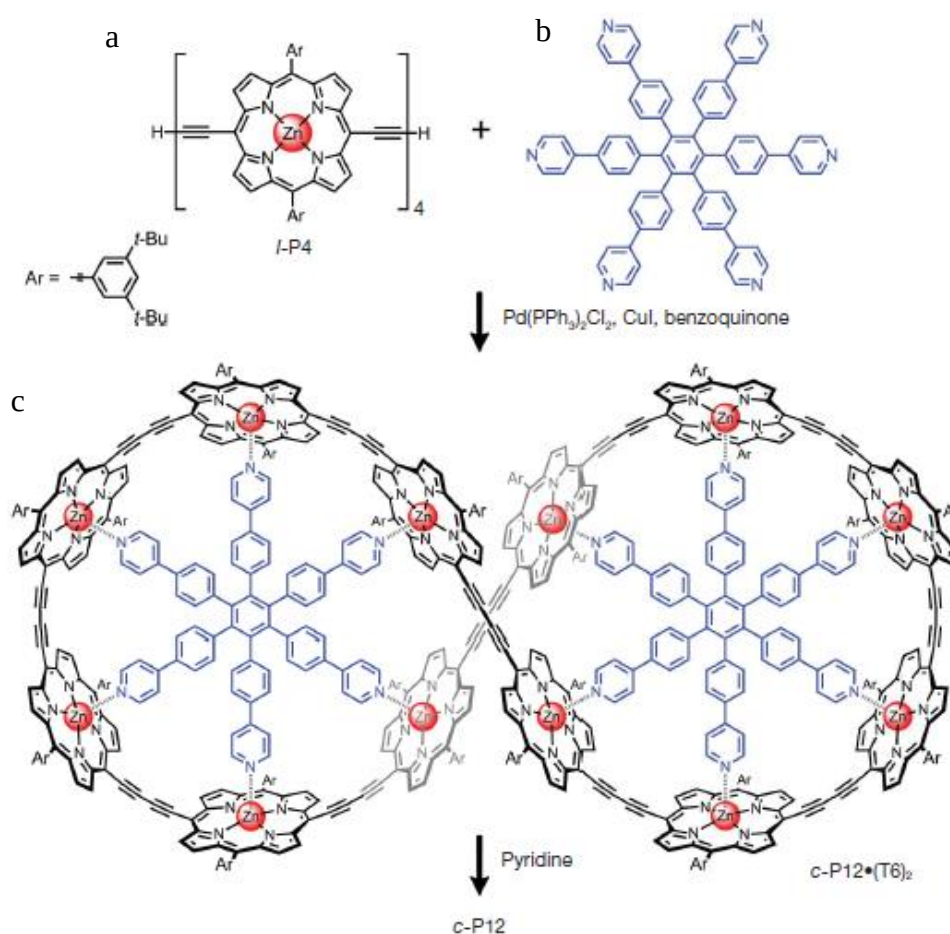


Figure 6.1.7: Vernier-templated synthesis of c-P12 in the presence of hexapyridyl template T6. a) Structure of linear oligomer (l-P4), b) structure of hexapyridyl template T6 c) generation of nanoring-template complexes c-P12·(T6)₂. Ar is a side group (3,5-bis(octyloxy)phenyl) attached to all the porphyrin to promote solubility of nanoring [12].

In addition, the Vernier template strategy is used to synthesise cyclic polymers using porphyrin oligomers that consist of 10 building blocks and circular molecular templates with 6 and 8 binding sites to form c-P30 and c-P40, respectively (Figure 6.1.8) [1].

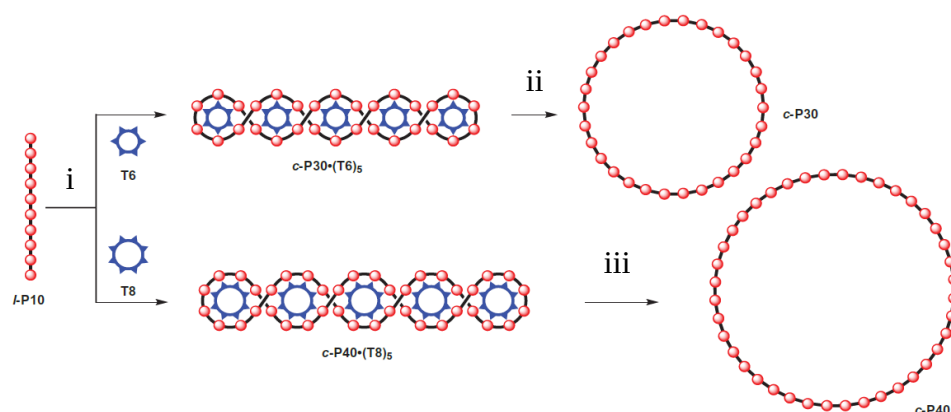


Figure 6.1.8: The Vernier template strategy is used to synthesise cyclic polymers using (i) porphyrin oligomer with 10 building block and circular molecular template with 6 and 8 binding site to form (ii) c-P30 and (iii) c-P40, respectively [1]

A schematic diagram of a cyclic polymer nanoring with 30-Zn porphyrin units bound together by butadiyne bridges is shown in Figure 6.1.9. Octyloxy side chains are attached by aryl groups porphyrin macrocycle in order to promote solubility. The Zn-Zn spacing between neighbouring porphyrin units in the linear polymer is 1.33 nm [15] indicating a diameter of 12.7 nm for a circular conformation, which is the separation of opposite Zn atoms within a circular ring.

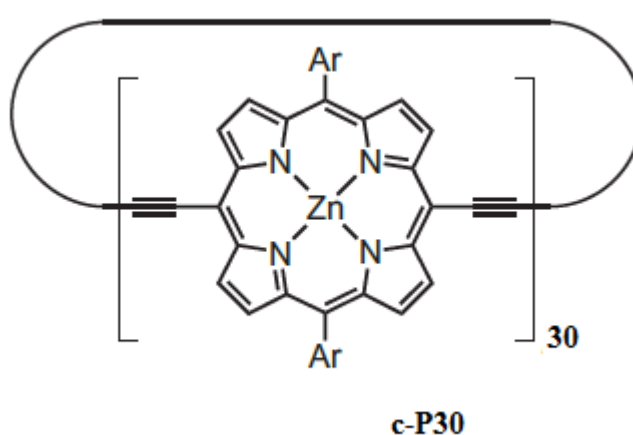


Figure 6.1.9: Chemical structure of a cyclic polymer nanoring with 30-Zn porphyrin units bound together by butadiyne bridge. Octyloxy side chains are attached via aryl groups (Ar) to promote solubility.

6.1.4 Porphyrins and intermolecular interactions (π - π interaction)

The π - π interaction is a non-covalent intermolecular interaction between aromatic rings, which occurs due to London dispersion forces [16]. This interaction plays a crucial role in stacking biological systems and organic molecules such as proteins and porphyrins. In 1990, a simple electrostatic model was suggested by Hunter and Sanders for π - π interactions, which can be described as a positively charged σ -framework around the periphery and also two negatively charged π -electron clouds in both aromatic faces [17] as shown in Figure 6.1.10.

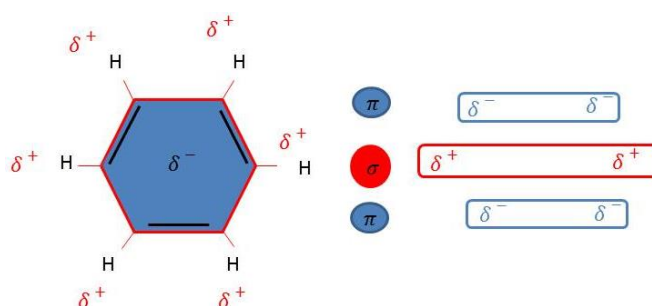


Figure 6.1.10: An sp^2 hybridised atom in aromatic system

There are several different forms of π - π interactions between aromatic rings due to multiple points of intermolecular interaction. These geometries include face-to-face stacked (sandwich), offset stacking (parallel displaced) and edge-to-face (T-shape stacking) as illustrated in Figure 6.1.11. The face-to-face stacked geometry shows an unfavourable electrostatic π - π repulsive interaction, but offset and T-shape stacking give a favourable π - σ attractive interaction [17].

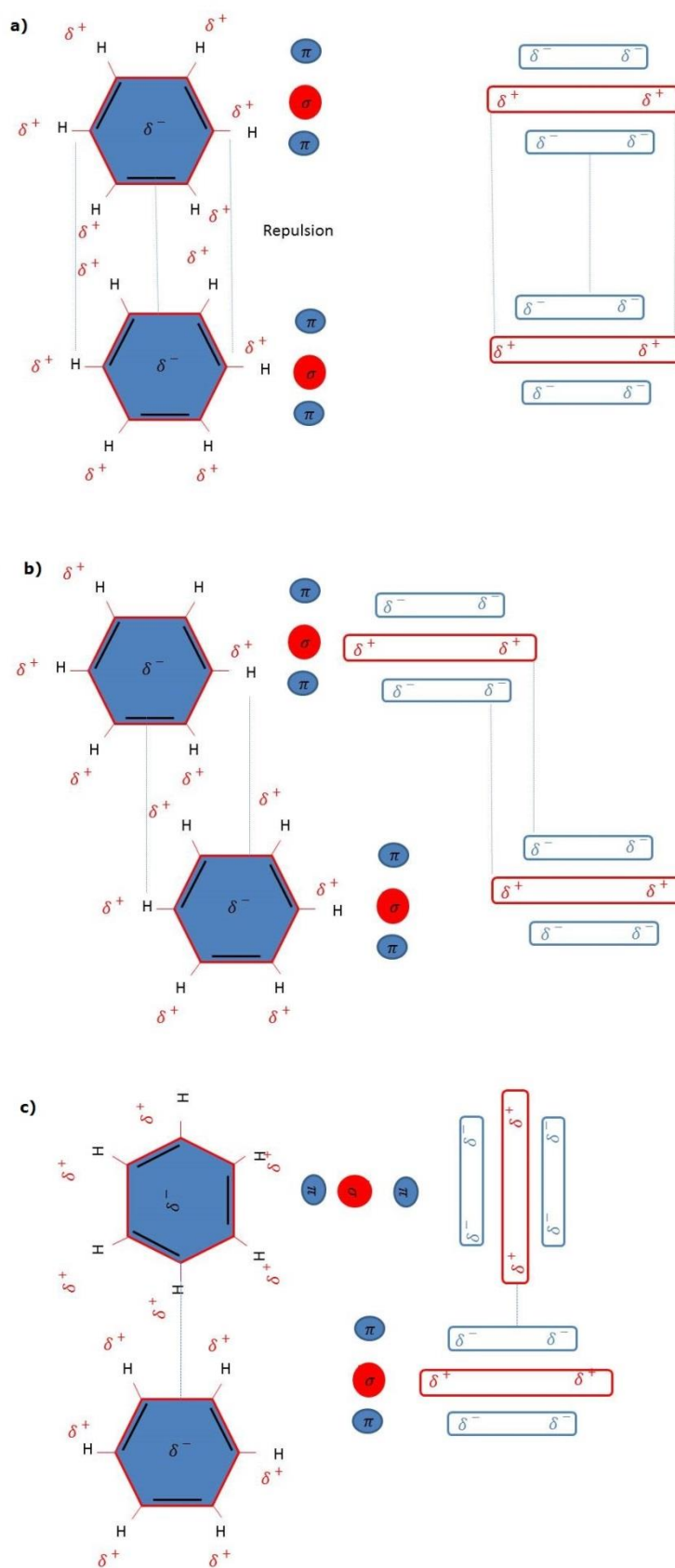


Figure 6.1.11: Forms of π - π interaction between two aromatic rings . a) face to face stacked ; b) offset stacked; c) Edge-face stacked.

