Optical Anisotropy and Molecular Orientation of CuPc Films and Optical Properties of Ultra-thin High-k Films

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vorgelegt von Dipl. Phys. Li Ding

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Gutachter: Prof. Dr. Dr. h.c. Dietrich R. T. Zahn

Prof. Dr. Norbert Esser

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Hafniumdioxid (HfO$_2$) ist ein heißer Kandidat für das Ersetzen des herkömmlich als Gate-Dielektrikum verwendeten SiO$_2$ mit dem Ziel, die Leckströme bei der weiteren Verkleinerung mikroelektronischer Bauelemente zu minimieren. Um amorpe Schichten, die vorteilhaft zur Minimierung der Leckströme sind, zu erhalten, werden die HfO$_2$-Schichten, die oft kristallin sind, mit Aluminiumoxid (Al$_2$O$_3$) (k-Wert: 9) kombiniert, das bei wesentlich höheren Temperaturen amorph bleibt. Zwei Serien von ultra-dünnen Proben wurden durch Atomlagenabscheidung hergestellt: Mischschichten Hf$_x$Al$_{1-x}$O$_2$ und Doppelschichten HfO$_2$ auf Al$_2$O$_3$. Die optischen Konstanten und Bandlücken wurden mittels SE im Energiebereich von 0,7 bis 10 eV bestimmt. Es hat sich gezeigt, dass die (effektive) Bandlücke der Misch- und Doppelschichten durch die Komposition abgestimmt werden kann. Nach Lagerung der High-k-Schichten für zwei Monate an Luft konnte ein Alterungseffekt beobachtet werden. Dieser wird auf die weitere Oxidation der dielektrischen Schichten, die durch Sauerstoffdiffusion aus der Umgebungsluft in die High-k-Schichten ermöglicht wird, zurückgeführt.

Schlagwörter:
Optische Anisotropie, molekulare Orientierung, CuPc, Ellipsometrie, Reflektions-Anisotropie-Spektroskopie, \textit{in-situ}, Oberflächenmodifizierung, Metall-organische Grenzflächen, optische Konstanten, Bandlücke, high-k-Dielektrika, Alterungseffekt
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1. Introduction

The investigation in the thesis is composed of two parts: copper phthalocyanine (CuPc) thin films and ultra-thin high-k films. CuPc thin films on vicinal Si(111) substrates with various offcut angles are explored by ex situ and in situ optical investigation. The effect of surface modification on optical properties and molecular orientation of CuPc thin films as well as metal-organic (In-CuPc) interface is studied by in situ optical techniques. At the end optical constants and the bandgap of ultra-thin high-k films prepared by the cooperation group are presented and discussed.

CuPc [1] as a type of organic semiconductor has been intensively studied because of its potential applications in organic solar cells [2-3], organic field effect transistors (OFETs) [4-5] and organic light emitting diodes (OLEDs) [6-7]. Vicinal Si(111) is an interesting substrate due to the steps and terraces which induce a surface anisotropy [8]. It is reported that film structures are greatly influenced by the steps and terraces [9]. As molecular orientation in organic thin films plays a significant role in device performance, the impact of vicinal Si(111) surfaces on molecular orientation is under investigation.

High-k materials are currently a hot topic as promising candidates for SiO$_2$ gate dielectrics to extend further scaling in microelectronic technology. [10-12] HfO$_2$ [13-17] and Al$_2$O$_3$ [18-19] are high-k materials with a $k$ value of 25 and 9, respectively. Ultra-thin high-k films with different structures (mixed layer and bilayer) are investigated using vacuum ultraviolet spectroscopic ellipsometry (VUVSE) in the energy range from 4 to 10 eV due to their wide bandgap above 5 eV.

Spectroscopic ellipsometry (SE) [20-24] is a non-destructive optical technique used to characterize thin and ultra-thin films. Film thicknesses and optical constants are commonly determined by fitting SE data. Furthermore, out-of-plane anisotropy and molecular orientation of organic thin films can be derived
Reflection anisotropy spectroscopy (RAS) also named reflectance difference spectroscopy (RDS) can be considered as SE operating at near normal incidence. It is capable to detect very small in-plane anisotropy and has been applied for many material systems such as semiconductor surfaces, metal surfaces and organic films. In situ SE and RAS have been separately employed to monitor the growth of organic thin films. Here these two techniques are combined to characterize CuPc thin films and the In-CuPc interface. Atomic force microscopy (AFM) is utilized to examine surface morphology of various samples.
2 Materials and thin films

A brief introduction to organic semiconductors and high-k dielectrics is given in this chapter. Particularly, specific materials investigated in the thesis are discussed. In addition, some basic concepts on thin film growth are described at the end.

2.1 Organic semiconductors

Organic semiconductors are organic materials which can act as semiconductors. [32-33] There are two types of organic semiconductors: small molecules and polymers. The most important difference between the two types of organic semiconductors is the preparation process to obtain thin films. Thin films of small molecules can be deposited by sublimation or evaporation whereas polymer films have to be processed in solutions by spin-coating or printing due to the large molecular weight.

2.1.1 Optical properties

Organic semiconductors commonly have a π-conjugated electron system forming by the p$_z$-orbitals of sp$^2$ hybridization in C atoms. Fig. 2.1 shows σ- and π-bondings taking ethane as the simplest example. The π-bonding is significantly weaker than the σ-bonding. The energy levels of bonding orbitals (σ- and π-orbitals) as well as antibonding orbitals (σ*- and π*-orbitals) are presented on the right in Fig. 2.1 The lowest electronic transition occurs between the π- and π*-orbitals. Here the π-orbital is the highest occupied molecular orbital (HOMO) and the π*-orbital corresponds to the lowest unoccupied molecular orbital (LUMO). The transition energy lies generally between 1.5 and 3 eV, resulting in absorption or emission in the visible light range. This stimulates photoelectronic devices based on organic semiconductors.
Optical properties of organic solids are rather different from that of inorganic ones due to the fact that organic solids are bonded via van der Waals force between molecules, which is much weaker than that of covalent bonds in molecules. In addition, the optical excitation of organic solids tends to be localized near individual molecules. Thus the properties of organic solids are quite similar to those of single molecule.

![Diagram of σ- and π-bondings in ethane and energy levels of a π-conjugated molecule.](image)

**Fig. 2.1** Left: σ- and π-bondings in ethane. Right: energy levels of a π-conjugated molecule.

The optical transitions of molecules are vibronic, implying that the transition changes the electronic and vibrational states of a molecule simultaneously. This is also true for organic solids. The basic of vibronic transitions of molecules is illustrated in Fig. 2.2. [34] The diagram shows absorption and emission between vibrational excited states and the ground state.
two electronic states: ground and excited states. The non-radiative relaxation in process (2) and (4) is a transition between vibrational states. It is obvious that the absorption occurs at a higher energy than the emission. This is very often found in organic solids. The energy difference between the maximum absorption and the maximum emission is called Stokes shift.

**2.1.2 Devices and applications**

Various electronic devices based on organic semiconductors [35] show wide potential applications due to their low-cost mass production in industry and low power consumption. Less weight, smaller size and flexibility of organic semiconductors makes them suitable to fabricate flexible portable products.

*Organic light emitting diodes (OLEDs)*

A film of organic semiconductors is utilized in OLEDs to emit light when a current is going through. Charge carriers are injected from electrodes to organic layers and then the combination of electrons and holes emits light. Consequently, metal-organic interfaces play an important role to achieve high efficiency OLEDs.

OLEDs are used in television screens, computer monitors, cell phones and other small screens. OLEDs can also be used as large-area emitting elements

*Organic photovoltaic cells (OPVCs)*

Another important optoelectronic device is organic photovoltaic cell (OPVC), named also organic solar cell. The advantage of OPVCs compared to inorganic devices is the relative strong absorption coefficient (usually $\geq 10^5$ cm$^{-1}$) whereas the disadvantage lies at the generally lower carrier mobility in organic semiconductors.

The first small molecule OPVC was produced on the basis of phthalocyanines (Pcs) and porphyrins. [36] Later, a power conversion efficiency of 1% was reported in 1986 using copper phthalocyanine (CuPc). [37] Nowadays a power conversion efficiency between 1.5 and 4% have been achieved for OPVCs.
**Organic field effect transistors (OFETs)**

OFETs utilize a film of organic semiconductor as the channel between source and drain contacts and the current density in the channel can be controlled by the applied voltage on a dielectric layer beneath the organic film. To achieve high carrier mobilities, highly ordered crystalline organic films are required. Special treatment of substrates and careful control of deposition conditions are necessary to obtain well-ordered and highly crystalline films. A high hole mobility of $3 \text{ cm}^2/\text{Vs}$ was reported for pentacene thin-film OFETs. [38]

### 2.1.3 Phthalocyanines (Pcs)

Phthalocyanines, a kind of organic semiconductor, are blue-green colored organic compounds which are used as dyes and pigments. As an example the molecular structure of copper phthalocyanine (CuPc) is shown in Fig. 2.3. CuPc is a planar molecule, whose Cu ion in the center can be substituted by different metal ions, such as Zn, Fe, Mn, Co, Ni, Pb, Sn. The Cu ion can also be replaced by two hydrogen atoms (H$_2$Pc) or other ions like VO, TiO. However, the oxygen atom of TiOPc and VOPc is out of the ring plane. Phthalocyanine derivatives are produced when the hydrogen atoms of the ring are substituted by functional ligands like halogens, hydroxy, amino, alkyl, aryl, thiol, alkoxy and nitro.

As mentioned above, phthalocyanines show a wide application in OPVCs due to their strong absorption in the visible light range. The physical properties of phthalocyanines can be tuned by various ions. The strong absorption band of phthalocyanines appearing in the region of 2 eV is named Q band, which is responsible for their blue-green color. [39-40] The Q band is interpreted as a result of the $\pi-\pi^*$ transition in phthalocyanine molecules. It should be pointed out that a Davydov splitting of the Q band is characteristically observed in all phthalocyanine molecules. [40-41] The absorption band in the ultraviolet (UV) region below 6 eV is known as the B band. [40] Fig. 2.4 shows optical constants of CuPc from 0 to 12 eV. The Q and B bands can be clearly observed.
CuPc can be used as a donor material in OPVCs [42], while it can serve as a hole injection layer [43] or emitting layer [44] in OLEDs. A high charge carrier mobility up to $1 \text{ cm}^2/\text{Vs}$ was reported for single crystal CuPc OFETs together with a low threshold voltage. [45] However, thin film CuPc OFETs exhibit much lower mobilities. CuPc thin films deposited with the substrate temperature at 125 °C show a mobility of $0.02 \text{ cm}^2/\text{Vs}$. [46] The high chemical stability of CuPc compared with other organic semiconductors, like pentacene and rubrene, motivates research on improving its electrical properties. [47]

![Fig. 2.3 Molecular structure of CuPc.](image)

![Fig. 2.4 Refractive index (n) and extinction coefficient of CuPc.](image)

CuPc exhibits two crystalline phases: the metastable $\alpha$-phase and the stable $\beta$-phase. CuPc thin films deposited at room temperature are in $\alpha$-phase [48-49] whereas films deposited at substrate temperature above 210 °C are in $\beta$-phase [50]. If $\alpha$-phase CuPc films are annealed at 290 °C, a complete transformation from the $\alpha$-phase to the $\beta$-phase occurs. [50] Single crystal CuPc in $\beta$–phase exhibits the monoclinic unit cell and the lattice constants are $a=14.6 \text{ Å}$, $b=4.8 \text{ Å}$, $c=17.3 \text{ Å}$ and $\beta=105.39^\circ$. [4] However, the geometry of $\alpha$–phase CuPc is not yet clear, which could be tetragonal, orthorhombic or monoclinic structure. The x-ray diffraction (XRD) patterns as well as the absorption spectra of CuPc in different phases are presented in Fig. 2.5. [51-52] It is obvious that the lineshape of the Q band differs greatly in the $\alpha$- and $\beta$-phases. There are energy shifts in the peak positions of the Q band. Furthermore, the peak at longer wavelength presents a
weaker intensity than the one at shorter wavelength for CuPc films in α-phase, which is on the contrary for β-phase.

Anisotropy is generally observed in organic thin films due to the ordering of molecular stacking (molecular orientation) and the asymmetry of molecules. CuPc molecule is symmetric as shown in Fig. 2.3. However, CuPc thin films exhibit out-of-plane anisotropy owing to a tilt angle of the molecular plane relative to the substrate plane (out-of-plane molecular orientation), leading to different optical constants (dielectric functions) between the in-plane and out-of-plane components. The intensity of the out-of-plane anisotropy is dependent on the magnitude of the tilt angle of molecules, which is determined by the strength of molecule-substrate interaction. Thus, it is possible to estimate the average tilt angle of molecules from the out-of-plane anisotropy determined by SE. A model is developed and discussed in the next subchapter. For upright standing molecules, the out-of-plane component should be much stronger than the in-plane one; for flat lying molecules, considerably weak out-of-plane component would be exhibited.

If CuPc molecules show an ordering in the in-plane stacking, in-plane anisotropy can be observed. Stronger in-plane anisotropy implies a higher in-plane order of molecules. The in-plane ordering of molecules could also lead to enhanced in-plane carrier mobility. [53] However, molecules usually tend to exhibit in-plane disordering in evaporated thin films. One way to induce in-plane ordering in molecules is to make use of regular step arrays on vicinal surfaces.
[54-55], which is the method used here to deposit CuPc thin films exhibiting in-plane ordering.

In this thesis, the out-of-plane and in-plane anisotropy are determined from SE and RAS, respectively.

2.1.4 **Perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA)**

PTCDA is a perylene derivative organic semiconductor and its molecular structure is shown in Fig. 2.6. An interesting phenomenon of PTCDA is that these molecules tend to lying flat on most of the substrates due to the formation of in-plane hydrogen bonding between neighboring molecules. [56-60] PTCDA thin films with flat-lying orientation were also observed on both standing-up and lying-down CuPc thin films. [58] Fig. 2.7 shows the in-plane herringbone structure of PTCDA molecules, which indicates an in-plane molecular ordering in the (102) plane of crystals. This stacking of molecules with molecular plane parallel to the (102) lattice plane appears in both α- and β-phase PTCDA. Due to the flat-lying molecules the dielectric function of PTCDA thin films shows very weak out-of-plane anisotropy [23], as indicated in Fig. 2.8.

2.1.5 **Octadecyltrichlorosilane (OTS)**

Surface modification is a pretreatment of surfaces to improve adhesion properties, to change wetting characteristics and to control surface chemistry. Producing a self-assembled monolayer (SAM) of OTS is a surface modification method to enhance carrier mobility in OFETs by two orders of magnitude and to improve device stability. [61] The chemical structural of OTS [CH$_3$-(CH$_2$)$_{17}$-SiCl$_3$] molecule is displayed in Fig. 2.9. OTS is an amphiphilic molecule with a long-chain alkyl group (C$_{18}$H$_{37}$–) and a polar head group (SiCl$_3$–), which forms closely packed ordered SAM (as shown in Fig. 2.10) on various oxidic substrates. [62] Different from flat-lying PTCDA, OTS molecules stand up on substrate surface.
The effect of these two differently oriented molecules on molecular orientation of CuPc thin films are investigated in the thesis.

Fig. 2.6 Molecular structure of PTCDA.

Fig. 2.7 Herringbone structure of PTCDA molecules on substrates.

Fig. 2.8 Dielectric function of PTCDA thin films deposited on glass or SiO₂/Si. [23]

Fig. 2.9 Chemical structure of OTS molecule.

Fig. 2.10 Closely packed ordered SAM of OTS on substrate.
2.2 High-k dielectrics

In the last decades the number of devices on an integrated circuit increased exponentially and the minimum feature size of a transistor decreases exponentially. However, the scaling can not go forever due to a limit in Moore’s law. The most serious problem is that the gate leakage current caused by direct tunneling of electrons through gate dielectrics rises sharply for ultra-thin SiO$_2$ films. Consequently, a desire to search new oxides to replace SiO$_2$ as gate dielectrics comes into being.

**2.2.1 Definition of high-k**

A standard of the resistance to the leakage current for gate oxides should be firstly figured out. The relative permittivity $\varepsilon_r$, also referred as relative dielectric constant, is a parameter which defines the capability of a material to store charges. Fig. 2.11 shows a sketch of a capacitor with a dielectric layer sandwiched between two metal plates. Its capacitance is given by

$$C = \frac{\varepsilon \varepsilon_0 A}{d}$$

(1)

where $\varepsilon_0$ is the vacuum permittivity, $A$ is the contact area between the dielectric layer and metal plates, and $d$ is the thickness of the dielectric layer. Thus the relative permittivity is proportional to the capacitance density ($C/A$).

The permittivity is generally expressed by $\varepsilon$. However, it should be noted that the Greek letter $\kappa$ is also used to represent the permittivity. Currently, high-k is an equivalent term of high-κ. Compared with the relative permittivity of SiO$_2$ ($k =$
3.9), materials with higher $k$ values are named as high-$k$ dielectrics and those with lower $k$ values as low-$k$ dielectrics.

An equivalent oxide thickness (EOT) of high-$k$ dielectrics is defined as

$$ EOT = d_{ox} = \frac{3.9}{k} d_{high-k} $$

(2)

The EOT magnitude gives an electrical thickness of another gate oxide in terms of its equivalent SiO$_2$ thickness.

