Control of pentacene thin film growth by supersonic molecular beam deposition

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Control of pentacene thin film growth by supersonic molecular beam deposition

Proefschrift

ter verkrijging van het doctoraat in de Wiskunde en Natuurwetenschappen aan de Rijksuniversiteit Groningen

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Contents

Chapter 1 ..................................................................................................................... 1
  1.1 Organic semiconductors in general................................................................. 2
  1.2 Overview of pentacene thin film studies......................................................... 2
    1.2.1 The pentacene molecule ................................................................. 3
    1.2.2 Initial growth of a thermally sublimated pentacene thin film ............... 4
    1.2.3 Effects of the substrate surface on pentacene growth ......................... 5
    1.2.4 Polymorphs of pentacene thin films............................................... 8
    1.2.5 Defects in pentacene thin films ..................................................... 9
    1.2.6 Supersonic molecular beam deposition of pentacene thin films ........... 11
  1.3 Purpose of the present research................................................................. 13
  1.4 Outline of the thesis..................................................................................... 14
References ............................................................................................................. 17

Chapter 2 ............................................................................................................. 21
  2.1 Supersonic molecular beam deposition ....................................................... 22
  2.2 Atomic force microscopy ........................................................................... 26
    2.2.1 Contact mode atomic force microscopy ............................................ 28
    2.2.2 Tapping mode atomic force microscopy ............................................ 31
  2.3 Contact angle measurement........................................................................ 34
Chapter 3........................................................................................................37

3.1 Introduction .................................................................................................. 38
3.2 Pentacene submonolayer growth on SiO\textsubscript{x} by supersonic molecular beam deposition................................................................. 39
  3.2.1 SiO\textsubscript{x} substrate preparation.................................................. 39
  3.2.2 Characterization of the supersonic molecular beam by time of flight mass spectroscopy.............................................................. 40
  3.2.3 Growth of pentacene submonolayers on SiO\textsubscript{x}................. 42
3.3 Investigation of pentacene submonolayer growth......................... 44
  3.3.1 Formation of pentacene islands............................................................ 44
  3.3.2 Morphological evolution of the pentacene submonolayer ....................... 54
  3.3.3 Crystallinity of first pentacene monolayer ........................................ 56
3.4 Conclusions .................................................................................................. 58

References ........................................................................................................... 59

Chapter 4...........................................................................................................63

4.1 Introduction .................................................................................................. 64
4.2 Experiments .................................................................................................. 65
4.3 Investigation of pentacene submonolayer growth with different E\textsubscript{k} and θ at RT.............................................................. 66
  4.3.1 Evolution of pentacene submonolayer morphology... 66
4.3.2 Investigation of pentacene island size and critical nucleus size................................................................. 73

4.4 Pentacene submonolayer growth with different $E_k$ and $\theta$ at 200K ........................................................................................................... 77

4.5 Conclusions .................................................................................. 81

References.........................................................................................82

Chapter 5.................................................................................................85

5.1 Introduction ..................................................................................... 86

5.2 Experiments..................................................................................... 88

5.3 Investigation of the morphology of pentacene films grown on a SiO$_x$ surface patterned with Au electrodes................. 89

5.4 Electrical characterization of pentacene ultrathin film based field effect transistors ......................................................... 97

5.5 Conclusions ..................................................................................... 102

References............................................................................................ 103

Summary ..............................................................................................107

Samenvatting .....................................................................................111

Acknowledgements ...........................................................................115

List of Publications ...........................................................................119
Chapter 1

Introduction

In the past decades, pentacene was intensively studied and identified as one of the most promising organic semiconductors for future device applications. However, various challenges concerning device reliability and electronic performance have to be met to reach the satisfactory levels for real applications. So far, there is wide agreement that achieving high quality pentacene crystalline thin films with large single crystalline grains and less grain boundaries is the most essential and effective way to improve the quality of devices such as pentacene thin film-based field effect transistors. In this chapter, I shall review past studies of the initial growth of pentacene thin films prepared by thermal sublimation and of the various polymorphs observed for this deposition method. I shall also illustrate how the growth is influenced by the specific substrate surface, what defects arise in the pentacene layer and how they influence charge carrier mobility. Next, I shall discuss some recent studies of pentacene thin films grown by supersonic molecular beam deposition as well as the latest achievements on pentacene transistors based on these films. Finally, I shall describe the purpose of the research presented in this thesis and give a brief introduction to the various chapters.
1.1 Organic semiconductors in general

Organic semiconductors were first discovered in the 1950’s and they include polymers, such as polyacetylene, polypyrrole and polyaniline, and oligomers, such as pentacene, rubrene and antracene. All have a conjugated \( \pi \) orbital structure, which is formed by the covalently bonded carbon atoms via alternating single and double bonds. In the conjugated \( \pi \) orbital structure, due to \( sp^2 \) carbon hybridization, the \( p_z \) orbital, which is occupied by an unpaired electron, can bond with another \( p_z \) orbital from a neighbouring carbon atom to form the bonding and anti-bonding levels, which are also called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively. Electrons from \( P_z \) orbitals have a high probability to delocalize along the overlapping \( \pi-\pi \) orbitals. Charge carrier transport in organic semiconductors with either amorphous or polycrystalline structure is believed to be based on the thermally activated carrier hopping mechanism \([1, 2]\) and measured mobility values are normally lower than 1 cm\(^2\)/Vs. However, in the single crystal organic semiconductors, the band like carrier transport is the dominating mechanism to explain the higher carrier mobility (normally >> 1 cm\(^2\)/Vs) and the mobility decreases with increasing the temperature \([2, 3]\). Currently, the advantages of organic semiconductor materials have been widely recognized: 1) the film preparation is easier and cheaper than for inorganic semiconductors; 2) the films have excellent mechanical flexibility and are light weight. For real industrial application, organic semiconductor materials are expected to be used in a number of products, such as large-area flat panel displays, radio frequency identification tags and smart cards.

1.2 Overview of pentacene thin film studies

The first pentacene thin film based field effect transistor was built by G. Horowitz et al. in 1992 \([4]\), stimulated intensive studies of pentacene thin film growth and relevant electronic devices by scientists in the field of physics, chemistry and materials science. Some of the most important achievements in the field of pentacene thin film based transistors have been the following: in 1997, Y. Y. Lin et al. \([5]\) first reported a high hole mobility (\( \sim 1.5 \) cm\(^2\)/Vs) measured in pentacene transistors, which were
Introduction

Fabricated with thermally sublimated pentacene thin films on the octadecyltric-chlorosilane (OTS) pre-treated SiO$_2$ surface. Then, in 2002, H. Klauk et al. reported a better performance of pentacene transistors with polymer dielectric material as a gate [6]. These devices were not only characterized by a high mobility, approaching $\sim 3 \text{ cm}^2/\text{Vs}$, but also by a low threshold voltage and a large on/off ratio. Recently, in 2006, S. Lee et al. realized an even higher hole mobility of $\sim 5 \text{ cm}^2/\text{Vs}$ in pentacene transistors by increasing the number of hydroxyl groups in the polymeric dielectric gate material [7]. Presently, pentacene is widely considered as a research model for the fundamental studies of semiconducting oligomers. Enormous efforts have been devoted to understanding the pentacene thin film growth mechanism and to developing new methods for the controllable production of high quality pentacene crystalline thin film since it is the crystalline quality of the film which is regarded as a crucial factor for the performance of pentacene based electronic devices.

![Chemical structure of pentacene](image)

Figure 1-1: Chemical structure of pentacene

1.2.1 The pentacene molecule

Pentacene ($\text{C}_{22}\text{H}_{14}$) is an organic molecule with a planar configuration formed by five fused benzene rings as shown in figure 1-1. Thermally sublimated pentacene molecules can be physically adsorbed on chemically inert surfaces, such as SiO$_2$, Al$_2$O$_3$ etc [8, 9] via van der Waals force interaction. After adsorption, the pentacene molecules aggregate into the solid condensed phase via the surface diffusion. On a chemically inert surface, the first layer of adsorbed pentacene molecules normally presents a
standing up orientation, testifying to the weak interaction between the molecules and the substrate. It was found that also in the following layers, that the pentacene molecules still pack in the standing up orientation, indicating a relatively weaker interaction among the pentacene molecules between different layers than that within the same layer [10, 11]. However, the standing up orientation can be changed to lying down if the surface changes from chemically inert to reactive, such as a cleaned silicon surface with unsaturated dangling bonds [12, 13], or to a metal surface, such as the surface of Au [14] or Cu [15], which may lead to the strong electronic interaction at the interface.

1.2.2 Initial growth of a thermally sublimated pentacene thin film

The initial growth of a pentacene thin film, especially the formation of the first monolayer, has attracted much interest from researchers based on two main reasons: 1) a controllable high quality pentacene monolayer can be used as a template for growing the subsequent pentacene layers with better quality; 2) the first several pentacene layers grown next to the electrode are the channel of charge transport and their crystalline quality can significantly affect the carrier mobility [16, 17, 18] measured in the pentacene transistors. In the formation of the first pentacene monolayer, nucleation, molecular island formation and island coalescence are three main steps, which can be identified from the surface morphology evolution. Pentacene nucleation and island formation on a SiO₂ substrate were systematically studied by S. Pratontep et al. [19, 20]. In that work, the nucleation density and average molecular island size were both found to be dependent on the applied deposition rate and substrate temperature, indicating a consistency with the rate equations formalism proposed by J. A. Venables et al. [21]. They established a correlated island growth mode and described it as a relation between the molecular diffusion length (λ_D) and inter-island distance (λ_NN). The authors pointed out that a correlation growth only occurred if 2λ_D > λ_NN, which meant that the molecular diffusive areas around the neighbouring molecular islands overlapped. Consequently, correlated island growth can lead to a uniform island size distribution. In addition, the molecular island structure also showed a dependence on the applied deposition rate and substrate temperature. With increasing deposition rate or decreasing substrate temperature, the
molecular island structure was found to shift from fractal to non-fractal. Furthermore, this structure transition was also noticed when changing the substrate hydrophilicity [22, 23].

The pentacene critical nucleus size is one of the important parameters in the study of the pentacene initial growth and indicates that one molecule less than the number of molecules is necessary to form a stable nucleus on the surface. The critical nucleus size of the thermally sublimated pentacene on SiO$_2$ at room temperature was first calculated and reported by R. Ruiz et al. [24] by using the general scaling function, established by J. G. Amar and F. Family [25]. In this work, it was found that the critical nucleus size was three pentacene molecules meaning that at least four molecules were needed to form a stable nucleus. Later on, M. Tejima et al. [26] investigated the pentacene critical nucleus size for growth at different temperatures and found that it decreased from 3 molecules, when the substrate was held in the temperature range from 304 or 342 K, to 2 molecules, when the substrate temperature was between 223 or 249 K during pentacene nucleation. The temperature induced change in critical nucleus size was also studied by D. Choudhary and co-workers in their computational simulation of pentacene initial growth [27]. They suggested that the increase in number of molecules needed for forming a stable nucleus when increasing the substrate temperature was due to the decrease of the molecular sticking coefficient.

During formation of the first monolayer, second layer nucleation often appeared when the coverage > 0.5 ML and indicated a trend towards island growth mode for the thermally sublimated pentacene monolayer. This phenomena has been demonstrated by both experimental work [28] and theoretically simulation [29]. In the work reported by F. J. M. Heringdorf etc [30], a simple model for explaining the 3-D island growth was presented. It stated that the second nucleation only takes place when the formula of $\pi R_c^2 N_1 < 1$ is satisfied. $N_1$ is the nucleation density; $R_c$ is the critical size of formed molecular island in the pentacene submonolayer and strongly dependent on the deposition rate (F), surface diffusion constant (D$_s$), and the diffusion barrier existing at the island edge, namely the Ehrlich - Schwoebel barrier [31].

1.2.3 Effects of the substrate surface on pentacene growth
In pentacene thin film growth, the nature of the substrate surface plays a very important role in determining the molecular orientation, the adsorption probability and the surface diffusivity. In 2001, F. J. M. Heringdorf and co-workers first successfully produced very large pentacene single crystal grains with an average size of ~ 0.1 mm by thermally sublimating the pentacene molecules on a cyclohexene (C₆H₁₀) pretreated Si surface [30]. This achievement indicated a very promising future for producing electronic devices based on films with large single crystalline pentacene grains. Recently, S. Pratontep et al. presented a fundamental study of pentacene sub-monolayer growth (coverage < 40%) on organic and inorganic surfaces where they compare the surface morphology obtained on various substrates [22]. In this work, the pentacene nucleation density was found to be higher on polymer-covered surfaces than on inorganic dielectric surfaces. This suggested a relatively higher surface diffusivity on organic substrates, such as PMMA, than on inorganic substrate surface, such as SiO₂ or Al₂O₃. The resulting island structure switches from fractal to non-fractal when changing the pentacene deposition from SiO₂ or Al₂O₃ to PMMA. This behaviour was confirmed by a similar work of B. Stadlober et al. [23] and explained by the higher island edge diffusion for pentacene molecules on a PMMA surface. Furthermore, more significant re-evaporation of the molecules was found to occur on SiO₂ than on PMMA indicating a lower pentacene adsorption energy. However, a contradicting result was presented by A.C. Mayer et al. [32] who used synchrotron x-ray scattering to study pentacene growth on SiO₂ and on hexadecyltrichlorosilane (HTS) treated SiO₂. They claimed that the pentacene desorption is more facile from HTS than from a UV ozone treated SiO₂ surface and attributed the discrepancy between their results and those obtained by S. Pratontep et al. to the different SiO₂ surface treatment.

Recently, self-assembled monolayers (SAM) are widely used as buffer layer on the dielectric gate material for growing pentacene thin films in transistor fabrication. Several authors demonstrated that the SAM could directly influence pentacene submonolayer growth resulting in different morphologies and crystallinity at the interface, which then affect the charge mobility measured in the transistors. In 2002, M. Shtein and coworkers reported a study of pentacene growth on octadecyltrichlorosilane (OTS) modified SiO₂ and on O₂ plasma treated SiO₂ and of the charge mobility measured in devices based on such films [33]. In this work, they found a relatively higher hole mobility (~ 1.6 cm²/Vs) for the transistor made of a
pentacene thin film grown on the OTS pretreated SiO$_2$ than for that fabricated with a pentacene thin film grown on O$_2$ plasma treated SiO$_2$ ($\sim$ 0.5 cm$^2$/Vs). X-ray diffraction studies of these films found a significant fraction of flat-lying pentacene molecules in the thin film grown on the OTS pretreated SiO$_2$ but this feature was nearly absent in pentacene thin films grown on O$_2$ plasma treated SiO$_2$. The authors attributed the observed pentacene flat-lying configuration to a better adhesion between pentacene molecules and OTS pretreated SiO$_2$ surface and concluded that this configuration combined with the obtained higher hole mobility implied a possibly enhanced $\pi$-$\pi$ orbital overlap between the molecules. Recently, a similar work was reported by H. Yang et al. [34], who proposed a direct correlation between the crystalline structure obtained in the pentacene submonolayers deposited on SiO$_2$ surfaces, modified by hexamethyldisilazane (HMDS) and OTS SAMs, and the mobility measured in the corresponding thick film transistors. These authors found that compact pentacene islands with crystalline facets were formed on the HMDS modified SiO$_2$ surface, whereas fractal pentacene islands were produced on OTS modified SiO$_2$ surface. Correspondingly, a higher hole mobility ($\sim$ 3.4 cm$^2$/Vs) was obtained in transistors made of pentacene thin films grown on the HMDS modified SiO$_2$ than for those grown on the OTS modified SiO$_2$ ($\sim$ 0.5 cm$^2$/Vs). This large mobility difference was interpreted as resulting from the compact molecular islands with crystalline facets formed on the HMDS modified SiO$_2$ surface. These islands may behave like single crystalline grains with much less internal defects and more straight grain boundaries in the completed pentacene monolayer. On the contrary, the fractal molecular islands with complex divergent polycrystalline structure formed on OTS modified SiO$_2$ surfaces imply a larger concentration of internal defects and non-straight grain boundaries in the first completed monolayer and hence an inferior charge mobility performance in the corresponding pentacene transistors.

The substrate surface roughness is another important issue in the discussion of how the surface affects pentacene thin film growth and charge carrier mobility. In the work presented by Heremans and coworkers [35], the pentacene grain size was found to be dramatically decreased when increasing the substrate surface roughness and attributed to the reduction of molecular surface diffusivity and the decrease of the energy barrier for nucleation. Meanwhile, these authors also found that the hole mobility measured in the transistors made with thermally sublimated pentacene thin films could decrease from 0.49 cm$^2$/Vs to 0.04 cm$^2$/Vs by increasing the
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surface roughness. They explained that the charge carriers moving at the interface could be trapped in potential valleys due to the roughness and only those trapped in shallow minima could move out and drifted along a certain horizontal potential gradient. S. E. Fritz et al. reported a similar work studying the effects of dielectric surface roughness on the hole mobility in the transistors made of thermally sublimated pentacene thin films [36]. They discovered a surface morphology variation of pentacene thin film grown on SiO$_2$ surfaces, which had been intentionally engineered into different surface roughness. Typical fractal pentacene grains were found on the top layer of the thermally sublimated pentacene thin film, which was grown on a “smooth” SiO$_2$ surface. On the contrary, very small, nodular pentacene islands, without any visible crystal facets, were formed on the “rough” SiO$_2$ surface. By increasing the root mean square surface roughness from 0.2 nm to 1.5 nm, the charge carrier mobility in the pentacene thin film based transistor decreased from 0.31 cm$^2$/Vs to 0.02 cm$^2$/Vs.[36]

1.2.4 Polymorphs of pentacene thin films

So far, there are two main pentacene polymorphs found in the thermally sublimated pentacene thin films on SiO$_2$ as shown in figure 1-2, namely a bulk phase with an interplanar spacing, $D_b$, ~ 14.4 Å and a thin film phase with $D_b$ ~ 15.4 Å. In the bulk phase, the unit cell has a triclinic structure containing two pentacene molecules arranged in a herringbone configuration [37], whereas the thin film phase shows a similar herringbone configuration but with an orthorhombic crystal symmetry [38, 39]. In 1996, C. D. Dimitrakopoulos and co-workers reported a study of pentacene thin film growth by molecular beam deposition and of the related transistor performance [40]. By using X-ray diffraction, these authors discovered that the thin film and bulk crystal structures could coexist in the pentacene thin films grown on SiO$_2$. Successive studies of thin films grown from thermally sublimated pentacene found that the formation of different polymorphs is dependent on various factors such as the nature of the substrate surface [41, 42], the substrate temperature during growth [43] and the thin film thickness [39, 43, 44]. Recently, A. C. Mayer et al. also found that the thin film and bulk phase could simultaneously appear in the early pentacene nucleation period but their nucleation and following growth were completely un-correlated [45]. Until now, the true mechanism of pentacene
polymorphs formation is still under investigation. With respect to the pentacene transistor performance, coexistence of pentacene polymorphs in the thin film implies disorder and this kind of structure non-uniformity may behave as a charge transport barrier degrading transistor performance.