Porphyrin π - π interactions were modelled using molecular mechanics calculations, which predicted face-to-face stacking, while Hunter and Sanders experimental studies demonstrated an offset geometry [17]. The latter geometry sets the pyrrole ring of one porphyrin exactly above the π -cavity at the center of the other porphyrin. This arrangement suppresses the π - π repulsion between the π -electrons of the stacked pyrrole ring, while increasing the attraction between a positively charged metallic atom in the central cavity of one porphyrin with the π -electrons of the pyrrole ring at the neighbouring porphyrin see Figure 6.1.12.



Figure 6.1.12: Offset stacking geometry of the cofacial porphyrin dimer

6.2 Single height structure of c-P12 and c-P24 nanorings

In previous studies [12, 13] the 12-porphyrin nanoring (c-P12) [12] and 24-porphyrin nanoring (c-P24) [13] were adsorbed on Au(111) from a mixture toluene-methanol (3:1 by volume with 5% pyridine) using electrospray deposition under vacuum conditions.

Several isolated nearly circular c-P12 molecules were observed by STM (see Figure 6.2.1a, b). They were adsorbed preferentially at surface step edges and had heights of 0.1-0.2 nm indicating monolayer height. The high resolution of STM images makes it possible to count the 12 porphyrin subunits, and the expected Zn $\cdots$ Zn diameter of 4.7 nm was measured for c-P12.

Figure 6.2.1b show the STM image of the c-P24 nanorings that were not only adsorbed preferentially at surface step edges as previously observed for c-P12 but also deviate from circular shape due to the flexibility of this larger cyclic polymer. Therefore, the Zn $\cdots$ Zn diameter deviates from the expected value of

10 nm. The topographic height shows that these nanorings are single layer with the height ~ 0.1 nm. This means they cover the surface as monolayer nanorings with porphyrin units parallel to the surface because the expected height for an edge-on porphyrin unit would be ~ 1 nm.

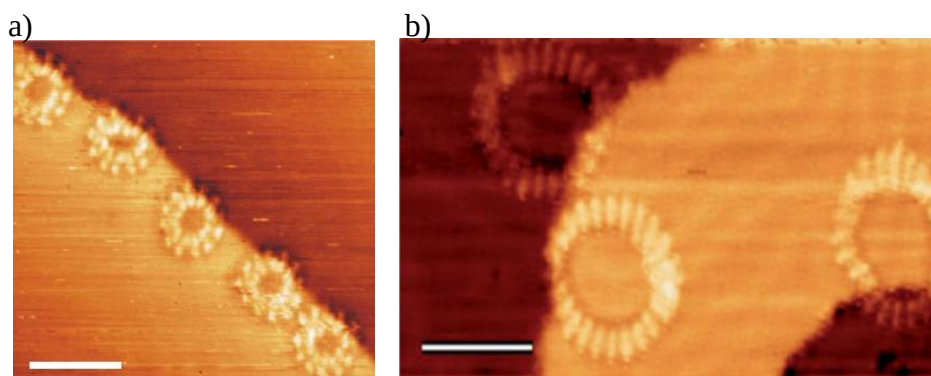


Figure 6.2.1: The STM images of 12-porphyrin nanoring (c-P12) (a) [12] and 24-porphyrin nanoring (c-P24) [13] (b) adsorbed on Au(111) from a mixture toluene-methanol (3:1 by volume, with 5% pyridine) using electrospray deposition. Scale bars 5 nm (a) and 10 nm (b)

6.3 Supramolecular stacking and nesting of nanorings

6.3.1 Stacking structure of c-P24 nanorings

Similar to the previous section [13], the 24-porphyrin nanoring was subsequently adsorbed on Au(111) by Svatek et al. using electrospray deposition. However, the c-P24 was dissolved in mixture toluene-methanol (3:1 by volume), without the addition of pyridine [14]. In this case, the c-P24 nanorings were adsorbed with different heights (see Figure 6.3.1 and 6.3.2) due to the formation of columnar stacks of c-P24. They also found that if pyridine is added to the solution, only single layer nanorings are adsorbed on surface. This implies that the stacking structure is dependent on solvent. This suggests that the stacking occurs in the solvent prior to deposition on surface.

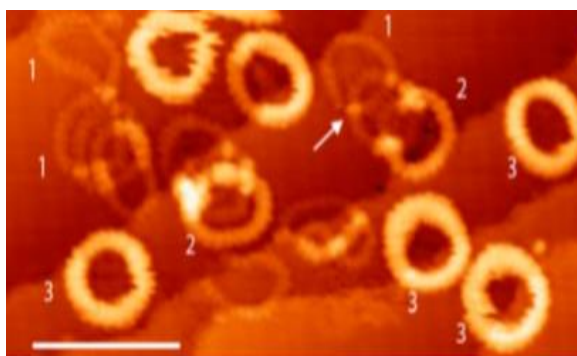


Figure 6.3.1: STM images of 24-porphyrin nanoring (c-P24) [14] adsorbed on Au(111) from toluene-methanol (3:1 by volume), without the addition of pyridine using electrospray deposition. Single ring marked by (1), double stack ring (2), triple stack ring (3). Scale bars 20 nm

Figure (6.3.2 a,b) shows the height profile along c-P24 nanorings identified by a colour labelled trace, which shows heights of 0.1 nm for single rings and 0.7 nm for triple stack.

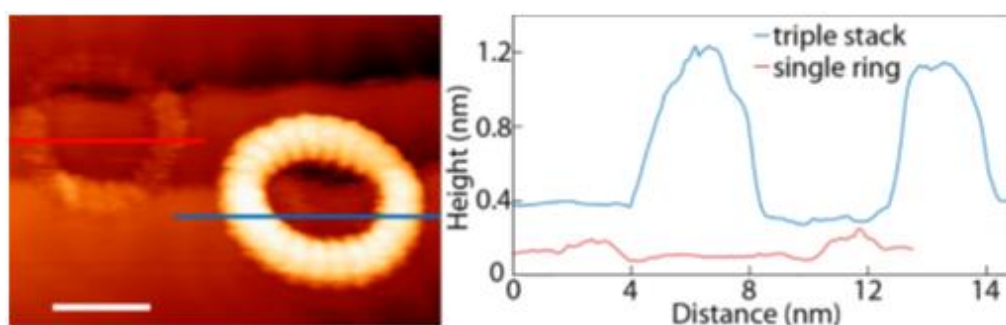


Figure 6.3.2: the height profile along c-P24 nanorings are identified by colour labelled trace, single ring (red) and triple stack (blue) [14].

Figure 6.3.3 show the schematic diagram of single ring, double and triple columnar stacks of nanorings with the layer spacing in the stacks.

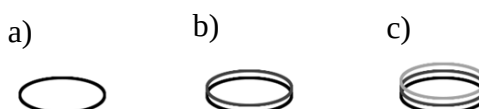


Figure 6.3.3: Schematic diagram of single ring (a), double (b) and triple stacks nanorings (c)

A histogram (Figure 6.3.4) shows heights of c-P24 nanorings [14]. The frequency shows that the most of the nanorings are clustered around a height of 0.1 nm, which corresponds to the single height nanorings following by two and three stacking layers, with heights of 0.4 nm and 0.7 nm, respectively.

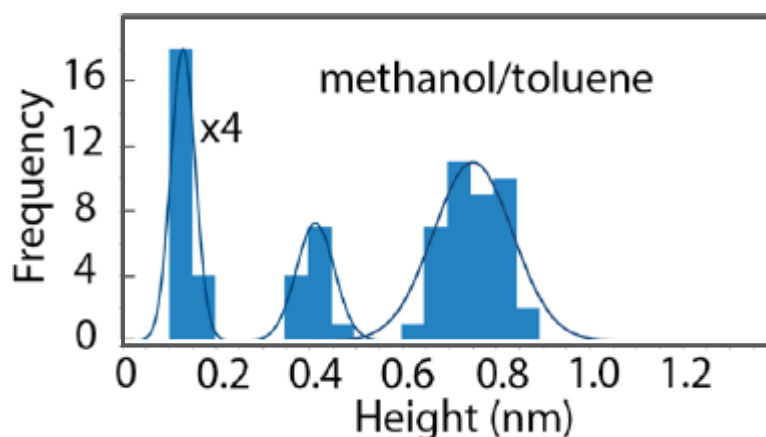


Figure 6.3.4: A height histogram of c-P24 nanorings adsorbed at Au(111) from methanol/toluene [14].

6.3.1.1 Flexibility and bending energy of cyclic polymers

The adsorption of c-P24 nanorings on a surface gives rise to the formation of single height rings with distorted shape and stacked nanorings (nearly circular shape). Equation 6.3.1 is used to determine the deviation, g , of a ring from a circular shape [14],

$$g = \frac{a}{b} - 1 \quad 6.3.1$$

where the long and short axes (Figure 6.3.5) of a nanoring are denoted by a and b , respectively. If the ring is circular, the deviation parameter g is equal to zero. Experimentally the value of g was found to be decrease for stacked nanorings with increasing height implying that the mechanical stiffness (rigidity) of stacked nanorings is increased [14].