### 2.2.2 Choice of high-$k$ dielectrics

High-$k$ dielectrics are excellent candidates for gate oxides to reduce the leakage current in the further scaling of device sizes. When a high-$k$ dielectric is chosen to act as a gate oxide, some issues must be taken into account.

Its $k$ value should be high enough for a reasonably long lifetime, preferably higher than 12. Furthermore, a reasonably wide bandgap is required for the band offset condition. Fig. 2.12 shows bandgap versus $k$ value for various candidate oxides. Since a wide bandgap and a high $k$ value do not coexist for one oxide, oxides with a relatively high $k$ value and a relatively wide bandgap have to be accepted. These oxides are marked out above the dashed curve in Fig. 2.12.

The chosen oxide must be chemically stable. It should not react with Si to form SiO$_2$ or a Silicide. The third issue is thermal stability. The oxide should be stable in a rapid thermal annealing for 5 s at 1000 °C during the processing flows. Higher leakage current may result from a crystalline oxide due to the grain boundaries. However, most of the oxides crystallize below 1000 °C except from Al$_2$O$_3$ and Ta$_2$O$_5$. Ta$_2$O$_5$ is excluded from the candidates because it is reactive. The crystallization could be inhibited by alloying the oxide with an amorphous oxide at high temperatures, such as Al$_2$O$_3$ and SiO$_2$, forming an aluminate or a silicate. [63-65]

The interface between the chosen oxide and Si should be of a good electrical quality, free of interface defects and a very small roughness. Using an
amorphous oxide helps to reduce the number of interface defects. This is most compatible with the current Si:SiO$_2$ process.

![Bandgap Diagram](image)

**Fig. 2.12** Bandgaps and k values for various candidate oxides. [10]

The oxide should act as an insulator. It means that the injection barriers for both electrons and holes into the oxide bands should be higher than 1 eV, [66-67] as shown in Fig. 2.13. Since the conduction band (CB) and the valence band (VB) of the gate oxide generally align asymmetrically with respect to those of Si, the bandgap of the oxide is preferred to be over 5 eV to have high enough carrier injection barriers.

![Band Offsets Diagram](image)

**Fig. 2.13** Sketch of band offsets determining carrier injection barriers into bands of the gate oxide.
The desired oxide must have few electrically active defects. These defects result in some extra energy states in the band gap of the oxide. Typical defects are impurities, excess or insufficiency of oxygen.

2.2.3 Hafnium dioxide (HfO₂)

Hafnium dioxide (HfO₂) is one of the excellent candidates due to a high k value of 25, a wide bandgap around 5.8 eV, and a good thermal stability. [13] HfO₂ has four phases: monoclinic, tetragonal, orthorhombic and cubic. In the bulk only the monoclinic phase is stable at room temperature. The cubic phase can be stabilized by defects or doping of rare earth elements. A phase transition occurs from monoclinic to tetragonal phase in bulk at 1720 °C. In thin films, the monoclinic phase could transform to either of the tetragonal, orthorhombic or cubic phases.

The optical properties [14-15,68], electrical properties [16,69] and nanostructures [14,17] of HfO₂ thin films have been widely investigated. Experimental work found that amorphous and nano-crystalline HfO₂ show similar leakage currents. [70-71] The fact that crystallized HfO₂ thin films do not give rise to higher leakage currents is beneficial to improve device performance using HfO₂ as gate dielectrics. Furthermore, nearly the same bandgap was observed for nano-crystalline and amorphous HfO₂ thin films. [72] Defect states due to oxygen vacancies or impurities were reported for nano-crystalline HfO₂ thin films [14,73-74], which can be suppressed by introduction of SiO₂ or Al₂O₃ to have amorphous films. Hence Hf silicate [75-77] or aluminate [78-80] is obtained.

Al₂O₃ has a k value of 9 and stays amorphous at high temperatures. [18] The bandgap of Al₂O₃ in bulk is around 8.8 eV. [19] Similar as the others, Hf aluminate does not crystallize easily at temperatures around 1000 °C. Another benefit of Hf aluminate is that it presents a higher k value than Al₂O₃ and a wider bandgap (higher carrier injection barriers) than HfO₂.
2.3 Thin films

The thickness of thin films can vary from monolayer in angstrom to several micrometers. Nowadays thin films show wide applications in electronic devices and optical coatings. In this subchapter thin films are discussed in two aspects: growth modes and specific issues on organic thin film growth.

2.3.1 Growth modes

The growth of thin films on a substrate is grouped into three modes by Bauer in 1958, [81] depending on the interaction strength between film materials and the substrate. The three growth modes are: (a) Frank-van der Merwe (FM) or layer-by-layer, (b) Volmer-Weber (VW) or 3D islands, and (c) Stranski-Krstanow (SK) or layer plus 3D islands growth. Fig. 2.14 illustrates the three growth modes of thin films for various thicknesses. FM mode is observed when the interaction between film materials and the substrate is larger than the interaction between particles of film materials. Conversely, VW mode is found if the interaction between film materials and the substrate is smaller than that within film. SK mode occurs for interaction strength intermediate between the above two cases. Theoretically a quantity of energy is defined as

\[ \Delta \sigma = \sigma_s - \sigma_f - \sigma_i \]

(3)

where \( \sigma_s \) and \( \sigma_f \) are the surface free energies of the substrate and the film, respectively, and \( \sigma_i \) the interfacial free energy. If \( \Delta \sigma > 0 \), FM mode may occur; if \( \Delta \sigma < 0 \), VW mode could be obtained. At some thickness (critical thickness) it is possible that the sign of \( \Delta \sigma \) changes from positive to negative due to the strain in layers, thus the growth transforms from FM to SK resulting in 3D islands on wetting layers.

2.3.2 Issues specific to organic thin film growth

As the general concepts of thin film growth are discussed above, a few specific issues on organic thin film growth [82] will be described in the following.
(1) Internal degrees of freedom exist for organic molecules as “extended objects” consisting of atoms. This is basically the most significant difference between growths of atoms and molecules.

The orientational degree of freedom gives rise to new phenomena due to the change of molecular orientation during the growth of organic thin films. Fig. 2.15 presents two extreme cases of molecular orientation for organic thin films: standing upright and lying flat. An intermediate case is commonly found that molecules show a tilt angle $\alpha$ ($0^\circ<\alpha<90^\circ$) relative to the substrate surface. The vibrational degree of freedom has also an impact on the interaction between organic films and the substrate, especially on the adsorption and diffusion behaviors of molecules on the surface.

![Fig. 2.14 Cross-section views of three growth modes of thin films for various thicknesses.](image)

(2) The interaction potential (molecule-molecule and molecule-substrate) differs from that in the case of atomic growth for inorganic films. Therefore, van der Waals interactions are much more important.

The effect of strain in organic films is different. Organic systems can accommodate more strain. The critical thickness in growth from layer to 3D islands (transformation from FM to SK mode) can be larger than that for
inorganic systems. Since there are no dangling bonds at organic surfaces due to closed-shell molecules and Van-der-Waals type crystals, the surface energies are usually weaker than those for inorganic surfaces.

![Diagram](image)

Fig. 2.15 Extreme cases of molecular orientation for organic thin films. (a) upright-standing, (b) flat-lying molecules.

(3) The size of molecule and the associated unit cells are larger than the unit cells of typical inorganic substrates.

The effective lateral variation of the potential is averaged over the size of the molecule. Hence, the molecule experiences a weaker effective corrugation potential of the substrate than atomic adsorbates. The size difference between molecular adsorbates and inorganic substrates indicates that there are more translational domains. Organic materials generally crystallize in low-symmetry structures, leading to not only translational but also orientational domains. Both of the domains contribute to sources of disorder, in addition to those known for inorganic systems, such as vacancies.

In short, most of the above mentioned points influence the interactions directly or indirectly. Thus, the growth dynamics of organic systems differs from inorganic systems.
3 Experimental

The chapter discusses experimental methods and techniques in three parts. Firstly, the way to prepare vicinal Si(111) substrates are described. Secondly, two deposition methods of different organic thin films are presented as well as atomic layer deposition (ALD) of ultra-thin high-k film. Finally, several characterization techniques of thin films are discussed in details, including spectroscopic ellipsometry (SE), reflection anisotropy spectroscopy (RAS) and atomic force microscopy (AFM).

3.1 Preparation of vicinal Si(111) substrates

P-type doped vicinal Si(111) wafers with a resistivity of 1-30 Ωcm and a diameter of 100 mm were purchased from Silchem Company. The vicinal Si wafers were offcut toward [11-2] direction with three different offcut angles: 0.35°, 3° and 6°. The purchased wafers were then cut manually with a diamond cutter to obtain small pieces for different purposes. Generally one substrate is in the size about 1.0 cm × 1.5 cm to have large enough light spot on the sample surface in optical measurements. Substrates for in situ investigations should be at least in the size of 2.5 cm × 3.0 cm in order to lower the difficulty in the alignment of in situ setup.

3.1.1 Cleaning

Vicinal Si substrates were cleaned in a standard procedure. Si substrates were firstly immersed into acetone and kept in an ultrasonic bath for 10 minutes. Secondly, isopropanol or ethanol was used to clean Si substrates in an ultrasonic bath for another 10 minutes. Then the substrates were rinsed with deionized water and dried using N₂ gas.
3.1.2 Hydrogenation

In order to investigate the influence of vicinal Si(111) surfaces on film properties, native oxide layers were removed by means of a dip in hydrofluoric (HF) acid. This is a wet chemical etching method for hydrogenation of Si. HF acid with three different concentrations was used: 40%, 5% and 1%. The dip time varied from 30s to 10 minutes. Finally the most suitable hydrogenation method was found out to have the surface as smooth and homogeneous as possible.

3.2 Film growth

In the thesis organic films (CuPc and PTCDA) were grown by organic molecule beam deposition (OMBD) in high vacuum (HV) whereas high-k dielectric films (HfO$_2$ and Al$_2$O$_3$) were prepared by atomic layer deposition (ALD). The OTS monolayer was obtained in solution from a chemical method. Details of the three film preparation techniques are discussed in this subchapter.

3.2.1 Organic molecular beam deposition (OMBD)

There are a number of deposition techniques for organic thin films, such as spin-coating and dipping for polymers, vacuum thermal evaporation and molecular beam epitaxy (MBE) for small molecules. Organic molecular beam deposition (OMBD) allows a deposition of thin films in a few nanometer or even monolayers with a good control of film thickness.

Knudsen cells are employed as source evaporator in OMBD systems. A typical Knudsen cell consists of a crucible made of quartz, heating filaments, water cooling system, thermal couple for temperature monitoring, heat shields and a shutter. Stable temperature and a stable growth rate for many materials can be obtained using a Knudsen cell.

A scheme of an OMBD chamber is depicted in Fig. 3.1. Knudsen cells are constructed at the bottom of the chamber. A quartz crystal microbalance (QCM)
is mounted near the sample holder to monitor the growth rate and film thickness. QCM measures a change in the resonant frequency due to the mass change resulting from deposited films on the crystal surface. The substrate is covered by a main shutter beneath unless a stable growth rate is obtained. When the desired film thickness is reached, the shutter is moved back beneath the sample.

![Fig. 3.1 A scheme of an OMBD chamber.](image)

During deposition the Si substrates were kept at room temperature. The base pressure before film growth in our OMBD chamber is below $8 \times 10^{-7}$ mbar and the growth rate of CuPc films is around 0.3 nm / min. The sublimation temperature of CuPc and PTCDA in Knudsen cells is around 400 and 300 °C, respectively.

In addition to CuPc and PTCDA thin films, In thin films were also deposited in the same chamber at a much higher growth temperature of 700 °C. Watering cooling system in Knudsen cells should be employed for the In growth due to the high temperature.

### 3.2.2 Chemical preparation of OTS monolayer

It is possible to use OTS as a surface modification layer by thermal evaporation in $N_2$ atmosphere [83] or chemical preparation. There are various
chemical methods to get an OTS monolayer [84-86], which are often based on OTS solution in hexane or toluene.

To obtain a good adhesion of the OTS monolayer, a vicinal Si substrate with native oxide instead of hydrogenated Si was used because SiO$_2$ helps to form covalent bonds with OTS. Here a similar preparation method was employed as described by Belgardt et al. [87] The Si substrate was cleaned separately in acetone and ethanol each in ultrasonic bath for 5 minutes and then washed with deionized water and dried via N$_2$ gas. Later the substrate was immersed in ‘piranha’ acid solution consisting of 2 parts of hydrogen peroxide (Merck KGaA, 30%) and 3 parts of sulphuric acid (Merck KGaA, 96%) in an ultrasonic bath for 30 minutes. Following this procedure the substrate was again washed with deionized water and dried using N$_2$. The clean substrate was then immersed in the OTS solution in toluene (Merck KGaA, 99.9%) with a concentration of 0.002 mol/L. After 1 hour reaction time in N$_2$ atmosphere, the sample with an OTS monolayer on top was taken out, and instantly put separately in toluene and dichloromethane (Merck KGaA, 99.8%) each in an ultrasonic bath for 3 minutes to remove the remaining OTS solutions on the surface. Finally the sample was rinsed by ethanol then deionized water, and dried with N$_2$ gas.

3.2.3 Atomic Layer deposition (ALD) of high-k films

3.2.3.1 Introduction to ALD

Atomic layer deposition (ALD) is a film growth technique based on sequential, self-limiting surface chemical reactions. [88-89] The ALD method grows thin films by sequential pulsing of precursor vapors into the chamber and each precursor produces one atomic layer on the surface through chemical reactions. Each reaction process should be self-limiting so that only one atomic layer is generated via pulsing of one precursor. Furthermore, the self-limiting nature results in a continuous and pinhole free film, which is a significant factor to achieve excellent dielectric films. [90]
Fig. 3.2 illustrates the film growth process in an ALD system taking $\text{Al}_2\text{O}_3$ as an example. The details of $\text{Al}_2\text{O}_3$ growth in ALD have been intensively discussed by Puurunen. [91] Here only the key points of this growth process will be mentioned. Mostly, trimethylaluminum (TMA) and $\text{H}_2\text{O}$ are used as precursors in the $\text{Al}_2\text{O}_3$ growth by ALD. The chemical reaction

$$2\text{Al}(\text{CH}_3)_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{CH}_4$$

is divided into the following two surface half-reactions:

(A) $\text{AlOH}^* + \text{Al}(\text{CH}_3)_3 \rightarrow \text{AlOAl}(\text{CH}_3)_2^* + \text{CH}_4$

(B) $\text{AlCH}_3^* + \text{H}_2\text{O} \rightarrow \text{AlOH}^* + 2\text{CH}_4$

where the asterisks denote the surface species. Fig. 3.2 (a) shows that the substrate surface is covered with hydroxyl groups (OH* species). When TMA($\text{Al}(\text{CH}_3)_3$) is pulsed into the chamber, it reacts with the OH* species and deposits AlCH$_3^*$ species on the surface as shown in Fig. 3.2 (b). The (A) reaction stops when all the OH* species are replaced by OAl(CH$_3$)$_2^*$ species. This ensures the uniformity of the single grown layer.

The excess TMA together with the reaction product methane (CH$_4$) is purged from the chamber via introducing an inert gas. Water vapor (H$_2$O) is then pulsed into the chamber (Fig. 3.2 (c)) and the (B) reaction occurs (Fig. 3.2 (d)), depositing the OH* species on the newly forming surface. Similarly the (B) reaction stops when all the CH$_3^*$ species are removed, producing another single layer (Fig. 3.2 (e)). The product of the (B) reaction CH$_4$ and the excess water vapor are pumped away using an inert gas for purging and the newly generated surface is ready for the next TMA pulse. Through cycles of the AB reactions an extremely smooth and uniform $\text{Al}_2\text{O}_3$ film is deposited on the substrate surface as illustrated in Fig. 3.2 (e). In one deposition cycle of the AB reactions a growth rate of 1.1 Å is achieved for ALD $\text{Al}_2\text{O}_3$ films [92].

Surface reactions in ALD are carried out in the temperature range between 200°C and 400°C to obtain a maximum growth rate. [94]

ALD precursors should meet the following requirements. [89] Precursors must be volatile with a high vapor pressure to ensure efficient transportation and thermally stable against self-decomposition. Precursors reacting aggressively
with each other are used to ensure a short reaction time and effective precursor utilization. Precursors should be chemisorbed on the surface and not allowed to etch or dissolve into the grown film, substrate or an underlying film. Precursors ought to produce unreactive byproducts so that byproducts can be easily purged from the reaction chamber.

Since the thickness of ALD grown films is linearly dependent on the number of deposition cycles, ALD is capable to provide an accurate and simple control of film thickness at atomic level. ALD grows a smooth, uniform and pinhole free film in large areas with a high quality. ALD can grow a multilayer structure in a continuous process and has a capability to create sharp interfaces. Oxides,
nitrides, metal, semiconductors are all possible to grow films using the ALD method.

One of the ALD applications is to grow ultra-thin high-k dielectrics in transistors and capacitors. ALD is also widely utilized to deposit high aspect ratio structures for Cu interconnects. ALD is capable to prepare nanolaminates and other nanostructures. Various coating layers can be produced by the ALD technique.

Fig. 3.3 illustrates a basic ALD system [95], which is composed of five key elements.