### 1.2.5 Defects in pentacene thin films

A pentacene polycrystalline thin film is generally defined as of better quality when showing large single crystal grains and low concentration of grain boundaries, impurities and dislocations. Understanding the formation of defects in the pentacene layers is very critical for further crystallinity improvement. Since in an OFET the pentacene layers closest to the interface function as the charge transport
channel, the quality of pentacene layer crystallinity has large implications for the pentacene transistor performance. Hence, possible defects close to the interface are even more significant than those in the more distant layers. In 2004, B. Nickel and co-workers reported a study of the dislocations in thermally sublimated pentacene thin films with a thickness ranging from 2 to 8 monolayers above the interface [46]. A relatively low density (~$0.5 \times 10^{11}/\text{cm}^2$) of dislocations was found in pentacene thin films grown on an OTS pre-treated SiO$_2$ compared to those obtained in the pentacene thin films grown on a cleaned SiO$_2$ or on a hydrogen terminated silicon surface. The authors also suggested that a high concentration of defects was a general physical phenomenon in the thermal sublimated pentacene thin films. Later on, K. Punbtambekar et al. directly observed and imaged the line dislocations in the second pentacene monolayer grown on SiO$_2$ by using the atomic force microscopy combined with a chemical etching process [47]. These authors stated that the line dislocations originated from the stress buildup inside the pentacene monolayer and remained confined within a region due to the high friction force and low surface potential. Additionally, the authors used Kelvin force microscopy to determine the small grain boundary potential in the first pentacene monolayer and found it to be comparable with the thermal energy at room temperature. Hence they interpreted the grain boundary potential as a shallow hole trap instead of a major charge transport barrier. Another interface study by A. C. Mayer et al. [48] found from synchrotron X-ray reflectivity measurements that a very thin water layer remained at the interface between the first pentacene monolayer and SiO$_2$ surface. These authors suggested that the water layer present at the interface could behave as an interface impurity and be responsible for charge trapping.

In addition to the defects formed during the pentacene thin film growth, other imperfections also can be introduced into the films during transistor fabrication. In the top contact configuration, a gold electrode is evaporated on the top surface of the film. In this process, due to the high heat load generated by the gold evaporator, the charge transport channel can be damaged by re-evaporating the pentacene molecules or by disordering the packing order of the molecules. Furthermore, gold atoms could penetrate into the pentacene film as reported by J. H. Cho et. al. [49], who also found that a sharp interface between gold and pentacene corresponding to a lower contact resistance could be achieved by fast gold electrode deposition. On the other hand, the bottom contact configuration, which is widely used in real industrial application for making the transistor...
Introduction

electrodes, implies preparing the gold electrodes directly on the dielectric material before growing the pentacene thin film. Large differences in surface morphology and crystallinity were found when comparing pentacene thin films grown on the gold surface and on the SiO₂ surface: pentacene grains formed on the gold surface have a much smaller grain size than those grown directly on the SiO₂ surface [50]. In addition, small pentacene grains, and hence a high density of grain boundaries, are also the dominating feature in the region close to the electrode, and the size of grains gradually increases as one moves further away from the electrode. This non-uniform pentacene morphology commonly observed at the border between gold and SiO₂ in the pentacene first monolayer growth is detrimental to charge injection and charge transport in pentacene transistors. To improve on this point, J. Kymissis et al. [51] and C. Bock et al. [52] grew pentacene thin film on a gold electrode surface modified with a thiol-based SAM. Both found that the morphological uniformity of the pentacene thin films at the border between SAM modified gold and SiO₂ was improved, the grains were larger in the region close to the electrode and the hole mobility was higher in the corresponding transistors.

1.2.6 Supersonic molecular beam deposition of pentacene thin films

In 2000, supersonic molecular beam deposition (SuMBD) was introduced as a new method for the organic crystalline thin film growth by S. Iannotta et al. [53]. The authors demonstrated that one could obtain highly ordered oligothiophene thin films based on the optical properties, which resembled those of single crystal material. In 2003, L. Casalis et al. [54] reported the use of SuMBD to grow pentacene thin film on a single crystal Ag (111) surface at relatively low substrate temperature (~ 200 K). Low energy He diffraction and X-ray reflectivity revealed a highly ordered pentacene crystalline structure with quasi layer-by-layer growth. The authors attributed the high order to efficient local annealing caused by the energy dissipation when the molecules impinge with high kinetic energy of ~ 5 eV (corresponds to a velocity of ~ 1850 m/s) on the Ag surface. In the same year, S. Iannotta and T. Toccoli [55, 56] presented another study where SuMBD was used to grow pentacene thin films on SiO₂ at room temperature. Relatively larger pentacene grains (> 1-2 µm) were obtained when imparting a higher kinetic energy (~ 5.5 eV) to the impinging
molecular beam but a very different surface morphology of pentacene thin film, showing an inferior crystalline quality was obtained at lower kinetic energy. Recently, a study concerning the initial growth of pentacene submonolayers on SiO$_2$ surfaces by using SuMBD was reported by A. S. Killampalli and coworkers [57], who found that the pentacene adsorption probability decreased with increasing the impinging molecular kinetic energy and incidence angle. Furthermore, scaling the maximum nucleation density with the growth rate by using a power law, they claimed that the pentacene critical nucleus size contained four molecules in all samples. One year later, the same group presented another study of pentacene initial growth using SuMBD on a HMDS modified SiO$_2$ surface [58]. The island density on the HMDS modified SiO$_2$ surface was found to be independent of the growth rate and much higher than that on the pristine SiO$_2$ surface. Based on the increased pentacene adsorption probability, authors concluded that molecular surface trapping was more efficient on the HMDS modified SiO$_2$ than on pristine SiO$_2$. In chapter 3 of this thesis, I shall present our recent studies of pentacene growth on SiO$_2$ [59] where we found that molecular kinetic energy, $E_k$, plays a very important role in pentacene submonolayer growth. By increasing $E_k$ to 6.4 eV, smaller islands with less fractal structure and a large island density were obtained, which resulted at higher coverage in a uniform pentacene monolayer with relatively large grain size and less grain boundaries. In the study of pentacene nucleation, we discovered a transition of the pentacene critical nucleus size from 3 to 2 molecules when increasing the impinging molecular kinetic energy beyond 5 eV and concluded that with SuMBD the pentacene submonolayer grows through a diffusion mediated growth mode.

Recently, an investigation of the hole mobility in transistors, based on SuMBD grown pentacene thin film on non-SAM modified SiO$_2$ gate dielectric with top gold electrodes, was carried out by T. Toccoli et al. [60]. They also discovered a grain size increase with increasing kinetic energy of the impinging molecules. For samples grown by the supersonic molecular beam with a kinetic energy of 6.5 eV, they demonstrated that single crystal like, large size pentacene grains with a very low roughness were obtained in the top surface of pentacene thin film. The hole mobility measurements of the pentacene transistors based on such films are shown in figure 1-3. The highest hole mobility of ~ 1.0 cm$^2$/V s was achieved in the pentacene thin film grown at highest kinetic energy of ~ 6.5 eV and was about five times higher than that obtained in pentacene thin films grown at lower kinetic energy, for example at ~ 3.5 eV. Furthermore, a linear relationship
Figure 1-3: OFET output of supersonic molecular beam grown pentacene thin films deposited with kinetic energy of (a) 3.5 eV; (b) 5.5 eV and (c) 6.5 eV. The highest hole mobility (~ 1.0 cm² V⁻¹ s⁻¹) is derived for pentacene thin film grown at a kinetic energy of ~ 6.5 eV [60].

between the hole mobility and temperature of the device was observed for samples grown at molecular kinetic energy of ~ 6.5 eV. This indicated a mobility decrease with increasing temperature which the authors attributed to a nearly band transport behavior, the typical charge transport feature occurring in single crystal pentacene [61].

1.3 Purpose of the present research

As outlined above, previous works demonstrated that, by using SuMBD, the pentacene thin film crystallinity and the corresponding transistor performance can be greatly improved. SuMBD also provides an alternative method to thermal sublimation for understanding the pentacene thin film growth and particularly, the formation of the first pentacene
monolayer on SiO$_x$ surface which is very critical for the quality of successive pentacene layers and also strongly affects charge transport in the transistor channel.

The aims of the research presented in this thesis were: 1) to understand, through surface morphology analysis, the growth mechanism of SuMBD grown pentacene submonolayers on SiO$_x$ and the significant differences between SuMBD and thermal sublimation; 2) to study the crystallinity of single pentacene molecular islands and of the first completed monolayer grown by supersonic molecular beams with different kinetic energy; 3) to elucidate the interaction between the impinging pentacene molecules and SiO$_x$ surface at different molecular kinetic energy, beam incidence angle and substrate temperature; 4) to improve the uniformity and crystallinity of the first pentacene monolayer grown on a surface patterned with bottom contact electrodes for transistor fabrication and to determine the charge mobility in the resulting devices.

### 1.4 Outline of the thesis

In chapter 2, our SuMBD system is introduced, including a description of the basic working principle, the structure of the entire setup, the general operational process and the characterization of the generated supersonic molecular beam. Then, we present the surface characterization technique – atomic force microscopy (AFM), which was the main tool for analyzing the surface morphology and crystallinity of the pentacene submonolayer. In this section, in addition to a detailed explanation of the working principle of AFM, I describe some important technical details, which are useful for obtaining high quality AFM images. In the final part of this chapter I illustrate the contact angle measuring system since it is an important tool for investigating the hydrophilicity of the surface before pentacene growth.

In chapter 3, we present a systematic investigation of the correlation between the kinetic energy of the incident molecules ($E_k =$ thermal energy, 3.3, 5.0, 6.4 and 6.7 eV) and the initial growth of pentacene submonolayer on the SiO$_x$ surface by using the supersonic molecular beam deposition (SuMBD). We found that the molecular kinetic energy plays a very important role in determining the critical nucleus size, the formation of the molecular island, the crystalline quality of the first completed monolayer and even the growth mode of the subsequent layers. With
increasing the $E_k \geq 5.0$ eV, the morphology in the submonolayer regime evolves toward higher island density with smaller island size. The SuMBD grown molecular islands show less fractal structure and smoother island edges than those resulting from organic molecular beam deposition (OMBD). The critical nucleus size was determined in the low coverage regime by using the general scaling function and found to show a transition from 3 to 2 pentacene molecules when the kinetic energy of the incident molecules exceeded 5-6 eV. From the comparison of pentacene islands grown by SuMBD with those grown by OMBD, we found that the pentacene island shape becomes more anisotropic, and the island size becomes more uniform, pointing to correlated island growth. Moreover, for OMBD 3D island growth is observed, SuMBD gives rise to the layer-by-layer growth at least for the first 2 layers. By comparing atomic force micrographs of the height and of the net transverse shear force, we found that when $E_k \geq 5.0$ eV, the first monolayer is composed of large single crystalline domains which extend over up to 10 micron. In these growth conditions not only the surface diffusivity is high, but energy dissipation occurring when the molecules hit the surface seems to lead to the reorientation of whole islands during island coalescence, resulting in the elimination of grain boundaries. The pentacene initial growth by SuMBD was interpreted by the diffusion mediated growth model and the conditions for pentacene initial growth were optimized.

In chapter 4, we report the investigation of the dynamics of pentacene submonolayers growth on SiO$_x$ by SuMBD when varying the kinetic energy, the beam incidence angle and the substrate temperature. Particularly, we focused on the influence of the kinetic energy of the impinging molecules and of the incidence angle. It is found that for a fixed $E_k$ of the incident molecules, the sticking coefficient decreases with increasing incidence angle, indicating that a larger parallel component of momentum favours molecule-surface scattering leading to desorption. This also agrees to the highly efficient molecular energy dissipation on the surface, which occurs for normal incidence. At constant incidence angle, the sticking coefficient shows a decrease with increasing $E_k$ and this is due to the large molecule – surface scattering caused by the excessive energy that the impinging molecules still have after their first inelastic collision. Concerning surfaces with different polarity, we find that the hydrophobic surface is more favourable for pentacene adsorption than the hydrophilic surface. For SuMBD at normal incidence onto a cooled substrate (~ 200 K), surface phonon assisted molecule-surface scattering which makes the
molecules rebound into vacuum, is suppressed, leading to a higher molecular sticking coefficient than that at RT. For SuMBD in grazing incidence and lower substrate temperature ($\sim 200$ K), the lower number of surface phonons prevents an efficient dissipation for molecules with large parallel momentum, therefore resulting in a lower sticking coefficient than for deposition on a substrate kept at RT. The island density and island size for the different growth conditions are strongly modulated by two important factors: molecular surface diffusivity and molecule – surface scattering. In the study of pentacene nucleation, we demonstrate that the critical nucleus size is essentially determined by the normal momentum. A critical nucleus size transition from 2 to 3 is found for samples grown at $E_k = 6.3$ eV when incidence angle moves away from the normal incidence. We suggest that the large molecule – surface scattering and increased molecular surface diffusivity due to the presence of the large parallel energy component are the key reasons why the formation of a stable nucleus requires more pentacene molecules.

In chapter 5, we present our results of growing the pentacene ultrathin films with nominal thickness of 1 ML and 6 ML by using the supersonic molecular beam deposition and of realizing the pentacene thin film based transistors with bottom contact Au electrodes. By modifying the Au electrode surface with SAM of (perfluoro) alkanethiols in the transistor, the quality of pentacene ultrathin films at the border between Au electrode and SiO$_x$ has been greatly improved. A highly uniform surface morphology and better crystallinity, which perfectly resemble those of pentacene films deposited on the bare SiO$_x$ surface are observed far away from the Au electrodes. The morphology transition area typically observed in the bottom electrode devices is completely eliminated and a sharp, seamless interface between the Au electrode and the pentacene film is established starting from the pentacene first monolayer up to several layers. The better morphology is reflected in a better transistor performance: drain current and hole mobility are three orders of magnitude higher than those obtained in the pentacene transistors without SAM modification and also the switch-on voltage is much lower ($\sim 0$ V) than for the transistors without SAM modification ($\sim 40$ V). For the Au surface modification, we applied two different kinds of SAMs: decanethiol and perfluorinated octanethiol, which give different Au Fermi level alignment respect to the pentacene HOMO level, resulting in an increased and decreased hole injection barrier, respectively. However, we found a high similarity of the electronic performance in transistors fabricated by both cases and this result stresses
that the surface morphology and crystallinity of the SuMBD grown pentacene ultrathin films at the border between the electrodes and SiO\textsubscript{x} substrate play the key role to determine the performance of the field effect transistor.

References

Chapter 2

Experimental facilities

In this chapter, we focus on the description of the facilities used for obtaining the experimental data discussed in this thesis. The supersonic molecular beam deposition system (SuMBD), the main equipment to grow the pentacene (sub-) monolayers and thin films, is introduced in the first part of this chapter. The entire setup of SuMBD, working principle and the operational conditions are described. A comparison between SuMBD and organic molecular beam deposition (OMBD) is made at end of this part. In the second part of this chapter, we present the main characterization technique – atomic force microscopy (AFM) - used for studying the surface morphology and crystallinity of pentacene (sub-) monolayers. We first give a brief general introduction of the AFM working principle, then we describe in detail the main AFM scanning techniques, namely contact and tapping mode, and their particularities. Transverse shear force microscopy (TSM), an effective AFM method for evaluating the crystallinity of our deposited pentacene (sub-) monolayers, is illustrated in detail. In the last part of this chapter, we explain contact angle measurements, a technique which has been intensively used for determining the hydrophilicity of the SiO₅ surfaces before pentacene growth.


## 2.1 Supersonic molecular beam deposition

A supersonic molecular beam was first realized by J. B. Fenn et al. [1, 2] in Princeton in 1963. Later on, this technique was extensively applied for studying the gas-surface interaction, dynamics of molecular adsorption on different surfaces [3, 4, 5, 6], inorganic and organic thin film growth and surface modification [7].

In the research presented in this thesis, we used a customer built supersonic molecular beam deposition system (SuMBD) for pentacene crystalline thin film growth. Figure 2-1 shows a photograph of the SuMBD system installed in our laboratory and a schematic drawing of its internal structure. Our SuMBD setup consists of:

1) three connected stainless steel high vacuum chambers;
2) a source housed in the first chamber and made of a 12 cm long quartz tube, with diameter 1 cm, as shown in figure 2-2. Pentacene powder is stored in a crucible inside the quartz tube. For the purpose of sublimation, a piece of tantalum foil is wrapped around the outer surface of the quartz tube for resistive heating. A chromel-alumel thermocouple placed close to the tantalum foil measures the temperature during the sublimation process. One end of the quartz tube is completely open and connected to a gas line and the other end is terminated with a nozzle, which has a cylindrical configuration (~ 180 - 200 µm in length and ~ 60 µm in diameter). Touching the nozzle, there is a tungsten filament for resistive heating and another chromel-alumel thermocouple for reading the temperature;
3) two skimmers: a first one (~ 0.3 mm in diameter) is mounted at the connection between first and second chamber, ~10 mm in front of the nozzle, and a second one (~ 3 mm in diameter) is mounted at the connection between second and third chamber;
4) A quartz microbalance, which can be moved in and out of the beam, is installed between the first and the second skimmer and serves to estimate the growth rate;
5) an entry lock connected to the third chamber is used for transferring the samples in and out of the deposition chamber. If maintained properly, the first and second vacuum chamber approach high vacuum after one day evacuation with large capacity rotary and turbo pumps. The high vacuum is crucial for the purpose of producing a high quality molecular beam and better quality pentacene thin films. Experimentally, the background pressure is kept at ~ $10^{-7} - 10^{-8}$ mbar in the first and second
Figure 2-1: Photograph of the supersonic molecular beam deposition system (up) and schematic drawing of the internal structure of the entire system (down)[8].
chamber and $\sim 10^{-10}$ mbar in the deposition chamber.

The pentacene thin film growth experiment is normally carried by two steps: first a stabilized, high quality supersonic molecular beam is generated and then the pentacene thin film is grown. In the first step, we feed the carrier gas – high purity helium with a certain pressure into the quartz tube, while simultaneously heating up the quartz tube body and the nozzle by sending a DC current through the tantalum foil and tungsten filament, respectively. Due to the large pressure gradient between the inside and the outside of the quartz tube, the sublimated pentacene molecules can seed into the helium gas and flow through the nozzle into the first chamber. At the exit of nozzle helium gas atoms and pentacene molecules collide, with an energy transfer from the light carrier gas atoms to the heavy molecules. Due to the aerodynamic acceleration process, the seeded molecules are accelerated and their kinetic energy increases. At the same time, the ro-vibrational modes of seeded molecules are relaxed due to energy exchange between molecules and gas atoms. All molecules are cooled down, losing their internal energies [7] and the higher the kinetic energy of the supersonic molecular beam, the lower is the temperature of the molecules. For pentacene supersonic molecular beam with a kinetic energy of 6 eV the seeded molecules can be cooled down to $\sim 20$-25 K [9]. In the SuMBD system, we are able to tune the kinetic energy of the
Experimental facilities

molecular beam from thermal energy up to several electron volts in several ways, namely by varying the nozzle configuration, the concentration of seeded molecules in the carrier gas and the nozzle temperature. When carrier gas (seeded with the molecules) flows through the nozzle into the first chamber, an isentropic gas expansion takes place, without collision between gas atoms and seeded molecules. By passing through two different kinds of skimmers, a supersonic molecular beam with high directionality and very narrow angular spread can be realized. After the applied temperature and pressure have stabilized, the molecular beam will be led into the deposition chamber to start the growth. This moment can be identified by the pressure increase by one order magnitude inside of deposition chamber. However, if a lower or no pressure increase is measured, this means that the molecular beam is misaligned with respect to the skimmers or that either the nozzle or the first skimmer are blocked, for example by previously deposited molecules.