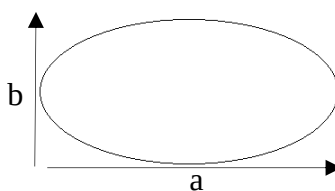


Figure 6.3.5: schematic diagram showing long and short axes of distorted ring

Equation 6.3.2 can be used to determine the deformation energy, E , [18], which is proportional to the bending stiffness, K_B , and a closed path integral of local curvature $C(s)$,

$$E = \frac{K_B}{2} \oint C(s)^2 ds \quad 6.3.2$$

For an elliptical shape the analytical method may be used to determine the relationship between E and g [19]. However, for irregular shapes of nanoring a numerical approach (Monte Carlo simulation) is used to calculate g , which is required to estimate the bending stiffness versus stack height.

From these simulations it is estimated that the bending coefficient is 0.03, 0.07 and 0.10 nNm² for single, double and triple layer nanorings, respectively.

6.4 Investigation of solution deposition of nanorings

The object of this study is to investigate whether nanorings can be deposited directly from solution and whether the apparent solvent effects on supramolecular order can be reproduced. In fact it is found that stacking and a new form of ordering which we refer to as nesting occurs. In these experiments we use a Au(111) substrate prepared as described in chapter 3 (see section 3.1.1).

6.4.1 Supramolecular self-assembly of c-P30 from toluene

Figure 6.4.1a shows STM images of the c-P30 cyclic polymer acquired following adsorption from toluene with high concentration, 133 µg/ml. Nanorings cover the surface and form highly disordered arrangements, with many nanorings partially overlapping and some adopting a structure like a parallel close packed arrangement of linear oligomers (see inset identified by while arrow) [15]. The distance, a , between Zn ... Zn porphyrins centre of linear porphyrin oligomers is 1.33nm. The perimeter $P=2\pi r$ of a cyclic polymer with radius r is equal to number of macrocycle group units N multiply by distance a . This implies that the diameter, $2r$, of c-P30 nanoring by assuming a circular

shape, is 12.7nm, equal to the value we measured 12.7nm. The distance between two porphyrin units on the two sides of the compressed rings is about 2.6 nm, which is consistent with the distance measured between two porphyrin groups of porphyrin oligomer that are arranged in a close packed structure [15]. A histogram (Figure 6.4.2a) shows nanoring heights are clustered around three discrete peaks, 1.4 nm, 1.1 nm and 0.8 nm, which are equivalent to heights of five, four and three stacking layers. This variation in height also accounts for the variation in apparent brightness in the images [14]. The height profiles (Figure 6.4.1f) identified by colour traces and arrows show stacks of five, four and three nanorings. Our results show that adsorption of cyclic c-P30 from toluene with high concentration results in a highly disordered arrangement on the surface.

Figure 6.4.1b shows that the adsorption of nanorings from toluene with lower concentration, 50 $\mu\text{g/ml}$, results in a significantly lower coverage. The cyclic polymer is adsorbed as a stacked nanoring with nearly circular conformation and forms random isolated groups. A histogram (Figure 6.4.2b) shows nanoring heights of four discrete values aggregates near 0.5 nm, 0.8 nm, 1.1 nm and 1.4 nm, which correspond to two, three, four and five stacking layers, respectively. The frequency shows that the most of the stacked nanorings are clustered around a height of 1.1 nm, which corresponds to a height of four stacked layers. In addition, height profiles (Figure 6.4.1g) identified by colour labelled traces and arrows show the different heights of stacked nanorings. Our results imply that deposition of c-P30 nanorings from diluted solution in toluene with 50 $\mu\text{g/ml}$ can result in less stacking, possibly due to dissociation of stacked nanorings in solution.

A new type of supramolecular order, nested self-trapping supramolecular structure is observed for c-P30 nanorings (see Figure 6.4.1c) deposited from a solution with lower concentration, 12.5 $\mu\text{g/ml}$. In this arrangement a tightly packed nanoring in a hairpin structure is trapped within a near circular nanoring. There are many single height nested nanorings on the surface in a disordered arrangement. Note also that a histogram (Figure 6.4.2c) shows that the nanoring heights have only one peak close to 0.18 nm, which is ascribed to monolayer height nanorings; for this sample there is no stacking. The height profile (Figure 6.4.1h) across nanoring is identified by a black marked trace.

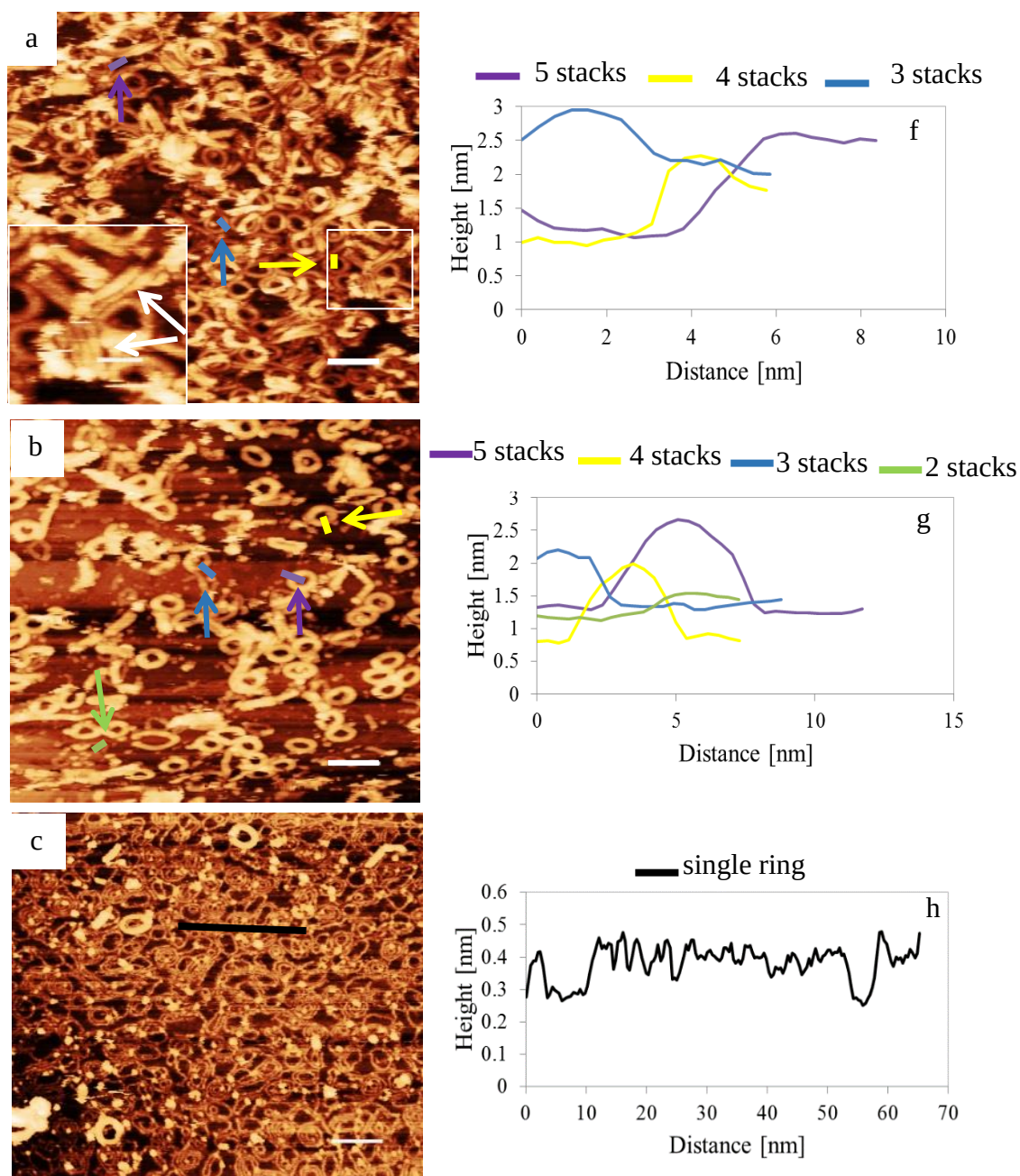


Figure 6.4.1: (Left) STM images of c-P30 deposited from toluene on a gold substrate Au(111) with concentrations (a) - 133 µg/ml inset: zoom of marked area to show compress stacking ring, (b) - 50 µg/ml, (c) - 12.5 µg/ml. The scale bars are 25 nm. The scanning parameters tunneling current and tip bias are 30 pA and 1V, respectively. (Right) height profile of the colour labelled trace along c-P30 nanorings shows different heights as a result of stacking nanorings, and single height ring. Profiles (f) show heights of 1.4 nm, 1.1nm, 0.77 nm corresponding to quintuple, quadruple, triple and double stacking nanorings, while profiles (g) show heights of 1.4 nm, 1.1nm, 0.77 nm and 0.47 nm corresponding to quintuple, quadruple, triple and double nanorings stack and profile (h) shows height 0.15 nm corresponding to single rings.

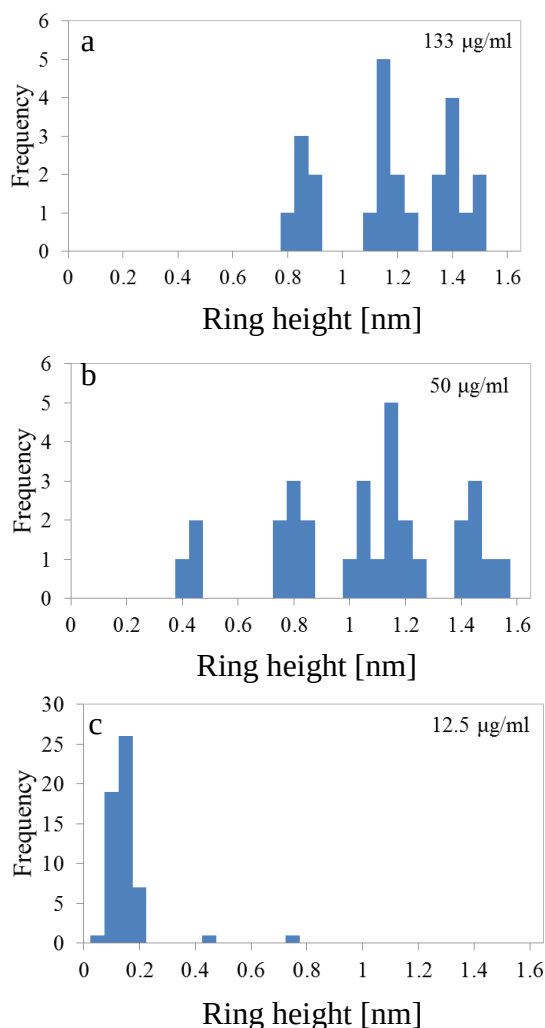


Figure 6.4.2: Histograms of heights, (a) showing quintuple, quadruple and triple stacked nanorings if nanorings are deposited from concentration 133 µg/ml, while (b) showing quintuple, quadruple, triple and double stacked nanorings if nanorings are deposited from concentration 50 µg/ml, (c) showing single rings if nanorings are deposited from 12.5 µg/ml.