(a) Two temperature-controlled liquid baths which provide vapor to the system.
(b) High speed valves to isolate each liquid bath from the system. With valves on precursor vapor pulses are introduced to the system.
(c) A wafer placed in the center of a small volume reaction chamber.
(d) A reaction chamber heated to initiate surface reactions for film deposition.
(e) A vacuum pump which maintains gas flow through the system enables rapid purging of the precursor gases between cycles.

![Fig. 3.3 A basic ALD system.](image)

### 3.2.3.2 ALD growth of HfO$_2$ and Al$_2$O$_3$

The research into high-k dielectric films is cooperation with Fudan University in China. High-k samples were prepared there. The details are shown below. Ultra-thin high-k films were deposited on hydrogenated Si(100) substrates by atomic layer deposition (ALD) at 300°C. The hydrogenation was done by means
of putting Si into 2% HF acid for 2 minutes. HfO$_2$ thin films were grown using Hf[N(CH$_3$)(C$_2$H$_5$)]$_4$ (TEMAH) as a metal precursor and H$_2$O as an oxidant precursor. Al$_2$O$_3$ thin films were obtained from Al(CH$_3$)$_3$ and H$_2$O precursors. The injection ratio of the metal precursor to the oxidant precursor was 1:1. Two series of high-k samples were prepared: mixed layers and bilayers. The sample structures are shown in Fig. 3. 4. Mixed layer samples (Hf$_x$Al$_{1-x}$O$_2$/H-Si) were deposited by modulating deposition cycles of HfO$_2$ and Al$_2$O$_3$ with a ratio of x to 1-x. The four Hf$_x$Al$_{1-x}$O$_2$ samples are labeled as MH2A8, MH4A6, MH6A4 and MH8A2 and the corresponding Hf fraction x varying as 0.2, 0.4, 0.6, and 0.8. Four bilayer samples (HfO$_2$/Al$_2$O$_3$/H-Si) are labeled as BH2A8, BH4A6, BH6A4 and BH8A2. The nominal thickness proportion of HfO$_2$ in the bilayer structure is 0.2, 0.4, 0.6, and 0.8 with a total nominal thickness of 10 nm.

3.3 Characterization techniques

3.3.1 Spectroscopic ellipsometry (SE)

Ellipsometry is a surface sensitive technique to characterize thin films, surfaces and material structures. [20, 96-98] The technique is discussed in this part from five aspects: fundamentals, optical elements, ellipsometric configurations, data acquisition and analysis.

3.3.1.1 Fundamentals

Ellipsometry is based on a change of the polarization states of light caused by reflection from a sample surface. $\rho$ is defined as the complex ratio of the reflection coefficients:
\[ \tilde{\rho} = \frac{\tilde{r}_p}{\tilde{r}_s} = \frac{r_p}{r_s} e^{i(\psi - \delta)} = \tan \psi \exp(i\Delta). \] (4)

\( \psi \) and \( \Delta \) are ellipsometric parameters, which describe the ratio of the magnitude and the phase change for p- and s-polarization.

The most common application of ellipsometry is to determine thickness and optical constants (dielectric functions) of thin films. Ellipsometry is also used to determine surface/interfacial roughness, optical anisotropy, crystallinity, alloy ratio and optical bandgap. Meanwhile, ellipsometry is also a powerful real-time monitoring technique. In the following some basic concepts in ellipsometry are discussed.

**Reflection of light**

Fig. 3.5 illustrates reflection of light on a surface. The incident beam, the reflection beam and the direction normal to the surface are in the same plane, which is defined as the plane of incidence. The effect of reflection depends on the polarization states of the incident beam and the angle of incidence. Polarization with the electric field vector parallel to the plane of incidence is defined as p-polarization. Polarization with the electric field vector perpendicular to the plane of incidence is defined as s-polarization.

**Brewster angle**

The Fresnel equations describe the behavior of light at an interface between two mediums, such as reflection and transmission. It is known from Fresnel equations that p-polarized light has no reflection if the incident angle meets the relation
\[ \theta_B = \arctan \left( \frac{n_2}{n_1} \right) \]

\( n_1 \) and \( n_2 \) are refractive indexes of the first and second medium, respectively. The equation is known as the Brewster's law and the angle \( \theta_B \) is defined as Brewster angle. Fig. 3.6 shows the dependence of reflection coefficient on the angle of incidence for different refractive indexes. It is seen that the difference in reflection coefficient between p- and s-polarization lies in the range near the Brewster angle. Therefore, ellipsometric measurements are usually performed with the angle of incidence in the range near the Brewster angle.

Fig. 3.6 Reflection coefficient as a function of the angle of incidence for different refractive indexes. The image is taken from webpage [99].

Interference

Optical interference occurs when light waves superpose. Interference is observed when light probes films deposited on a substrate. Thickness of films is determined from interference effect in ellipsometric data. As shown in Fig. 3.7, the incident beam firstly reflects on the film surface and secondly on the...
film/substrate interface. The two reflected beams superpose and interference occurs. The phase difference between the two beams is given by

$$\frac{4\pi d}{\lambda} \sqrt{n_1^2 - n_0^2 \sin^2 \theta}$$  \hspace{1cm} (5)$$

where $d$ is the film thickness, $\lambda$ is the wavelength, $\theta$ is the incident angle, $n_0$ and $n_1$ are refractive indexes of air and film. In addition, the reflected wave undergoes a $\pi / 2$ phase shift when $n_2 > n_1$ but no phase shift when $n_2 < n_1$.

**Depolarization effect**

When a depolarization effect occurs, the polarized light in ellipsometry can be transformed to partially polarized light, leading to a larger measurement error. The phenomena that can show depolarization effect upon reflection are summarized as follows: [98]

1. light scattering caused by a large surface roughness of a sample,
2. thickness inhomogeneity of a thin film deposited on substrate,
3. backside reflection when the substrate backside is polished and the substrate absorbs little light,
4. variation in the incident angle resulting from the weak collimation of light,
5. variation in wavelength originating from the finite bandwidth of the monochromator.

**Kramers-Kronig relations**

The refractive index and extinction coefficient (or the real and imaginary parts of the dielectric functions) are not independent quantities, which are correlated by the Kramers-Kronig relations. The relationships between $n$ and $k$ are given by

$$n(E) = 1 + \frac{2P}{\pi} \int_0^\infty \frac{E'k(E')}{E'^2 - E^2} dE'$$

$$k(E) = -\frac{2E}{\pi} \int_0^\infty \frac{n(E')}{E'^2 - E^2} dE'$$

where $P$ denotes the Cauchy principle value and $E$ denotes the energy. It implies that the refractive index can be calculated from the known extinction coefficient by Kramers-Kronig relations, and vice versa.
The similar relationship exists between $\varepsilon_1$ and $\varepsilon_2$, using $\varepsilon_1 (\varepsilon_2)$ to replace $n (k)$.

**Jones vector and matrix**

Jones vector is a mathematic expression of polarization states of light whereas Jones matrix is a matrix representation of variations in polarization, such as optical elements and optical measurements. Jones matrixes are linear operation with Jones vectors.

Because ellipsometric measurements take into account the relative change in magnitude and phase, the Jones vector is generally expressed in normalized light intensity. Accordingly, linearly polarized light parallel to the x- and y-direction are given by

$$
E_x = \begin{bmatrix} 1 \\ 0 \end{bmatrix}, \quad E_y = \begin{bmatrix} 0 \\ 1 \end{bmatrix}.
$$

(8)

Generally linearly polarized light having an angle $\beta$ inclined to the x axis can be written as

$$
E_y = \begin{bmatrix} \cos \beta \\ \sin \beta \end{bmatrix}.
$$

(9)

The right- and left-circular polarization are expressed by

$$
E_r = \frac{1}{\sqrt{2}} \begin{bmatrix} 1 \\ i \end{bmatrix}, \quad E_l = \frac{1}{\sqrt{2}} \begin{bmatrix} i \\ 1 \end{bmatrix}.
$$

(10)

Elliptical polarization is given by

$$
E_{\text{ellip}} = \begin{bmatrix} \sin \chi \exp(i\Delta) \\ \cos \chi \end{bmatrix}.
$$

(11)

Jones matrix of a coordinate rotation by an angle of $\gamma$ is written as

$$
\begin{bmatrix} \cos \gamma & \sin \gamma \\ -\sin \gamma & \cos \gamma \end{bmatrix}.
$$

(12)

The variation of change in polarization on a sample can be given by

$$
S = \begin{bmatrix} \sin \Psi \exp(i\Delta) & 0 \\ 0 & \cos \Psi \end{bmatrix}.
$$

(13)
3.3.1.2 Ellipsometer configurations

The basic ellipsometer configuration is based on five elements: source, polarizer, sample, analyzer and detector. There are three primary types of ellipsometers: null, polarization modulation and rotating element ellipsometers. [100]

Both the null and polarization modulation ellipsometers are constructed with a retarder after the polarizer. It is also possible to configure ellipsometers with just two polarizers (polarizer and analyzer). There are several advantages to using only two polarizers. Polarizers can be fabricated with nearly ideal optical behavior. Polarizers are achromatic over wide spectral ranges. Polarizers are relatively easy to construct and align in a system. However, two drawbacks come into being without a retarder. One drawback to rotating element ellipsometers without a compensator is the large uncertainty of $\Delta$ values when $\Delta$ is nearly $0^\circ$ or $180^\circ$. Another drawback is that the measured quantity in rotating element ellipsometers is $\cos \Delta$ rather than $\Delta$. Hence it is not clear whether $\Delta$ lies between $0^\circ$ and $180^\circ$ or between $180^\circ$ and $360^\circ$. This means that left- and right-circularly polarized light entering the analyzer and then the detector can not be distinguished in rotating element ellipsometers without a compensator.

The ellipsometer VASE® with AutoRetarder™ used in our lab is such a rotating analyzer ellipsometer (RAE) with an adjustable retarder, which turns out to be a very powerful research tool. The configuration of RAE with an adjustable retarder can alleviate the two drawbacks discussed above. The adjustable retarder is a variable compensating element placed between the polarizer and the sample. The polarizer and compensator combination can generated any polarized light as the incident beam on the sample. Thus the polarization state of the incident beam is adjusted to make sure that the reflected beam is always close to circularly polarized ($\Delta \sim 90^\circ$), when the rotating analyzer is the most accurate. In a word, the hybrid system is capable to measure $\Delta$ precisely in the range of $0^\circ$ – $360^\circ$. 

Recently imaging ellipsometer has been developed based on null ellipsometer, which allows measurements of a two-dimension plane with a very high thickness sensitivity of 0.1 nm. [101-103] The spatial resolution is 1 μm.

### 3.3.1.3 Data acquisition

In this section a general procedure of data acquisition using VASE® with AutoRetarder™ is described. [100]

**Sample cleaning**

Ellipsometry is very sensitive to microscopic surface quality like surface roughness. Surface contaminants and roughness could have a strong effect on the reflected light.

Sample surfaces should be as clean and dry as possible. Normally it is enough to remove room dust from surfaces using a dust blower.

**Calibration of the system**

Three parameters should be determined for a RAE system before ellipsometric measurements: the polarizer ($P_s$) and analyzer ($A_s$) angles relative to the plane of incidence, the relative attenuation ($\eta$) of the AC component to the DC component of the detector signal caused by the signal processing electronics. The determination procedure of the three parameters is called calibration of the system.

A sample should be mounted and aligned to calibrate the system. A Si(100) wafer with 30 nm thermal oxide on top is used in our lab as the calibration sample. The Fourier coefficients of the detector signal ($\alpha$ and $\beta$) are then recorded as a function of the polarizer angle as well as the residual, which is defined by the relation $1-\alpha^2-\beta^2$. Both $\alpha$ and $\beta$ can be expressed as a function of the three parameters $P_s$, $A_s$ and $\eta$ together with $\psi$ and $\Delta$. [100] The calibration is usually done at 75° angle of incidence and 2.48 eV (500 nm wavelength) for UV-VIS light and 1.05 eV (1177 nm wavelength) for near-IR light. Fig. 3.8 shows an example of the measured and fitted Fourier coefficients and residual.
minimum of the residual parabolic curve is the polarizer angle which lies in the plane of incidence. The fit curves agree extremely well with the measured data, implying that the ellipsometer system works in a nearly ideal situation. Accurate system calibration is necessary for accurate measurement data.

This calibration technique can be performed on any sample, if necessary. For in situ SE measurements the substrate was used as the calibration sample.

Data acquisition

After the system calibration, ellipsometric measurements of samples can be performed. All the samples investigated in the thesis were measured in a reflection mode from sample surfaces. The spectra range is normally chosen to be the range of the VASE system (0.7 – 5 eV). Three incident angles 65°, 70° and 75° are chosen for variable angle measurements, in the vicinity of Brewster angle (75° at 2.5 eV) for an air/c-Si interface. The maximum slit width is set to be 1700 μm with auto slit adjustment. Dynamic averaging is employed to increase the integration time of data acquisition for a high signal-to-noise ratio. All the ex situ measurements of organic thin films were performed with AutoRetarder. However, AutoRetarder is not available for in situ applications. The ellipsometric data of ultra-thin high-k films were acquired without AutoRetarder to reduce the acquisition time, since the measurements with AutoRetarder turn out to be exactly the same due to the fact that the Δ values here lie between 0° and 180°.
Errors in ellipsometric measurements

Errors in ellipsometric measurements can be divided into two groups: random and systematic. [96] Random errors (noise) seem to have little effect on the accuracy of the measured data and this effect can be reduced by averaging. Systematic errors can be caused by errors in the calibration of polarizer and analyzer positions, misalignment of the optical elements, errors in the determination of the incident angle, and errors in the wavelength calibration of the monochromator. Systematic errors greatly influence the accuracy of the measured data. A precise calibration of the system prior to measurements helps to reduce systematic errors to some extent. Practically it is extremely difficult to eliminate all systematic errors. As a result, systematic errors are commonly ignored.

3.3.1.4 Data analysis

Ellipsometry data are usually handled using linear regression analysis. This is described below. In the analysis, dielectric function modeling is necessary and optical modeling is employed to describe sample structures.

Optical model

The construction of an appropriate optical model for sample structures is one of the most important steps in ellipsometry data analysis. Fig. 3.9 illustrates various optical models used in the data analysis of ellipsometry for films grown on substrates. Fig. 3.9 (a) shows the simplest model for a film deposited on a bulk substrate. Then surface roughness (Fig. 3.9 (b)) and the interface (Fig. 3.9 (c)) between film and substrate are taken into account in the model. One dielectric function modeling is enough to represent the dielectric functions of an isotropic film. However, more dielectric functions modeling are required to describe anisotropic samples. Two dielectric function modeling are needed to represent the in-plane and out-of-plane dielectric functions for uniaxial samples. And three dielectric function modeling are necessary to model dielectric functions along three orthogonal axes.
Effective medium approximation (EMA)

An effective medium approximation (EMA) layer is used to model surface roughness, determining optical constants by an average of two or more sets of optical constants. Three EMA theories were proposed [104] by Aspnes choosing different materials as the host. Surface roughness has been successfully modeled by mixing 50% void and 50% material underneath. If the surface roughness layer is very thick, it is possibly necessary to use several layers, each with a different Bruggeman EMA fraction of void and the underlying material.

Cauchy model

The Cauchy dispersion formula is given by

$$n(\lambda) = A + B/\lambda^2$$

where \( n \) is the refractive index, \( A \) and \( B \) are fitting coefficients, and \( \lambda \) is the wavelength. Film thicknesses can be determined using the Cauchy formula in the transparent range (\( k = 0 \)) of the material.

Point-by-point fit

When film thickness is determined from the Cauchy model, point-by-point model is used to fit the optical constants one wavelength at a time. The fitted optical constants can be taken as reference spectra for a normal fit varying the optical constants of all wavelengths at a time. Gaussian functions are employed to model optical constants in a normal fit in the thesis. The Gaussian lineshape in \( \varepsilon_2 \) is defined as

$$\varepsilon_{n2} = A_n e^{-\left(\frac{E-E_n}{\sigma}\right)^2} - A_n e^{-\left(\frac{E-E_n}{\sigma}\right)^2},$$

(16)
\[
\sigma = \frac{Br_n}{2\sqrt{\ln(2)}}
\]  

(17)

where \(A_n\), \(E_n\) and \(Br_n\) are the fitted amplitude, energy position and broadening parameters of the \(n\)th oscillator, respectively. \(\varepsilon_i\) is then given according to the Kramers-Kronig relation.

The point-by-point model usually works well for isotropic samples.

**Multiple sample analysis**

Multiple sample analysis is often employed for anisotropic organic films due to a large number of fitting parameters. Ellipsometric data of several samples with different thicknesses are supposed to have the same optical constants. Those data are fitted together in multiple sample analysis so that the number of measured parameters exceeds that of fitting parameters, enhancing the accuracy of the determined optical constants. The disadvantage of multiple sample analysis is that this method can not determine differences in optical constants between different samples. Normally in multiple sample analysis each film thickness is above 30 nm because too thin organic films would exhibit a thickness dependence of optical constants because of the evolution in film structure and molecular orientation. Consequently, for \textit{in situ} SE spectra of CuPc films, single sample analysis is employed to investigate the dependence of optical constants on film thickness. All the SE data of ultra-thin high-k films were fitted using single sample analysis, which results in sufficiently precise optical constants for isotropic samples.