For investigating the quality of the generated pentacene supersonic molecular beam before carrying out the pentacene thin film growth, we used time of flight mass spectroscopy, which can be connected to the deposition chamber and well aligned on the axis of the impinging molecular beam. In this technique, the neutral pentacene molecules seeded in the helium carrier gas are first photoionized with a laser pulse from Nd:YAG laser (a wavelength 266 nm, pulse time 15 ns and frequency 8 Hz); then, the ionized molecules are accelerated by an electric field applied to the plate electrodes along the way to the detector. An optimized signal received by the detector is transformed into the ToF mass spectrum, which reveals useful information on the molecular beam such as the presence of impurities or of molecular clustering, the average velocity of the molecules, their kinetic energy and the relative beam flux. In addition to ToF mass spectroscopy, we also used a quartz microbalance to quantify the growth rate at different applied temperature for pentacene sublimation. However, this growth rate is only a reference for estimating the deposited pentacene layer thickness since the microbalance is not located in the same position as the substrate, which is placed further downstream inside of the deposition chamber. For more accurate thickness measurements, we have to rely on the AFM.

In comparison to the thermal sublimation technique (also named organic molecular beam deposition (OMBD)) [10, 11, 12], SuMBD presents several advantages: 1) a properly generated supersonic molecular beam can have a higher intensity with a narrower angular distribution than
Experimental facilities

a thermally produced organic molecular beam and presents a very uniform velocity distribution of the molecules hitting the substrate after passing through two skimmers; 2) the kinetic energy of the molecules can be varied and reach much higher values (up to ~ 7 eV in our setup). This leads to a larger molecular surface diffusivity, which is favourable for growing high quality thin films on a surface kept at room temperature. In fact, the surface diffusivity of thermally sublimated molecules can only be increased by heating up the substrate and this may lead to the molecular desorption, especially in the case of pentacene growth on a chemically inert surface; 3) After impinging on the substrate, molecules with higher kinetic energy can introduce local annealing by dissipating a certain amount of energy. This is very helpful to rearrange the molecular packing and achieve better crystallinity. However, nothing is perfect, so disadvantages of SuMBD also exist: compared to OMBD, SuMBD is more complicated and expensive. Moreover, the pentacene thin film growth rate in SuMBD is much lower than for OMBD because a certain amount of molecules are scattered away from surface, especially when we increase the kinetic energy of the impinging molecules.

2.2 Atomic force microscopy

Atomic force microscopy (AFM) is a well known characterization technique commonly used to study surface morphology with very high, sometimes even molecular or atomic resolution. It was invented by G. Binning and H. Rohrer in 1985 and they won the Nobel price for discovering the scanning tunneling microscopy and atomic force microscopy in 1986.

The AFM system used in these studies is the Nanoscope IV multimode scanning probe microscope, produced by the Digital Instruments, Veeco Metrology Group, U.S.A.. The basic structure of the AFM system is sketched in figure 2-3. Its working principle can be simply described as a measurement of the forces acting on the scanning tip via detecting the deflection of the moving cantilever. The interaction force between the scanning tip and sample surface is the essential parameter to determine the AFM scanning mode. In the force – distance diagram illustrated in figure 2-4, the contact and non-contact regime are clearly indicated as the function of the distance between tip and sample surface. By
Figure 2-3: Sketch of the setup for atomic force microscopy.

Figure 2-4: Interaction force between tip and the sample surface as function of distance.
decreasing the gap between the scanning tip and sample surface, the interaction forces can change from attractive to repulsive. With further reducing the gap, the repulsive force can dramatically increase due to the Pauli exclusion principle and become the dominant interaction. With varying the interaction force, the cantilever deflects in different ways. It can be bent upward, downward or twisted. In the studies described in this thesis, we intensively used contact mode or intermittent contact mode (also named tapping mode) AFM to explore the surface morphology of pentacene thin films.

2.2.1 Contact mode atomic force microscopy

In the AFM contact mode the tip is so close to the sample surface that it feels a repulsive force caused by the overlap between the electron clouds of atoms of the tip and of the surface (Pauli exclusion principle). Generally, contact mode AFM is applied to measure a relatively hard material by direct tip contact to the sample surface during operation. However, this scanning mode may cause some damage either to the tip making it loose its sharpness, or, especially for the soft matter material, to the sample surface. In our measurements, the height of the piezoelectric scanner is constant. When moving the sample with respect to the fixed scanning tip, a cantilever deflection is caused by the tip-surface interaction in different surface regions and can be detected by the highly sensitive quadrant photodiode onto which the laser beam reflected from the top surface of cantilever. The obtained laser signal is redirected into a well constructed feed back loop to adjust the vertical scanner displacement, which keeps the cantilever deflection constant. Therefore, the surface topography can be recorded by monitoring the motion of the piezoelectric scanner. Before collecting contact mode scanning images, it is crucial to perform a force calibration, by which key parameters such as deflection set point, ramp size and Z scan start are adjusted correctly.

In AFM contact mode, in addition to collect data of the surface height, the surface friction can also be recorded at the same time. In fact, when the tip is moving over the surface, different materials will give rise to a different surface friction and this can be identified by detecting the lateral torque on the cantilever while the tip is scanning in the direction perpendicular to its long cantilever axis. This technique is termed lateral force microscopy (LFM) and commonly used to determine the domain
boundaries in a film after coalescence of islands. LFM is, however, not sensitive enough to detect differences in surface friction of different domains caused by different molecular orientation. When scanning the tip along the direction of the cantilever long axis instead of perpendicular to it, we are able to measure the net transverse shear force, resulting from the changes in the tip-surface interaction when the tip is scanning over regions where the molecules pack with different orientation [13, 14]. This technique is named transverse shear microscopy (TSM). By mapping the variation in transverse shear force with different colour contrast, we can qualitatively determine the crystallinity inside a single molecular island or the monolayer. Based on this technique, the single or polycrystalline structure of a pentacene (sub-) monolayer can easily be determined. Recently, K. Puntambekar et al. applied this technique to study a pentacene monolayer on SiO$_2$ prepared by OMBD [15]. One of their results is shown by figure 2-5 as an example. The left image shows the height image of the first pentacene monolayer covered by some second layer islands which gives information on the morphology but not on the crystallinity. However, the right image obtained by TSM of the same surface, shows a clear colour contrast. The brighter a certain area, the larger is the transverse shear force acting on the tip when it scans over a certain grain. This implies that the
monolayer has a typical polycrystalline structure, where for example the grains marked with G1 and G2 have the same molecular orientation within the grain but a different rotation of the crystallite with respect to the substrate. On the contrary, the colour for the grains marked with G3 and G4 is less pronounced, indicating that their orientation mismatch is relatively small.

For the TSM measurements presented in this thesis, we used NP-20 AFM tips produced by Veeco Metrology and Instrument, U.S.A.. These tips are made of silicon nitride and attached to a very flexible triangular shaped cantilever, which has a spring constant of 0.58 N/m and must be properly mounted on a removable probe holder, which is laterally fixed inside of the SPM head. Before collecting the TSM images, the laser beam path has to be adjusted: by turning the knobs attached on the SPM head the laser beam can be moved along two directions (X, Y) on the top surface of the cantilever and the position is adjusted so that the scanning tip is right below the laser spot. A cross-shaped light pattern should be observed when the light is reflected properly from the triangular shaped cantilever. After laser position adjustment, we maximize the sum signal by tuning the position of photodetector mirror inside of the SPM head and set the vertical deflection signal to be -3 ~ -2 V and the horizontal signal to be 0. Then, a force calibration is carried out by engaging the tip on a small scanning area on the sample surface. Through this step, we are able to reach an appropriate scanning condition for achieving a high resolution image and can also evaluate the quality of the used tip. An optimized force calibration is plotted in figure 2-6. When approaching the surface (following the blue arrows) the cantilever deflection is monitored by means of the piezoelectric scanner extension when tip is engaged to the surface. The nearly horizontal line indicates that there is no cantilever deflection when the tip is far away from the surface. Once the tip is brought close to the surface, the tip is attracted as indicated by the small dip in the curve in Fig. 2-6. As the tip keeps moving even closer to the surface, the cantilever gradually bends upwards, as seen by the following straight line following the deflection in figure 2-6. When the tip is drawn back again, the cantilever first relaxes as shown by the straight line moving to down and right and marked by red arrows. Note that the relaxation of the tip overshoots at the point where repulsion had started when approaching the surface, and the attraction continues as the piezoelectric scanner is further retracted until the connection between tip and surface breaks and the cantilever rebounds back to its free standing position, giving rise to the second much deeper dip in
the plot. In the contact mode scanning, the deflection set point is the parameter mostly tuned for achieving a better resolved image. Although increasing the deflection point setting is sometimes helpful to obtain better images, the large interaction between tip and surface in these conditions can reduce the tip lifetime and/or introduce scratching lines in the images. In an optimized setting, the tip-surface interaction will be such that a good image resolution is obtained but damage on the tip is avoided.

Figure 2-6: Plot of the force calibration for the AFM contact mode [16].

**2.2.2 Tapping mode atomic force microscopy**

For tapping mode AFM operation, also called intermittent contact mode operation, the detected signal originates from the amplitude variation of the cantilever, which oscillates at a certain frequency during scanning. Since the tip approaches and then retracts from the surface periodically, the energy dissipated is much lower than when the tip is constantly very close to surface as in the contact scanning mode. This makes tapping mode technique more suitable for investigating delicate soft matter, such as pentacene or other organic materials. In the tapping mode, by using the piezoelectric actuator, the cantilever can be acoustically excited into a vertical oscillation at a certain amplitude in a range between 10 -100 nm with a frequency close to or equal to the cantilever’s resonance frequency. The free motion of the cantilever in air is described by a harmonic oscillation using the second order differential equation (2-1) [17], in which
m the mass of cantilever, \( z \) the vertical displacement, \( k \) the spring constant of cantilever; \( A_0, \omega \) the driving amplitude and frequency respectively; \( \omega_0 \) the resonance frequency of the cantilever; \( Q \) the quality factor and \( F_{ts} \) the tip-surface interaction force.

\[
m \frac{d^2z}{dx^2} + kz + \frac{m \omega_0}{Q} \frac{dz}{dx} = F_{ts} + A_0 \cos(\omega t) \quad (2-1)
\]

In air, the cantilever with free oscillation can have maximum amplitude. However, when the tip is physically contacting the surface, the oscillation amplitude is reduced due to the increased energy dissipation and the resonance frequency of the cantilever changes. This relation is well modeled by the amplitude dependent excitation frequency equation (2-2) [17]. In the tapping mode, the cantilever’s oscillation amplitude is kept constant with the help of a feedback loop which adjusts the vertical displacement of the piezoelectric scanner. Similar to the contact mode, the surface image can be obtained by monitoring the scanner movement.

\[
A(\omega) = \frac{F_0 / m}{\sqrt{\left(\omega_0^2 - \omega^2\right)^2 + \left(\omega \omega_0 / Q\right)^2}} \quad (2-2)
\]

Specified AFM probes (Tap 300 purchased from Budget Sensor) are required for tapping mode scanning. Such probes are made of silicon single crystals. A very sharp tip with a very small tip radius, typically less than 10 nm, is located at the end of the cantilever. Generally, a better resolution image can be easily achieved if the tip radius is smaller or close to the size of the measured objects. A Tap 300 AFM probe has a relatively stiff cantilever (force constant = 40 N/m) that can prevent the tip from being trapped by the surface during the scan. The process of AFM probe mounting and laser beam adjustment are similar to that described for the contact mode AFM: the focused laser spot gives rise to an elliptic light pattern on the top surface of the cantilever; its position should be adjusted to be right above the tip. We maximize the signal by tuning the
photodetector mirror inside the SPM head and move the reflected laser beam close to the centre of the quadrant photodiode detectors. Before each measurement, it is always useful to tune the tip via the auto-tune function of the operational system of the AFM. In this step, important information, such as, driving frequency, driving amplitude and set point amplitude are fixed. The driving frequency is normally set to a value close to the tip resonant frequency. However, if tip damage or material attachment on the tip are detected, the resonance frequency will change and the driving frequency will change as well. Hence, the tip tuning procedure also allows us to verify the quality of the tip. Image size, scanning speed and required image resolution are all defined before starting the measurement. For the investigations presented in this thesis, the scanning area \((10 \times 10 \ \mu m^2)\) was always selected near the centre of the deposited pentacene layer since that is the area with the most uniform morphology. We often set a slow scanning speed (i.e 1-1.5 Hz) for the purpose of achieving the best quality image. However, faster scanning speeds can also be useful for preview images or for preventing the tip drift on the surface. During the measurement, the set point amplitude, the drive amplitude, the proportional gain and the integral gain are frequently adjusted to assure proper scanning conditions for the various surface topographies encountered for the same sample.

Three kinds of data can be collected in the tapping mode surface measurement, namely surface height images, amplitude images and phase images. The signal of surface height is obtained by monitoring the vertical movement of the piezoelectric scanner. The exact surface height can be determined by using the cross-section profile. Parallel to the height image, the amplitude, obtained by measuring the cantilever deflection, can be simultaneously recorded. In the amplitude image, the edge features of scanned objects show much better resolution than those observed in the height image since they are not affected by the large surface height difference. Hence, this data is helpful for observing the detailed structure of a surface with a relatively complicated topography. The phase image from the scanned sample can also be obtained in parallel with the height image. At fixed vibrational amplitude, the phase signal is derived from the phase lag of the oscillating cantilever with respect to the input drive signal. Phase measurements are an efficient tool to study the structure and chemical composition of the surface on the nanometer scale because different material may give different phase shift and the lateral resolution of this technique can be easily approached within 10 nm.
Experimental facilities

All AFM measurements of pentacene films presented in this thesis were carried out in air at room temperature. Pentacene crystalline thin films are characterized by a relatively high stability in air after having been taken out of the ultrahigh vacuum chamber. However, after long period of air exposure (i.e. usually 3 weeks) a quality degradation of the pentacene layer is observed.

The detailed analysis of all obtained AFM data was performed with the help of the WSxM (Nanotec electronica S.L.) software. This software allows us to extract the basic topographic information, such as coverage, molecular island density, average island size, layer thickness and surface height profile.

2.3 Contact angle measurement

The contact angle measurement is an efficient and widely used technique for investigating the hydrophilicity, adhesion and surface tension of a solid surface. When a liquid drop is deposited on a solid surface in the air, it will adopt a certain shape dictated by the surface tension generated from the equilibrium state of the three interacting phases (solid/liquid/gas) as sketched in figure 2-7. The contact angle that is measured is the angle between the tangent line drawn at the edge of the liquid drop and prolonged down to the surface, and the surface horizontal as shown in figure 2-7. Mathematically, the contact angle can be expressed by using Young’s equation written in 2-3.  is the contact angle that we can obtain in the measurement. In the experiments, when the liquid drop spreads on the solid surface, a low value of results, which is typical for a high wettability of the surface. However, if the deposited drop contracts into a ball-like shape, a high value of is measured, indicative of a surface with less wettability. If the used liquid is pure water, the solid surface with the high/low wettability can be interpreted as a hydrophilic/hydrophobic surface. For the studies reported in this thesis, we use static contact angle measurements on a 1.25 µl droplet of highly purified, de-ionized water,

\[
\gamma_{GL} \cos \theta = \gamma_{GS} - \gamma_{SL} \quad (2-3)
\]
Experimental facilities

deposited with a Hamilton micro-syringe, to determine the hydrophilicity of the SiO\(_x\) substrate surfaces prior to pentacene deposition. The measurement was carried in air at a fixed temperature (~20\(^\circ\)C) by the sessile drop method [18] in a homebuilt microscope – goniometer system. The cross-section of the water droplet was recorded with a CCD camera, controlled by a homebuilt operational computer software. Usually, it takes about 60 seconds for the water droplet to stabilize after deposition, so the images for the contact angle measurement were taken after that waiting period. The contact angles on both the left and the right side of the droplet were derived by a fitting process, which is a function available in the homebuilt software. In order to achieve a reliable result, we always carried out contact angle measurements in four or five different areas of the same sample surface and extracted an average value as the final result. Since, as demonstrated by AFM measurements, the SiO\(_x\)/Si wafer used for pentacene thin film growth has a very low root mean square surface roughness, the contact angle variation due to surface roughness [19, 20] can be completely excluded in our experiments.

![Figure 2-7: Schematic of the contact angle and different surface tensions at solid/liquid (\(\gamma_{SL}\)), the gas/solid (\(\gamma_{GS}\)), and the gas/liquid (\(\gamma_{GL}\)) interfaces.](image)

References

9. Private communication with T, Toccoli.
Chapter 3

Initial growth of pentacene controlled by the kinetic energy of the incident molecules *

This chapter presents a systematic investigation of the correlation between kinetic energy of the incident molecules (E_k = thermal energy, 3.3, 5.0, 6.4 and 6.7 eV) and initial growth mode of the pentacene submonolayer on the silicon oxide surface by using the supersonic molecular beam deposition (SuMBD). We found that the molecular kinetic energy plays a very important role in determining the critical nucleus size, the formation of the molecular island, the crystalline quality of first completed monolayer and even the growth mode of the subsequent layers. With increasing E_k ≥ 5.0 eV, the morphology in the submonolayer regime evolves towards the higher island density with smaller island size. SuMBD grown molecular islands present a less fractal structure and smoother island edges than those resulting from organic molecular beam deposition (OMBD). The critical nucleus size was determined in the low coverage regime by using the general scaling function and showed a transition from 3 to 2 pentacene molecules when the kinetic energy of the incident molecules exceeded 5-6 eV. With respect to pentacene islands grown by OMBD, those resulting from SuMBD are more anisotropic in shape, and more uniform in size, pointing to correlated island growth. Moreover, for OMBD 3D island growth is observed while SuMBD gives rise to the Stransky- Krastanov growth in the pentacene initial growth. By comparing atomic force micrographs of the height and of the net transverse shear force, we established that when E_k ≥ 5.0 eV, the first monolayer is composed of large single crystalline domains which extend over up to 10 micron. In these growth conditions not only the surface diffusivity is high, but energy dissipation occurring when the molecules hit the surface seems to lead to the reorientation of whole islands during island coalescence, resulting in the elimination of grain boundaries. The pentacene initial growth by SuMBD was interpreted by the diffusion mediated growth model and the conditions for pentacene initial growth were optimized.