Figure 6.4.3a presents a clear zoom of c-P30 single height nested structure (marked A and B). The bright features show partially overlapping of a single nanoring. Also some nanorings break into linear polymer chains. Figure 6.4.3b presents a high resolution image of a c-P30 single height nested structure (marked A). In this image it is possible to resolve and count 30 porphyrin units around the perimeter of the inner and outer c-P30 nested structure. The distance between two opposite porphyrin units in the inner and outer nanoring of the nested structured is about 2.7 nm, consistent with the distance measured between porphyrin groups in neighboring close packed linear oligomers [15].

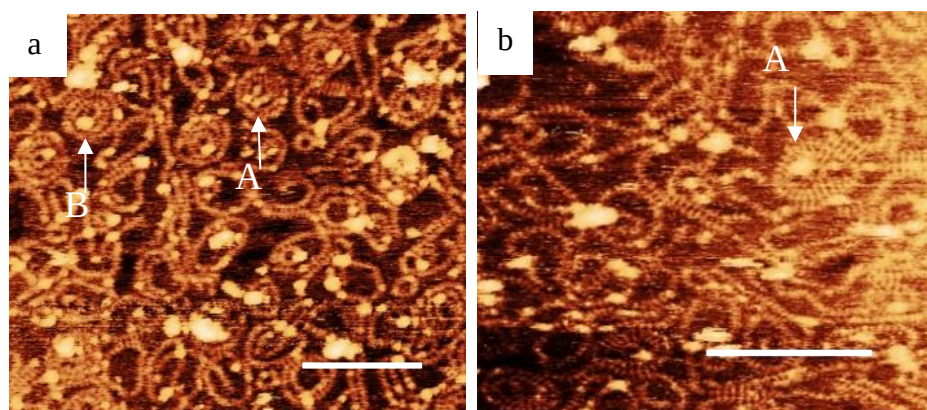


Figure 6.4.3: (a) Zoom image of c-P30 nested single height structure. (b) The high resolution image of c-P30 nested single height structure. The scale bars are 25 nm.

Our results show single height nesting supramolecular structure on the surface if the c-P30 cyclic polymers are deposited from solution with low concentration. We argue that nested self-trapped nanostructures arise following deposition on the surface due to the flexibility of nanoring which can result in a highly deformed non-circular shape. Initially, the stacked nanorings are pre-formed in solution prior to deposition and then rearrange following adsorption on the surface.

A schematic diagram of porphyrin positions in a nested nanoring structure is shown in (Figure 6.4.4) in order to evaluate the elastic bending energy, E_B , that is present in the nested conformation, which consists of 30 segments i with bending angle, α_i , between two sequence segments i th and $(i+1)$ th. Therefore, the bending energy can be expressed as follows [1].

$$E_B = \frac{K_B}{2a} \sum_i^N \alpha_i^2 \quad 6.4.1$$

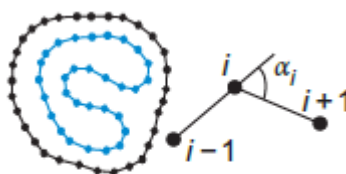


Figure 6.4.4: schematic diagram of porphyrin positions in nested nanoring structure

Unfortunately, there are always bright features within the nested single-height nanoring (see Figure 6.4.3a marked B), which are attributed to the porphyrin

groups that may be nonparallel to the substrate or inner nanoring is self-overlapping at this region, which makes the resolution of some porphyrin problematic. Therefore it is difficult to calculate the elastic bending energy here, but it was calculated for the nested double-height nanoring that was adsorbed using electrospray deposition and estimated to be $E_B \sim 2.6$ eV [1].

We have seen nested structures with monolayer inner and outer nanorings (as discussed above), but there is no observation of tightly packed stacked ring inside another stacking nanoring or stacking inside single height ring which was as reported for c-P30 deposited by electrospray [1].

In other work, it has been shown that cyclic porphyrin polymers adsorb on Au(111) with a distorted non-circular shape because the nanorings show flexibility [14], and also the nano-ring can represent a trap container to confine other species such as sublimed C_{60} [20]. For self-trapping where one nanoring is placed inside another nanoring, the maximum area enclosed by outer nanoring $\pi (Na/2\pi - d/2)^2$ must be greater than the chain length area of the inner nanoring (Nad see Equation 6.4.2), where d is the chain width 2.1 nm, which is equivalent to the separation measured between porphyrin units in two close packed porphyrin oligomer [15]. Therefore the following equation must be satisfied for one nanoring to be tightly coiled inside a near circular nanoring,

$$\pi (Na/2\pi - d/2)^2 > (Nad) \quad 6.4.2$$

This indicates that the cyclic polymer should consist of 29 or more porphyrin groups $N \geq 29$, for clarification see Table 6.4.1. As a result, nesting structures were not seen for c-P12 and c-P24 nanorings.

Table 6.4.1: Estimation for minimum size of nanoring could be possible to self-trap within another nanoring when number of porphyrin units is equal or more than 29

N	Nad	$\pi(Na/2\pi - d/2)^2$	supramolecular nesting
12	33.5	6.9	no
24	67.0	51.0	no
30	83.8	88.3	yes

6.4.2 Supramolecular self-assembly of c-P30 from toluene:methanol

Figure 6.4.5a shows STM images of c-P30 nanorings adsorbed on Au(111) from a toluene:methanol (3:5) mixture by volume and concentration 50 $\mu\text{g/ml}$ using the immersion method (see section 3.1.2). The nanorings cover the surface mainly in a densely packed stacking configuration and also many of them are observed overlapping, identified by bright features for overlap sites, which have double height compared with non-overlapping rings [14]. There are areas where nanorings are arranged in partially ordered arrangements, a quasi-hexagonal close packing conformation on surface. The stacked nanorings are distorted from a circular shape, due to their flexibility and possibly, their interactions with neighbour. Thus the nanorings show different dimensions for long and short axes with averages 12.8 nm, 9.6 nm respectively. A histogram (Figure 6.4.6a) shows that the heights of nanorings are assembled in three discrete values, which show peaks around 1.1 nm, 0.77 nm and 0.5 nm equivalent to the height of four, three and two stacking layers. Height profiles (Figure 6.4.5d) across stacked nanorings of different contrast are identified by colour marked trace, which confirms that the nanorings adsorbed from this concentration form different stacking layers. Our results show that the self-assembly of nanorings from a concentrated solution in toluene:methanol 3:5 cover the surface in a disordered stacked arrangement while a few areas adopt quasi-hexagonal close packing.

In Figure 6.4.5b we show STM image of c-P30 nanorings acquired following deposition from a mixture toluene:methanol with the same volume ratio 3:5, while the c-P30 solution concentration is reduced to 25 $\mu\text{g/ml}$. The nanorings self-assemble on the surface in columnar stacks, and nearly circular shape. The average diameter for long and short axes are close and equal to 12.8 nm and 11.4 nm, respectively. The uniformity of contrast implies that the stacking nanorings have a similar height. The stacking nanorings form an ordered arrangement of hexagonal close packed structures. The distance between macrocyclic porphyrins in neighboring stacked nanorings in a close packed structure is 2.7 nm, consistent with the distance measured between porphyrin groups of neighboring close pack in linear oligomers structure [15]. A histogram (Figure 6.4.6b) shows the heights of nanorings with a peak 0.5 nm. This value corresponds to the height of double stacked layers. The height profile (Figure

6.4.5e) through porphyrin nanorings is identified by a green marked trace, which shows that the height of the nanorings is roughly constant. Our results imply that the self-assembly of uniform stacking layers of nanoring can be controlled using diluted solution in 3:5 toluene:methanol, which also can result in arrangement nanorings in highly ordered configuration of hexagonal close packed structures.

Figure 6.4.5c shows the self-assembly of nanorings from a solution with concentration 12.5 $\mu\text{g/ml}$. In this case we observe, similar to the deposition from pure toluene; there are nested structures where a tightly packed single height nanoring is enclosed by a near circular single height ring (see nanoring in zoom image 6.4.5g, labelled A). However, there are also example of stacked nanorings forming nested structures. For example a tightly packed single height nanoring is enclosed by a near circular stacked nanoring of double layers (see ring in zoom image 6.4.5g, labelled B), but there is no observation of a tightly packed stacked ring inside another stacking nanoring or stacking inside single height ring as formed by electrospray deposition [1]. The height profile (Figure 6.4.6h) identified by the black and green marked traces across stacked and nested structures in Figure 6.4.5g shows the height of both single and double layers, which have height difference close to the value expected for space between two stacking layers 0.34 nm [14]. Also here we observe that the surface is about half covered by single height rings and half stacked rings. A histogram (Figure 6.4.6c) shows that the nanoring heights are clustered around peaks of 0.48 nm and 0.17nm, equivalent to heights of double and single nanorings, respectively. The height profile (Figure 6.4.5f) of the green labelled trace along nanorings confirms that the double stacked nanorings have heights about 0.48nm, while the single nanorings with black marked trace has height nearby 0.17nm.

The shape of nested nanorings is resolved (Figure 6.4.5g). for a single in single nested nanoring (A) and single in double nested nanoring (B), where the inner nanoring is folded into three hairpin structures with the angle of curvature about 180° , in which a nanoring adopts (C) conformation.