**Linear regression analysis**

Fig. 3.10 illustrates a flow chart of linear regression analysis in ellipsometry. A optical model is firstly constructed to describe sample structures and then the dielectric functions of each layer in the optical model are selected (if known) or modeled (if unknown). The fitting parameters are utilized to calculate \((\psi, \Delta)\) to fit the measured spectra. Then a fitting error MSE is evaluated, indicating how well the fit agrees with experimental data. The parameter MSE is defined as
\[
MSE = \sqrt{\frac{1}{2N-M} \sum_{i=1}^{N} \left( \frac{\psi_{\text{mod},i} - \psi_{\text{exp},i}}{\sigma_{\psi,i}} \right)^2 + \left( \frac{\Delta_{\text{mod},i} - \Delta_{\text{exp},i}}{\sigma_{\Delta,i}} \right)^2}
\]  

(14)

where \( N \) is the number of measured \((\psi, \Delta)\) pairs and \( M \) is the total number of real valued fit parameters.

The optical model or dielectric function modeling is optimized until the fitting error is sufficiently small. Finally the thickness and dielectric functions of samples can be determined with a minimum MSE. However, the result of a good fitting with a minimum MSE is not necessarily physically reasonable and hence should be further optimized.

In some cases, reasonable fitting or sufficiently low fitting error can not be acquired. This can be due to the following reasons.

(a) measured \((\psi, \Delta)\) spectra are not accurate,
(b) either dielectric functions or the optical model employed in data analysis are not appropriate,
(c) the sample has a depolarization effect.
The difficulty in data analysis can be seen later in the CuPc/In/Si sample system.

**Thickness determination of metal films**

Because there is no transparent range from 0.7 to 5.0 eV for metal films, Cauchy model can not be employed to determine thickness of In films. The thickness of In film is determined from the total frequency shift recorded by QCM and a ratio of the film thickness to the frequency shift. The investigation of Cu films gives rise to a ratio between the film thickness and the frequency shift of QCM. A frequency shift of 60 Hz corresponds to 1 nm Cu film. Taking the mass density of Cu and In into account, it is calculated that 1 nm In film corresponds to a frequency shift of 50 Hz.

### 3.3.1.5 Model to determine the average tilt angle of CuPc

A model has been developed to determine the average tilt angle of disk-like molecules with two perpendicular dipoles in the molecular plane (such as Pcs) in thin films from ellipsometric data. [105] Absorption intensity $I$ is proportional to the square of the transition dipole moment $\mu$ which induces the absorption. Assuming that the dipole moment of one optical transition has an in-plane projection $\mu_{xy}$ and out-of-plane projection $\mu_z$ relative to the substrate surface, the ratio of the out-of-plane to the in-plane absorption intensity is related to the ratio of the out-of-plane to the in-plane projection of the transition dipole moment as

$$\frac{I_z}{I_{xy}} = \left(\frac{\mu_z}{\mu_{xy}}\right)^2.$$  \hfill (18)

Suppose $\alpha$ is the tilt angle of CuPc molecules relative to the substrate surface. The Q band of CuPc molecules stems from the two transition dipoles nearly perpendicular to each other in the molecular plane. The out-of-plane ($z$ direction) projection of the transition dipole $\mu$ is $\mu \sin \alpha$. And the transition dipole projection along $x$- and $y$-direction is $\mu$ and $\mu \cos \alpha$, respectively. The in-plane absorption intensity is an integral over the in-plane orientation angle $\delta$:
\[
\int (\mu^2 \sin^2 \delta + \mu^2 \cos^2 \alpha \cos^2 \delta ) = \frac{1}{2} \mu^2 (1 + \cos^2 \delta) .
\] 

(19)

Thus the ratio of the out-of-plane to the in-plane absorption intensity is given by

\[
\frac{I_z}{I_{xy}} = \frac{\mu^2 \sin^2 \alpha}{1/2 \mu^2 (1 + \cos^2 \alpha)} = \frac{2\sin^2 \alpha}{1 + \cos^2 \alpha} .
\]

(20)

As the integrated area of the Q band in the extinction coefficient is proportional to the integral absorption intensity, the following equation is obtained

\[
\frac{A_z}{A_{xy}} = \frac{I_z}{I_{xy}} = \frac{2\sin^2 \alpha}{1 + \cos^2 \alpha} .
\]

(21)

\(A_z\) and \(A_{xy}\) are the integrated areas of the Q band for the out-of-plane and in-plane components of the extinction coefficient, respectively. Finally, the average tilt angle of molecules relative to the substrate surface \(\alpha\) can thus be estimated by

\[
\alpha = \cos^{-1} \left( \frac{2 - A_z / A_{xy}}{2 + A_z / A_{xy}} \right) .
\]

(22)

The error bar is determined by varying the \(A_z/A_{xy}\) ratio by 10% if not specified.

The limit in the model is that the estimated average tilt angle is far from the real one if molecules are almost lying flat. For an \(A_z/A_{xy}\) ratio of 0.1, the estimated tilt angle is 18°. Even if the \(A_z/A_{xy}\) ratio is as small as 0.03, a tilt angle of 10° is obtained. The two examples give us a clear expression about the limit of this model.

### 3.3.2 Reflection anisotropy spectroscopy (RAS)

Reflection anisotropy spectroscopy (RAS) is a non-destructive optical technique to investigate surfaces. [25-28] The principle and instrument of RAS systems are described in this section as well as some theoretical understanding.

#### 3.3.2.1 Principle

RAS measures the difference in reflection along two orthogonal axes in the surface plane:
\[
\frac{\Delta \tilde{r}}{\tilde{r}} = \frac{\tilde{r}_x - \tilde{r}_y}{(\tilde{r}_x + \tilde{r}_y)/2} = \text{Re}(\frac{\Delta \tilde{r}}{\tilde{r}}) + i \text{Im}(\frac{\Delta \tilde{r}}{\tilde{r}})
\] (23)

where \( \tilde{r} \) are the complex Fresnel reflection coefficients. Hence the technique is also named reflection difference spectroscopy (RDS). RAS signals are also complex with real and imaginary parts.

### 3.3.2.2 Instrument

Experimentally RAS can be considered as a development of ellipsometry [106-107]. RAS uses linearly polarized light reflected at nearly normal incidence onto the surface. The original RAS system without phase modulation was proposed by Aspnes [108]. Nowadays phase modulating RAS systems are often used and the scheme is shown in Fig. 3.11. [25] Light from the source passes through a polarizer, reflects on the sample surface, then goes through a photoelastic modulator (PEM) and an analyzer, through a monochromator, and finally hits a detector. The PEM introduces a phase retardation between linear polarizations parallel and perpendicular to the modulation axis. Phase modulating RAS makes it possible to measure both the real and imaginary parts of \( \frac{\Delta \tilde{r}}{\tilde{r}} \).

The optical axes of the polarizer and analyzer should be 45° inclined while the PEM modulation axis is set to be the same as the optical axis of the polarizer.

Fig. 3.12 illustrates the mechanism of PEMs. When stress is applied to an optically isotropic material, the material shows an optical anisotropy. This phenomenon is known as photoelasticity. And the birefringence induced by photoelasticity is proportional to the applied stress. The phase shift changes sinusoidally as a function of time with a PEM. A PEM can be fabricated by cementing a piece of crystal quartz and fused quartz. When an alternating voltage (AC) is applied on the crystal quartz with metal layers as electrodes, a resonance occurs along the long axis of the crystal. The resonant frequency of the transducer is determined by the size and shape of the crystal quartz, which is normally set to be 50 kHz. The amplitude of the resonance depends on the magnitude of the applied AC voltage. The resonance of the transducer gives rise to a periodic stain in the fused quartz. When the fused quartz is in tension (Fig. 44.
3.12 (a)) or compressed (Fig. 3.12 (b), a positive or negative phase shift occurs between the two components of the light at the resonant frequency. The strongest birefringence effect is in the center of the fused quartz.

The RAS setup in our lab is home built. A Xenon arc lamp is used as the light source to provide light with sufficient intensity from 1.5 eV to 5.0 eV. Aluminum coated concave mirrors are employed to collimate the emitted light from the lamp. Calcite Glain-air prism polarizers are used as the polarizer and the analyzer. A grating monochromator with the grating angle under computer control via a stepping motor is used. And it is placed after the analyzer in the optical path so that white light is available for optical alignment. A multi-alkali cathode photomultiplier tube (PMT) is used as the detector, which is designed for low light intensity applications due to the high gain and low noise. A lock-in amplifier is utilized to convert the photocurrent to a voltage signal, behaving as the electronics of the PMT detector.
3.3.2.3 Surface symmetry

Though RAS has been widely employed to investigate various surfaces and materials, a theoretical understanding of RAS is still under research, leading to difficulties in the interpretation of RAS spectra. However, some understanding of the dependence of RAS spectra on surface symmetry is available, providing important insights into surface investigations and processes.

Fig. 3.13 [25] illustrates atomic structures of various surfaces including (100), (111) and (110) surfaces of face centered cubic (FCC) crystals and (110) surface of body centered cubic (BCC) crystals. It is obvious that the (100) surface of FCC crystals is optically isotropic, resulting in no reflection anisotropy. The FCC (111) surface is optically isotropic derived from the following argument. The optical response of the FCC (111) surface along the direction inclined by an angle to the x axis (shown in Fig. 3.13 (b)) is expressed as

$$
\varepsilon (\theta) = \varepsilon_{xx} \cos^2 \theta + \varepsilon_{yy} \sin^2 \theta
$$

(24)

where $\varepsilon_{ij}$ is the $ij$ component of the dielectric tensor. As the (111) surface is three-fold symmetric, $\varepsilon (0) = \varepsilon (2\pi / 3)$. Then
\[ \varepsilon_{xx} = \varepsilon(0) = \varepsilon(2\pi/3) = \varepsilon_{xx} \left( \frac{1}{2} \right)^2 + \varepsilon_{yy} \left( \frac{\sqrt{3}}{2} \right)^2 \]  

and hence

\[ \varepsilon_{xx} = \varepsilon_{yy}. \]  

The (100) and (111) surfaces of the BCC crystals are found to be optically isotropic in the same manner.

The (110) surfaces of both the FCC and BCC crystals are clearly seen to be anisotropic from Fig. 3.13 (c) and (d). Therefore, the (110) surfaces become the primary focus of RAS studies. Similar to BCC, FCC crystal structures, the diamond cubic crystal Si has optical isotropic surfaces (100) and (111) and anisotropic surface (110).

A series of vicinal substrates are found to be optically anisotropic due to steps and terraces on the surface. [109-113] Therefore, vicinal surfaces are also widely investigated using RAS. Vicinal Si(111) wafers offcut toward [11-2] direction by 0.35°, 3° and 6° are used as substrates in this thesis. The offcut direction is
marked by the blue arrow in Fig. 3.14. These vicinal surfaces have contributions of RAS signal from the [110] surface and the RAS intensity is determined by the offcut angle. [8]

![Fig. 3.14 Offcut orientation of vicinal Si(111) surfaces toward [11-2].](image)

### 3.3.2.4 Data acquisition

For general measurements a rotatable sample holder with scales in degree is constructed to read the precise azimuth position of samples. For *in situ* experiments the manipulator marked with scales is designed to make 360° azimuth rotations of samples in the OMBD chamber possible.

Before each RAS measurement a good optical alignment of the system was obtained to make sure that the beam hits the centers of all the optical elements. RAS measurements were performed twice for one sample with an azimuth rotation of 90° and the effect of the optical elements and the measurement environment on RAS spectra can be removed by a substraction of the two spectra.
3.3.3 Setup

3.3.3.1 In situ setup combining SE and RAS

The *in situ* setup combining SE and RAS is shown in Fig. 3.15. The optical path of SE is indicated by the blue arrows. The polarizer is constructed on one side of the OMBD chamber, and the analyzer together with a detector on the other side. The incident angle is set to be 70°. Light goes through an optical fiber into the polarizer. The polarizer was connected to the computer by a cable as well as the analyzer and the detector. The input head of the cable connecting the polarizer is perpendicular to the plane of incidence as well as that of the analyzer. The optical path of RAS is marked in red. The RAS system is placed vertically beneath the chamber. The distance between the sample and the light source is around 1.4 m to ensure the near normal incidence of RAS. The sample is fixed facedown horizontally. The Knudsen cells are constructed at the bottom of the chamber. There is a distance of about 0.5 m between the sample and the Knudsen cells, large enough to deposit films with uniform thicknesses.

![Fig. 3.15 The *in situ* setup combining SE and RAS with the OMBD chamber.](image)
The growth rate and thickness of films are monitored by quartz crystal microbalance (QCM). When the desired thickness is reached, film growth is interrupted and spectra of SE and RAS are recorded. Two RAS spectra are recorded with a 90° rotation of the sample to remove the background effect.

The challenge of \textit{in situ} SE and RAS experiments is to obtain good alignments for SE and RAS simultaneously. The first step is to get SE signal as high as possible by fine adjusting of the positions of the polarizer and the detector. A fine adjustment of the sample via three screws on the manipulator is also possible. The difficulty of \textit{in situ} RAS alignments lies mainly on the achievement of the reflection beam through a small window hitting the center of the PEM. In addition, the rotation of the manipulator with the sample facedown should be in the plane perpendicular to the plane of incidence for RAS, so that after a rotation of 90° the spot of the reflected beam on the PEM is not much deviated from the one before rotation.

\subsection*{3.3.3.2 Vacuum ultraviolet spectroscopic ellipsometry (VUV SE)}

Fig. 3.16 illustrates a sketch of the VUV SE system at BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung). Synchrotron radiation is taken as the light source of ellipsometer. The energy range we use to characterize high-k films is from 4 eV to 10 eV. Samples are at first loaded into the load lock chamber and then transferred to the main chamber. The incident angle is around 67.5°, which is obtained by rotating the main chamber 20°. The rotation axis is parallel to the incident beam from synchrotron radiation.

The combination of VUV SE data with VASE data recorded in our lab gives ellipsometric data in a whole energy range of 0.7 - 10 eV. The parameters of VUV SE measurements can be fitted to make the <\varepsilon> curves overlap with those of VASE data in the range between 4 and 5 eV. These parameters include sample offset, analyzer offset, and the incident angle. In this manner, SE data from two ellipsometric systems can be combined.
3.3.4 Atomic force microscope (AFM)

Atomic force microscopy (AFM) is a technique to provide a 3D file of a surface in the nanometer scale. The big advantage of AFM is the capability to image surfaces of nearly any type of materials, such as metals, isolators, semiconductors and organics.

3.3.4.1 Principle

AFM is designed on the basis of measuring forces between the tip and sample. Fig.3.17 shows the force dependence on the tip-sample distance. If the tip is quite far away from the sample surface, almost no forces exist. When the tip comes closer to the surface, the attractive Van der Waals force is dominant. The Van der Waals force is dominantly repulsive if the tip is even closer, nearly in contact with the surface.
The tip in AFM is mounted at the end of a flexible cantilever. The force is measured by the spring constant of the cantilever and the tip-sample distance. Hook’s law describes the force in the following equation

\[ F = -kz \]  \hspace{1cm} (27)

where \( F \) is the force, \( k \) is the spring constant of the cantilever and \( z \) is the cantilever deflection.

![Diagram showing force and tip-sample distance](image)

Fig. 3.17 Relation between the force and the tip-sample distance. [114]

### 3.3.4.2 Instrument

A scheme of an AFM system coupled with an inverted optical microscope is illustrated in Fig. 3.18. [115] The optical microscopy gives simultaneously an optical image of the surface with the surface topography from AFM. A laser beam impinges on the back of the cantilever and is then reflected onto a photodiode detector to amplify the cantilever deflection. Thus the force between the tip and sample can be monitored. The relative motion of the tip to the sample is performed by a piezo scanner. In almost all the AFM operating modes, a feedback circuit, connected to a cantilever deflection sensor, keeps the tip-sample force at a constant value controlling the tip-sample distance. The amount of the feedback signal, measured at each scanning point, contributes to a third quantity in z direction-the surface topography.

AFM tips are usually made from Si or Si$_3$N$_4$ by micromachining technology. [116-118] Typical radius of tips is from a few to tens of nanometers.
3.3.4.3 Operating modes

Basically non-contact and contact modes are developed in the attractive and repulsive regime (shown in Fig. 3.17), respectively. If the net force between the tip and the sample is always repulsive and the tip is constantly in contact with the sample, this operation mode of AFM is a contact one. The tip-sample distance in a contact mode is normally below 0.5 nm. If the tip experiences only the attractive force with the sample and it is away from the sample surface, non-contact mode is employed with a tip-sample distance from 2 to 10 nm. If the tip-sample force changes from repulsive to attractive from time to time, the operation mode is named as intermittent-contact mode or tapping mode. The tip-sample distance in the tapping mode is also medium, from 0.5 nm to 2 nm.

Contact mode is used if flat and rather rigid samples are investigated, enabling the highest resolution. For loosely bound to the substrate and easily damageable materials, such as organics, tapping mode is employed. The cantilever is oscillating at a frequency close to its resonance frequency and the amplitude of oscillations is monitored. By maintaining a constant oscillation amplitude a constant tip-sample force is maintained. To get a high resolution in non-contact mode, a UHV environment is required to image the surfaces.
All the AFM images in the thesis were obtained in an intermittent contact mode (tapping mode) using the NanoWizard® I (JPK Instruments, Berlin, Germany) system. The probe tip was uncoated Si tip with a typical radius of 10 nm purchased from the MikroMasch company.