* This chapter is based on Yu Wu, Tullio Toccoli, Norbert Koch, Erica Iacob, Alessia Pallaoro, Petra Rudolf and Salvatore Iannotta, “Controlling the early stages of pentacene growth by supersonic molecular beam deposition” published on Physics Review Letter 98, 076601 (2007) and based on Yu Wu, Tullio Toccoli, Jian Zhang, Norbert Koch, Erica Iacob, Alessia Pallaoro, Salvatore Iannotta and Petra Rudolf, “Key role of molecular kinetic energy in early stages of pentacene island growth” submitted to Applied Physics A.
3.1 Introduction

Pentacene is one of the most promising candidates for organic electronics applications [1] and recently very high hole mobilities (up to 5.5 cm²/Vs) [2] have been achieved in pentacene thin film based field effect transistors. Nonetheless, the difficulty in determining and controlling key properties such as structure, morphology and interfaces of the organic layer is still a major factor limiting the electronic properties. The charge mobility is a crucial parameter for device performance and previous studies have demonstrated that it is highly sensitive to the crystallinity of the deposited pentacene thin film, i.e. to the grain size [3, 4], defect density [5, 6] and crystal polymorph [7, 8]. In particular, further progress in device development requires the production of highly ordered large size pentacene crystals [9], possibly eliminating grain boundaries [1, 1]. In the past few years, several studies based on the OMBD grown pentacene layers have demonstrated that the pentacene grain size can be modulated via changing the deposition rate, the substrate temperature or modifying the substrate surface with organic self assembled layers [10, 11, 12, 13, 14]. Recent reports illustrated that supersonic molecular beam methods [15, 16, 17] represent a viable and promising approach to improve the pentacene crystallinity based on the idea of tuning and controlling the energy of the incident molecules. Since the film quality is determined by the early stages of growth and since the first few molecular layers are crucial for charge transport in organic thin film transistors (OTFTs) [18, 19], we focused our studies on the submonolayer regime on a chemically inert, flat SiOₓ/Si surface. Recently, Killampalli et al. [20] studied the deposition of pentacene monolayers on SiOₓ/Si by supersonic molecular beams at various kinetic energies (1.5-6.7 eV). They reported an adsorption probability that decreases for increasing incident kinetic energy, an island density that did not change appreciably during island growth, and the critical nucleus size requires four molecules. On the other hand, studies of thermally sublimated pentacene grown on SiOₓ, find a critical nucleus size of three [21, 22].

In this work, we show that, by carefully tuning flux and energy of the incident molecules, one can establish the correlation between kinetic energy of incident pentacene and morphology of the deposited pentacene submonolayers at different growth stages. In particular, we demonstrate that at moderate fluxes: a) the island density depends markedly on the kinetic energy; b) the critical nucleus size determined by applying the
Initial growth of pentacene controlled by the kinetic energy of the incident molecules

general scaling function [23], has a transition from 3 to 2 when the $E_k > 5-6$ eV; c) with increasing $E_k$ correlated island growth becomes more pronounced and the island structure changes from fractal to less fractal and becomes anisotropic; d) Stransky-Krastanov growth mode is observed in the pentacene initial growth. With the help of transverse shear microscopy (TSM) we could establish the conditions for producing highly ordered pentacene layers containing large single crystal grains and a minimum density of grain boundaries. Although a polycrystalline structure is found for all pentacene monolayers, the single crystal grain size strongly depends on the kinetic energy of the impinging molecules and reaches up to ~10 µm for the sample grown at $E_k = 6.4$ eV.

3.2 Pentacene submonolayer growth on SiO$_x$ by supersonic molecular beam deposition

3.2.1 SiO$_x$ substrate preparation

To obtain a clean silicon oxide surfaces with few impurities and defects, SiO$_x$ layers were prepared by wet chemical oxidation of silicon wafers (Si(100), p-type with boron dopant, resistivity 1 to 10 Ω cm$^{-1}$, purchased from Silicon Quest International, USA). Before subjecting them to chemical oxidation, the silicon wafers were cleaved into 15 mm × 13 mm pieces and initially cleaned by sonication in de-ionized water (Milli-Q, 18.0 MΩ) and in acetone (analytical reagent A.R., Labscan Ltd, Ireland) for 15 min. Then, they were transferred to a fresh acetone bath and heated to the boiling point for 15 min in order to remove the impurities from the surface. The chemical oxidation process comprised the following steps: 1) after the general cleaning, the samples were transferred to a H$_2$SO$_4$ (97%, pro analysi, Merck, Germany): H$_2$O$_2$ (30% Merck, Germany) = 1:3 solution and heated up to ~ 70° for 30 min. Samples were then cleaned by de-ionized water for several times and the surface became totally hydrophilic. 2) Samples were transferred into HCL (37%, pro analysi, Merck, Germany) + H$_2$O$_2$ (1:1) piranha solution and heated up to 30° for 15 min. This was a very strong chemical reaction producing a large amount of visible gas bubbles. Finally, samples were again repeatedly washed by de-ionized water to remove any solution traces. To avoid contamination through
prolonged exposure to the air, the substrates were stored in a small vacuum chamber before using them for pentacene submonolayer growth. This treatment resulted in very thin (~3 nm) SiO$_x$ layers, as determined by ellipsometry measurements.

These SiO$_x$ substrates showed a relatively low root mean square roughness of ~0.5-1 nm as measured by atomic force microscopy in tapping mode on the freshly prepared surface. However, a few bright spots (area density of ~2.5×10$^7$/cm$^2$) presumably due to contamination still showed up in AFM images. To check the hydrophilicity of the substrates, the contact angles were measured in air by using the sessile drop method [24] in a custom built microscope-goniometer system. A 1.25 µl drop of de-ionized water was deposited onto the freshly prepared SiO$_x$ substrate surface using a Hamilton micro-syringe and the contact angle was measured after 60 s. For each surface, we collected data at four different places in order to check the uniformity of surface polarity and to calculate the average contact angle. All substrates showed contact angles of 35 ± 2° and are therefore hydrophilic.

### 3.2.2 Characterization of the supersonic molecular beam by time of flight mass spectroscopy

Time of flight mass (ToF) spectroscopy was employed to characterize the generated supersonic molecular beams, namely to ascertain that no chemical impurities or molecular clustering were present in the beam and to determine the average molecular velocity and hence the kinetic energy of the molecules in the beam. Figure 3-1 (a) shows the ToF spectra recorded for beams with three different kinetic energies. Based on the relation between the flight time and the charge/mass ratio of the photo-ionized molecules, pentacene is identified as the only chemical component in all beams. Pentacene molecular isotopes are recognized as small shoulders on the right of the main peaks. There is no any evidence of pentacene molecular clusters, which would be identifiable by a larger mass. The peaks corresponding to the three molecular beams are centered at 37.04 µs, 37.14 µs and 37.26 µs, from which mean kinetic energies of 6.4 eV, 5.0 eV and 3.3 eV are deduced. The signal of the molecular beam with kinetic energy of 6.4 eV shows a full width at half maximum (FWHM) of 0.04 µs, indicative of a narrow molecular velocity distribution. On the
Figure 3-1: (a) Time of flight mass spectra of supersonic molecular beams of pentacene molecules: the peaks are centered at 37.04 µs, 37.14 µs and 37.26 µs correspond to average kinetic energies of 6.4 eV, 5.0 eV and 3.3 eV; (b) The molecular kinetic energy as a function of carrier gas pressure.
Initial growth of pentacene controlled by the kinetic energy of the incident molecules

Contrary, the molecular beam with kinetic energy of 3.3 eV has a large FWHM value of 0.08 µs corresponding to a velocity distribution, which is similar to that of a thermally sublimated pentacene molecular beam [25]. When keeping the nozzle at a constant temperature, the velocity of the pentacene in the molecular beam and hence its kinetic energy could be tuned by varying the carrier gas pressure, which in turn changes the concentration of seeded molecules in the carrier gas. To obtain the same flux in all experiments, the incident molecular beams have been adjusted in such a way as to achieve the same peak area in the mass spectra of all molecular beams. Figure 3-1 (b) shows the increase of the molecular kinetic energy as a function of helium pressure and indicates a very good reproducibility of the experimental conditions to obtain a certain kinetic energy with a certain carrier gas pressure.

3.2.3 Growth of pentacene submonolayers on SiO$_x$

The SiO$_x$ substrates were first introduced in the entry lock, which was pumped to ultrahigh vacuum ($7-8 \times 10^{-8}$ mbar) and then transferred one by one into the preparation chamber when they were needed for the growth experiments.

Purified pentacene powder of a dark blue colour (99.98%, purchased from Sigma Aldrich, Corp.) was further purified by vacuum sublimation under a temperature gradient [26]. This purification was carried out at 430 K for 70 hours in the dark to protect the molecules against UV degradation. The purified pentacene powder was carefully loaded into the quartz tube in the first vacuum chamber of the supersonic molecular beam system and outgassed for at least 3-4 hours at a pressure of $3-4 \times 10^{-7}$ mbar before starting the experiments.

The supersonic molecular beam with a specified kinetic energy was generated by extraction through the nozzle under a pressure gradient formed between the inside and the outside of the source. Pentacene sublimation was achieved by sending a DC current ($\sim 8-9$ A) through the tantalum foil wrapped around the quartz tube and heating it to $\sim 480$ K. To control the energy transfer in the collision between the molecules and helium atoms, the nozzle was heated to $\sim 430$ K by sending DC current ($\sim 1.1$ A) through a tantalum filament placed closeby. Generally, it took about 2-3 hours to stabilize the experimental conditions. The SiO$_x$ surface was
positioned vertically facing the incident supersonic molecular beam, which covered a spot with an area of 10 mm in diameter. All pentacene growth experiments described in this chapter were performed with the substrate at room temperature. With deposition times of 10, 20, 30 and 50 min we could monitor the evolution of pentacene submonolayer coverage for each kinetic energy of the molecular beam. The typical flux was about $6 \times 10^{11}$ molecules/(s·cm²) estimated from equation 3-1 [27] where $P_0$ is vapour pressure of thermally sublimated pentacene, $T_0$ the real temperature of pentacene during sublimation and $m$ the mass of molecule.

$$I(0) \propto \frac{P_0}{\sqrt{mT_0}} \quad (3-1)$$

$T_0$ and $P_0$ [28] were measured in the experiment of pentacene thermal sublimation, where the sublimation rate was regulated to give the same peak area in the ToF spectra as those shown in figure 3-1(a). A growth rate of 1 ML/45 min as determined by a crystal microbalance and calibrated with the thickness measurement by ex-situ tapping mode AFM, was applied for all experiments and could be adjusted by simply changing the sublimation temperature. Four different kinetic energies (3.3 eV, 5.0 eV, 6.4 eV, and 6.7 eV) were obtained by properly tuning the helium carrier gas pressure while monitoring the flux of seeded pentacene molecules through ToF spectroscopy. The pressures for our beams were 300 mbar, 760 mbar, 2000 mbar and 2400 mbar. 6.7eV was the highest kinetic energy achievable in the experimental conditions used for the investigation presented in this chapter. After pentacene deposition the sample was transferred back to the entry lock and stored there in UHV and in the dark before further characterization.

One set of pentacene submonolayers was prepared by organic molecular beam deposition (OMBD) as described in reference [29]. The deposition rate was ~ 1 ML/45 min, as measured by a quartz crystal microbalance. The substrate was kept at room temperature during deposition.

The deposited pentacene submonolayers were imaged by ex-situ tapping mode atomic force microscopy, TM-AFM, (Multimode Scanning Probe Microscope, Digital Instruments, Veeco Metrology Group, U.S.A.) with a silicon tip with nominal radius less than 10 nm as scanning probe.
Initial growth of pentacene controlled by the kinetic energy of the incident molecules

We selected five scanning regions around the centre of the deposition area and fixed the scanning size to 10\times10 \, \mu m^2. The detailed analysis of AFM data was carried out with the WSxM software (version 8.7, Nanoteclectronica S.L., Spain, see ref. 30). The statistical analysis of the AFM data was performed with the help of specific software (Origin 7.0, OriginLabs Inc., U.S.A.)

We also employed AFM to perform transverse shear microscopy (TSM) [31, 32, 33]. In this technique, a triangular shaped silicon nitride AFM tip (NP-20 Veeco Metrology and Instrument, U.S.A.) with a spring constant of 0.58 N \, m^{-1} is scanned in contact mode parallel to the cantilever’s long axis. Like this one can measure the net transverse shear force, resulting from the changes in the tip-surface interaction when the tip is scanned over regions where the molecules pack with different orientation [33]. By mapping the variation in transverse shear force with colour contrast, we could qualitatively determine the crystallinity of a single molecular island or of the monolayer. 10\times10 \, \mu m^2 TSM images were collected in parallel with the AFM height images for samples grown by OMBD and SuMBD presenting a nearly completed first monolayer.

3.3 Investigation of pentacene submonolayer growth

3.3.1 Formation of pentacene islands

Figure 3-2 presents TM-AFM micrographs illustrating the morphology of pentacene layers corresponding to ~ 0.3ML coverage and resulting from different growth conditions. All SuMBD samples (Fig. 3-2 (b-d)) consist typically of lobular islands with smooth edges, while the OMBD sample (Fig. 3-2 (a)) is characterized by islands with rougher edges as well as by the presence of smaller dendritic islands, as minority species. If one ignores the minority species, the samples grown by OMBD (Fig. 3-2 (a)) and by SuMBD with \( E_k = 3.3 \, \text{eV} \) (Fig. 3-2 (b)) are rather similar in that they both show a larger average island size and lower nucleation density than the samples grown by SuMBD at \( E_k = 5.0 \, \text{eV} \) and \( E_k = 6.4 \, \text{eV} \), shown in Figs. 3-2 (c) and 3-2 (d), respectively.
Figure 3-2: Tapping mode AFM (10×10 µm²) micrographs of pentacene submonolayers grown by OMBD (a) and by SuMBD at \( E_k = 3.3 \text{ eV} \) (b), \( E_k = 5.0 \text{ eV} \) (c) and \( E_k = 6.4 \text{ eV} \) (d). The inset of figure (d) shows the angle of 82° formed by two island edges.

The nucleation density (N) as a function of the kinetic energy of the impinging molecules, plotted in figure 3-3 (a), quantifies this observation. To derive N, the molecular island number was averaged from five AFM images collected in different regions on each sample, by using the flooding function in the WSxm 8.7 software. For the sample grown with pentacene at \( E_k = 6.4 \text{ eV} \), N is \( \sim 57\% \) higher than for the OMBD sample and \( \sim 45\% \) higher than for the SuMBD sample grown at \( E_k = 3.3 \text{ eV} \) but it is only \( \sim 5\% \) higher than for the SuMBD sample grown at \( E_k = 5.0 \text{ eV} \). We suggest that this difference is generated by the different
Initial growth of pentacene controlled by the kinetic energy of the incident molecules

molecular surface diffusivity due to the different growth regimes. In fact, the experimental evidence indicates that pentacene monomers with high $E_k$ ($\geq 5.0$ eV) may sample many adsorption sites before being adsorbed or desorbed with roughly an equal probability to either integrate into a preformed islands or form a new nucleus on the empty surface in between the islands. On the other hand for samples grown with pentacene at low $E_k$, such as in OMBD and SuMBD with $E_k = 3.3$ eV, the probability for an incoming monomer to irreversibly integrate into the preformed molecular islands becomes dominant with respect to forming new nuclei in an uncovered substrate region [14].

We calculated the average island size for each sample from the sum of four island area histograms obtained from four AFM images collected in different regions of each sample. The sum histograms are presented in figure 3-3 (b) and the average island size is derived by fitting the data with a lognormal function. We found average island sizes of $0.13 \pm 0.02 \mu m^2$, $0.12 \pm 0.01 \mu m^2$ and $0.11 \pm 0.01 \mu m^2$ for SuMBD samples, where pentacene impinges with $E_k = 3.3$ eV, $5.0$ eV and $6.4$ eV. An average island size of $0.22 \pm 0.07 \mu m^2$ was determined for the OMBD sample. From figure 3-3 (b), one clearly sees that the island size distribution becomes narrower and peaked at smaller values when the kinetic energy increases. This trend towards a more uniform island size that is characteristic of a changeover towards correlated island growth as proposed by S. Pratontep et al [34, 35], where the overlap area of the capture zones of neighbouring islands is large. The broader island size distribution is observed for the sample deposited with the $3.3$ eV beam and with the thermal energy growth. An insight into the growth of pentacene islands from hyperthermal beams can be achieved by considering that it is a diffusion limited process [21,22]. When colliding with the surface, the initial kinetic energy of pentacene is converted (partially) into kinetic energy parallel to the surface via a complex mechanism involving inelastic molecule-molecule and molecule-surface energy transfer processes [36, 37, 38, 39]. It is therefore reasonable to assume, by extending consolidated growth models [21, 22, 23], that molecules with higher kinetic energy diffuse over longer distances before aggregating with other diffusing molecules or before being captured by pre-formed molecular islands. This would result in a more uniformly dispersed pattern of small molecular islands. On the contrary, molecules with a lower kinetic energy travel shorter distances on the surface and have a lower probability to form new
Initial growth of pentacene controlled by the kinetic energy of the incident molecules

Figure 3-3: (a) Molecular island density obtained from submonolayers grown by OMBD and by SuMBD at $E_k$ of 3.3 eV, 5.0 eV and 6.4 eV; (b) Molecular island size distribution for the same samples.
Another important issue that we investigated is the role played by the kinetic energy of the impinging pentacene molecules in determining the island shape. To this end we considered the islands at low coverage where coalescence has not started yet (see Fig. 3-2 (a-d)) and determined the fractal dimension for each growth condition. The island fractal dimension ($D_f$), as illustrated in figure 3-4 (a-d), is calculated by the area-perimeter relationship $P = kA^{2/D_f}$, proposed in [40], where $P$ the island perimeter, $A$ its area, $k$ a scaling constant and $D_f$ the fractal dimension. When the $D_f = 2$ it means the measured structure has the typical fractal shape because of the highest self similarity, which means that the object is exactly or approximately similar to a part of itself, such like the coastline. The mean $D_f$ turns out to be decreasing from $1.40 \pm 0.05$ for the SuMBD samples grown at $E_k = 3.3$ eV to $1.39 \pm 0.04$ for those deposited with $E_k = 5.0$ eV and $1.30 \pm 0.03$ for the layer formed when $E_k = 6.4$ eV. The data points are more and more scattered as $E_k$ decreases (see Fig. 3-4(c)) due to the larger dispersion in island size distribution but the $D_f$ values never approach those typical of a fractal island structure, in agreement with the island morphology observable in Fig. 3-2. For the islands grown by OMBD, the mean $D_f$ can not be correctly derived by one linear fit because of the presence of two types of islands (see discussion Fig. 3-2 (a) above) causes a much larger scattering of the data points. However, as shown in figure 3-4 (d), if two different linear fittings are carried out for the majority and the minority species of islands, one obtains a large mean $D_f = 1.69 \pm 0.05$ for the small dendritic islands (reversed filled triangles in the figure), and $D_f$ of $1.60 \pm 0.05$ for the data corresponding to the larger islands (labeled by filled diamonds). Dendritic or fractal islands occur naturally during growth in systems where island edge diffusion is restricted.