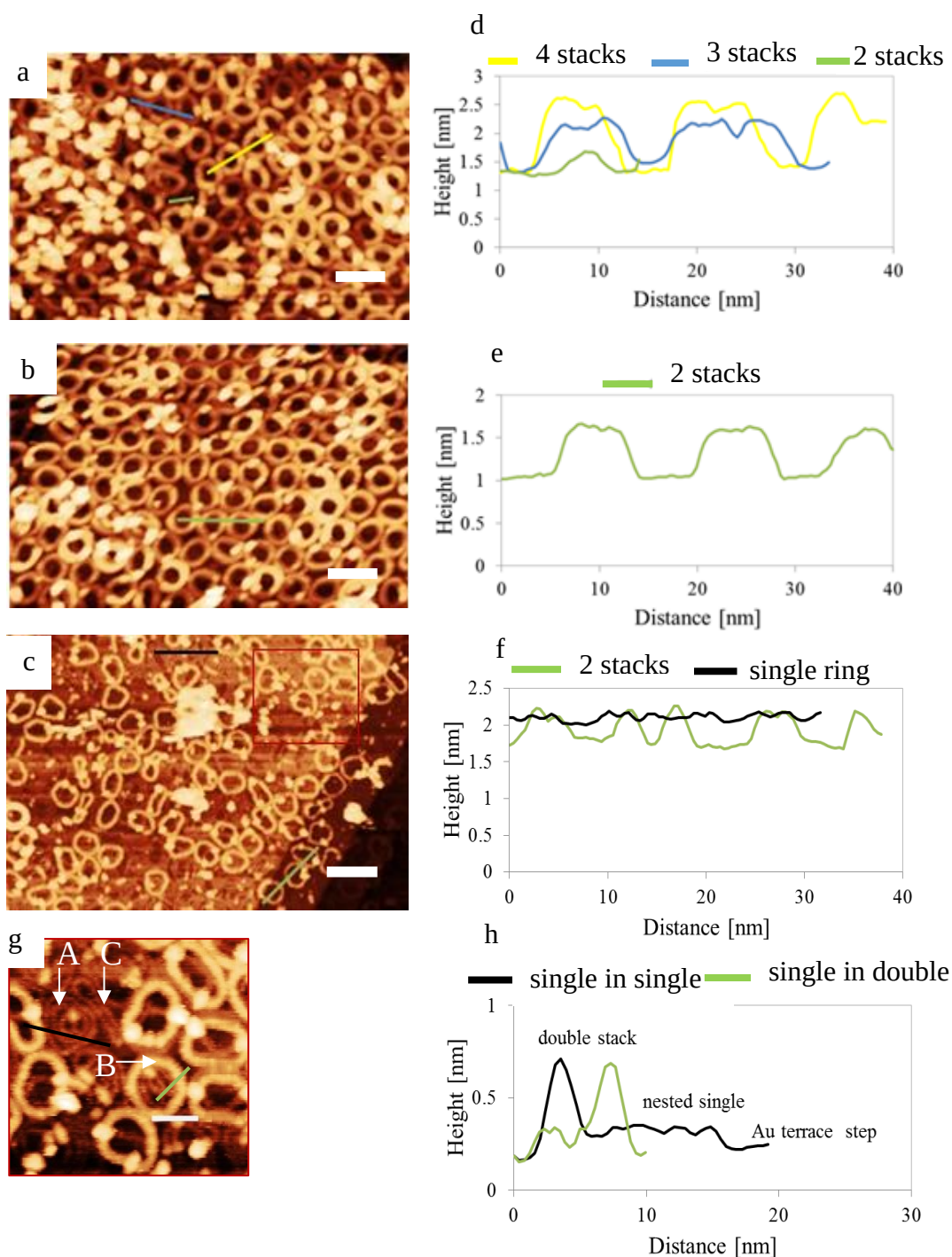


Figure 6.4.5: (Left) STM images of c-P30 deposited from a toluene – methanol mixture 3:5 by volume on a gold substrate with concentrations (a) - 50 $\mu\text{g/ml}$, (b) - 25 $\mu\text{g/ml}$, (c) - 12.5 $\mu\text{g/ml}$. The scale bars are 25 nm. The scanning parameters tunneling current and tip bias are 30 pA and 1V, respectively (Right). Height profile of the colour marked trace along c-P30 nanorings shows the different heights as a result of stacked nanorings, profile (d) show heights of 1.1nm, 0.77 nm and 0.47 nm corresponding to quadruple, triple and double nanorings stack, while profile (e), (f) show height 0.5 corresponding to double nanoring stack. g, Zoom image of highlighted region red colour in c showing single in single and single in double nested structure. (h) the black and green height profiles show the height of stacked and nested structures in (g).

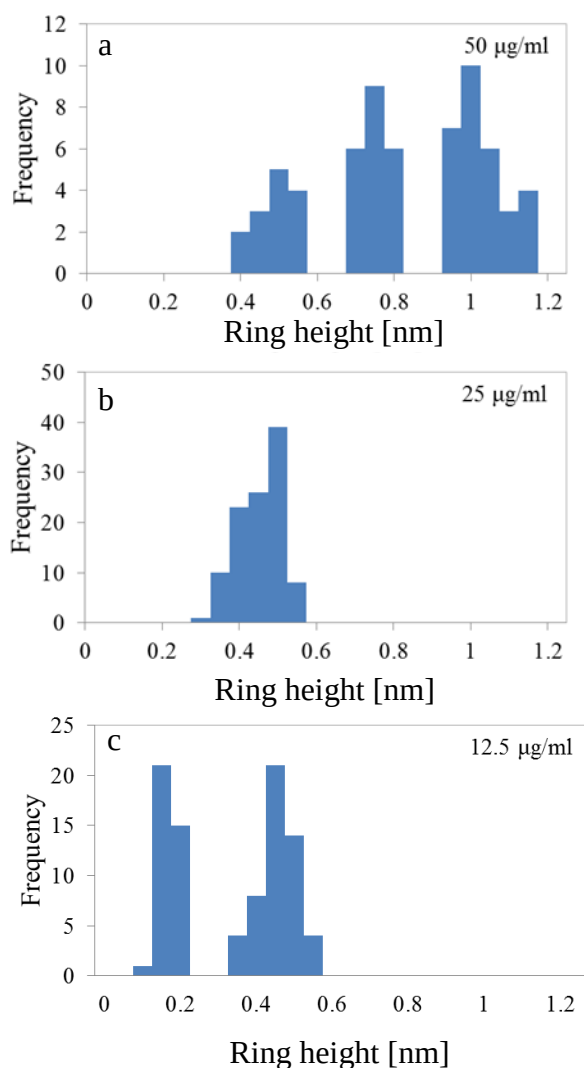


Figure 6.4.6: Histograms of heights, (a) showing quadruple, triple, double stacked nanorings if nanorings are deposited from concentration 50 µg/ml, while (b), (c) showing double nanorings stacked if nanorings are deposited from 25 µg/ml and 12.5 µg/ml.

Figure 6.4.7a, b, c shows STM images of c-P30 nanorings adsorbed from a diluted solution, where the toluene volume are relatively higher than methanol (a fixed to 1 part) as follow: 159:1, 79:1, 50:1 with the concentration 2.5, 5, 7.75 µg/ml, respectively. The nanorings covered the surface mainly as single height nanoring or/and single nested nanoring with less stacked nanorings, but single nested nanorings suppressed to adsorb in the case of very high toluene volume Figure 6.4.7a.

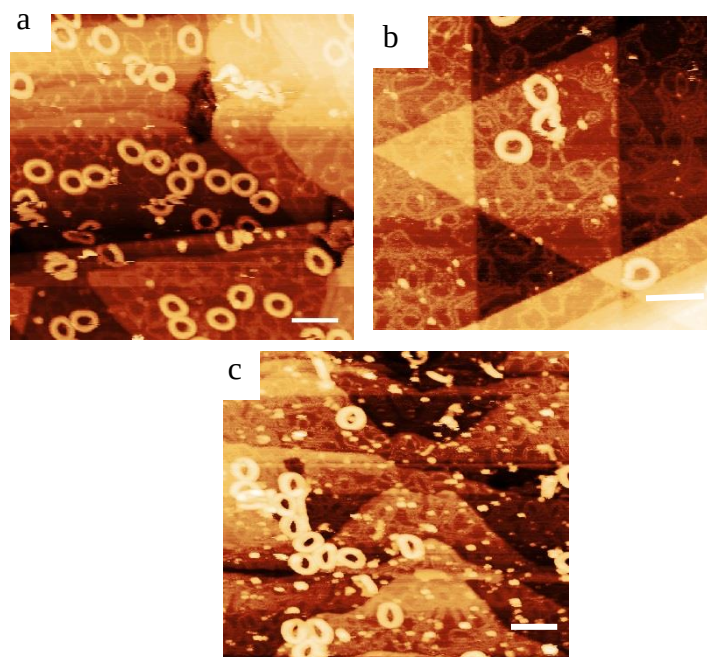


Figure 6.4.7: STM images of c-P30 nanoring deposited from mixture toluene-methanol with volume ratio (a) - 159:1, (b) - 79:1, (c) -50:1. The scale bars are 25 nm

Figure 6.4.8a, b shows STM images of c-P30 nanorings adsorbed from a diluted solution by keeping the toluene volume fixed to 9 part while adding methanol as follow: 9:5, 9:10 with concentration 63, 50 $\mu\text{g/ml}$, respectively. The nanorings cover the surface in stacked configurations. we also observed that when the methanol volume became larger than toluene by a factor of 4, the nanorings are not adsorbed. We have attributed this to the removal of nanorings from the solution.

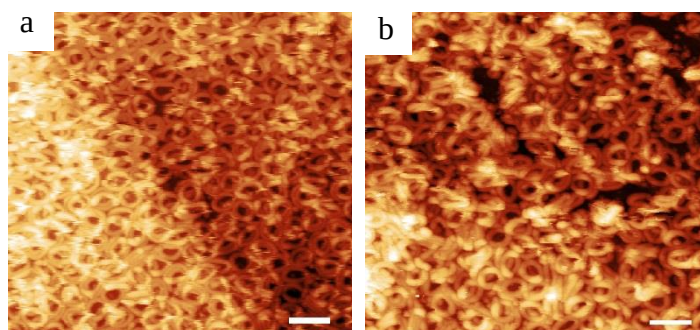


Figure 6.4.8: STM images of c-P30 nanoring deposited from mixture toluene-methanol with volume ratio (a) – 9:5, (b) – 9:10. The scale bars are 25 nm

Figure 6.4.9 shows an AFM image for c-P30 nanorings following deposition on Au(111) from toluene-methanol 3:5 with concentration 50 $\mu\text{g/mL}$. This image clearly exhibits Au(111) terrace steps with image size 1 $\mu\text{m} \times 1 \mu\text{m}$, where stacked nanorings cover the surface. The average Zn-Zn diameter of the nanorings is about 12 nm, which is similar to that measured in STM images of c-P30. Notice that this sample is the same that we have imaged by STM in Figure 6.4.5b.