The roughness (rms) value shown in this thesis is a root mean square average of height deviations taken from the image plane, which is expressed as

\[ \sqrt{\frac{\sum Z_i^2}{N}}. \]  

(28)
4 Morphology of hydrogenated vicinal Si(111) substrates

Vicinal Si(111) surfaces present steps and terraces in different sizes and directions depending on the offcut angle and direction. [8,111] From the interplanar distance of bulk Si(111) 3.14 Å, the width of the single height step is estimated to be around 51 nm, 6 nm and 3 nm for the offcut angles 0.35°, 3° and 6°, respectively. This evaluation is confirmed by the experimental work that an average single step width of 10 nm was observed by UHV-STM for 1.8° offcut H-Si(111) toward [11-2] direction when a special chemical treatment was employed to achieve atomically flat and homogeneous H-Si(1 1 1) surfaces. [119]

In the chapter a proper wet chemical etching method (dip in 5% HF for 2 min) was found to obtain a smooth and homogeneous vicinal Si(111) surface. All the vicinal Si(111) substrates used in the thesis are then hydrogenated applying the same method.

AFM was employed to investigate the morphology of hydrogenated vicinal Si(111) surfaces using different passivation methods. After hydrogenation, the Si(111) surface was measured by AFM immediately to reduce the impact of re-oxidation in the ambient air. Fig. 4. 1 shows the morphology of Si(111)-6° passivated in 40% HF acid for different time. Fig. 4. 2 and Fig. 4. 3 present the morphology of Si(111)- 6° passivated in 5% and 1% HF acid, respectively. The roughness (rms) of hydrogenated Si(111) surfaces is given on the bottom of each image. It is found that Si(111)-6° passivated in 5% HF for 2 min results in the smoothest and most homogeneous surface as shown in Fig. 4.4. Fig. 4. 5 illustrates the morphology and roughness of Si(111)-0.35° passivated in 40% and 5% HF acid for 2 min. Both of them give rise to very smooth surfaces. So all the
vicinal Si(111) substrates are hydrogenated in 5% HF acid for 2 min to get a smooth and homogeneous surface.

All the AFM images in this chapter are scaled by 1000 nm × 1000 nm.

Fig. 4. 1 The morphology and roughness of Si(111)-6° passivated in 40% HF acid for (a) 30 s, (b) 2 min, (c) 5 min.

(a) (0.308 ± 0.046) nm    (b) (0.168 ± 0.065) nm     (c) (0.142 ± 0.038) nm

Fig. 4. 2 The morphology and roughness of Si(111)-6° passivated in 5% HF acid for (a) 30 s, (b) 2 min, (c) 5 min, (d) 10 min.

(a) (0.287 ± 0.082) nm    (b) (0.132 ± 0.020) nm     (c) (0.151 ± 0.062) nm    (d) (0.171 ± 0.041) nm
Fig. 4.3 The morphology and roughness of Si(111)-6° passivated in 1% HF acid for (a) 30 s, (b) 2 min, (c) 5 min.

(a) (0.568 ± 0.057) nm  (b) (0.219 ± 0.020) nm  (c) (0.304 ± 0.021) nm

Fig. 4.4 The roughness of Si(111)-6° surfaces passivated in different methods.

Fig. 4.5 The morphology and roughness of Si(111)-0.35° passivated for 2 min in (a) 40% HF acid, (b) 5% HF acid.

(a) (0.079 ± 0.007) nm  (b) (0.089 ± 0.008) nm

Atomic steps are not observed in the AFM images of hydrogenated Si(111)-6° surfaces. It is mainly due to the preparation method of Si surfaces. Normally the steps and terraces can be observed after the treatment of thermal annealing procedure, which means that the surfaces should be degassed for half an hour.
by raising the temperature slowly up to 700 °C, flashed to 1260 °C for 10 s, and cooled to 1060 °C for 1 min. However, Si surfaces here were passivated in HF. It was reported that an immersion in boiling water for 10 mins after HF etching resulted in atomically flat surfaces homogeneously covered with silicon monohydride (–SiH) while HF etched Si surfaces without the treatment in boiling water are atomically rough with a higher defect density. [120] The effect of the immersion in boiling water was confirmed by clearly observed atomic steps on H-Si(111)-1.8° surfaces via STM [119]. Furthermore, Higashi et al. [121] also found that HF etching produces atomically rough surfaces. This explains that HF etched Si surfaces do not display atomic steps here.
5 Optical Anisotropy of CuPc films on vicinal H-Si(111) substrates

Despite of the fact that groups of regular steps and terraces could not be observed for hydrogenated vicinal Si(111) surfaces prepared by a wet chemical etching method, it is interesting to know the influence of different vicinal Si(111) surfaces on the properties of organic films. Optical anisotropy together with molecular orientation of CuPc films grown on various vicinal Si(111) substrates was analyzed via SE and RAS in the chapter. The film morphology was investigated by means of AFM.

In order to investigate the influence of vicinal substrates on film structure, Si(111) with offcut angles of 0.35°, 3° and 6° are used as substrates in one growth run to exclude the impact of the growth parameters.

5.1 Out-of-plane anisotropy: SE results

Two samples of different thicknesses were coupled in the fitting for multiple sample analysis. The thickness of the samples produced in the first run is (35.4 ± 0.3) nm and the film thickness produced in the second run is (91.3 ± 0.6) nm.

Fig. 5.1 shows Ψ and Δ of 91 nm CuPc film on Si(111)-0.35°. The ellipsometry measurements were performed at incident angles between 65° and 75°. The fit agrees well with the experimental data. The refractive index (n) and extinction coefficient (k) of CuPc films on Si(111)-0.35° deduced from the model fit are presented in Fig. 5.2. Fig. 5.3 shows the extinction coefficient (k) of CuPc films on 3° and 6° offcut Si(111). The spectra of films on various vicinal Si(111) show a similar lineshape. The difference between the in-plane and out-of-plane components of the extinction coefficient indicates an out-of-plane anisotropy in the film. In-plane means parallel to the plane of the substrate and out-of-plane perpendicular to the substrate.
Fig. 5.1 $\Psi$ and $\Delta$ of CuPc films on Si(111)-0.35°. The scattered lines are experimental data at the incident angles of 65°, 70° and 75°. The solid lines are model fit.

Fig. 5.2 The refractive index (n) and extinction coefficient (k) of CuPc thin films on Si(111)-0.35°.

Fig. 5.3 The extinction coefficient of CuPc thin films on 3° and 6° offcut Si(111).

The relative intensity of the two absorption peaks in the Q band indicates that the CuPc films are $\alpha$-phase. The average tilt angle of molecules in the film on 0.35°, 3° and 6° offcut Si(111) is calculated to be 62.8° ± 3.6°, 42.8° ± 2.0° and 41.7° ± 2.0°, respectively.
5.2 In-plane anisotropy: RAS results

Fig. 5.4 presents the real parts of the RAS spectra of various vicinal Si(111) surfaces with native oxide. The hydrogenated surfaces easily reoxidize in air. As we know from Ref. [122], the hydrogenated and oxidized vicinal Si surfaces show almost the same RAS spectra. Hence the spectra in Fig. 5.4 describe the hydrogenated vicinal Si(111) surfaces quite well. The Si(111) surface is optical isotropic but the anisotropic Si(110) surface contributes to a small anisotropy of the vicinal Si(111) surfaces due to the offcut orientation. The RAS features appear in the range of 3.4 eV and 4.3 eV, which are the E$_1$ and E$_2$ electronic transitions of bulk silicon. It can be easily understood that the anisotropy strength increases with increasing offcut angles. The vicinal surface with larger offcut angles has bigger contribution from the anisotropy of the Si(110) surface, which is clearly seen in Fig. 5.4. The heights of the E$_2$ peak in the spectra for offcut angles of 3° and 6° are 0.23 and 0.48, respectively. This is in accordance with the conclusion that for very small offcut angles the magnitude of RAS feature is nearly proportional to the offcut angle [8].

Fig. 5.5 shows the RAS spectra of CuPc thin films on vicinal Si(111). The magnitude of the RAS features increases with increasing offcut angles, which indicates the influence of the substrate anisotropy on the film. Four RAS features are observed for 35 nm CuPc films. The two RAS features at around 2 eV (the insert of Fig. 5.5) are related with the Q band of CuPc, implying that the anisotropy comes from the CuPc film. This in-plane anisotropy suggests that CuPc molecules in the film are oriented with azimuthal alignment due to the step structures on vicinal Si(111) surfaces. If the molecules are randomly oriented, the film will be in-plane isotropic. The magnitudes of these features at around 3.3 and 4.6 eV are hundred times larger than those of vicinal Si(111) surfaces. The contribution from the B band of CuPc films in this energy range is rather small, which can be deduced from the magnitude of RAS features at the Q band. So the two RAS features are mainly related to the vicinal Si(111) surfaces. This behavior is similar to the one observed for PTCDA on GaAs(001) surface [31] and thus the much larger magnitude may predominantly be attributed to interference effect.
The spectra in Fig. 5.5 were measured at the angle with the maximum RAS intensity. Moreover, the angle position of the maximum intensity of the film anisotropy agrees with that of the substrate anisotropy. The substrate induced in-plane anisotropy of CuPc films indicates that CuPc molecules are aligned along the step edges on vicinal Si(111) surfaces.

![Fig. 5.4 Real and imaginary parts of RAS spectra of vicinal Si(111) surfaces.](image1)

![Fig. 5.5 The RAS spectra of 35 nm and 91 nm CuPc thin films on vicinal Si(111).](image2)

The RAS spectra of 91 nm CuPc films on vicinal Si(111) surfaces are more complicated. The RAS features at the Q band are not observable. The magnitude of the features at around 3.3 and 4.6 eV is much smaller. Furthermore, three additional RAS features are observed at around 2.4, 4.0 and 5.0 eV (marked by the arrows), which are caused by interference. From the simulation result performed in the same procedure as described in Subchapter 6.1.3, it is known that the anisotropy of 91 nm CuPc film on Si(111)-6° is negligible due to the shielding of the substrate anisotropy.
5.3 Film morphology: AFM image

Similar morphology of CuPc films grown on different vicinal Si(111) substrates are found by AFM. Fig. 5.6 illustrates an AFM image of 91 nm CuPc grown on 6° offcut Si(111).

![AFM image of 91 nm CuPc/Si(111)-6°](image)

Fig. 5.6 The morphology of 91 nm CuPc/Si(111)-6°.

**Conclusion**

In summary, CuPc films grown on hydrogenated vicinal Si(111) substrates were investigated by optical spectroscopy. The VASE data were fitted using a uniaxial model and the optical constants \((n, k)\) of CuPc films were determined. The difference between the in-plane and out-of-plane components of the optical constants indicates out-of-plane anisotropy and molecular orientation. RAS spectra of CuPc films show that their in-plane anisotropy increases with increasing offcut angles of vicinal Si(111). The much stronger RAS features of 35 nm films at around 3.3 and 4.6 eV imply that the molecules are aligned along the step edges of vicinal Si(111) surfaces. For 91 nm films the RAS features are weaker due to the reduced influence of the substrate on the top layers of the film.
In situ optical investigation of CuPc films on vicinal H-Si(111)

SE and RAS are both excellent tools for real time investigations of film growth process because of their surface sensitivity. In situ SE and RAS spectra of CuPc films with various thicknesses recorded simultaneously are analyzed and discussed in the chapter to investigate the evolution process of film structure, and optical anisotropy during film growth.

This chapter consists of two parts. In the first part in situ SE and RAS spectra are analyzed to investigate the optical anisotropy and molecular orientation of CuPc films grown on H-Si(111)-6°. The second part focuses on the effect of the surface modification layer on the properties of CuPc films. The OTS monolayer or PTCDA film were prepared on Si(111)-6° surfaces as a modification layer.

6.1 Optical anisotropy and molecular orientation of CuPc/H-Si(111)-6°

In situ SE and RAS spectra of CuPc/H-Si(111)-6° are shown and analyzed in the subchapter. In situ SE spectra are fitted separately to check whether the optical constants of CuPc films change with increasing thickness or not. In situ RAS spectra are analyzed to explore the impact of the surface anisotropy of H-Si(111)-6° on the in-plane anisotropy of CuPc films.

6.1.1 In situ SE spectra

Fig. 6.1 shows the imaginary parts of the pseudo dielectric function $\varepsilon_2$ of the in situ SE spectra of CuPc grown on Si(111)-6° for various thicknesses. The $E_2$ peak of Si at around 4.3 eV is very sensitive to changes occurring on the Si surface. Its intensity is strongly decreasing due to the deposition of molecules.
onto the surface. Even for only 1.2 nm CuPc film, the \( E_2 \) peak is obviously reduced as revealed in Fig. 6.1 (a). With increasing film thickness the intensities of both Si peaks at around 3.4 and 4.3 eV decrease and an accompanying shift towards lower energy is also observable. The features occurring at around 2 eV, on the other hand, are attributed to the Q band feature of CuPc. It is beneficial for its observation that the Si spectrum is featureless in the Q band energy range. The CuPc Q band features are clearly seen even for the film as thin as 1.2 nm confirming that SE has the capability to detect ultra-thin layers on the surface.

The Q band features increase with increasing film thickness up to about 30 nm. For films thicker than 30 nm the Q band features begin to decrease due to interference effects as can be clearly confirmed by the simulation of the spectra (shown in Fig. 6.1 (c)). The simulated spectra were obtained in the Wvase® software by taking the optical constants of CuPc and varying the film thickness. The change in \( <\varepsilon_2> \) for thicker films as seen in Fig. 6.1 (b)) is less pronounced compared to the thinner ones.

\( <\varepsilon_2> \) of the in situ SE spectra for CuPc grown on Si(111)-0.35° are very similar to those shown for CuPc grown on Si(111)-6°.

### 6.1.2 Fitting of SE spectra

The fitting procedure commenced with the fitting of the ex situ data obtained for the final film thickness since measurements at three incident angles were available and consequently the reliability in obtaining the optical constants for the optically anisotropic system is best. Thereafter the single incident angle in situ spectra were fitted using the ex situ results as starting point. The fitting of the ex situ data was performed using a uniaxial model and the extinction coefficient \( (k) \) obtained for CuPc thin films are presented in Fig. 6.2.

The average tilt angle of molecules relative to the substrate surface on 6° and 0.35° offcut Si(111) is calculated to be 41.5° ± 2.0° and 81.1° ± 6.5°. The reason that vicinal Si(111) surfaces induce a different out-of-plane molecular orientation from nearly flat Si(111) surfaces is still under investigation. It needs to be pointed out that the average tilt angle of molecules in CuPc/Si(111)-6° agrees very well
with the previous one step grown films. However, the tilt angle in CuPc/Si(111)-0.35° is not exactly the same, which turned out to be $62.8° \pm 3.6°$ for the one step grown films. This difference in the tilt angle could be ascribed to the difference in growth procedures. The films in this chapter were grown step by step with time intervals of about 4 hours for recording the SE and RAS spectra. For Si(111)-6° substrates the steps and terraces obviously play a more dominant role for determining the molecular orientation. Hence the same average tilt angle of

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**Fig. 6.1 (a)(b)** The imaginary parts of the pseudo dielectric function of the *in situ* SE spectra for CuPc/Si(111)-6° with different film thicknesses, (c) the simulation of $<\varepsilon_2>$ for thicker films.
molecules is achieved. In the case of nearly flat Si(111)-0.35° the growth methods could be the dominating factor for molecular orientation.

In addition, it should be mentioned that we have only one sample available for fitting in this study. This analysis leads to a higher uncertainty in the lineshape of the Q band than the previous multi-sample analysis, especially for the out-of-plane components. However, it is found that this higher uncertainty contributes scarcely to the average tilt angle of molecules.

Fig. 6.3 (a) presents the thicknesses of CuPc films grown on Si(111)-6° determined by different methods. The rectangular symbols indicate the thickness calculated from the frequency shift measured by QCM using the ratio 0.12 nm / Hz. The triangular ones (fit 1) are the thicknesses fitted by using an isotropic model taking the optical constants of the in-plane component of the ex situ fitting results (applying a uniaxial model for fitting the in situ data is complicated since data are available for only one incident angle). For films thicker than 45 nm, the thicknesses determined by QCM and fit 1 are in good agreement. However, fit 1 overestimates the thickness of thinner films. This implies that the optical constants of thinner CuPc films are different from those of thicker ones, which are actually underestimated due to an overestimation of the thickness. The difference in the thickness determined by QCM and fit 1 is illustrated in Fig. 6.3 (c) implying the trend in the change of the CuPc optical constants with increasing film thickness.
Fig. 6.3 (a) The film thicknesses of CuPc/Si(111)-6° determined by different methods. (b) The fitted extinction coefficient of fit 2 using the isotropic model. The two series of thicknesses are determined by QCM and fit 2 (these shown in brackets), respectively. (c) Difference in the thicknesses determined by QCM and fit 1. (d) Dependence of the integrated area of the Q band shown in (b) on the film thickness.