To better understand how the molecular island shape is correlated with the kinetic energy of the impinging molecules, we performed a statistical analysis of the ratio ($R$) between the large ($L_L$) and small ($L_s$) dimensions of pentacene islands, the result of which is plotted in figure 3-5. The average $R$ values were obtained by measuring 50 molecular islands randomly chosen for each sample. Although the error bars are relatively large, there is an indication of a trend towards the formation of anisotropic
Initial growth of pentacene controlled by the kinetic energy of the incident molecules

Figure 3-4: Mean fractal dimension ($D_f$) obtained from (a) sample prepared by SuMBD at 6.4 eV with $D_f = 1.30 \pm 0.03$; (b) sample prepared by SuMBD at 5.0 eV with $D_f = 1.39 \pm 0.04$; $S$ is the measured area and $P$ is the perimeter of the individual island.
Initial growth of pentacene controlled by the kinetic energy of the incident molecules

Figure 3-4: Mean fractal dimension ($D_f$) obtained from (c) sample prepared by SuMBD at 3.3 eV with $D_f = 1.40 \pm 0.05$; (d) sample prepared by thermal evaporation with the $D_f = 1.60 \pm 0.05$ and $D_f = 1.69 \pm 0.05$. $S$ is the measured area and $P$ is the perimeter of the individual island.
Initial growth of pentacene controlled by the kinetic energy of the incident molecules

![Graph showing the ratio \( R = \frac{L_L}{L_s} \) between the large length \( L_L \) and small length \( L_s \) of deposited pentacene islands in different submonolayers prepared by OMBD and by SuMBD at \( E_k \) of 6.4 eV, 5.0 eV and 3.3 eV. Inset shows the definition of \( L_L \) and \( L_s \).]

islands when \( E_k \) increases. This anisotropic island formation cannot be due to an anisotropy in surface diffusion of pentacene since SiO\(_x\) is chemically inert and amorphous, we suggest instead that it is caused by the molecular diffusion at island edges, which can also trigger the formation of a non-fractal structure [41, 42].

A quantitative assessment of the initial growth process was achieved by determining the critical nucleus, \( i \) (\( i+1 \) = number of molecules forming a stable nucleus), on the basis of the general scaling function (3-2) introduced by Amar and Family [23] and extended to pentacene growth by Ruiz et al. [21], and hence reproposed by Tejima et al. and Stadlober et al. [43, 44]. \( C_i \) and \( b_i \) are constants determined by hypergeometrical equations (3-3), (3-4) for \( i=0 \) to 3 that assure normalization and proper asymptotic behaviour of \( f_i(u) \); \( u = a/A(\theta) \) (\( a \) is the area of each molecular island extracted in the pentacene submonolayer, \( A(\theta) \) is the average island size); \( \Gamma \) is the gamma function, which is an extension of the factorial function to real and complex number.
Initial growth of pentacene controlled by the kinetic energy of the incident molecules

\[ f_i(u) = C_i u^i e^{-ib_i u^{\frac{1}{b_i}}} \]  \hspace{1cm} (3-2);

\[ (ib_i) = \frac{\Gamma[(i + 2)b_i]}{\Gamma[(i + 1)b_i]} \]  \hspace{1cm} (3-3);

\[ (C_i) = \frac{[(ib_i)^{(i+1)b_i}]}{[b_i \Gamma[(i + 1)b_i]]} \]  \hspace{1cm} (3-4);

Figure 3-6(a) compares the properly normalized island size distributions of pentacene submonolayers grown at \( E_k = 3.3 \) eV and \( E_k = 6.4 \) eV with the predictions of the general scaling model calculated for \( i = 1, 2 \) and 3. For the highest \( E_k \) used here, we systematically observed a much better agreement for \( i=2 \), as confirmed by the \( \chi^2 \) criterion. At \( E_k \) lower than about 5.5-6.0 eV, the experimental island size distribution is better reproduced by the \( i=3 \) distribution, as was previously reported for submonolayers deposited on similar substrates and temperatures by thermal sublimation [21, 43, 44]. Analyzing series of different sets of data by best fitting procedures, we confirmed that the critical nucleus decreases from 3 to 2 over a threshold of \( E_k \) of the molecules in the beam as shown in figure 3-6(b).

The diffusion growth model confirms the important role played by \( E_k \) in regulating the formation and the growth of pentacene islands. The probability that three free molecules with high surface diffusivity meet is higher than that four free molecules with lower diffusivity come together and this is the basic mechanism that explains the high nucleation density with a dispersive nuclei distribution obtained for samples grown at \( E_k \geq 5.0 \) eV in the low coverage regime. Furthermore, the high nucleation density can proportionally reduce the average island-island distance, which is favourable to the growth of the highly correlated molecular islands. Since the growth is diffusion mediated, such a higher density shifts the onset of the island-island coalescence process to a much earlier stage. The final outcome is a process where the smaller and more mobile islands can merge easier in a crystalline film with reduced number of grain boundaries.

When comparing our findings to the ones of Killimpally et al. [20],
Initial growth of pentacene controlled by the kinetic energy of the incident molecules

Figure 3-6: (a) The properly normalized island size distributions of films formed at $E_k=6.4$ eV (■) and $E_k=3.3$ eV (○) indicate different critical nucleus sizes, respectively $i=2$ and $i=3$, in the framework of the scaling function predictions reported in the plot as broken line ($i=3$), continuous line ($i=2$) and dotted line ($i=1$) (see text), $N(\theta)$ is island size distribution, $A(\theta)$ is average island size and $\theta$ is coverage; (b) Critical nucleus sizes extracted from the experimental island distributions as a function of $E_k$ of pentacene molecules, for 10 min deposition time. The lines for $i=2$ and $i=3$ are shown as guide the eye. A transition between two different growth regimes is observed at ~5.5-6.0 eV.
Initial growth of pentacene controlled by the kinetic energy of the incident molecules

one notices important differences in the $E_k$-dependence of the coverage and of the morphologies as well as of the critical nucleus. Our results demonstrate that remarkably different regimes of growth can be achieved in SuMBD by carefully tuning kinetic energy and flux (the growth rates in our experiments were about a factor 50 lower than that in [20]).

3.3.2 Morphological evolution of the pentacene submonolayer

Figure 3-7 shows the TM-AFM micrographs of layers obtained with the same deposition conditions as in Fig. 3-2 but for longer deposition times. When the coverage increases up to $\sim 0.5 - 0.65$ ML, island coalescence is observed for all samples (Fig. 3-7 (a-d)). From the surface morphology one concludes that second layer nucleation occurs at this coverage for the OMBD grown pentacene layer in agreement with a previous report [14]. On the other hand, second layer nuclei are extremely rare for all SuMBD samples. When further extending the deposition to a time where the coverage of all samples is close to completion of their first monolayer (see figure 3-7 (e-h)), all pentacene islands are connected to each other via coalescence, while grain boundaries appear. For all samples the monolayer is $1.5\pm0.2$ nm thick confirming that pentacene molecules

Figure 3-7: Tapping mode AFM (10×10 $\mu$m²) micrographs of pentacene submonolayers grown by OMBD (a and e)
Initial growth of pentacene controlled by the kinetic energy of the incident molecules.

Figure 3-7: Tapping mode AFM (10×10 µm²) micrographs of pentacene submonolayers grown by SuMBD at $E_k = 3.3$ eV (b and f), $E_k = 5.0$ eV (c and g) and $E_k = 6.4$ eV (d and h).
Initial growth of pentacene controlled by the kinetic energy of the incident molecules

... pack upright. Second and third layer nuclei typical of the Vollmer-Weber growth mode are now very clearly visible for the OMBD sample. While a few second layer islands are also present on top of the first layer of SuMBD sample grown at $E_k = 3.3$ eV (Fig. 3-7 (f)), SuMBD samples produced at higher kinetic energies still hardly show any second layer formed on the top of first monolayer implying the Stransky-Krastanov growth mode. This is a strong indication that at high $E_k$ the diffusivity of pentacene, after landing on top of the first layer islands, is sufficiently high to always sample the island edge and its energy is large enough to overcome the edge barrier or “Schwoebel barrier” [45], which otherwise hinders the impinging pentacene from moving down to the substrate. This assumption receives support from the fact that we often observe an island shape as shown in the inset of figure 3-2 (d): the angle of $\sim 82^\circ$, formed by two island edges is very close to that formed by the $a$-$b$ lattice vectors in the pentacene (001) crystal plane as reported by J. E. Northrup et al. in the calculation of pentacene packing in the single layer [46].

3.3.3 Crystallinity of first pentacene monolayer

To learn more about the quality of the first monolayer and in particular to determine the size of single crystal domains, we carried out transverse shear microscopy studies. When scanning over the surface of a polycrystalline layer, the tip feels a different friction on crystal domains with different pentacene orientation and packing. The distribution of crystal domains is identified by the friction force contrast that is visualized by different colours.

Figure 3-8 compares the contact mode AFM micrographs where colour represents height on sample surface together with the corresponding TSM images for samples grown by OMBD and by SuMBD at $E_k$ of 3.3 eV and 6.4 eV. The OMBD sample (Fig. 3-8 (a, b)) shows a typical polycrystalline structure with random in-plane orientation of the single crystalline domains in the first monolayer. The domain size reaches 1-2 $\mu$m that corresponds very closely to the average size of isolated pentacene islands before the onset of aggregation. The coalescence process seems not to influence the orientation alignment of the merging islands (see arrows in figure 3-8 (b)), in agreement with previous findings [33] so that a large number of grain boundaries is present in the first monolayer. The second

56
Initial growth of pentacene controlled by the kinetic energy of the incident molecules

Figure 3-8: Contact mode AFM height images and transverse shear force micrographs of pentacene monolayers grown on a SiO$_x$ surface by OMBD ((a) and (b), respectively) and by SuMBD where the molecules impinge on the surface with a kinetic energy of 3.3 eV ( (c) and (d), respectively) and of 6.4 eV ((e)and (f), respectively). White arrows point to single crystal grains.
layer islands, which cover about 1/5 of the monolayer, show a typical dendritic shape and most of them are composed of several crystalline domains. The SuMBD sample grown at $E_k = 3.3$ eV (Fig. 3-8 (c, d)) displays larger single crystalline domains (see arrows in figure 3-8 (d)) with more regular shape and sharp edges. The islands have merged after coalescence and hence the number of grain boundaries are much less than in the OMBD grown sample. Furthermore, in the second layer, covering about 1/4 of the first one, the percentage forming single-crystalline islands is much higher than in the OMBD sample. In the film grown at $E_k = 6.4$ eV (Fig. 3-8 (e, f)) the size of single crystal domains in the first monolayer increases dramatically. The largest single crystalline domain within the $10 \times 10 \mu m^2$ scanning area, indicated by the arrow in Fig 3-8 (f), spans 9-10 $\mu m$. The second layer covers about 1/3 of the monolayer and all of its molecular islands are larger than those of the other two samples and show a single crystal structure. There is hence a strong indication that the majority of the second layer islands grow epitaxially on the underlying crystal domain since they show the same friction force contrast as the layer below. This implies that at high kinetic energies of the impinging pentacene, the island growth is highly correlated with a mechanism that favours orientational alignment of the islands before coalescence occurs. On the basis of our experimental evidence and in particular in order to explain the generation of the observed large domains, we speculate that the reorientation of entire islands should be part of the energy dissipation mechanisms characteristic of SuMBD growth. Theoretical studies would be helpful to further clarify this question.

### 3.4 Conclusions

We have demonstrated that the kinetic energy of pentacene molecules, landing on a silicon oxide surface, plays a crucial role in determining island structure, shape, size distribution and even the quality of the first monolayer as well as of upper layers. By increasing $E_k$ the island structure reverts from fractal to non-fractal structure in the low coverage regime, the island shape becomes more anisotropic due to the molecular diffusion along the island edges and the island size becomes more uniform because of correlate island growth. We interpreted the impact of $E_k$ in terms of the diffusion mediated model, and found that the critical nucleus reduces
Initial growth of pentacene controlled by the kinetic energy of the incident molecules

from i=3 (typical for OMBD) to i=2 for $E_k \geq 5$-6 eV. The completion of the first layer before the second one starts to form has been clearly observed from all samples grown by SuMBD indicating the Stransky-Krastanov growth mode. The quality of first monolayer is greatly improved when $E_k \geq 5.0$ eV presenting very few grain boundaries. The formation of single crystalline domains spanning over up to $\sim 10 \mu m$ in the monolayer is successfully achieved in the growth at the high kinetic energies. To explain the formation of single crystalline domains spanning over up to $\sim 10 \mu m$ in the monolayer, we suggest that this is consistent with the reorientation of entire island, which is part of the energy dissipation at these high kinetic energies, during coalescence.

References

Initial growth of pentacene controlled by the kinetic energy of the incident molecules

Initial growth of pentacene controlled by the kinetic energy of the incident molecules

Initial growth of pentacene controlled by the kinetic energy of the incident molecules
Chapter 4

Dynamic growth of pentacene submonolayers on SiO$_x$ by supersonic molecular beam deposition*

Pentacene submonolayer growth on SiO$_x$ surface by supersonic molecular beam deposition at different kinetic energies (E$_k$), incidence angle ($\theta$) and substrate temperature was studied. When increasing the incidence angle at constant E$_k$, the pentacene sticking coefficient ($S_0$) decreases due to the enhanced molecule-surface scattering, induced by parallel to normal momentum conversion. However, with increasing E$_k$ at constant $\theta$, $S_0$ also decreases because when the impinging molecules retain more energy after the initial inelastic collision, their probability of being scattered away from the surface is higher. Surface phonon assisted molecule - surface scattering is suppressed for growth at lower substrate temperature ($\sim$ 200 K) at normal incidence as evidenced from an increased pentacene sticking coefficient with respect to room temperature (RT) deposition in the initial growth period. For growth at $\theta = 75^\circ$, however, the relatively lower surface phonon density at $\sim$ 200 K seems to hamper the energy dissipation of molecules during their diffusion parallel to the surface since a lower initial sticking coefficient is observed than for RT growth. The nucleation density and island size for different growth conditions are strongly influenced by the effects of molecular surface diffusivity and molecule - surface scattering. The critical nucleus size, determined by the general scaling function, shows a strong dependence on the normal component of E$_k$ and a transition from 2 to 3 molecules as critical nucleus size is found for growth at E$_k$ = 6.3 eV when $\theta$ is increased, moving away from the normal incidence.

* This chapter is based on Yu Wu, Tullio Toccoli, Salvatore Iannotta and Petra Rudolf “Dynamic growth of pentacene submonolayers on SiO$_x$ by supersonic molecular beam deposition”, manuscript in preparation.
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4.1 Introduction

Pentacene, a promising candidate for highly efficient and high quality organic electronic devices, is widely studied. Recent efforts intended to improve the crystalline quality of pentacene thin films focused on supersonic molecular beam deposition (SuMBD) as a new method for pentacene thin film growth [1, 2]. With this technique the kinetic energy of impinging molecules can be easily tuned from thermal energy up to several eV by means of changing the seeded molecular concentration in the carrier gas. Several reports appeared on the initial growth of pentacene submonolayers [3, 4, 5, 6, 7], on the comparison between pentacene submonolayer morphologies for layers grown by SuMBD and by thermal sublimation [8] as well as on the carrier transport in field effect transistors based on SuMBD grown pentacene thin films [9]. So far, it has been demonstrated that the critical nucleus size, the crystallinity of the first monolayer and the structure of molecular islands in the first pentacene layer are all strongly correlated with the kinetic energy at which the molecules impinge on the substrate surface. Moreover, with SuMBD, the first pentacene monolayer is completed before the second layer starts to grow, and a better quality pentacene monolayer with larger single crystal grains and much less grain boundaries was realized when $E_k > 5 - 6$ eV [4]. Improved carrier transport (hole mobility $\approx 1.0 \text{cm}^2\text{V}^{-1}\text{s}^{-1}$) was achieved in transistors based on SuMBD grown pentacene thin films [9]. A fundamental study of the interaction between energetic pentacene molecules and a SiO\textsubscript{x} surface by A. S. Killampalli et al. [3] proposed that the decrease of pentacene adsorption probability with increasing $E_k$ was dominated by a trapping mediated process [10]. The influence of parallel and normal momentum were found to be equally important for adsorption in these conditions, as demonstrated by applying the energy scaling process in a regime between the normal energy scaling [11, 12] and the total energy scaling [13, 14]. However, so far no detailed study of the critical nucleus size, the variation of molecular island size and the evolution of submonolayer coverage for SuMBD growth at different $E_k$ and $\theta$ has been carried out. This is what we aimed for in this investigation of pentacene submonolayers deposited by SuMBD on a silicon oxide surface, where we varied the kinetic energy of the impinging molecules, the incidence angle and the temperature of the substrate during growth. We find that all three parameters strongly influence the molecular sticking coefficient, the
molecular island density and the size distribution as well as the critical nucleus size.

4.2 Experiments

Experiments were conducted with a home-built SuMBD setup. In the first set of experiments, pentacene submonolayers were grown with the same beam fluxes but with two different kinetic energies (\(E_k\)), 6.3 eV and 2.9 eV, of the impinging molecules arriving at the surface (kept at room temperature (RT)) at three different \(\theta\) (which is the angle formed between the direction of the incidence beam and of the substrate normal): in normal incidence, at 45° and 75°. In the second set of experiments, pentacene submonolayers were grown at constant \(E_k\) of 6.3 eV, two different \(\theta\), namely normal incidence and 75°, and two different substrate temperatures, RT and ~ 200 K. 500 nm and 280 nm thick SiOₓ / Silicon wafers (purchased from Silicon Quest International, USA) with a low root mean square surface roughness (~ 5-6 Å) were used as substrates in the first and second series of experiments, respectively. These wafers were cleaved into 10 × 10 mm² pieces and cleaned by boiling in acetone for 1 minute, followed by sonication for 20 s. Then, the wafers were transferred into isopropan-2-ol ((CH₃)₂CHOH) solution and sonicated for another 30 s. Finally they were dried by spinning and blowing with N₂ (99.995%) gas. Contact angle measurements gave 55 ± 2° for the substrate terminated with a 500 nm thick SiOₓ layer and 17.6 ± 2° for the one with the 280 nm thick SiOₓ layer, indicating that the latter was a more hydrophilic surface.