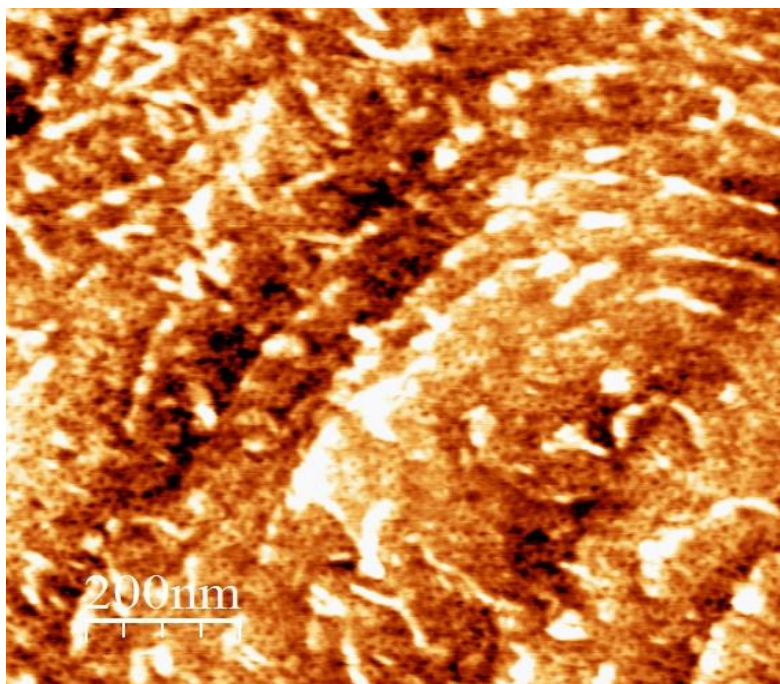


Figure 6.4.9: AFM topography for c-P30 nanorings on Au(111) deposited from toluene - methanol 3:5 with a concentration of 50 $\mu\text{g/ml}$

We observed a significant difference between stacking of nanorings adsorbed from various solvents. For deposition from toluene, we show that highly disordered stacked and overlapping noncircular nanorings are present on the surface. In contrast, the stacked nanorings from toluene:methanol show a much more ordered arrangement. These results imply that the choice of solvent can be used to control the arrangement of nanorings.

We have observed that the shapes of supramolecular adsorption on surface are dependent on concentration. For high concentration, the adsorption from toluene/methanol or pure toluene, leads to supramolecular stacking of nanorings on surface with up to six layers, much higher than previously observed. In

contrast, self-assembly from low concentration 12.5 $\mu\text{g/mL}$ in toluene:methanol, shows supramolecular nesting of nanoring, which has two conformations, single in single nesting nanostructures consisting of single folded nanoring inside a nearly circular single height nanoring, and single in double nesting nanostructure consist of single folded ring inside a nearly circular double height stacking rings. Also, the adsorption of nanorings from only toluene with low concentration shows supramolecular nesting of nanorings, but in this case the supramolecular structure has only single in single nesting structures and very few stacking nanorings. Our results imply that the supramolecular shape and height are dependent on concentrations.

In Figure 6.4.10 the peak heights in the histograms show a linear increase with peak number, and its gradient is equivalent to the layer spacing between stacking nanorings about (0.31 ± 0.012) nm, the spacing of parallel porphyrin units stabilised by π - π interaction [14].

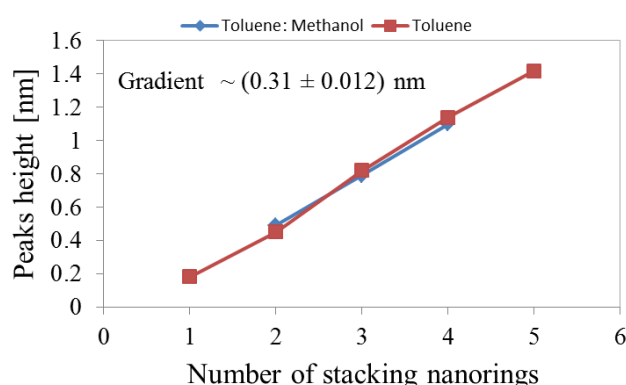


Figure 6.4.10: Peaks height in the histograms versus number of stacking

The surface density of single, stacked, single in single nested and single in double nested cyclic polymer c-P30 conformations are summarised in Table 6.4.2, demonstrating that the stacked nanorings are most, at high concentration, while supramolecular nested geometry dominates the surface at low concentrations.

Table 6.4.2: Surface density of single, stacked and nested nanorings conformations from solution deposition under ambient conditions

Concentrations	surface density of c-P30 (ring/ μm^2) from toluene:methanol 3:5				Surface density of c-P30 (ring/ μm^2) from Toluene		
	single		single		single		
	in		in		in		
	single		double		single		
	single	stacking	nested	nested	single	stacking	nested
133 $\mu\text{g/ml}$					0	5000	0
50 $\mu\text{g/ml}$	0	5400	0	0	0	2600	0
25 $\mu\text{g/ml}$	0	5600	0	0			
12.5 $\mu\text{g/ml}$	2800	2700	700	600	4100	0	800

6.5 Summary

We have shown that artificial covalently bonded cyclic macromolecules can be deposited from solution, resulting in supramolecular nanostructures on a surface, such as stacked columnar rings, single in single ring nested structure and single in double rings nested structure, and also stacked nanorings arranged in a uniform height hexagonal close packed structure. Stacking nanorings can result in a reduction of the effect of the flexibility of the cyclic polymer, and result in a nearly circular shape for supramolecular nanostructures on a surface. In addition we have shown that the height of supramolecular stacks can be controlled by solution concentration. Stacked nanostructures arise in solution prior to adsorption on the surface using solution phase deposition. The c-P30 cyclic polymer deposited from toluene results in monolayer nested structures for low concentration and disordered stacking columnar for high concentration. The cyclic polymer studied here is important due to its extended π -conjugation and large size, and holds promise for electronic nanodevices. This study shows that the cyclic polymers tend to self-organize in three dimensions using non-covalent interaction when deposited from solution.

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Chapter 7

Conclusion

This chapter provides a summary of the whole thesis by reviewing the main results that have been found.

In this thesis, we investigated the growth of metal-free naphthalocyanine (Nc) and copper naphthalocyanine (CuNc) thin films on both bare Si/SiO₂ and octadecyltrichlorosilane (OTS) modified Si/SiO₂ surface, and their morphology was characterised using atomic force microscopy (AFM). We observed that the increase of substrate temperature during growth affects the morphology, preferential molecular orientation and degree of crystallinity of molecular thin films. This was investigated using X-ray diffraction (XRD). The organic field effect transistors (OFETs) were fabricated, and their electrical characteristics were measured under both vacuum and atmospheric conditions and exhibit p-type field effect operation. In addition, we studied the self-assembly of the cyclic porphyrin polymer c-P30 on Au(111) from solution under ambient conditions. Scanning tunneling microscopy (STM) and AFM are used to image the adsorbed polymers on the substrate

In chapter 4, the effects of growth conditions, in particular substrate temperature, on film morphology, the crystallinity and the preferential molecular orientation have been investigated. Increasing the substrate temperature during thin film growth on Si/SiO₂ leads to a more crystalline structure, and changes in molecular orientation and thin film morphology. For example, the naphthalocyanine molecules grow in an amorphous arrangement (grain structure) at low surface temperature $T_s < 120$ °C. However, at higher surface temperature the molecules stood edge-on direction with stacking axes parallel to the substrate and form a crystalline configuration (needle-like structure).

In chapter 5, we first reported on the fabrication of Nc and CuNc OFETs. Their electrical characteristics were measured in vacuum and air. We found that the device parameters were affected by preparation conditions such as substrate temperature, OTS-modification of the substrate, exposure to ambient conditions

and post annealing. Firstly, the OFETs charge carrier transport is enhanced by increasing substrate temperatures until reaches peak then decreases by further increasing the substrate temperature. We found that the optimum substrate temperature during growth is achieved at 200 °C, for which Nc thin film on SiO₂ and OTS shows the best electrical properties. The electrical properties improve because the direction of current flow is in direction of the π -stacking of molecules, which stood edge-on direction as described in chapter 4. The optimized growth temperature for CuNc thin films on SiO₂ and OTS-terminated substrates was determined to be 180 °C and 160 °C, respectively. In addition, the chemical modification of SiO₂ with a self-assembled monolayer of OTS leads to change of surface morphology and reduction of surface traps. This gives rise to improve a field-effect mobility and reduced hysteresis. Furthermore, the exposure to atmosphere of Nc and CuNc OFET devices leads to changes in carrier transport, hysteresis and threshold voltage stability due to the introduction of excess holes and filling of hole traps. We have found that the density of charge carrier trap is $\sim 3.7 \times 10^{12} \text{ cm}^{-2}$ and $1.8 \times 10^{12} \text{ cm}^{-2}$ for top-contact and bottom-contact OFET devices, respectively. Moreover, the top-contact devices are annealed at 100 °C-120 °C for 3 hours in vacuum that lead to reduced hysteresis, threshold voltage and improved performance of devices as compared for the same device as prepared in air. This is possibly due either to degassing of oxygen from semiconductor layer that lead to decrease hole concentration in semiconductor, or reduction in the contact resistance after annealing. Finally, the mobility of the top-contact OFET devices are always higher than that of bottom-contact OFET devices. This is possibly due to adsorption of molecules in a different film morphology at the interface between metal and SiO₂ surface for top and bottom-contact configurations see Figure 5.3.2.

In chapter 6, we have investigated the self-assembly of c-P30 the cyclic polymer (nanoring) with 30 porphyrin units on Au(111) from solution by immersion in different solvents at various concentrations. We observed that the cyclic polymer is adsorbed in different supramolecular configurations such as stacked columns, uniform height hexagonal close packed structure of stacked columnar, single in single ring nested structures and single in double rings nested structure. Stacking

nanorings lead to reduced flexibility of cyclic polymer and a nearly circular shape on a surface. We argue that the stacked nanostructure arises in solution prior to adsorption on the surface. We argue that the nested self-trapped nanostructure arise following deposition on the surface due to the flexibility of nanoring which can result in a highly deformed non-circular shape. We observe that the height of supramolecular stacked columnar and their arrangement can be controlled by solvent and solution concentration. The c-P30 cyclic polymers deposited from mixture toluene:methanol or only toluene result in monolayer nested structure for low concentration and disordered stacking columnar for high concentration. This study shows that the cyclic polymers tend to self-organize in three dimensions using non-covalent interaction when deposited from solution. The cyclic polymer studied here is important due to its extended π conjugation and large size, and holds promise for electronic nanodevices.

There are several plan for future work based on this thesis as follows: Firstly we are planning further studies on the growth of organic heterostructures at Si/SiO₂ substrate by depositing C₆₀ on naphthalocyanine thin films grown at high substrate temperature. This may give an OFET that can be operated both as a p-channel and n-channel device. In addition, further study can be suggested to investigate the growth of naphthalocyanine on boron nitride surface and formation of monolayer supramolecular structures of naphthalocyanine. Finally, further studies on the adsorption of nanorings from a mixture of solutions of c-P24 and c-P30 to investigate the self-trapping of small nanorings in larger ones.