Fit 2 was performed using the isotropic model having both the film thickness and optical constants as fitting parameters. The fitted thickness is presented by the circles in Fig. 6.3 (a), showing the same slope as that by QCM but with a parallel shift. This parallel shift is attributed to the systematic error bar of applying the isotropic model for in situ data of the anisotropic CuPc films. The fitted extinction coefficients of representative thicknesses are illustrated in Fig. 6.3 (b). It can be seen that the lineshape of the Q band changes for different film thicknesses. The evolution of the lineshape can be divided into three groups. The first group shows an obvious valley between the two peaks in the Q band for films above 46 nm. The valley in the second group is rather shallow for films...
around 36 nm. There is no valley in the third group for films below 26 nm but the first peak at 1.8 eV reduces to a shoulder of the second peak at 2 eV. This change in the lineshape of the Q band suggests that structural changes occur in the film with increasing film thickness. Furthermore, the integrated area of the Q band in Fig. 6.3 (b) presents a decreasing trend with increasing film thickness, as shown in Fig. 6.3 (d). The trend in change is similar to that shown in Fig. 6.3 (c) supporting the validity of fit 2.

The isotropic model was also used to fit the in situ SE data of CuPc films grown on Si(111)-0.35°. However, good fitting results could not be obtained. This is because the films have a strong out-of-plane anisotropy caused by the standing molecules, which is outside the validity range of the isotropic model.

**6.1.3 In situ RAS spectra**

The real parts of the in situ RAS spectra of CuPc films grown on Si(111)-6° are illustrated in Fig. 6.4. The inset shows the RAS spectra of the substrate and ultra-thin films. The Si features at 3.4 and 4.3 eV are clearly seen for the Si(111)-6° substrate, the lineshape of which is changed due to the adsorbed molecules on the surface. The features at around 2 eV are attributed to the Q band of CuPc because Si itself is again featureless in this range. The pronounced Q band features of 1.2 nm CuPc film demonstrate the sensitivity of the RAS technique to the molecular deposition. In the higher energy range three features develop at around 3.4, 4.5 and 5.2 eV. The position of the third feature at around 5.2 eV shows a red shift due to interference effects. The RAS features of CuPc present the in-plane optical anisotropy of the grown film. The comparatively small Q band features indicate that CuPc related RAS features in the higher energy range should also be weak while three strong features are observed above 3 eV. The large magnitude of these three features for thicker films agrees with the previous one-step grown films.

The details of the Q band features in the RAS spectra are shown in Fig. 6.5 (a). The valley between the two peaks becomes more and more pronounced and the splitting between the two Q band features increases with increasing film
thickness. This phenomenon is also observed in simulated RAS spectra when taking the constant difference between the dielectric functions along x- and y-directions and varying film thickness. [123] Thus it is attributed to interference effect. The linear dependence of the two peak heights and the total integrated area on the thickness is shown in Fig. 6.5 (b). This means that the strength of the

Fig. 6.4 Real part of the in situ RAS spectra of CuPc/Si(111)-6° for different film thicknesses.

Fig. 6.5 (a) The Q band features in the RAS spectra of CuPc/Si(111)-6°, (b) the dependence of the peak heights and the integrated area on the film thickness.

RAS signal of CuPc films is linearly dependent on film thickness in the thickness range presented. The pronounced RAS signal implies a strong in-plane optical anisotropy of the films which is induced by the surface anisotropy of the Si(111)-
6° substrate. Here we interpret the in-plane optical anisotropy of CuPc films as a result of the in-plane order of molecular alignment. Note that the last three thicknesses show a smaller slope compared to all the others. This is probably due to the weakened substrate influence on the structure of top layers in the film. The order of the in-plane molecule orientation in the top layers is not as good as in the bottom. Hence the optical anisotropy of each 2.4 nm layer on the top is decreased.

For CuPc thicker films above 30 nm, the \textit{in situ} RAS spectra of representative thicknesses are illustrated in Fig. 6. 6 (a). The complicated lineshape of the RAS spectra is caused by interference effect. The inset presents the details of the Q band features. It does not show an obvious regularity in the lineshape of the Q band. The dependence of the integrated area of the Q band on the film thickness is illustrated in Fig. 6. 6 (b). An abrupt reduction occurs at the critical thickness of 34 nm then it starts to increase again with increasing film thickness. Giving a certain difference between the dielectric functions along \(x\), and \(y\) directions, the in-plane anisotropy of CuPc thin films can be simulated varying film thickness. This abrupt reduction is not found in the simulation, implying a structural change in the film. This agrees with the conclusion from the \textit{in situ} SE analysis. The extraordinarily large magnitude at 58.8 nm can be seen in both experiment and simulation which is ascribed to interference effect.

![Fig. 6. 6 (a) The \textit{in situ} RAS spectra of thicker CuPc films grown on Si(111)-6°. The inset shows the Q band features. (b) The dependence of the integrated area of the Q band on the film thickness.](image)
For comparison the in situ RAS spectra of CuPc films grown on nearly flat Si(111)-0.35° are presented in Fig. 6.7. The RAS features of Si(111)-0.35° are not noticeable due to the very small offcut angle. Only the three features above 3 eV are seen for thick CuPc films and extremely weak compared to those grown on Si(111)-6°. The Q band features of CuPc films are too weak to be observed. This suggests that the optical in-plane anisotropy of CuPc films grown on Si(111)-6° is indeed induced by the substrate anisotropy.

**Conclusion**

In short, in situ SE and RAS are combined to monitor film growth of CuPc on vicinal Si(111) substrates. The in situ SE data of CuPc/ Si(111)-6° are analyzed and discussed. The change in the lineshape of extinction coefficient and the abrupt increase in the Q band area imply that structural changes occur during film growth. The fitting of the ex situ SE data using the uniaxial model illustrates different molecular orientations. The average tilt angle of molecules relative to the substrate surface is calculated to be 41.5° ± 2.0° on Si(111)-6° and 81.1° ± 6.5° on Si(111)-0.35°. The in situ RAS spectra show that the substrate anisotropy leads to in-plane ordering of CuPc molecules and thus optical anisotropy of CuPc films grown on it. The RAS intensity of CuPc films is linearly dependent on film thickness in the range below 30 nm. Moreover, the abrupt decrease in the RAS intensity confirms the structural change deduced from the analysis of the SE data.
6.2 Effect of surface modification on film properties

In the last subchapter *in situ* investigation of CuPc on hydrogenated Si-6° was discussed. Here surface modified H-Si(111)-6° was used as substrate to see how the modification layer influences both the out-of-plane and in-plane molecular orientation of CuPc in thin films. Two surface modification methods were used: thermally evaporated PTCDA layers and chemically prepared OTS monolayer. Literature suggest that OTS forms upright standing monolayer [83-84] whereas PTCDA molecules are lying flat [56-57] on substrates. Reports have shown organic molecules grown on OTS are aligned more or less in a standing way [83] while those grown on PTCDA stack almost in a flat lying way. [59-60] Thus it is no doubt that both OTS and PTCDA influence significantly the out-of-plane molecular orientation of organic films. However, it is unclear that whether the surface modification layers show an impact on the in-plane orientation or not. It is possible that the modification layer presents some in-plane anisotropy resulting from the vicinal Si-6° substrate similar as CuPc (shown in the last subchapter) and hence influences the in-plane orientation of the top grown CuPc molecules.

6.2.1 OTS modification

It was reported that OTS monolayer could introduce upright standing molecules in organic electronic device thus greatly improve the carrier mobility. [83-84] Fig. 6.8 (a) illustrates that OTS monolayer leads to a stronger out-of-plane component than the in-plane one in the extinction coefficient on the Si-6° substrate with native oxide. And the corresponding average tilt angle of molecules relative to substrate surface is $69.3° \pm 4.1°$, larger than $41.5°$ on unmodified Si-6° surface. This agrees with the other reports that upright standing OTS monolayer greatly influences the out-of-plane molecular orientation in films grown on it. However, OTS monolayer does not present an obvious impact on the in-plane orientation of CuPc shown by the *in situ* RAS spectra in Fig. 6.8 (b).
The RAS spectrum of OTS/Si-6° is extremely similar as that of Si-6° without OTS monolayer. Furthermore, the RAS spectrum of 3.6 nm CuPc/OTS/Si-6° keeps nearly unchanged. For CuPc film as thick as 12.0 nm, only a shift in the background of RAS spectra is observed. The RAS intensity of Si features at 3.4 and 4.3 eV is well preserved but no Q band features of CuPc are seen. This could be explained by the phenomenon that the 12.0 nm CuPc films form random islands but not continuous films on OTS/Si-6°. Thus the in-plane random distributed CuPc islands do not show RAS features because of the in-plane isotropy. The OTS/Si-6° substrate was probably partly covered by CuPc molecules, leading to the RAS intensity of Si features as strong as the bare substrate.

Fig. 6.8 (a) Extinction coefficient of a 48.1 nm CuPc film on OTS modified Si-6° substrate. (b) In situ RAS spectra of CuPc films with various thicknesses deposited on OTS/Si-6°.

### 6.2.2 PTCDA modification

In the following CuPc films grown on PTCDA modified Si-6° substrate are mainly discussed.

#### 6.2.2.1 Optical properties of PTCDA

Fig. 6.9 (a) shows RAS spectra of PTCDA/H-Si-6° with different thicknesses and the inset is extinction coefficient of PTCDA films. For 6.4 nm PTCDA layers grown on Si-6° three features at about 2.3, 2.7 and 5 eV are easily found, which match the three strong absorption peaks of PTCDA. RAS spectra of PTCDA, by
a subtraction of the substrate spectra, are presented in Fig. 6.9 (b). The other two small features are additionally observed, corresponding to the weak absorption of PTCDA at 3.2 and 3.5 eV.

![Graphs](image)

Fig. 6.9 RAS spectra of (a) PTCDA layers on Si-6° and (b) PTCDA layers subtracting Si substrate.

### 6.2.2.2 Analysis of the in situ SE and RAS spectra

Fig. 6.10 shows imaginary parts of the in situ pseudo dielectric functions of CuPc thin films grown on 6.4 nm PTCDA using Si-6° as a substrate. The black curve is SE spectrum of hydrogenated Si-6°, showing two Si features at around 3.4 and 4.3 eV. For 6.4 nm PTCDA layers, the E₂ peak of Si at 4.3 eV decreases drastically due to adsorbed layers on the surface. In addition, two features are weakly seen at around 2.3 and 2.7 eV, which turn out to be absorption features of PTCDA layers. The Q band features of CuPc at around 2 eV are observable for films above 18 nm. This gives a first hint that CuPc molecules present a small tilt angle to the substrate surface.

Ex situ SE spectra of 59.3 nm CuPc films were recorded by VASE at three different incident angles of 65°, 70° and 75°. The fitted optical constants using anisotropic model are shown in Fig. 6.11. The out-of-plane components are much weaker than the in-plane ones. The average tilt angle of CuPc molecules relative to the substrate surface is calculated to be 19.7° ± 8.0° taking the formula (22).
Fig. 6.10 Imaginary parts of the \textit{in situ} pseudo dielectric functions of CuPc thin films grown on 6.4 nm PTCDA on Si-6°.

Fig. 6.11 Refractive index (n) and extinction coefficient (k) of 59.3 nm CuPc films grown on 6.4 nm PTCDA on Si-6°.

Fig. 6.12 presents thicknesses determined by different methods for the \textit{in situ} SE spectra. The final thickness 59.3 nm determined from \textit{ex situ} VASE spectra corresponds to the frequency shift 460 Hz determined by QCM, giving a ratio of 0.13 nm/Hz. Black rectangles are \textit{in situ} thicknesses calculated from this ratio and the frequency shift. Red circles represent thicknesses fitted in an isotropic model taking the in-plane components of optical constants shown in Fig. 6.11. Blue triangles indicate thicknesses fitted in an anisotropic model taking the optical constants in Fig. 6.11. It is seen that the blue triangles agree quite well with the black rectangles, both showing a linear dependence on the frequency.
shift with a slope of 0.13 nm/Hz. This means that the optical constants of CuPc films keep nearly the same for different thicknesses during growth as well as molecular orientation. The linear dependence is not presented by red circles because CuPc films here show a very strong out-of-plane anisotropy due to the PTCDA template.

![Graph](image)

**Fig. 6.12** Thicknesses determined by different methods.

**Fig. 6.13** Extinction coefficient (k) of 51.1 nm CuPc on 1.2 nm PTCDA on Si-6°.

When the thickness of PTCDA template layer decreased to 1.2 nm, a 51.1 nm CuPc film was prepared with the extinction coefficient shown in Fig. 6.13. The out-of-plane component is not as weak as that on 6.4 nm PTCDA. The average tilt angle of molecules is 36.6° ± 1.7°, in the range between 19.7° for the 6.4 nm PTCDA growth template and 41.5° for Si-6°. The average integrated area of the Q band for extinction coefficient (k) is defined as \( \overline{A} = \frac{2A_{xy} + A_z}{3} \) where \( A_{xy} \) and \( A_z \) is the integrated Q band area of the in-plane and out-of-plane k component, respectively. This quantity \( \overline{A} \) is proportional to the absorption, which is found be correlated with film density. [124] The intensity of absorption increases when the film density is increased. The parameter \( \overline{A} \) is calculated for CuPc films grown on three different substrates: H-Si-6°, 1.2 nm PTCDA/H-Si-6° and 6.4 nm PTCDA/H-Si-6°. And the magnitude of \( \overline{A} \) for the three samples is 0.4575, 0.4154 and 0.3846 whereas the corresponding average tilt angle of molecules relative to the substrate surface is 41.5°, 36.6° and 19.7°, respectively. Furthermore, the magnitude of \( \overline{A} \) corresponding to the average tilt angle of 62.8° and 81.1° for CuPc films on H-Si-0.35° shown in previous chapters is 0.4472 and 0.3788,
respectively. The relation between the magnitude of $\bar{A}$ (dependent on film density) and the average tilt angle of molecules is shown in Fig. 6.14. It is seen that the highest film density is obtained in the vicinity of 45°. As one stacking way of molecules could give rise to two different tilt angles with a sum of 90° (as 20° and 70° shown in Fig. 6.14 (b)), film density is expected to be symmetry with a central axis at 45°. Thus, the maximum or minimum of film density would be observed in the range of 45°. However, the reason that the highest density occurs at around 45° is not yet clear.

![Graph](image)

**Fig. 6.14 (a)** The dependence of the magnitude of $\bar{A}$ (the intensity of absorption) on the average tilt angle of molecules. (b) Two different tilt angles for one stacking way of molecules.

**In situ** RAS spectra of CuPc films grown on 6.4 nm PTCDA on Si-6° are presented in Fig. 6.15 (a). The RAS intensity of Q band features for CuPc on the PTCDA template is much weaker than that on Si-6°. For ~30 nm CuPc films, the height of Q band features is only 0.3 compared with 7 for CuPc on Si-6°. Similar to SE spectra, a shoulder is clearly observed at around 2.2 eV due to the PTCDA template. Fig. 6.15 (b) shows the RAS spectra of CuPc films on 1.2 nm PTCDA. The RAS intensity of Q band features is between the above two cases: without PTCDA and on 6.4 nm PTCDA. The dependence of the integrated area of the Q band in RAS spectra on film thickness is presented in Fig. 6.16. A roughly linear dependence is observed for CuPc films on 1.2 nm PTCDA. For the 6.4 nm PTCDA template, the linear dependence disappears. In addition, the RAS intensity is one order of magnitude lower resulting from the pre-covered PTCDA.
layers, which inhibits the effect of the surface anisotropy of vicinal Si-6° substrate on CuPc films.

Fig. 6.15 In situ RAS spectra of CuPc films grown on (a) 6.4 nm, (b) 1.2 nm PTCDA on H-Si-6°.

In addition, two more samples were prepared on 3.4 nm PTCDA with thicknesses of 55.8 and 100.5 nm, respectively. The optical constants of CuPc were fitted by coupling two samples together. The extinction coefficient is shown in Fig. 6.17, which confirms the considerably weak out-of-plane component. The average tilt angle of CuPc on 3.4 nm PTCDA is calculated to be 20.0° ± 8.0°, nearly the same as that (19.7°) on 6.4 nm PTCDA. It implies that 3.4 nm PTCDA is thick enough to fully cover the Si-6° substrate surface. Therefore, the
orientation of CuPc molecules is dominated by the PTCDA growth template with flat lying molecules.

The RAS spectra of CuPc films on 3.4 nm PTCDA are not presented here because they do not exhibit optical anisotropy as those in Fig. 6.15. It should be pointed out that the reproducibility of optical anisotropy of CuPc grown on PTCDA template is very low. This is dependent on whether the PTCDA molecules in the template layers on the Si-6° substrate show an in-plane ordering or not. Only when the PTCDA layers exhibit in-plane anisotropy as seen in Fig. 6.9, the following deposited CuPc molecules could have the chance to align and thus show in-plane anisotropy. However, it is more difficult to control the in-plane ordering of PTCDA molecules than CuPc due to the strong hydrogen bonding between neighboring PTCDA molecules.

Fig. 6.16 The dependence of the integrated area of the Q band in RAS spectra on film thickness.

Fig. 6.17 Extinction coefficient (k) of CuPc films on 3.4 nm PTCDA/H-Si-6° from the fit by coupling 55.8 nm and 100.5 nm films.