Purified pentacene powder with dark blue colour (99.98%, purchased from Sigma Aldrich, Corp.) was carefully loaded into a quartz tube and outgassed in the source chamber of the SuMBD setup for at least 3 hours at a pressure of 10⁻⁸ mbar. Thermally sublimated pentacene molecules were seeded into the helium carrier gas and extracted through the resistively heated nozzle (\(\phi \sim 50 \, \mu\text{m}\)) at one end of the quartz tube. A focused molecular beam with an optimized directionality was formed after passing through a skimmer (\(\phi \sim 0.7 \, \text{mm}\)) located at the connection between the source chamber and the preparation chamber. Before starting the deposition experiments, the pentacene molecular beam was characterized by a home-built time of flight mass spectrometer (ToF) in order to extract the average kinetic energy and velocity distribution of the seeded molecules.
in the generated supersonic molecular beam and to assure that no chemical impurities, molecular dissociation or cluster formation were present in the beam. The carrier gas pressures and the nozzle temperature are used to tune the $E_k$ in the produced supersonic molecular beam. To obtain the appropriate $E_k$ of 6.3 and 2.9 eV, a nozzle temperature of $\sim 400$ K and a helium carrier gas pressure of $\sim 2000$ mbar and $\sim 300$ mbar, respectively, were applied. The aligned molecular beam impinging in the centre of substrate surface, covering a round spot with a diameter of $\sim 10$ mm. We used three growth times, namely 10, 20 and 30 min, for the purpose of monitoring the morphological evolution of the pentacene submonolayer for each growth condition.

Ex-situ tapping mode atomic force microscopy (AFM) was performed with Multimode Scanning Probe Microscope, Digital Instruments, Veeco Metrology Group, U.S. using a silicon tip with radius <10 nm as the scanning probe for best image resolution. The measurements were carried out right after completing the pentacene submonolayer growth in order to avoid any ageing effect after exposing samples to ambient air. Five different $10 \times 10 \mu m^2$ scanning regions around the center of each sample were chosen for imaging the surface morphology with $512 \times 512$ scanning lines. The detailed analysis of AFM data was performed with the WSxM software (version 8.7, Nanotec electronica S.L.[15]) and the statistical analysis of the AFM data was carried out with the help of software (Origin 7.0, OriginLabs Inc.).

4.3 Investigation of pentacene submonolayer growth with different $E_k$ and $\theta$ at RT

4.3.1 Evolution of pentacene submonolayer morphology

Figure 4-1 shows the surface morphology of the pentacene submonolayers obtained in the first set of experiments as revealed by AFM. For samples grown with $E_k=2.9$ and 6.3 eV at normal incidence, $\theta = 45^\circ$ and $\theta = 75^\circ$, the average height of measured molecular islands indicate the values close to the nominal length ($\sim 1.5$ nm) of the long axis of single pentacene molecule, indicating that the thickness of all pentacene
submonolayers achieved in this set of experiment corresponds to a single layer. For the initial growth period, corresponding to the AFM micrographs collected after the first 10 min growth and shown in the first row of figure 4-1(a, d, g, j, m, p), a morphology variation with the incidence angle of the molecular beam is easily distinguished: both submonolayer coverage and molecular island size decrease when $\theta$ increases from normal incidence to $75^\circ$ implying a drop of the molecular sticking coefficient. The island density is obtained by simply counting the number of islands within the fixed scanning area. To obtain statistically relevant results, we averaged the number of islands obtained in all five scanned regions of each sample. At normal incidence, we found that a higher island density of $\sim 1.35 \, \mu m^{-2}$ is obtained for samples grown at $E_k = 6.3$ eV than for sample grown at $E_k = 2.9$ eV ($\sim 1.22 \, \mu m^{-2}$), in agreement with our previous results [3]. When $\theta$ is increased to $45^\circ$, the effects of molecule – surface scattering and of the energy component parallel to the surface have to be taken into account simultaneously to explain the surface morphology. The island densities of samples grown with this geometry are similar to those obtained at normal incidence. As one would have expected a lower island density because of the scattering the observed similar island density implies that the larger parallel energy component may enhance the surface diffusivity and hence increase the probability of nucleation. However, due to the increased molecule – surface scattering, the island growth can be slowed down as evidenced by the smaller island size when the beam impinges at $\theta = 45^\circ$ as compared to normal incidence. When the molecules hit the surface at $\theta = 75^\circ$, we obtained a much lower nucleation density than that at $\theta = 45^\circ$, namely $\sim 0.46 \, \mu m^{-2}$ for the sample grown at $E_k = 6.3$ eV and $\sim 0.64 \, \mu m^{-2}$ for the one grown at $E_k = 2.9$ eV, and an even smaller island size. It seems therefore that the molecule – surface scattering is more pronounced at $\theta = 75^\circ$ than at $\theta = 45^\circ$ and this leads to a decreased probability of island nucleation or capture by a preformed island.

When extending the growth time to 20 minutes, the molecular islands are all enlarged for samples grown at normal incidence and $\theta = 45^\circ$ as shown in figure 4-1(b, e, h, k), but apparently not for samples grown at $\theta = 75^\circ$, see figure 4-1(n, q). The island density has saturated at this point or maybe even earlier since the number of islands for all samples is close to that obtained after the first 10 min of growth. The molecular islands evidently keep expanding laterally after island density saturation and, for
Dynamic growth of pentacene submonolayers on SiO_x by supersonic molecular beam deposition

Figure 4-1: AFM images of the surface morphology of pentacene grown at RT on SiO_x at E_k = 6.3 and 2.9 eV, incidence angle of the supersonic molecular beam: \( \theta = 0^\circ \). Each pentacene submonolayer deposition was carried independently.
Dynamic growth of pentacene submonolayers on SiOₓ by supersonic molecular beam deposition

Figure 4-1: AFM images of the surface morphology of pentacene grown at RT on SiOₓ at Eₐ = 6.3 and 2.9 eV, incidence angle of the supersonic molecular beam: θ = 45°. Each pentacene submonolayer deposition was carried independently.
Dynamic growth of pentacene submonolayers on SiO\textsubscript{x} by supersonic molecular beam deposition

Figure 4-1: AFM images of the surface morphology of pentacene grown at RT on SiO\textsubscript{x} at $E_k = 6.3$ and 2.9 eV, incidence angle of the supersonic molecular beam: $\theta = 75^\circ$. Each pentacene submonolayer deposition was carried independently.
samples grown at both normal incidence and $\theta = 45^\circ$, figure 4-1 (b, e, h, k) gives clear evidence that the coalescence process has started. More connections between neighbouring islands can be noticed after 30 min of growth in figure 4-1(c, f, i, l) while pentacene second layer growth is still hardly observed even on the top surface of large islands as already seen from the average height measurement discussed above. However, particularly for samples grown with $E_k = 6.3$ eV and at $\theta = 75^\circ$, the morphological variation seems rather small if one compares the images obtained after 20 min and 30 min of growth depicted in figure 4-1(n) and (o), respectively. This points to very important molecule – surface scattering during the growth, which slows down the expansion of the individual islands and prevents the nucleation of new ones.

To investigate how the sticking coefficient changes for different growth condition, we calculated the ratio between the number of adsorbed molecules on the surface after first 10 min of growth and the incoming molecular flux, taking into account that with increasing $\theta$ the effective area of beam – surface interaction increases from $\sim 79$ mm$^2$ at normal incidence to $\sim 111$ mm$^2$ at $\theta = 45^\circ$ and $\sim 304$ mm$^2$ at $\theta = 75^\circ$. This means that the effective flux decreases from $\sim 6000$ s$^{-1}$µm$^{-2}$ determined at $\theta = 0^\circ$, to an estimated 4500 s$^{-1}$µm$^{-2}$ at $\theta = 45^\circ$ and 1600 s$^{-1}$µm$^{-2}$ at $\theta = 75^\circ$. Figure 4-2 shows the sticking coefficient, calculated based on the coverage after 10 min deposition, as a function of the incidence angle and the kinetic energy of the incident molecules. Three important trends can be distinguished: 1) with increasing $\theta$, $S_0$ decreases for all the samples; 2) at fixed $\theta$, $S_0$ is always lower for growth at $E_k = 6.3$ eV than for growth at $E_k = 2.9$ eV, by 8.6% for normal incidence, by 14.5% for deposition at $\theta = 45^\circ$ and by 68.4% when the beam hits at $\theta = 75^\circ$; 3) $S_0$ drops by $\sim 40\%$ with increasing $\theta$ from normal incidence to $75^\circ$ for the sample grown at $E_k = 6.3$ eV whereas only $\sim 7\%$ decrease of $S_0$ is found for the sample deposited with lower kinetic energy. These observations can be understood based on classical molecular dynamics simulations for SuMBD of ethane on Si(100) [10], a system where a similar sticking behaviour was observed experimentally. These simulations showed that energy exchange on first impact with the surface largely dictates whether the incident molecule will stay on the surface: during the first collision with the surface, the normal component of momentum is dissipated very effectively, whereas the parallel component of momentum is not. This process leaves the molecule in a vibrationally and rotationally excited state, which allows it to make
subsequent impacts with the surface and undergo further energy dissipation processes. However, molecules with a large parallel momentum were found to retain a substantial fraction of it after the initial impact with the surface [10]. Parallel momentum, as well as any energy stored in rotations, can be converted into normal momentum during subsequent impacts, causing the molecules to scatter back into the vacuum. Therefore, molecules with high kinetic energy impinging at glancing angles may scatter from the surface before the parallel momentum can be dissipated. This implies that the lowest sticking coefficient will result for the highest $E_k$ and the largest $\theta$ as observed in our experiments.

Next we wanted to understand the evolution of the growth for longer deposition time where also the preformed islands influence the surface diffusion. For this we investigated the pentacene submonolayer coverage by analyzing the AFM images, normalized it to the impinging molecular flux. The data are reported in figure 4-3 as a function of growth

![Graph showing sticking coefficient as a function of incidence angle](image_url)

**Figure 4-2:** The molecular sticking coefficient of pentacene deposited at different kinetic energy of 6.3 eV and 2.9 eV as function of different incidence angle.
Figure 4-3: Normalized coverage of pentacene sub-monolayers obtained in different SuMBD growth conditions as a function of growth time from the analysis of the AFM images. The linear fits of the data give the growth rate for each set of kinetic energy and different incidence angle.

time and seen to increase monotonically for all samples. The growth rates for the various deposition conditions characterized each by a certain kinetic energy and incidence angle are determined by the linear fits, also shown in figure 4-3. Samples grown at \( E_k = 2.9 \text{ eV} \) show very similar growth rates (\( \sim 0.018 - 0.019 \text{ ML/min} \)) for all incident angles of the molecular beam. However, for samples grown at \( E_k = 6.3 \text{ eV} \), the growth rate slightly decreases (from \( \sim 0.019 \text{ ML/min} \) to \( \sim 0.016 \text{ ML/min} \)) with increasing \( \theta \) from normal incidence to \( 45^\circ \), and further drops to \( \sim 0.011 \text{ ML/min} \) for \( \theta = 75^\circ \). These results indicate that the applied molecular kinetic energy is an important factor determining the growth rates of deposited pentacene submonolayers.

### 4.3.2 Investigation of pentacene island size and critical nucleus size
Our detailed morphology investigation included analyzing the AFM data for samples obtained in the first sets of experiments to extract the island size distribution and the average island size (A_{av}). We considered only the images collected from pentacene submonolayers after first 10 min deposition where no island coalescence had yet occurred. In figure 4-4 (a, b) we report the histograms of the island size (A) for different growth conditions as obtained from a scanning area of 10 × 10 µm², together with the fit (using a log normal function) with a single peak. The average island size is given by the position of the peak in the distribution curve. To assure reliable results, ~ 400 islands were included in the average island size calculation for each sample. The obtained average island sizes are 0.15±0.02, 0.09±0.01 and 0.06±0.01 µm² for samples grown at E_k= 6.3 eV, at normal incidence, θ = 45° and 75° and 0.19±0.03, 0.14±0.02 and 0.07±0.01 µm² for samples grown at E_k= 2.9 eV, at normal incidence, θ = 45° and 75°. The average island size decreases with increasing θ and for each incidence angle, the average island size obtained for samples grown with E_k= 2.9 eV is always larger than the one of samples grown with E_k = 6.3 eV. This suggests that less molecule – surface scattering and lower surface diffusivity caused by the smaller E_k favor lateral expansion of the islands via trapping of more molecules on the surface. With increasing θ, the distribution of island sizes obtained for the growth becomes narrower for both the kinetic energies used. The full width at half maximum (FWHM) of the peak drops from 0.10 µm² (0.12 µm²) at normal incidence to 0.06 µm²(0.10 µm²) at θ = 45° and to 0.05 µm² (0.05 µm²) at θ = 75° for samples grown with E_k = 6.3 eV (2.9 eV). This indicates that higher island size uniformity is achieved in the growth at large incidence angle.

Investigating the critical nucleus size for the different growth conditions is another interesting issue in this work since, so far, there is no study of the pentacene critical nucleus size for growth on SiO_x for molecules impinging not along the surface normal. In the submonolayer regime, the average island size and number of islands with a certain size in a unit area can be scaled by using the formula of \( N_s \sim \alpha x A_{av}^2 f_i(A/A_{av}) \) (4-1) [16] where \( \alpha \) is the coverage and \( f_i \) is the general scaling function \( f_i(u)= C_i u^i e^{-iu^i} \) (4-2) introduced by Amar and Family [17]. The term of ‘i’ presents the critical nucleus size, which is one molecule less than the number of pentacene needed for forming a stable nucleus, and can...
Dynamic growth of pentacene submonolayers on SiOₓ by supersonic molecular beam deposition

Figure 4-4: Island size distribution of pentacene submonolayers grown on SiOₓ by 10 min exposure to the supersonic beam operated at two different kinetic energies (a) $E_k = 6.3 \text{ eV}$ and (b) $E_k = 2.9 \text{ eV}$ at normal incidence, $\theta = 45^\circ$ and $\theta = 75^\circ$. 
Figure 4-5: The critical nucleus size obtained from pentacene submonolayers after 10 min of deposition of molecules with kinetic energies of 6.3 and 2.9 eV, plotted as function of θ at normal incidence, 45° and 75°. The lines are shown as guided the eye.

be extracted by performing the nonlinear least square fitting of the rescaled island size distribution as reported by Ruiz et al.[18], Tejima et al.[19] and B. Stadlober et al. [20]. C_i and b_i are constants determined by hypergeometrical equations for i = 1 to 3 that assure normalization and proper asymptotic behavior of f(u). Values of 1, 2 and 3 are assigned to the term ‘i’ in the scaling function in each fitting process and the best value is on the one giving the lowest fitting error and χ^2. In figure 4-5, the critical nucleus size is plotted as function of E_k and θ. For samples grown with E_k = 2.9 eV, the critical nucleus size is 3 for all incidence angles, meaning that at least 4 molecules are required to form a stable nucleus. However, for samples grown with E_k = 6.3 eV, at normal incidence, the critical nucleus size is 2 molecules. More molecules are needed to form a stable nucleus in the growth with E_k = 6.3 eV at larger incidence angle, probably by reason of the high probability of dissociation of unstable nuclei caused by molecules diffusing on the surface with large parallel momentum and by
strong molecule - surface scattering, which induces pentacene desorption. By calculating the normal energy components of impinging molecules with \( E_k \) of 6.3 eV at \( \theta = 45^\circ \) and \( \theta = 75^\circ \), they are \( \sim 4.5 \) and \( \sim 1.6 \) eV, respectively, which exactly fall into the range of \( E_k < 5 \) eV indicating a good agreement with our previous calculation of \( E_k \) dependent pentacene critical nucleus size [4]. This seems to indicate that it is the momentum normal to the surface which determines the critical nucleus size, possibly due to its highly efficient dissipation upon first impact. The change in critical nucleus size observed here is analogous to findings of a previous study on thermally sublimated pentacene submonolayer growth at different substrate temperatures [19, 21], in which the higher substrate temperatures lead to a high probability of pentacene desorption on the surface.

4.4 Pentacene submonolayer growth with different \( E_k \) and \( \theta \) at 200K

To better understand the molecule – surface scattering and in particular the role of the surface phonons in such processes, we performed a second set of SuMBD experiments, where we grew pentacene submonolayers on SiO\(_x\)/Si with \( E_k = 6.3 \) eV but at two different substrate temperatures, RT and \( \sim 200 \)K, and two different incidence angles, normal incidence and \( \theta = 75^\circ \). The beam flux was regulated to be nearly the same as in the first set of experiments for the deposition at normal incidence. The flux applied in the growth at \( \theta = 75^\circ \) was increased and estimated on the readings of the quartz microbalance to be about three times higher than that at normal incidence. The morphology of the layers obtained in this set of experiments is shown in figure 4-6 as revealed by AFM. By carrying out average height measurements, the deposited submonolayers were again proved to correspond to the thickness of a single pentacene layer. For growth at normal incidence at RT, the samples presented in figure 4-6 (a-c) show the typical dendrite island structure, with relatively lower island density than those shown in figure 4-1 (a-c). This variation is attributed to the more hydrophilic character of the substrate, which changes molecular adsorption and surface diffusivity as reported by S. Pratontep et al. and A. S. Killampalli et al. [22, 23]. Samples deposited at \( \sim 200 \) K, at normal incidence (Fig. 4-6 (d-f)) show relatively smaller islands but a larger island density than those deposited on a surface at RT (Fig. 4-6 (a-c)). These
Figure 4-6: AFM images show the morphology of pentacene submonolayers grown on SiOₓ at E_k = 6.3 eV, at RT and 200K at θ = 0° (1st and 2nd column, respectively). Each pentacene submonolayer deposition was carried independently.
Dynamic growth of pentacene submonolayers on SiO$_x$ by supersonic molecular beam deposition

Figure 4-6: AFM images show the morphology of pentacene submonolayers grown on SiO$_x$ at $E_k = 6.3$ eV, at RT and 200K at $\theta = 75^\circ$ (1$^{st}$ and 2$^{nd}$ column, respectively). Each pentacene submonolayer deposition was carried independently.
phenomena can be interpreted as follows: with decreasing surface temperature, the density of surface phonons is reduced and this limits the possibilities to slow down the diffusing molecules. The pentacene molecules are therefore able to travel relatively longer distances before being captured by preformed islands and the probability of forming new nuclei is increased, giving rise to a uniformly dispersed pattern of small islands. For OMBD grown pentacene submonolayer on SiOₓ, the molecular island density was found to depend on substrate temperature as follows:

\[ N \propto K^{\delta} \exp\left[\left(k_B T_s\right)^{-1} \times E_N\right] \] (4-3) [7] (where \( K \) is the growth rate, \( k_B \) is the Boltzmann constant, \( T_s \) is the substrate temperature, \( E_N \) is the activation energy for homogenous nucleation and \( \delta \) depends on the type of substrate [24]). By calculating the ratio of the island density of \( N_{200K} / N_{300K} \) and ratio of \( \exp(k_B \times 300K) / \exp(k_B \times 200K) \) for two different group of samples grown at normal incidence with different substrate temperature (Fig. 4-6 (a-c) and (d-f)), a similar result of ~ 0.7 was achieved. Therefore, for SuMBD grown

Figure 4-7: Molecular sticking coefficient of pentacene with kinetic energy of 6.3 eV incident on silicon oxide at two different incidence angles as the function of substrate temperature.
pentacene at normal incidence it seems that they are consistent with the relationship indicated in (4-3). For growth at θ = 75°, the samples are presented in figure 4-6 (g-i) also show the dendrite island structure due to the hydrophilic substrate. Pentacene submonolayers grown at 200 K (Fig. 4-6 (j-l)) indicate much smaller coverage, which is about 50% lower than those grown at RT (Fig. 4-6 (g-i)).