Appendix A

A.1 Copper naphthalocyanine organic field effect transistor with bottom-contacts

A.1.1 Effect of atmospheric exposure on OFET characteristics for thin films on SiO₂ at T_s = 160 °C

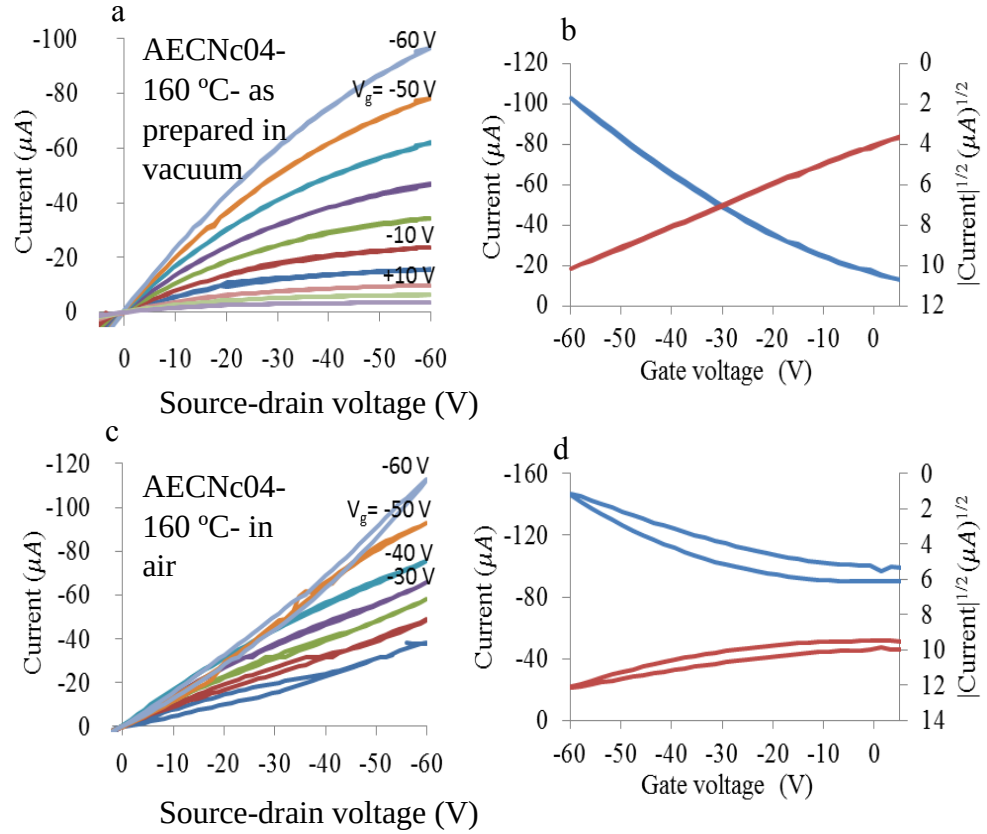


Figure A.1.1: Output characteristics (a, c) corresponding to transfer characteristics (b, d) of CuNc OFETs on bare Si/SiO₂ named AECNc04 that prepared at 160 °C and measured in vacuum and in air.

Appendix A

A.1.2 Effect of atmospheric exposure on OFET characteristics for thin films on SiO₂ at T_s = 340 °C

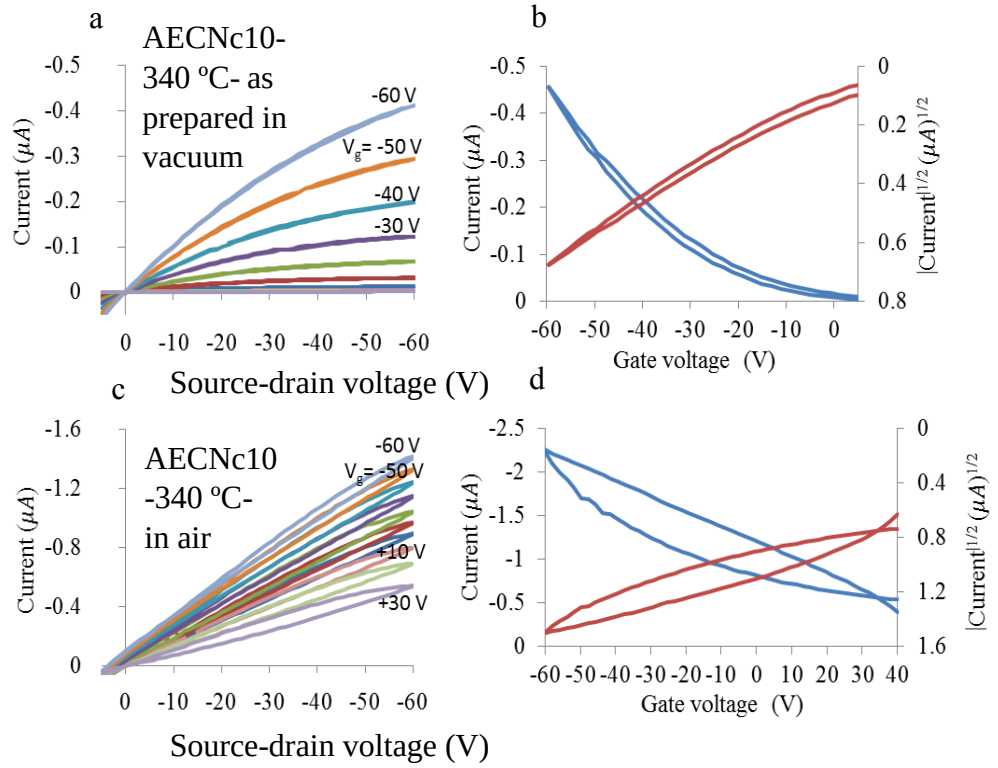


Figure A.1.2: Output characteristics (a, c) corresponding to transfer characteristics (b, d) of CuNc OFETs on bare Si/SiO₂ named AECNc10 that prepared at 340 °C and measured in vacuum and in air.

A.1.3 Effect of substrate temperature on OFET characteristics in vacuum for thin films on OTS treated oxide

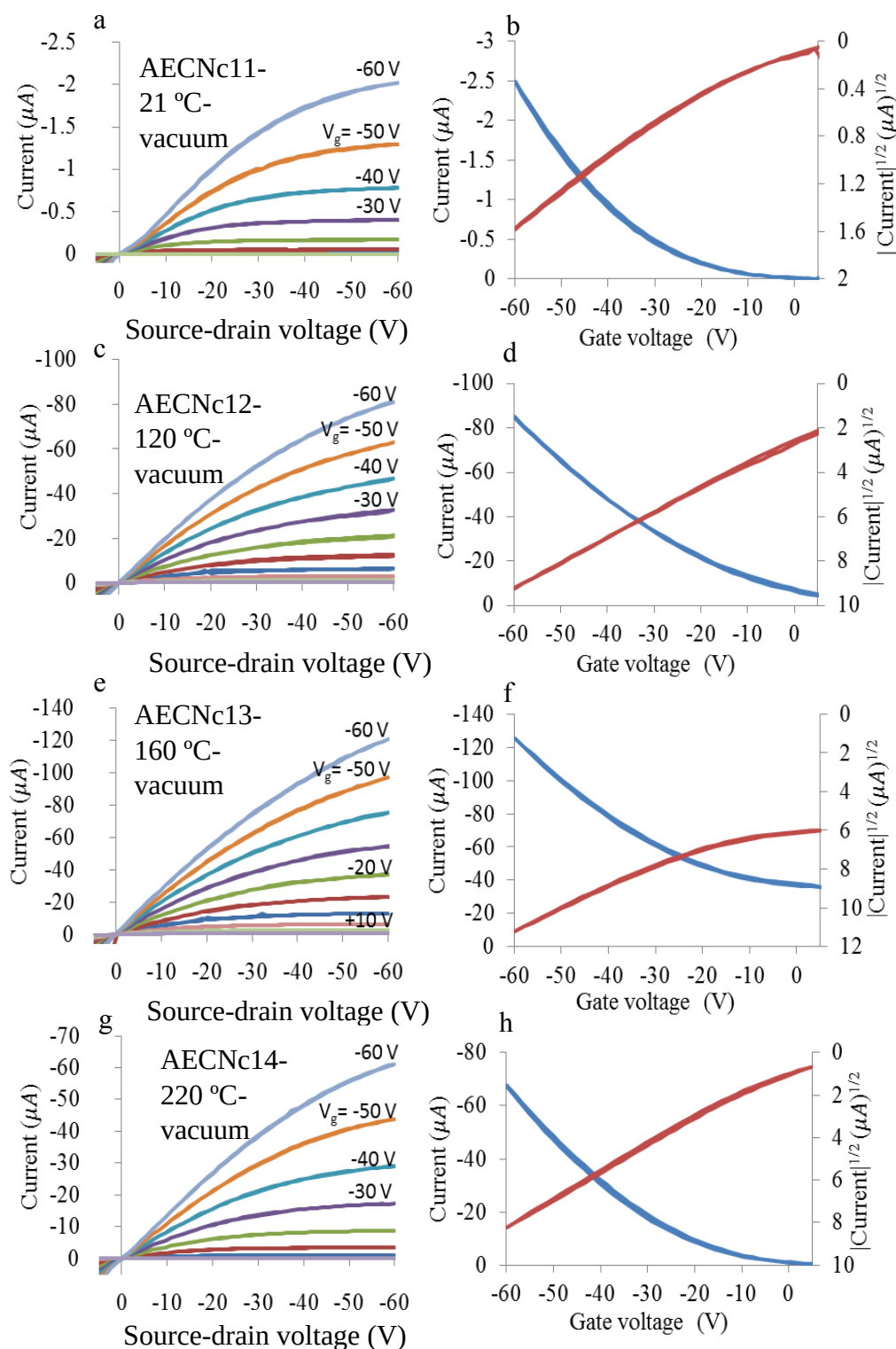


Figure A.1.3: Output characteristics (a, c, e and g Left column) corresponding to transfer characteristics (b, d, f and h right column) of CuNc OFETs on OTS-modified oxide named AECNc11, 12, 13, 14 and prepared at different substrate temperatures (21 °C, 120 °C, 160 °C, and 220 °C, respectively) that measured in vacuum and dark.