### 6.2.2.3 Growth mode of PTCDA

From the above results it is known that nearly flat lying CuPc molecules are found on 3.4 and 6.4 nm PTCDA but not on 1.2 nm PTCDA. The average tilt angle of CuPc on 1.2 nm PTCDA (36.6°) is quite close to that (41.5°) on H-Si-6°, which gives a hint that 1.2 nm PTCDA do not fully cover the H-Si(111)-6° surface. Thus it can be concluded that PTCDA molecules form a film on the H-
Si(111)-6° substrate in an island growth mode (Volmer-Weber mode or 3D growth). In the last decades there are plenty of reports on the PTCDA growth on various substrates. Sazaki et al. [119] found PTCDA films were grown in islands of Volmer-Weber type on the H-Si(111)-1.8° substrate at 150°C by molecular beam epitaxy (MBE) in an UHV chamber. Chen et al. [125] identified the growth process of evaporated PTCDA on H-Si(111) as a Volmer-Weber mechanism. Gustafsson et al. [126] concluded that for a thickness of 0.5-2 ML PTCDA molecules form islands on H-Si(001), leaving the substrate partly uncovered.

When the thickness is above 5 ML, a complete monolayer is formed and covers the substrate totally. In our case 1.2 nm is around 3-4 ML. These reports support our conclusion that 1.2 nm PTCDA does not cover the substrate completely. It also explains that the partly uncovered H-Si-6° substrate induce the medium in-plane anisotropy shown in the RAS spectra.

There are also reports that the growth of PTCDA on single crystal metal surface is in a layer-by-layer mode below 2 ML and then an island mode for thicker films [127-129], i.e., a Stranski-Krastanov mode. It indicates that the formation of the wetting layer of PTCDA is critically dependent on the surface conditions. On a well-defined surface such as a single crystal the wetting layer of PTCDA can be developed due to the strong molecule-substrate interaction. Thus the wetting layer of PTCDA is not observed on our hydrogenated Si surface by chemical etching.

**Conclusion**

Summarily, the effect of two methods of surface modification on film properties was under research. OTS monolayer was found to show a significant influence on the out-of-plane anisotropy but little impact on the in-plane anisotropy. The average tilt angle of molecules relative to the substrate surface changes from 41.5° ± 2.0° on H-Si-6° to 69.3° ± 4.1° resulting from the OTS monolayer. Nearly flat lying CuPc molecules are observed on the PTCDA layer thicker than 3.4 nm, giving an average tilt angle of 19.7° ± 8.0°. The RAS
intensity of the Q band features for CuPc on 6.4 nm PTCDA is much weaker than that on H-Si-6°. For 1.2 nm PTCDA both the out-of-plane and in-plane anisotropy of CuPc films are dominated by the vicinal substrate due to the partly uncovered substrate surface. The average tilt angle of molecules for CuPc on 1.2 nm PTCDA is $36.6° \pm 1.7°$, close to the angle of $41.5° \pm 2.0°$ on H-Si-6°. The RAS intensity of the Q band for CuPc/1.2 nm PTCDA is moderate compared with the other two cases.
7 In situ optical investigation of In-CuPc interface

Metal-organic interface is commonly found in organic electronic devices. Thus it is important to understand what happens at metal-organic interfaces. For metal growth on organic, metal could diffuse deeply into organic thin films [130-132], or form clusters [133-134] on top of organic films. Besides the chemical stable cases, it is also possible that metal reacts with organic films. [135-136] Aristov et al. [136] reported a strong diffusion of Indium into CuPc film and a product of In$_2$CuPc from chemical reactions.

The growth of In on CuPc films has also been investigated in our group. In situ Raman spectroscopy reveals a diffusion behavior of In into CuPc film but no chemical reaction was found. [137] The chemical and electronic structures shown by photoemission spectroscopy (PES) suggest that the In/CuPc system is not a reactive one. [138] Here in situ SE and RAS were employed to investigate the In/CuPc system from the electronic structure and the optical constants.

7.1 In situ SE spectra

Fig. 7.1 shows real and imaginary parts of the pseudo dielectric functions of in situ SE spectra for various In thicknesses grown on 27.0 nm CuPc film. For 0.5 nm In, nearly no changes in the spectra are observed except from a very small reduction of the peaks at around 2.5 eV. The reduction goes further with increasing In thickness until 4.6 nm. Then the pseudo dielectric functions jump to larger magnitudes in the region for a deposition of 6.9 nm In. Moreover, a strong change occurs in the energy range below 1.5 eV. For even thicker In films, the change shows similar trends as that of 6.9 nm In.

In other words, the in situ SE spectra of 0.5, 2.1 and 4.6 nm In on CuPc are similar to those of bare CuPc film. When the thickness of In increases further,
drastic changes in the spectra are seen. The in situ SE spectra of In on CuPc could be interpreted as follows. At first, the deposited In atoms diffuse into the CuPc film beneath, which explains the similarity between the spectra of In as thick as 4.6 nm on CuPc and those of bare CuPc film. After the diffusion reaches saturation, more deposited In atoms start to nucleate on the surface of CuPc film and In clusters are formed. As a result, strongly different SE spectra are shown when the In thickness is above 6.9 nm.

Fig. 7.1 Real and imaginary parts of the pseudo dielectric functions of in situ SE spectra for various In thickness grown on 27.0 nm CuPc film.

To fit the optical constants of In film on top, it is necessary to know those of the 27.0 CuPc film underneath. Thus, a CuPc film with the same thickness was deposited as a reference sample. The refractive index and extinction coefficient of the 27.0 nm CuPc film are shown in Fig. 7.2. The experimental and model fit data are presented in Fig. 7.3, implying a good agreement. Notice that the lineshape of the Q band here is different from that for the 58.8 nm film shown in Fig. 6.2 (a), but similar to that of the comparable thickness (26.4 nm) in Fig. 6.3 (b). It confirms the existence of the dependence of the Q band lineshape on film thickness.

The optical constants of In were reported from thin film measurements by Theye and Devant [139], as shown in Fig. 7.4 (a). Very thin (10 – 20 nm) In films were prepared by evaporation in ultra-high vacuum onto fused silica at 100 K. The films were slightly annealed up to 180 K and then cooled back to 100 K. Introducing N₂ gases into the vacuum to a pressure of 1 Torr, the samples were
then brought back at room temperature without granulation. These In thin films turned out to be continuous with good uniformity of thickness. The optical constants of these thin films are found to be not dependent on film thickness and agree well with those of much thicker (bulk like) films.

![Fig. 7.2 Refractive index (n) and extinction coefficient (k) of a 27 nm CuPc film.](image)

The optical constants of In (shown in Fig. 7.4 (a)) are utilized to fit film thickness taking the known optical constants of the 27.0 CuPc film shown in Fig. 7.2. Different optical models are employed to evaluate the SE data, such as a roughness layer on top, an interfacial EMA layer between In and CuPc, an ultra-thin In$_2$O$_3$ layer on the surface. None of these models gives a good or reasonable fitting. In all the cases the fit data in the near-IR range are largely deviated from the experiment, indicating that the optical constants of In shown in Fig. 7.4(a) might be incorrect for the specific thin film. As the optical constants of metal thin films are commonly known to be dependent on various film properties, like film
thickness, crystalline structure, surface morphology and grain size, the optical constants of the In specific film grown here should be firstly figured out.

One more sample of In thin film grown on Si was prepared as a reference. The film thickness is determined to be 46.0 nm from the calculation, which is comparable to the magnitude of 46.8 nm from SE data. The fitted optical constants using isotropic model are shown in Fig. 7.4 (b). The experimental and model fit data are presented in Fig. 7.5, exhibiting a very good agreement. Comparing with the literature data, the fitted extinction coefficient is much smaller, less than half of the magnitude in the range of 0.7 – 2 eV, whereas the refractive index is relatively larger in the region below 1 eV. In addition, the energy of the inter-band transition shifts toward a lower energy. The strong difference is attributed to totally different film morphologies. The 46.8 nm In film presents a significantly high roughness, as shown in Fig. 7.6 (a). Numerous islands in the size of hundreds of nanometers are observed with a height of about 100 nm. It is in expectation that the In film consisting of large islands exhibits different optical response from continuous and smooth In films.

The surface morphology of 13.8 nm In film grown on CuPc is presented in Fig. 7.6 (b) as well as that of 27.0 nm CuPc film in Fig. 7.6 (c). The CuPc thin film is continuous and quite smooth (roughness: 3.4 nm). When In film is grown on top, the smooth surface is preserved (roughness: 4.4 nm) but the island size increases obviously. The In film on CuPc shows a significantly different morphology from that on Si. Therefore, different optical response would be expected. Consequently, taking the optical constants of In film on Si to evaluate the SE data of the In/CuPc/Si system does not work successfully, either.
Fig. 7.4 Optical constants of In thin films: (a) literature data, (b) a 46.8 nm In film on Si.

Fig. 7.5 Experimental data and model fit of the 46.8 nm In thin film.

Fig. 7.6 AFM images of (a) 46.8 nm In film, (b) 13.8 nm In on 27.0 nm CuPc, (c) 27.0 nm CuPc.
As neither of the optical constants of In from the literature nor of the reference film on Si are suitable for In grown on CuPc, the last possibility is to model the optical constants of In directly. However, no good fitting from this method can be obtained. The failure of the method implies that the optical constants of CuPc film below should be modified. This supports the interpretation for the *in situ* SE spectra that the deposited In atoms firstly diffuse into the underneath CuPc film. As a result, the CuPc film with In atoms in the matrix shows different optical responses from the pure CuPc film. However, a solution to the optical response of CuPc with diffused In atoms inside has not yet been found.

It is possible to model the total optical response of the In/CuPc structure. The optical constants from a Point-by-Point fitting by a given film thickness are shown in Fig. 7.7. Fig. 7.8 presents experimental and model fit data of the In/CuPc structure, implying a good agreement. Varying the film thickness, the magnitude in extinction coefficient is changed but the lineshape is kept. Taking the optical constants in Fig. 7.7 as reference, the Gaussian Oscillator fitting gives rise to very similar results, implying a Kramers-Kronig consistency. It indicates that the optical constants in Fig. 7.7 can describe the total optical response of the In/CuPc structure very well. The band at ~ 2 eV is obviously ascribed to the Q band feature of CuPc. The absorption below the Q band should originate from In but the magnitude is much smaller than that of pure In films. The absorption between 2.4 and 5 eV, which could be attributed to In since the magnitude of k (~ 1.5) is close to that of In film as shown in Fig. 7.4 (b).

### 7.2 *In situ* RAS spectra

Fig. 7.9 presents real parts of *in situ* RAS spectra of the In/CuPc/Si system with various In film thicknesses. The Q band areas of the *in situ* RAS spectra are shown in Fig. 7.9 (b). The Q band feature of 0.5, 2.1 and 4.6 nm In on 27.0 nm CuPc in RAS are similar to that of bare CuPc film. This could be attributed to nearly unchanged CuPc film surface resulting from the In diffusion into CuPc film. A shoulder appears in the Q band at ~ 2.2 eV for 4.6 nm In, suggesting that
some In atoms start to form clusters on the CuPc film surface. For thicker In films, the Q band features of CuPc show rapidly reducing intensity due to the cover of CuPc by In. Therefore, RAS measures the optical anisotropy of In film instead of the CuPc film underneath. The features at higher energy (3 – 5.5 eV) present a red shift due to interference effect with increasing film thickness. The nearly featureless RAS spectrum of 11.5 nm In on CuPc implies that In films are optical isotropic.

![Graph 1](image1)

**Fig. 7.7** Optical constants of the In/CuPc structure from a Point-by-Point fitting. The dashed line is the in-plane component of the extinction coefficient for the 27.0 nm CuPc film.

![Graph 2](image2)

**Fig. 7.8** Experimental and model fit (Point-by-Point) data of the In/CuPc structure.

The change trend of the *in situ* RAS spectra is in accordance with that of the *in situ* SE spectra, confirming the conclusion that In atoms firstly diffuse into the beneath CuPc film and later form thin films on CuPc.
Fig. 7.9 Real parts of \textit{in situ} RAS spectra for various In film thicknesses on 27.0 nm CuPc film.

**Conclusion**

Briefly, the In/CuPc/Si system was investigated by \textit{in situ} SE and RAS. It suggests that In atoms diffuse into CuPc film at first and later form clusters on top of CuPc. The In clusters were confirmed by the film morphology revealed via AFM. It is not possible to find a solution to model the optical response of In and CuPc separately in the In/CuPc structure due to the diffusion of In atoms into the underneath CuPc film. The total optical response of the In/CuPc system can be described by modeled optical constants of one effective layer. However, there are challenges to interpret the effective optical constants. More efforts are needed to further understand the In/CuPc system and the interface.
8 Optical properties and aging effect of ultra-thin high-k films grown by ALD

Hf aluminate is one of the promising high-k candidates to replace SiO$_2$ as gate dielectric in microelectronic technology. Optical constants and bandgap of ultra-thin high-k films are determined by SE in the chapter. The influence of mixed layer and bilayer of HfO$_2$ and Al$_2$O$_3$ on bandgap is investigated and discussed. Film stability after storage in air is also explored.

8.1 Optical constants and bandgap

The thicknesses obtained for all the high-k films are listed in Table I. The optical constants (refractive index $n$ and extinction coefficient $k$) of each sample are determined from SE data using a Gaussian Oscillator model which implies Kramers-Kronig consistency. The model ensures the best match between fit and measured data which is of particular importance for evaluation of the ultra-thin films. The Tauc-Lorentz (TL) model [140] which has the advantage to deliver $E_g$ directly as a fit parameter was also tested and found to be unsuitable for application to ultra-thin films because of the larger mismatch between the best fit curve and measured data. Combinations of several Tauc-Lorentz functions and of Tauc-Lorentz with Gaussian functions were additionally tried leading also to higher error bars compared to the Gaussian model. Furthermore, $E_g$ becomes uncertain or even meaningless due to the superimposed functions and the high correlation of fitting parameters.

Figs. 8.1 (a-b) show the optical constants of mixed layers and reference samples HfO$_2$ and Al$_2$O$_3$. The refractive index of mixed layers increases with increasing Hf fraction in the range between pure Al$_2$O$_3$ and pure HfO$_2$. The change in the position of the onset of extinction coefficient indicates a related change in the bandgap.
Table I  Film thickness \( d \) and bandgap \( E_g \) are determined for as-received samples while \( d' \) and \( E_g' \) are values determined for aged samples after two months. \( \Delta d \) and \( \Delta E_g \) indicate the difference in \( d \) and \( E_g \) between aged and as-received samples. The error bar in thickness and bandgap is \( \pm 0.2 \) nm and \( \pm 0.02 \) eV, respectively.

<table>
<thead>
<tr>
<th>Sample</th>
<th>HfO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>MH2A8</th>
<th>MH4A6</th>
<th>MH6A4</th>
<th>MH8A2</th>
<th>BH2A8</th>
<th>BH4A6</th>
<th>BH6A4</th>
<th>BH8A2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d/)nm</td>
<td>7.4</td>
<td>7.3</td>
<td>10.5</td>
<td>10.8</td>
<td>9.7</td>
<td>8.9</td>
<td>11.8</td>
<td>8.1</td>
<td>7.6</td>
<td>9.6</td>
</tr>
<tr>
<td>( d'/)nm</td>
<td>8.9</td>
<td>8.7</td>
<td>12.0</td>
<td>12.6</td>
<td>10.8</td>
<td>9.8</td>
<td>12.7</td>
<td>9.6</td>
<td>8.8</td>
<td>10.1</td>
</tr>
<tr>
<td>( \Delta d )</td>
<td>1.5</td>
<td>1.4</td>
<td>1.5</td>
<td>1.8</td>
<td>1.1</td>
<td>1.1</td>
<td>0.9</td>
<td>1.1</td>
<td>1.5</td>
<td>1.2</td>
</tr>
<tr>
<td>( E_g/)eV</td>
<td>5.77</td>
<td>6.71</td>
<td>6.53</td>
<td>6.29</td>
<td>6.14</td>
<td>5.99</td>
<td>6.20</td>
<td>6.05</td>
<td>6.16</td>
<td>5.79</td>
</tr>
<tr>
<td>( E_g'/)eV</td>
<td>5.69</td>
<td>6.40</td>
<td>6.46</td>
<td>6.19</td>
<td>6.06</td>
<td>5.89</td>
<td>6.15</td>
<td>5.95</td>
<td>6.02</td>
<td>5.71</td>
</tr>
<tr>
<td>( \Delta E_g )</td>
<td>-0.08</td>
<td>-0.31</td>
<td>-0.07</td>
<td>-0.10</td>
<td>-0.08</td>
<td>-0.10</td>
<td>-0.05</td>
<td>-0.10</td>
<td>-0.14</td>
<td>-0.08</td>
</tr>
</tbody>
</table>

Fig. 8.1 (Effective) optical constants of mixed layer samples (a-b) and bilayer samples (c-d) including reference samples of pure HfO\(_2\) and Al\(_2\)O\(_3\).

The dependence of the absorption coefficient \( \alpha \) on the energy is expressed by the relationship [141-143]:

\[
\alpha = C(hv - E_g)^m / hv
\]

where \( C \) is an energy-independent constant, \( hv \) is the energy, and \( E_g \) is the optical bandgap. The exponent \( m \) is a constant which indicates the transition type: \( m = 1/2 \) and 2 for direct and indirect allowed transitions, respectively. Therefore one can plot \((\alpha E)^{1/m}\) versus energy \( E \), and the extrapolation of the linear part to the \( x \) axis provides the value of the
optical bandgap $E_g$. The absorption coefficient $\alpha$ is defined as $\alpha = 4\pi k/\lambda$. The optical bandgap can also be determined from the linear part in the plot of $(n\alpha E)^{1/m}$ versus $E$. [144-146] The investigated ultra-thin high-k films are found to show an indirect bandgap ($m = 2$), as seen in Fig. 8.2. For all the samples, the plot of $(aE)^{1/2}$ gives a value of $\sim 0.02$ eV lower than that of $(n\alpha E)^{1/2}$. All the values of $E_g$ listed in Table I are determined from the plot of $(n\alpha E)^{1/2}$.