In figure 4-7 we report the sticking coefficient for pentacene impinging at normal and glancing angle as a function of substrate temperature. The values for S₀ were calculated based on the coverage extracted from AFM data obtained after the first 10 min of growth. At normal incidence, S₀ for growth at RT is about 30% lower than that for growth at ~ 200 K. This can be explained by the fact that surface phonons have to participate in the scattering events by which the molecules rebound into the vacuum and therefore one expects that the adsorption probability is higher for pentacene growth at lower substrate temperature where the population of thermally activated surface phonons is reduced and the surface phonon assisted molecule - surface scattering is suppressed. Furthermore, the S₀ obtained at RT, normal incidence in the second series of experiment is ~ 20% lower than that obtained in the first one shown in figure 4-2 indicating that the hydrophobic surface is favoured for the pentacene adsorption. If one considers the sticking coefficient for grazing incidence, one notices that it goes down (~ 50%) when the substrate temperature is lowered, contrarily to what is observed for normal incidence. This emphasizes the important role of the surface phonons in parallel momentum dissipation. In fact, in order for a molecule to trap, it must dissipate enough of its translational energy to remain in the physical adsorption potential well and since the only difference between the depositions at RT and ~200 K is the surface phonon population, the latter must be responsible for the lower adsorption probability at lower substrate temperature.

4.5 Conclusions:

We analyzed the surface morphology of pentacene submonolayers grown by supersonic molecular beam deposition on a SiOₓ/Si surface kept at room temperature or at ~200 K. In particular, we focused on the influence of the kinetic energy of the impinging molecules and of the
Dynamic growth of pentacene submonolayers on SiOₓ by supersonic molecular beam deposition

incidence angle. We found that for a fixed Eₖ of the incident molecules, the sticking coefficient decreases with increasing incidence angle, indicating that a larger parallel component of momentum favours molecule-surface scattering leading to desorption. This also agrees with a more efficient molecular energy dissipation on the surface for normal incidence than at larger θ. At constant incidence angle S₀ shows a decrease with increasing Eₖ and this is attributed to the large molecule – surface scattering caused by the excessive energy that the impinging molecules still have after their first inelastic collision. For SuMBD at normal incidence onto a cooled substrate (~ 200 K), surface phonon assisted molecule-surface scattering, which makes the molecules rebound into vacuum, is suppressed, leading to a higher molecular sticking coefficient than that at RT. For SuMBD in grazing incidence and lower substrate temperature (~ 200 K), the lower number of surface phonons hampers an efficient dissipation of the (large) parallel momentum. This is not compensated by the lower probability of backscattering into the vacuum, and therefore results in a lower sticking coefficient. The island density and island size for the different growth conditions are strongly modulated by two important factors: molecular surface diffusivity and molecule – surface scattering. In the study of pentacene nucleation, we demonstrate that the critical nucleus size is essentially determined by the normal momentum. A critical nucleus size transition from 2 to 3 is found for samples grown at Eₖ = 6.3 eV when θ moves away from the normal incidence. We suggest that the large molecule – surface scattering and increased molecular surface diffusivity due to the presence of the large parallel energy component are the key reasons why the formation of a stable nucleus requires more pentacene molecules.

References

Dynamic growth of pentacene submonolayers on SiO$_x$ by supersonic molecular beam deposition

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In this chapter, we show how supersonic molecular beam deposition can be employed to realize high quality pentacene ultrathin films for application in field effect transistors with bottom contact Au electrodes. In particular, we modified the Au electrode surface in the transistor structure with a self assembled monolayer (SAM) of (perfluoro)-alkanethiols to decouple the metal surface from pentacene. By covering the Au electrodes with a SAM of decanethiol (DT) or 1H,1H,2H,2H-perfluoro octanethiol (PFOT), the quality of pentacene ultrathin films (nominal thicknesses 1 ML and ~ 6 MLs) grown at the interface between Au electrode and SiO$_x$ could be dramatically improved and a highly uniform surface morphology and crystallinity could be achieved, which were also successfully extended to the centre of the transport channel. Our devices did not show the morphology transition area which is normally observed in the vicinity of a bare Au electrode and which is characterized by isolated 3D grains with high concentrations of grain boundaries. Instead, a sharp and seamless interface between the Au electrodes and the first pentacene layer was realized. The field effect transistors constructed with such pentacene ultrathin films show much better electronic and transfer characteristics when the electrodes were modified with a SAM before pentacene deposition than when the films were grown on bare electrodes. The Au electrodes’ surface modified by DT has a different work function than that covered by PFOT. One would therefore expect a different energy level alignment at the Au contact in the two cases, leading to an increased or decreased hole injection barrier and consequently to high or low contact resistance. However, the experimentally obtained electronic characteristics for the two types of devices are very similar. This result stresses that the morphology and crystallinity of the grown pentacene ultrathin film at the Au/SiO$_x$ interface play a crucial role in determining the performance of the pentacene based field effect transistors.

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5.1 Introduction

In the past decades many efforts have been devoted to the improvement of electronic properties of pentacene thin film-based field effect transistors [1, 2, 3, 4, 5]. Growing a high quality polycrystalline pentacene thin film with lowest possible density of grain boundaries and large single crystal grains is regarded as one of the key steps to achieve an electronic device with high performance. So far, the best characteristics [6] have been realized with top contact geometry (produced by shadow mask evaporation) on large grain pentacene thin films grown on flat, chemically inert intrinsic SiO$_x$, a commonly used dielectric gate material in transistor applications. However, on the same intrinsic SiO$_x$ surface patterned with bottom Au contacts, pentacene thin film growth turns out to be more problematic [7] and the performance of the corresponding devices becomes much worse than those with top contact electrodes. The degradation of both surface morphology and crystallinity of the deposited pentacene thin film at the interface between Au and SiO$_x$ is observed. The degradation is most severe when only one pentacene monolayer is deposited. As first reported by C. D. Dimitrakopoulos et al. [8], a morphology transition area is formed, which contains small pentacene grains with high concentration of grain boundaries and often some parts of the SiO$_x$ surface remain uncovered by the organic material. This causes a poor connectivity between the pentacene layer and the Au electrode and leads to a relatively high contact resistance, which hampers efficient charge injection and charge transport.

In 2001, I. Kymissis et al. [9] reported a high performance pentacene thin film based field effect transistor (FET) with bottom contact electrodes by engineering the Au surface with a SAM, namely 1-hexadecanethiol. They claimed a considerable mobility increase by a factor of 7 and 5 extracted from the linear and saturation regime, respectively, with respect to similar devices realized without the SAM modification. The improved surface morphology and large grain size were evident on the top surface of the thermally sublimated thicker pentacene films. However, no information on the quality of the first pentacene monolayer buried far below the visible top surface was provided in that work. Very recently, a similar study but with using another SAM, namely, aromatic anthracene-2-thiol (AnT), to modify the bottom contact Au electrode was reported by C. Bock et al. [10]. Also these authors obtained a uniform surface morphology of the thermally sublimated pentacene thin film with a
Pentacene ultrathin film growth controlled by pre-deposition of a self assembled monolayer for application in a field effect transistor with bottom Au electrodes

thickness of ~ 100 nm extending from the AnT modified Au electrode into the transport channel. By decreasing the film thickness down to 8 nm (~ 5 monolayers), pentacene grains with relatively larger size were found on the sample with the AnT modified Au electrodes, however, the deposited pentacene did not form a continuous layer between two Au electrodes, (source/drain) and showed the typical island growth. Furthermore, many bare patches of SiO$_x$ surface were noticed in the region close to the edges of Au electrodes, indicating a very poor interface connection between the pentacene layer and Au electrodes. Apparently, with decreasing the film thickness, it becomes harder to control the morphology and crystallinity at the border between Au and SiO$_x$. To our knowledge, there are so far no studies reporting the electronic characteristics of FETs with Au bottom contact electrodes based on thermally sublimated pentacene films thinner than 6 monolayers (ML). This is rather surprising since R. Ruiz et al. [11] demonstrated with their systematic studies of the thermally sublimated pentacene thin film based transistors with the top contact Au electrodes that the early growth of pentacene thin films (from 1 to 6 ML) plays a very important role determining the transistor performance. These authors found that the mobility depends on the thickness of the deposited film and saturates when the latter reaches approximately 6ML.

In this chapter, we present our results concerning the growth of pentacene films with nominal thickness of 1 ML and 6 ML by SuMBD for the realization of transistors with bottom contact Au electrodes, which were unmodified or modified by (perfluoro) alkanethiols SAM. We also report on the electronic measurement of the devices fabricated in this fashion. We found that the first pentacene monolayer presents a highly uniform surface morphology and a better crystallinity, reaching from the edge of the Au electrode to the centre of the transport channel in the transistor when the electrodes were modified with a SAM before pentacene deposition. A sharp and seamless interface between Au electrode and the first completed pentacene monolayer was successfully achieved. Better electronic and transfer characteristics were found for pentacene transistors with SAM modification than for those without the SAM modification. The high similarity of the electronic characteristics obtained for pentacene transistors where the electrodes were modified with different SAMs implies that the morphology and crystallinity of grown pentacene ultrathin films at the border between Au and SiO$_x$ play the main role in determining the FET performance.
Pentacene ultrathin film growth controlled by pre-deposition of a self assembled monolayer for application in a field effect transistor with bottom Au electrodes

5.2 Experiments

The FET structure was fabricated by conventional lithography and obtained from Philips Research Laboratories in Eindhoven, the Netherlands [12]. 250 nm thick thermally grown SiO$_x$ was used as the gate insulator. By using conventional lithography, gold source and drain contacts were patterned with a finger geometry with 5 nm of titanium as adhesion layer. The SiO$_x$ with FET structures were dipped in a Piranha solution (demi water 100 ml + ammonia (30 %) 20 ml + H$_2$O$_2$ 20 ml) for 60 s at 70 ºC to remove all organic impurities from the surface of both the metal and the oxide. Then the samples were sonicated in acetone for 5 minutes and subsequently dried by spinning before being treated with UV-Ozone for 20 minutes. For the self-assembly process, (perfluoro) alkanethiols were dissolved in ethanol (~1 – 3×10$^{-3}$ M) and the samples were immersed in the SAM solution overnight. After the self-assembly process, the substrates were thoroughly rinsed with ethanol, toluene, and 2-propanol, and dried by the N$_2$ flow. Two different SAMs, namely, decanethiol (DT) (CH$_3$-(CH$_2$)$_9$-SH) and perfluorinated octanethiol (PFOT) (CH$_3$-(CF$_2$)$_5$-(CH$_2$)$_2$-SH), which was synthesized according to reference [13], were used for modifying the Au electrode surface.

Pentacene ultrathin film growth was performed with the home-built supersonic molecular beam deposition (SuMBD) system [14, 15] described in chapter 2 of this thesis. Here we adopted the optimized condition for growing the best quality pentacene ultrathin film determined as described in chapter 3 and reported in [16], namely a beam impinging at normal incidence and delivering molecules of 6.4 eV kinetic energy onto the substrate kept at room temperature. We took care to stabilize the generated supersonic molecular beam over a period of 2-3 h prior to starting the pentacene film growth. The working pressure inside of deposition chamber was maintained at 1.7×10$^{-7}$ mbar through the entire growth. A very low growth rate of ~ 0.4 Å/min, monitored by the quartz crystal microbalance and calibrated by AFM coverage measurements, was used. In these conditions the first pentacene monolayer on SiO$_x$ was completely closed after ~ 40 min of deposition.

Electrical measurements of the realized FETs was carried out in a home-built probe station under high vacuum of ~ 10$^{-6}$ mbar with a Keithley 4200 semiconductor analyzer at room temperature.
Pentacene ultrathin film growth controlled by pre-deposition of a self assembled monolayer for application in a field effect transistor with bottom Au electrodes

The morphology of pentacene ultrathin films was studied by using the ex-situ tapping mode AFM (Nanoscope IV multimode scanning probe microscope, produced by the Digital Instruments, Veeco Metrology Group, U. S.) analogously to the studies reported in the chapters 3 and 4 of this thesis. Each AFM characterization was carried out at room temperature in atmosphere shortly after the electronic measurement. Both AFM height and amplitude images with highest resolution (512×512 pixels) over area sizes of 10×10 µm² and 3×3 µm² were systematically collected for each sample. The AFM data were analyzed with the help of the WSxM (Nanotec electronica S.L. [17]) software.

The crystal structure of a pentacene film with a nominal thickness of 6 ML on intrinsic SiOₓ was investigated by X-ray diffraction (Philips X’pert diffractometer), employing monochromatic K_{α₁} radiation (λ =1.54059Å). A θ - 2θ XRD scan coupled with the symmetric reflection mode was used to determine the lattice parameter.

5.3 Investigation of the morphology of pentacene films grown on a SiOₓ surface patterned with Au electrodes

Figure 5-1 presents the surface morphology, as determined by AFM, of pentacene ultrathin films with two different nominal thicknesses, 1 ML and 6 ML, grown on the bare SiOₓ surface far away from the Au electrodes. Figure 5-1(a) shows the height image obtained from a pentacene ultrathin film with a thickness of ~ 1.3 ML. After 50 min growth, the first pentacene monolayer is completely closed, presenting a very flat surface and a highly uniform morphology. The second pentacene monolayer growth initiated after the completion of the first monolayer and reached a coverage of ~ 30%. All the molecular islands in the second layer have a more fractal structure, probably due to the different diffusivity of the molecules on top of the pentacene monolayer as compared to that on the silicon oxide surface [18]. In some regions molecular islands in the third and fourth layer can also be observed indicating a trend towards island growth. This result is consistent with our previous studies of initial pentacene growth on SiOₓ [16]. When prolonging the film deposition up to the nominal thickness of 6 ML as shown in figure 5-1(b), Stransky – Krastanov growth is observed. For a more detailed observation, a high
Figure 5-1: AFM images of pentacene ultrathin films grown by SuMBD on a SiO$_x$ substrate pre-patterned with Au electrodes. The data were collected in surface regions far away from the gold electrodes: (a) AFM height image of a film with nominal thickness 1.3 ML showing a complete first monolayer and 1, 2 and 3 layer thick islands; (b) AFM height image of a film with nominal thickness ~ 6 ML; (c) high resolution (3×3 µm$^2$) AFM height image; (d) the line profile measurement of the same surface as presented in (c).
resolution AFM height image (3×3 µm²), recorded in the centre of the pentacene film, is presented in figure 5-1(c). Contrarily to the second layer shown in figure 5-1(a), in the upper layers of the thicker film the molecular islands show a more compact structure with regular shape and relatively sharp, straight island edges. We attribute this change in morphology to the local annealing caused by the continuous flow of energetic molecules which, being normally incident on the surface, dissipate energy very efficiently during the first impact ([19] as seen also in Chapter 4). Furthermore, as often observed in homoepitaxial growth, the shape of molecular islands formed in the upper layer mimics that of those directly underneath. This sort of pyramidal structure is due to screw dislocations originating at defects on the surface [20]. As described in chapter 3 of this thesis, in our study using transverse shear force microscopy [21] we could demonstrate the very good crystallinity of a pentacene monolayer grown on SiOₓ by SuMBD at kinetic energy of 6.4 eV. Hence, by employing such a pentacene monolayer as a template, the quality of the first few subsequent layers can be improved as well. The line profile measurement on the AFM height image shown in figure 5-1(d) serves to determine the number of completed pentacene layers above the interface. From this profile we can estimate that there are at least two pentacene layers completed in the growth of the pentacene film with nominal thickness of 6 ML.

X-ray diffraction was used for characterizing the crystal structure of a pentacene ultrathin film grown on the bare SiOₓ surface. As shown in figure 5-2 (a) four very sharp, narrow diffraction peaks with high intensity corresponding to the (00l) indexes are obtained and the inter-plane distances of ~ 15.5 Å, which corresponds to the thin film phase as reported previously [22, 23, 24], is derived based on Bragg’s law for the (001) crystal surface. However, in the detailed structure of (001) diffraction peak shown in figure 5-2 (b), different phases are observed: inter-plane distances of ~ 14.4 Å derived for the small peak right to the (001) peak corresponds to the single crystal phase [25, 26] and the inter-plane distances of ~ 16.4 Å derived from the small peak left to the (001) peak has been ascribed to a configuration, in which pentacene molecules stand up at 90° angle with respect to the substrate surface [27]. However, in the SuMBD grown pentacene ultrathin film these coexisting minority phases make up a very small fraction of the film, as evidenced by the extremely low X-ray diffraction intensity. This suggests that the thin film phase is the main
Figure 5-2: (a) X-ray diffraction spectra of pentacene ultrathin films with nominal thickness ~ 6 ML grown by SuMBD on a SiOₓ substrate; (b) detail structure of the (001) diffraction peak.
crystal structure in the SuMBD grown ultrathin pentacene film.

Figure 5-3 summarizes our investigation of the surface morphology of the pentacene monolayer in the vicinity of a Au electrode. Here we deposited pentacene on the SiO\textsubscript{x} surface patterned with Au electrodes and compared three situations: i) growth on the bare Au/SiO\textsubscript{x} interface and ii) growth on a Au/SiO\textsubscript{x} interface where the Au electrode has been modified with a PFOT SAM or a DT SAM prior to pentacene SuMBD. Since the Au electrode is \~150 nm thick, while the pentacene monolayer has a thickness of \~1.5-2 nm, there is an extremely large contrast caused by the surface height difference at the border between Au and SiO\textsubscript{x} and this severely degrades the image quality. To achieve a high resolution on this rather complex surface, we recorded the amplitude image simultaneously with the height image. A high resolution amplitude image (3\times3 \mu m\textsuperscript{2}) of the completed monolayer at the border between SiO\textsubscript{x} and bare Au electrode is shown in figure 5-3 (a); while analogous images recorded on the monolayers grown on the interfaces where the Au electrode was modified

Figure 5-3: AFM amplitude images of a pentacene film with a nominal thickness of 1 ML grown by SuMBD on a SiO\textsubscript{x} surface pre-patterned with Au electrodes. (3\times3 \mu m\textsuperscript{2}) images collected at the border between the SiO\textsubscript{x} surface and (a) the bare Au electrode; (b) the Au electrode modified with a PFOT SAM.
with a PFOT or a DT SAM are presented in figures 5-3 (b) and 5-3 (e), respectively. To ascertain the presence of the first pentacene monolayer, we collected height images in areas where the amplitude images gave indication for exposed SiO_x surface patches. In these areas, the first pentacene monolayer can be identified from a height measurement. If one compares the pentacene monolayers of figure 5-3 (a, b, e) with that grown on bare SiO_x of figure 5-1(a), one can conclude that at the centre of the transport channel these films all perfectly resemble each other since the former show similar large, flat pentacene grains with highly uniform morphology and crystallinity. As shown in figure 5-3 (a), for pentacene
Pentacene ultrathin film growth controlled by pre-deposition of a self assembled monolayer for application in a field effect transistor with bottom Au electrodes
grown on the substrate with the bare Au electrode, the uniform morphology of the pentacene monolayer stops at ~ 1 µm from the edge of the Au electrode where a morphology transition area starts. Within this transition area, the continuous monolayer is replaced by isolated aggregated pentacene grains with sub-micron size. It is these small pentacene grains which assure the connectivity at the interface between continuous pentacene monolayer and Au electrode, while large patches of bare SiO_x surface are also visible as indicated in figure 5-3 (a). This change in morphology close to the Au electrode can degrade the performance of the transistor because: 1) the injected charges can be trapped by the high density of grain boundaries present in those small grains; 2) the poor connectivity between pentacene and Au electrode reduces the efficiency of charge transport through the interface due to the limited area of the latter. We also have to take into account that pentacene interacts differently with bare Au than with SiO_x as illustrated in the schematic drawing presented in figure 5-3 (c): the big difference in interaction is well known from past studies [28, 29], which demonstrated that the first layer of pentacene adopts a lying down configuration on Au, while the weak van der Waals interaction between pentacene and SiO_x leads to the standing up configuration for 1 ML pentacene on that surface. When the different interactions are simultaneously present at the border between bare Au and SiO_x, the pentacene growth results strongly disturbed and disordered molecular packing with a high concentration of internal defects is observed. This favours 3D molecular island growth.