Appendix A

A.1.4 Effect of atmospheric exposure on OFET characteristics for thin films on OTS treated oxide

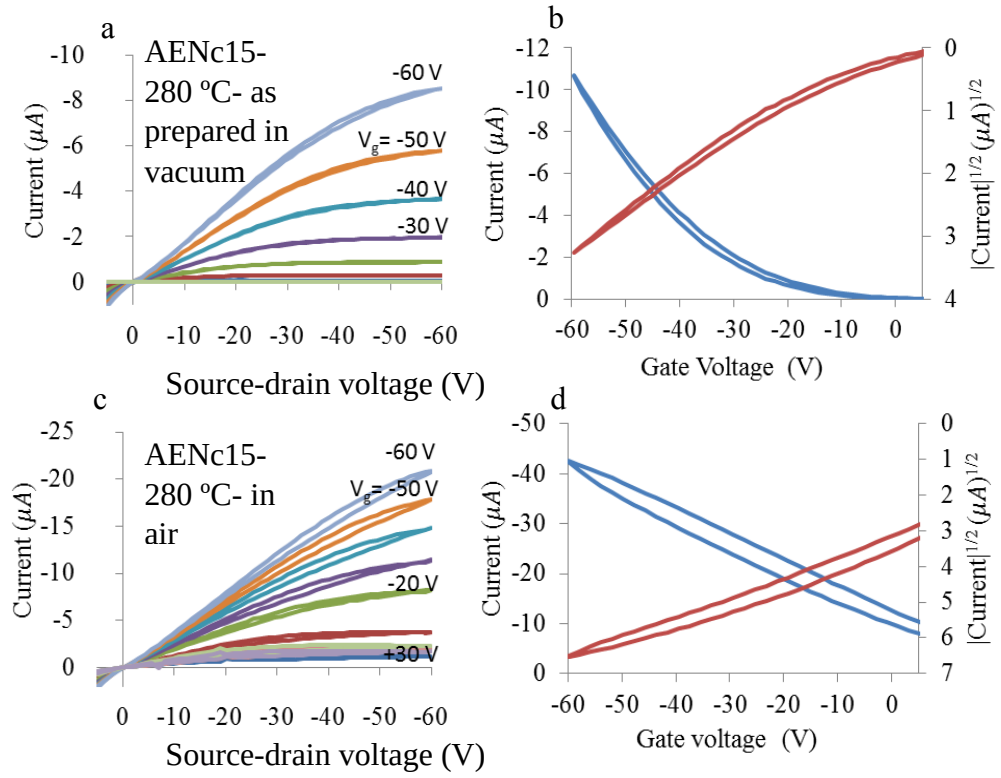


Figure A.1.4: Output characteristics (a and d) corresponding to transfer characteristics (b and d) of an CuNc OFET on OTS named AECNc15 that prepared at 280 °C and measured in vacuum, and in air.

Appendix A

A.2 Copper naphthalocyanine organic field effect transistor with top-contacts

A.2.1 Effect of annealing sample and atmospheric exposure on OFET characteristics

Note that for the following measurements: symbols AA refers to after annealed sample, and BA refers to before annealing sample.

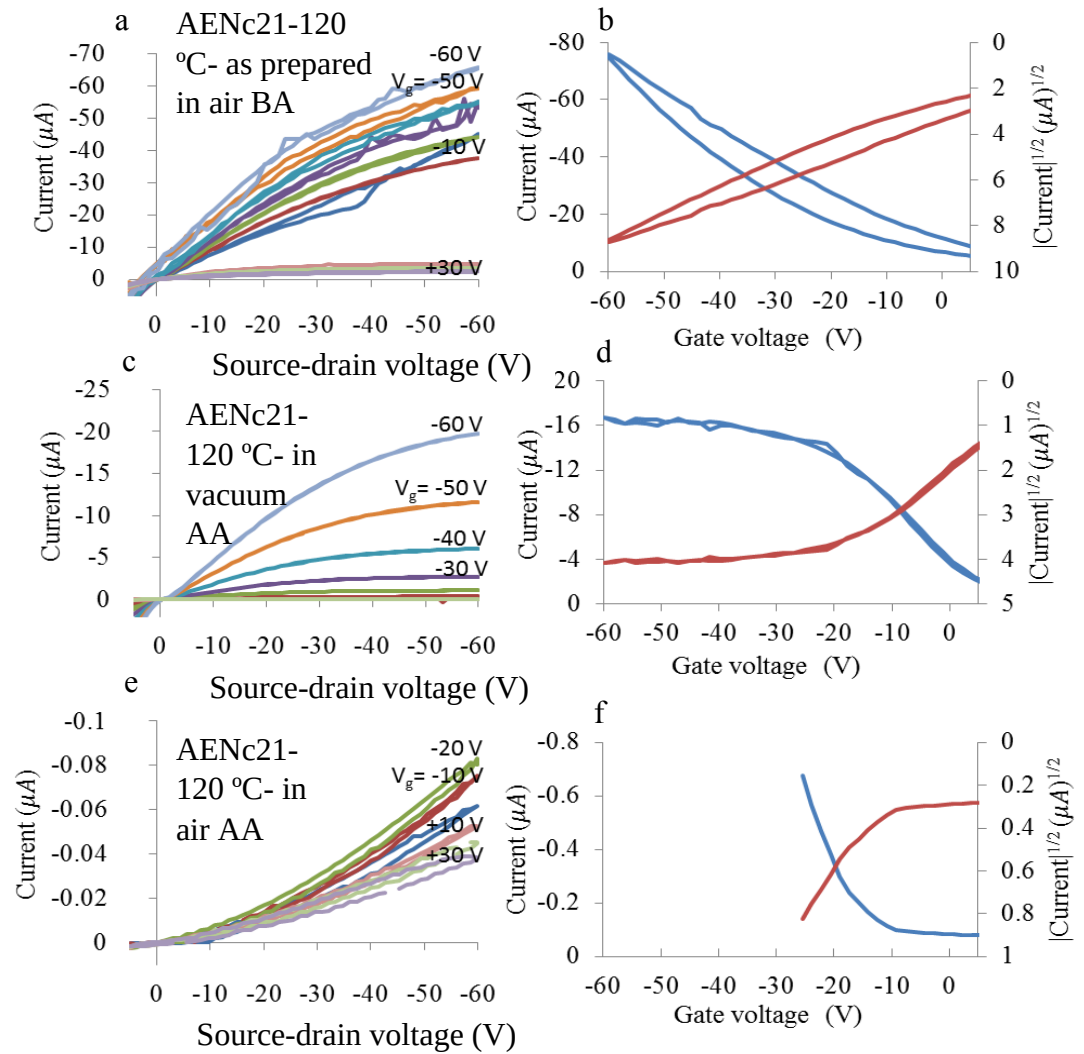


Figure A.2.1: Output characteristics (a, c and e) corresponding to transfer characteristics (b, d and f) of top contact CuNc OFET on bare Si/SiO₂ named AECNc21 that prepared at 120 °C and measured in air as prepared, annealed in vacuum and in air, respectively.

A.2.2 Effect of annealed sample for OTS treated oxide substrate and atmospheric exposure on OFET characteristics

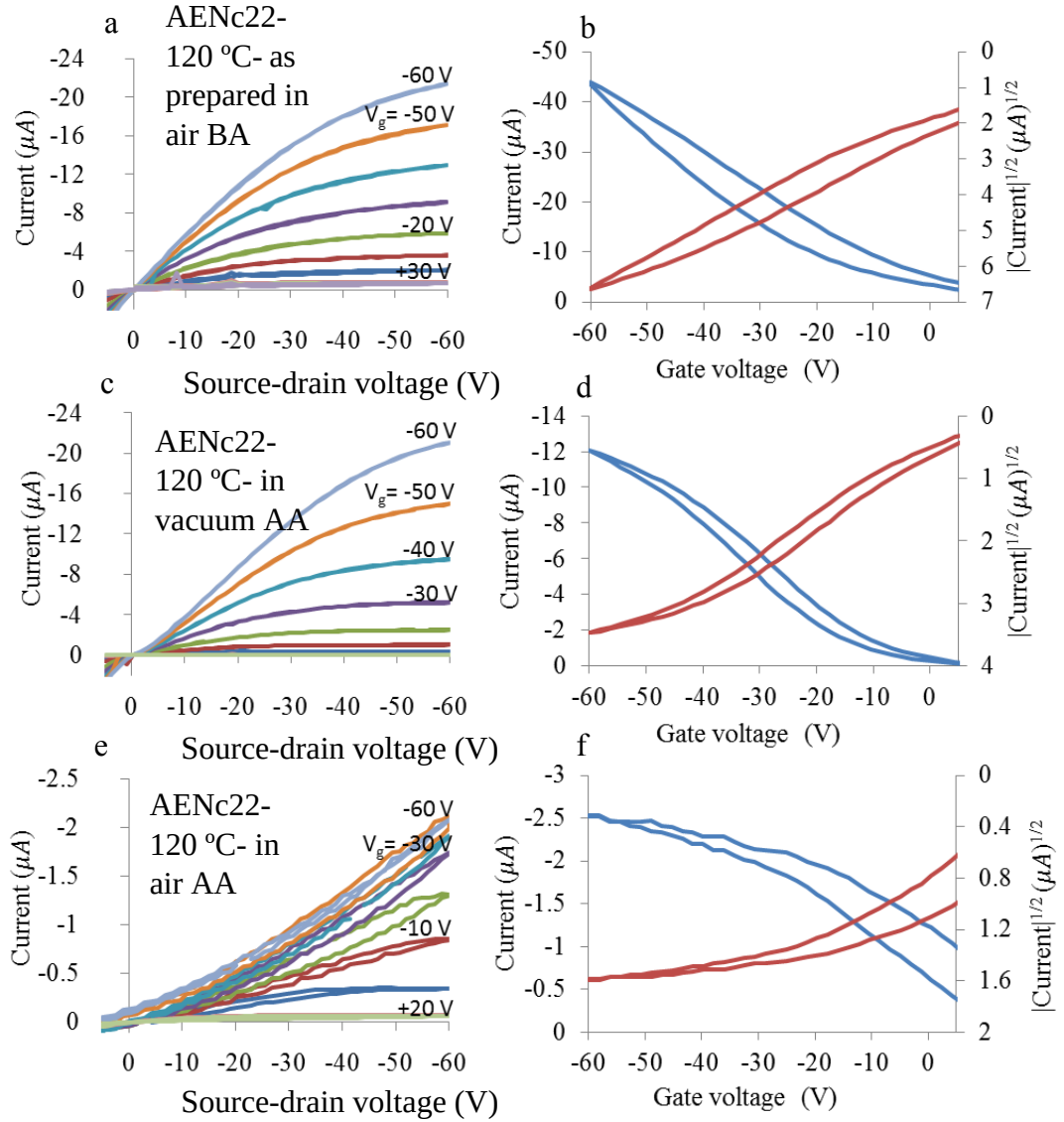


Figure A.2.2: Output characteristics (a, c and e) corresponding to transfer characteristics (b, d and f) of top contact CuNc OFET on OTS-modified oxide named AECNC22 that prepared at 120 °C and measured in air as prepared, annealed in vacuum and in air, respectively.