Fig. 8.2 Tauc plots of $(n\alpha E)^{1/2}$ and $(aE)^{1/2}$ for a 7.4 nm HfO$_2$ film to determine the optical bandgap.

The bandgap of HfO$_2$ film is determined to be $(5.77 \pm 0.02)$ eV, in agreement with the reported values from 5.3 to 5.8 eV for ALD films [144,147-148]. The Al$_2$O$_3$ film reveals a bandgap of $(6.71 \pm 0.02)$ eV, which is again in the range of 6.4-7.1 eV observed for ALD films. [147-149] The bandgap of Hf$_x$Al$_{1-x}$O$_z$ layers is linearly dependent on the Hf fraction ($x$) between that of HfO$_2$ film (6.71 eV) and Al$_2$O$_3$ film (5.77 eV) (shown in Fig. 8.3 (a)). Yu et al. [147] found that the bandgap of mixed layers as determined via X-ray photoelectron spectroscopy (XPS) changes linearly with the Hf fraction. A linear relationship was also observed by Licitra et al. [148] employing spectroscopic ellipsometry in an energy range from 1.5 eV to 8.0 eV.

In the fitting of SE data for bilayer samples a single layer is used to describe the effective optical response of the whole structure, since one of the aims of this work is to investigate the influence of structure (mixed layer or bilayer) on the
bandgap. Therefore, the determined optical constants and bandgap are effective values for the whole ultra-thin bilayer structure.

Fig. 8.3 The dependence of (effective) bandgap ($E_g$) and refractive index ($n$) on Hf fraction for mixed layers (a-b) and bilayers (c-d).

The effective optical constants of bilayers are shown in Fig. 8.1 (c) and (d). The determined values of the effective $E_g$ are presented in Table I. Fig. 8.3 (c) illustrates that the effective $E_g$ does not show a linear dependence on its nominal HfO$_2$ thickness proportion in the bilayer structures. The simulation results of the effective $E_g$ for bilayer structures (HfO$_2$/Al$_2$O$_3$/H-Si) are shown in Fig. 8.4 (a), implying that the effective $E_g$ of bilayers decreases with increasing HfO$_2$ thickness proportion. The lower effective $E_g$ of BH4A6 compared to BH6A4 shown in Fig. 8.1(c-d) indicates that BH4A6 has actually a little larger HfO$_2$ thickness proportion than BH6A4. Both the simulation and experimental values of the effective $E_g$ for bilayers are lower than that of mixed layers with a similar Hf fraction. The simulation of different bilayer structures (HfO$_2$/Al$_2$O$_3$/H-Si: 2H8A and Al$_2$O$_3$/HfO$_2$/H-Si: 8A2H) in Fig. 8.4 (b) shows that the effective optical constants are dominated by the top layer. The lineshape and the magnitude of the effective extinction coefficients of bilayers are closer to those of the top layer, suggesting
that the top layer has a more pronounced influence on the total optical response of bilayer structures.

![Graph](image)

Fig. 8.4 (a) Experimental and simulated values of the effective optical bandgap of bilayers. (b) Simulated effective extinction coefficients of two different bilayer structures.

### 8.2 Aging effect

The SE spectra of the samples were first recorded 1 week after the deposition (as received), then they were measured again after two months. All spectra changed over time in a similar way. Fig. 8.5 (a) exhibits as an example the change in the measured data of sample MH2A8. A curve shift and weakened Si features at ~ 3.4 and 4.3 eV are observed in the pseudo dielectric function \(<\varepsilon_2>\). This phenomenon can be caused either by a thickness increase or morphological changes associated with an increased surface roughness. Fig. 8.5 (b) shows an AFM image of the aged sample MH2A8 exhibiting a very smooth surface with a roughness of about 0.2 nm. The smoothness of aged films excludes the possibility of increased surface roughness. As displayed in Table I all aged samples show an increase in film thickness. The average increase in film thickness is 1.25 nm. Furthermore, the aged samples present decreased refractive indexes and bandgaps as shown in Fig. 8.3. The bandgap is decreased by an average value of 0.08 eV except for pure Al<sub>2</sub>O<sub>3</sub>, which shows a
drastic reduction of 0.31 eV. The bandgap of aged mixed layers preserves its linear dependence on Hf fraction.

Fig. 8.5 Mixed sample MH2A8: (a) imaginary parts of the pseudo dielectric function, (b) AFM: surface morphology after aging. (c) HRTEM image of the aged sample BH6A4.

The aging effect is attributed to further oxidation of high-k films in atmosphere. Oxygen was reported to diffuse from the ambient into (HfO$_2$)$_x$(Al$_2$O$_3$)$_{1-x}$ films even when they were annealed in oxygen-rich N$_2$ at around 1000°C for 20 s. [150] The oxygen diffusion from the ambient is suppressed only when films were annealed in high vacuum. In a similar manner, oxygen can diffuse from ambient air which has a much higher oxygen concentration into high-k films kept in air for two months. Since the injection ratio of the metal precursor to the oxidant precursor during the ALD process is 1:1, the films were prepared
under oxygen-deficient conditions. Thus some oxygen is accommodated in the film, leading to an increase in film thickness as well as a decrease in refractive index and bandgap. A high resolution transmission electron microscopy (HRTEM) image of aged sample BH6A4 is shown in Fig. 8.5 (c). No interfacial layer is observed between Al$_2$O$_3$ and H-Si substrate, implying that oxygen diffusion from high-k films into Si substrate is inhibited due to the barrier layer Al$_2$O$_3$. [150-152] Heo et al.[153] observed that the refractive index of ALD grown SnO$_x$ films declines with increasing ratio of oxygen. This supports our conclusion that the decrease in refractive index for the aged films is due to an enlarged amount of oxygen in the film composition.

Costina and Franchy [18] reported that the much lower bandgap of Al$_2$O$_3$ thin films compared to the bulk value is correlated with defect-induced states located in the band gap. More defects may occur in the structure of aged films resulting from the introduction of oxygen. This could explain the remarkable reduction of 0.31 eV in the bandgap of pure Al$_2$O$_3$ film.

**Conclusion**

In summary, two series of ultra-thin high-k samples were investigated using SE. The (effective) optical bandgap of both mixed layer and bilayer structures can be tuned by the film composition. The bandgap of mixed layers is linearly dependent on Hf fraction from 5.77 eV for pure HfO$_2$ film to 6.71 eV for pure Al$_2$O$_3$ film. The effective bandgap of bilayer structures does not show a linear dependence on HfO$_2$ thickness proportion and it is lower than that of mixed layers for a comparable Hf fraction. The film thickness increases, while the (effective) optical bandgap and refractive index decrease for aged films after storage of samples for two months in atmosphere. This is attributed to further oxidation of oxygen-deficient high-k films in air.
9 Summary

Two different materials were studied in the thesis: copper phthalocyanine (CuPc) and (HfO$_2$)$_x$(Al$_2$O$_3$)$_y$ high-k dielectrics. CuPc thin films were investigated by \textit{(in situ)} spectroscopic ellipsometry (SE) and \textit{(in situ)} reflection anisotropy spectroscopy (RAS) to determine the out-of-plane and in-plane optical anisotropy and molecular orientation, respectively. Ultra-thin high-k films prepared by atomic layer deposition (ALD) were researched employing VASE and VUV SE in the energy range of 0.7-10 eV.

In order to obtain a smooth and homogeneous hydrogenated surface, morphology of vicinal Si(111) wafers passivated in HF solutions varying the HF concentration and the dip time was investigated using AFM. It is found that a dip in 5\% HF for 2 min gives rise to the smoothest and most homogeneous hydrogenated vicinal Si(111) surfaces. All the substrates in the thesis were hydrogenated in the same procedure except from the one pretreated with OTS monolayer (ML), on which native SiO$_2$ was kept to improve the adhesion of OTS molecules.

Vicinal Si(111) wafers with three offcut angles (0.35\°, 3\° and 6\°) were utilized as substrates in one growth run to exclude the impact of various growth parameters of CuPc thin films by organic molecular beam deposition (OMBD). A significant influence of offcut angles on both out-of-plane and in-plane molecular orientation is found. Larger offcut angle results in stronger RAS signal of the Q band feature of CuPc (at ~ 2 eV), indicating higher in-plane anisotropy of CuPc film due to a preferential in-plane orientation of molecules. The average out-of-plane tilt angle of molecules relative to the substrate surface and in-plane anisotropy of CuPc films on various vicinal Si substrates are shown in Table II. A larger out-of-plane tilt angle together with extremely low in-plane anisotropy is reported for CuPc films on Si(111)-0.35\°. Close out-of-plane tilt angles are observed for films on Si(111)-3\° and -6\°.
In situ SE and RAS were combined to monitor the growth of CuPc films on vicinal substrates as well as on surface modified Si(111)-6°. The average out-of-plane molecular tilt angle and in-plane anisotropy of CuPc thin films are presented in Table III. The larger out-of-plane tilt angle of CuPc molecules in the in situ grown film on nearly flat Si(111)-0.35° is attributed to the difference in growth conditions compared with the one-step grown film on the same substrate. CuPc films of the in situ investigation were grown step by step with a time interval of about 4 hours for recording the SE and RAS spectra. For Si(111)-6° substrates, the substrate influence is dominant in the out-of-plane molecular orientation, resulting in almost the same molecular tilt angle.

Table II The average out-of-plane tilt angle of molecules and in-plane anisotropy of CuPc films on vicinal Si substrates with various offcut angles.

<table>
<thead>
<tr>
<th>offcut angle</th>
<th>out-of-plane tilt angle</th>
<th>in-plane anisotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.35°</td>
<td>62.8° ± 3.6°</td>
<td>extremely low</td>
</tr>
<tr>
<td>3°</td>
<td>42.8° ± 2.0°</td>
<td>medium</td>
</tr>
<tr>
<td>6°</td>
<td>41.7° ± 2.0°</td>
<td>high</td>
</tr>
</tbody>
</table>

Table III The average out-of-plane tilt angle of molecules and in-plane anisotropy of CuPc thin films for in situ growth on various substrates.

<table>
<thead>
<tr>
<th>substrate</th>
<th>out-of-plane tilt angle</th>
<th>in-plane anisotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Si(111)-0.35°</td>
<td>81.1° ± 6.5°</td>
<td>extremely low</td>
</tr>
<tr>
<td>H-Si(111)-6°</td>
<td>41.5° ± 2.0°</td>
<td>high</td>
</tr>
<tr>
<td>OTS/Si-6°</td>
<td>69.3° ± 4.1°</td>
<td>negligible</td>
</tr>
<tr>
<td>1.2 nm PTCDA/H-Si-6°</td>
<td>36.6° ± 1.7°</td>
<td>medium</td>
</tr>
<tr>
<td>3.4 nm PTCDA/H-Si-6°</td>
<td>19.7° ± 8.0°</td>
<td>low</td>
</tr>
<tr>
<td>6.4 nm PTCDA/H-Si-6°</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The fitting results of the in situ SE data of CuPc/H-Si(111)-6° including a change in the Q band lineshape and an abrupt increase in the Q band area imply
that a structural change occurs during film growth, which is confirmed by the abrupt decrease in the integrated area of the Q band in the \textit{in situ} RAS spectra. The RAS intensity of CuPc films is linearly dependent on film thickness in the range below 30 nm. It suggests that the preferential in-plane orientation of CuPc molecules is preserved for films as thick as 30 nm. When film thickness is further increased, the preferred in-plane ordering of molecules in the top layers decreases due to the weakened substrate influence on film structure.

The impact of surface modification on optical anisotropy and molecular orientation was investigated. Chemically prepared OTS ML with upright standing molecules shows a significant influence on the out-of-plane anisotropy with an average out-of-plane tilt angle of 69.3° ± 4.1° but little impact on the in-plane anisotropy. The featureless RAS spectra of CuPc/OTS/Si-6° indicate that molecules do not show a preferential in-plane orientation due to the fully covered Si-6° surface by the OTS ML. Nearly flat lying CuPc molecules are observed on thermally evaporated PTCDA layers thicker than 3.4 nm, giving an average tilt angle of 19.7° ± 8.0° due to the flat lying PTCDA molecules on Si. Meanwhile, the in-plane anisotropy of CuPc is much lower than that without PTCDA. 1.2 nm PTCDA layers do not form a continuous film on Si-6° and thus show an impact on the out-of-plane and in-plane molecular orientation of CuPc to some extent. The influence of the PTCDA layer thickness on molecular orientation can be explained by the island growth mode of PTCDA.

In-CuPc was chosen to be a sample system in order to study metal-organic interface employing \textit{in situ} SE and RAS. When In was evaporated onto CuPc film, both the SE and RAS spectra suggest that In atoms firstly diffuse into the CuPc film underneath and later form clusters on top. The In clusters were illustrated by the film morphology revealed via AFM. The difficulty in the SE fitting is that a solution can not be found to model the optical response of In and CuPc separately in the In/CuPc structure due to the In diffusion into CuPc.

Two series of ultra-thin high-k samples were deposited by ALD: mixed layers Hf\textsubscript{x}Al\textsubscript{1-x}O\textsubscript{z} and bilayers HfO\textsubscript{2} on Al\textsubscript{2}O\textsubscript{3}. The nominal thickness of each sample is 10 nm. The Hf fraction x varies as 0.2, 0.4, 0.6 and 0.8 in four mixed layers.
Hf$_x$Al$_{1-x}$O$_z$, respectively. The HfO$_2$ thickness in bilayer varies as 2, 4, 6 and 8 nm, respectively. The corresponding Al$_2$O$_3$ thickness in bilayer varies as 8, 6, 4 and 2 nm, respectively. Optical constants and bandgap were then determined using VUV SE. The (effective) optical bandgap of both mixed layer and bilayer structures is found to be tuned by the film composition. The bandgap of mixed layers is linearly dependent on Hf fraction from $(5.77 \pm 0.02)$ eV for pure HfO$_2$ film to $(6.71 \pm 0.02)$ eV for pure Al$_2$O$_3$ film. The effective bandgap of bilayer is lower than that of mixed layers for a comparable Hf fraction. Optical properties of bilayers are dominated by the top layer. Aging effect of high-k films was observed after storage of samples in air for two months, leading to an increase in film thickness and a decrease in bandgap energy. This is caused by further oxidation of the dielectric films due to the oxygen diffusion from ambient air to high-k films. The HRTEM image of an aged bilayer sample shows that the oxygen diffusion from high-k films to the H-Si substrate is inhibited by the barrier layer Al$_2$O$_3$ as no interfacial layer was observed between them.
References


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Selbständigkeitserklärung

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbstständig angefertigt, nicht anderweitig zu Prüfungszwecken vorgelegt und keine anderen als die angegebenen Hilfsmittel verwendet habe. Sämtliche wissentlich verwendete Textausschnitte, Zitate oder Inhalte anderer Verfasser wurden ausdrücklich als solche gekennzeichnet.

Chemnitz, den 14. November 2011

Dipl. Phys. Li Ding
Curriculum Vitae

Name: Li Ding
Date of Birth: Jan.14, 1984
Nationality: Chinese
Gender: female

Vettersstr. 72/311
09126, Chemnitz
Phone: +49-371-531 37492
Email: li.ding@physik.tu-chemnitz.de

Education
07.2008-
Ph. D student in Chemnitz University of Technology, Germany
08.2006-06.2008
Diplom of Physics, RWTH Aachen University, Germany
09.2002-06.2006
Bachelor of Science, Zhejiang University, China

Research Experience
07.2008-
Ph. D thesis: “Optical anisotropy and molecular orientation of organic thin films and bandgap of ultra-thin high-k films” in the group of Semiconductor Physics (Prof. Dr. Dietrich R. T. Zahn), Chemnitz University of Technology, Germany
02.2007-04.2008
Diploma thesis: “Infrared spectroscopic study of intermolecular interaction and molecular orientation in perylene films” in the I. Institute of Physics (IA) (Prof. Dr. Matthias Wuttig), RWTH Aachen University, Germany
10.2005-05.2006
Bachelor thesis: “Magnetic, structural and optical properties of transition metal doped ZnO films” at Zhejiang University, China
04.2004-05.2005
Subject “Aggregation of Atoms on Liquid Substrates” in Student Research Training Program of Zhejiang University

Teaching Experience
08.2005
Assistant teacher in the summer school of physics at Zhejiang University

Language Skills
Chinese: Mother tongue
English: fluent, TOEFL score 623 taken in 08.2005
German: Score 2.3 (good) of Deutsche Sprachprüfung für Studierende in englischsprachigen Master-Studiengängen (DSM) in 08.2007

Honors
2004-2005
The second prize scholarship (top 5%), Excellent Student Scholarship, Ferrotec scholarship, Zhejiang University
2003-2004
The second prize scholarship (top 10%), Zhejiang University
2002-2003
National Fellowship, China
Publications