If the Au surface is modified with a SAM of (perfluoro) alkanethiols, it becomes less reactive [30, 31] and the differences in interaction between the electrode surface and the SiO_x can be minimized, thus resulting in a similar configuration of the adsorbed pentacene as indicated by the schematic drawing of figure 5-3 (d). Figures 5-3 (b) and (e) show that this strategy yields a dramatic morphological improvement of the pentacene monolayer at the border between electrode and SiO_x. The highly uniform surface morphology of the pentacene monolayer continues from the centre of the charge transport channel to the edge of the Au electrode and the morphological transition area is completely eliminated. In the large scale AFM amplitude image (10×10 µm^2) of the single pentacene layer grown at the interface between the Au electrode modified with the PFOT SAM and SiO_x surface presented in figure 5-3(f), a continuous seamless interface is distinguished along the Au electrode. To our knowledge, this is
Figure 5-4: AFM amplitude images (3×3 µm²) of a pentacene film with a nominal thickness of 6 ML grown on a SiOₓ surface pre-patterned with Au electrodes. The images were collected on three different devices at the border between the gold electrode and the SiOₓ surface: (a) one where the gold electrode is left bare before pentacene SuMBD; (b) one where the gold electrode was modified with a PFOT SAM before pentacene SuMBD; (c) one where the gold electrode was modified with a DT SAM before pentacene SuMBD.
the first time that such a high quality pentacene monolayer deposited on SiO$_x$ with bottom contact Au electrodes is achieved.

Figure 5-4 presents the AFM data collected in the interface region between SiO$_x$ and Au electrode from the pentacene films with nominal thickness of 6 ML grown on (a) bare Au electrodes; (b) Au electrodes modified with a PFOT SAM and (c) Au electrodes modified with a DT SAM. As explained before, because of the large height difference between the electrode and the SiO$_x$ surface, amplitude images were collected simultaneously with height images to be able to study the topography with high resolution. From figure 5-4 (a), one sees that even when increasing the film thickness, the morphological transition area is still distinguishable by the sub-micron size 3D islands, which connect the Au electrode to the continuous pentacene film at the centre of the transport channel. However, these 3D islands are decidedly bigger and characterized by better crystal facets than those in the morphological transition area of the sample with only a single pentacene layer (figure 5-3 (a)). One can safely presume that due to the strong interaction between pentacene and bare Au, pentacene piles up disorderedly along the side wall of the Au electrode occasionally breaking up into 3D islands. Therefore, in many places the bare SiO$_x$ surface is still exposed at the interface, even after a relatively long deposition time. As shown in figure 5-4 (b, c), for pentacene films grown on substrates with SAM modified Au electrodes, a very different scenery results: a highly uniform surface morphology and better crystallinity are successfully obtained in the vicinity of the Au electrode for the thicker film as already seen for the single pentacene layer and again the films in the border area resemble those grown on bare SiO$_x$ in the centre of the transport channel. Homoeptaxial growth occurs also in the area close to the SAM modified Au electrodes. The growth is of Stransky – Krastanov type yielding a fully covered SiO$_x$ surface. The results presented in figure 5-4 demonstrate that the quality of subsequent pentacene layers depends very much on the quality of the first monolayer.

5.4 Electrical characterization of pentacene ultrathin film based field effect transistors

By applying the two different SAM (PFOT and DT) to modify the Au electrode surface, we have demonstrated the quality improvement of
Pentacene ultra-thin film growth controlled by pre-deposition of a self assembled monolayer for application in a field effect transistor with bottom Au electrodes

pentacene ultrathin film at nominal thickness of 1ML and 6ML. From the point view of energy level alignment, it is already known that modifying Au surface with a PFOT SAM can increase the Au work function from ~4.9 eV to 5.5 eV due to the presence of a dipole at the interface [13]. This implies that the Fermi level of the electrode is well aligned with the pentacene HOMO level to create an Ohmic contact, favouring charge injection. However, modifying Au surface with a DT SAM, an opposite interface dipole can decrease the Au work function from ~4.9 eV to 4.1 eV to form an energy barrier for the hole injection [13, 32, 33]. Therefore, after applying the SAM, two parameters, which may strongly influence the pentacene transistor performance, have to be considered: 1) the change of the energy level alignment; 2) the modification of the surface energy. Hence, the question is: which one plays the crucial role or do they have equal weight in determining the pentacene transistor performance?

For revealing the dominant factor controlling the pentacene transistor performance, electrical measurements were carried out on three

Figure 5-5 Output characteristics of bottom Au electrode transistors based on pentacene thin films of nominally 6 ML thickness deposited by SuMBD on bare electrodes (a). The measured transistors have a channel length / channel width of 10 µm /10000 µm.
Pentacene ultrathin film growth controlled by pre-deposition of a self assembled monolayer for application in a field effect transistor with bottom Au electrodes

Figure 5-5 Output characteristics of bottom Au electrode transistors based on pentacene thin films of nominally 6 ML thickness deposited by SuMBD on electrodes modified by a DT SAM (b), on electrodes modified by a PFOT SAM (c). All measured transistors have a channel length / channel width of 10 µm /10000 µm.
different transistors based on the pentacene films with a nominal thickness of ~ 6 ML whose morphology was presented in figure 5-4 (a-c). Let us start discussing the output characteristics of each transistor shown in figure 5-5. As seen in figure 5-5 (b, c), they show excellent current amplification and have a much large drain current, which is about three orders of magnitude higher than transistors without the SAM modification shown in figure 5-5 (a). In the transfer characteristic reported in figure 5-6 (a, b, c), the transistor where the electrodes were left bare prior to pentacene SuMBD has a relatively large switch-on voltage of approximately ~ 40 V. The mobility for this device, derived from the saturation regime of the transfer characteristics presented in figure 5-6 (a), is close to $10^{-4} \text{cm}^2\text{V}^{-1}\text{s}^{-1}$. However, it is about two orders of magnitude lower than those (~ 0.02–0.05 cm$^2$V$^{-1}$s$^{-1}$) extracted from the saturation regime of the transfer characteristics shown in figure 5-6 (b) and (c) of transistors where the Au electrodes were modified with a DT SAM and a PFOT SAM, respectively.

Figure 5-6 Transfer characteristics of bottom Au electrode transistors based on pentacene thin film of nominally 6 ML thickness deposited by SuMBD: (a) with non-modified Au. The measured transistors have a channel length / channel width of 10 µm /10000 µm.
Pentacene ultrathin film growth controlled by pre-deposition of a self assembled monolayer for application in a field effect transistor with bottom Au electrodes

Figure 5-6 Transfer characteristics of bottom Au electrode transistors based on pentacene thin films of nominally 6 ML thickness deposited by SuMBD: (b) with Au modified by a DT SAM, (c) with Au modified by a PFOT SAM. All measured transistors have a channel length / channel width of 10 µm /10000 µm.
prior to pentacene SuMBD. In fact, the mobility derived in these cases is close to that achieved in the pentacene single layer transistor because there are only two completed layers formed in the grown pentacene ultrathin film with the nominal thickness of 6ML. The superior electronic properties of the transfer characteristics are observed in the pentacene transistors with SAM modification of the electrodes: 1) one finds a high on/off ratio (> $10^6$); as well as 2) a large saturation current with much lower switch-on voltage (coming close to zero volt); 3) a relatively higher mobility is derived in the saturation regime. However, a pronounced hysteresis phenomenon is noticed in the transistors with pentacene multilayers. This is probably caused by charge trapping at the grain boundaries of the discontinuous pentacene upper layers. At first glance it is surprising that there is very little difference in performance between the transistors of which the electrodes have been modified with different SAMs. We calculated the contact resistance in the saturation regime [34] and found that the resistance of the bare Au electrode is about three orders of magnitude higher than that of the electrode modified with the PFOT SAM electrode and one order higher than that of the DT SAM modified one. However, by comparing the transfer characteristics, one notes that, with the improved morphology and crystallinity at the interface of pentacene with the SAM modified Au, the charge injection barrier induced by the interface dipole can easily be overcome via increasing the applied gate voltage. If we consider the performance improvement of the pentacene transistors with SAM modified Au electrodes based on the concept of the alignment of the electronic energy levels at the contacts, we find it is not consistent with the current results that indicate the high similarity of output and transfer characteristics of pentacene transistors with different SAM modification. Therefore, we conclude that the improved morphology and crystallinity of the pentacene films at the border between Au electrode and SiO$_x$ is the crucial factor controlling the transistor performance.

5.5 Conclusions:

By modifying the bottom contact Au electrode surface with a SAM of DT or PFOT in the transistor, the quality of SuMBD grown pentacene ultrathin films (nominal thickness of 1 ML & 6 MLs) at the interface between Au electrode and SiO$_x$ has been greatly improved. In both cases
Pentacene ultrathin film growth controlled by pre-deposition of a self assembled monolayer for application in a field effect transistor with bottom Au electrodes

this area presents a highly uniform surface morphology and better crystallinity, which perfectly resemble those of pentacene films deposited on the bare SiO$_2$ surface far away from the Au electrodes. Consequently, the morphology transition area, typically observed in bottom electrode devices, is completely eliminated and a sharp seamless interface between the Au electrode and the pentacene film is established starting from the pentacene first monolayer up to several layers.

The better morphology is reflected in better transistor performance: drain current and hole mobility are about three and two orders of magnitude higher than those obtained in the pentacene transistors without SAM modification and also the switch-on voltage is much lower (~0 V) than for the transistors without SAM modification (~40 V). Modification of the Au electrodes with a DT SAM gives a different energy level alignment with respect to the pentacene HOMO level than modification with a PFOT SAM, resulting in the first case in an increased and in the second case in a decreased hole injection barrier as we could see from the contact resistance at the respective contacts. However, we found a high similarity of the electronic performance in both cases and this result stresses that the surface morphology and crystallinity of the SuMBD grown pentacene ultrathin films at the interface between the electrodes and SiO$_2$ substrate play the key role to determine the performance of the field effect transistor.

References

Pentacene ultra-thin film growth controlled by pre-deposition of a self-assembled monolayer for application in a field effect transistor with bottom Au electrodes

Pentacene ultrathin film growth controlled by pre-deposition of a self assembled monolayer for application in a field effect transistor with bottom Au electrodes

Pentacene ultra-thin film growth controlled by pre-deposition of a self assembled monolayer for application in a field effect transistor with bottom Au electrodes
Summary

Most people associate the word “plastics” with things like garden furniture, toys and plumbing, however, nowadays plastic materials are being created with increasingly useful electronic and optical properties and integrated into "smart" electronic devices such as identification tags, programmable credit cards and flat-panel displays.

Figure S-1: a foil of ~ 50 plastic programmable bit-pattern generators made by Dago de Leeuw’s group at Philips Labs in the Netherlands.

For the past 20 years the goal of plastic electronics has motivated all over the world an increasing research effort, which aims at providing plastic films with the electronic properties needed for practical circuitry. Organic molecules with conjugated system have shown great potential for such applications - they are carbon based materials, have high mechanical flexibility and light weight and readily processed into devices. These special properties are very promising for the fabrication of foldable and portable plastic electronic devices, when one can tolerate quite low digital data rates and small currents, so that the relatively poor conductivity of organics is not a problem. Volume production may reduce costs enough that, for example, identification tags based on all-organic circuitry become viable alternatives to conventional bar codes in shopping and inventory control. These new tags have the potential to store far more information.
than today's passive tags, and they would not need the manual manipulation required by laser-scanned optical bar codes.

As far as materials are concerned, pentacene, a well known organic semiconductor, has been widely recognized as a prototype in studies of organic crystalline thin film growth and the relevant electronic device physics. In the past, many studies have been devoted to improving the quality of pentacene thin films in order to enhance device performance.

In this thesis, we present a series of fundamental studies of pentacene thin film growth on SiO$_x$ aimed at understanding its growth mechanism by means of surface morphology analysis. The novel aspect of our investigation is that we employed an unconventional organic thin film growth technique - supersonic molecular beam deposition (SuMBD); this is a relatively new method for growing thin pentacene layers if compared to the more commonly employed organic molecular beam deposition (OMBD). In chapter 2, we described in detail its working principle and how it differs from OMBD. The main characterization tool in our pentacene thin film morphology studies was atomic force microscopy. We employed it both in the tapping mode to collect height images and in the contact scanning mode to perform transverse shear microscopy.

In the results presented in chapter 3, we demonstrated that the kinetic energy ($E_k$) of the impinging molecules is the crucial factor which dominates surface morphology and crystallinity of the pentacene submonolayer. Growth with different $E_k$ results in different molecular surface diffusivity, as evidenced by the variation in island density and island size distribution. With increasing $E_k$, the island density increases and the island size decreases ensuing more uniform island size and a dispersed pattern of molecular islands, which indicate in turn correlated island growth. A less fractal island structure is observed for SuMBD growth pointing towards island edge diffusion, which is interpreted by the diffusion mediated growth mechanism. Another important parameter for describing the growth process is the size of the critical nucleus, i.e. one less than the number of molecules needed to form the smallest stable island. By using the general scaling function a transition of the critical nucleus size from 3 to 2 is found when $E_k > 5$-6 eV and this result explains the island density variation between samples grown with high and low $E_k$. Furthermore, the island – island coalescence starts at an earlier stage for growth with higher $E_k$ and produces a much more uniform and less defected monolayer than deposition with low $E_k$. This is demonstrated by the investigation of the crystallinity of the first pentacene monolayer with transverse shear
Microscopy: when pentacene impinges on the silicon oxide surface with a kinetic energy of 6.4 eV the monolayer is made up of large single crystal grains (spanning ~ 10 µm) with flat surface and very few grain boundaries and has therefore a much better quality than layers produced by OMBD, which have typically a polycrystalline structure with many small grains (~1-2 µm) and a high concentration of grain boundaries.

In Chapter 4 we reported our studies focused on how the incidence angle, θ, of the molecular beam and the substrate temperature, T_s, influence submonolayer growth, again for pentacene hitting the surface with different E_k. We examined the interaction of energetic pentacene with the SiO_x surface by investigating the sticking coefficient, S_0, island size distribution and critical nucleus size. With increasing θ at constant E_k, S_0 decreases due to enhanced molecule-surface scattering induced by efficient parallel to normal momentum conversion. However, with increasing E_k, at constant θ, S_0 also decreases because when the impinging molecules retain more energy after the initial inelastic collision, their probability of being scattered away from the surface is higher. Surface phonon assisted molecule-surface scattering is suppressed in a growth at lower T_s (~200 K) at normal incidence as evidenced from an increased pentacene sticking coefficient with respect to room temperature (RT) deposition in the initial growth period. For growth at grazing incidence of the beam, however, the relatively lower surface phonon density at ~ 200 K seems to hamper efficient energy dissipation of molecules during their diffusion parallel to the surface. In fact, a lower initial sticking coefficient is observed than for RT growth. Our studies demonstrate that nucleation density and island size for different growth conditions are strongly influenced by the effects of molecular surface diffusivity and molecule-surface scattering. The critical nucleus size determined by the general scaling function shows a strong dependence on the normal component of E_k and a transition from 2 to 3 molecules of the critical nucleus size is found for growth at E_k = 6.3 eV when θ is increased, moving away from the normal incidence.

In the last part of this thesis, we illustrated how to employ SuMBD grown high quality pentacene films in field effect transistors (FET) with the bottom contact Au electrodes. We modified the Au electrode surface in the transistor structure with a self-assembled monolayer of (perfluoro)-alkanethiols to decouple the metal surface from pentacene. The main achievement of this work was that for the first time a high quality pentacene monolayer was produced at the interface between Au and SiO_x. The morphology transition area which is normally observed in the vicinity
of a bare Au electrode and characterized by isolated 3D grains with high concentration of grain boundaries was completely eliminated in our devices. The field effect transistors constructed with such ultrathin pentacene films show much better electronic and transfer characteristics.

To conclude, the three achievements presented in this thesis were:

1) we demonstrated that the kinetic energy of pentacene landing on SiO\textsubscript{x} is the key factor to determine the surface morphology and the quality of the deposited films;

2) we discovered that the sticking coefficient of pentacene on SiO\textsubscript{x} surface is strongly influenced by the molecular kinetic energy, the incidence angle of the molecular beam and the applied substrate temperature;

3) we succeeded in producing high quality pentacene ultrathin films for application in field effect transistors with the bottom contact Au electrodes.

The next challenge will be to demonstrate that with SuMBD grown films one can produce devices with better characteristics than the best ones fabricated with OMBD grown films.
Samenvatting

De meeste mensen associëren het woord "plastic" met dingen als tuinmeubelen, speelgoed of sanitair, maar tegenwoordig worden plastic materialen geproduceerd met steeds nuttigere elektronische en optische eigenschappen. Ze worden geïntegreerd in "slimme" elektronische apparaten, zoals identificatiechips, programmeerbare creditcards en flatpanel beeldschermen.

Figuur S-1: een folie van 50 plastic programmeerbare bit-patroongeneratoren gemaakt door de groep van Dago de Leeuw bij Philips Labs in Nederland.

In de afgelopen 20 jaar heeft het doel van plastic elektronica geleid tot een toenemende inspanning voor onderzoek over de hele wereld. Dit doel is gericht op het verschaffen van plastic lagen met de elektronische eigenschappen die nodig zijn voor praktische schakelingen. Organische moleculen met geconjugeerd systeem zijn veelbelovend voor dergelijke toepassingen: ze zijn koolstof gebaseerde materialen, hebben een hoge mechanische flexibiliteit en zijn lichtgewicht en zijn gemakkelijk te verwerken in apparaten. Deze bijzondere eigenschappen zijn veelbelovend voor de fabricage van plastic inklapbare en draagbare elektronische apparaten, als men vrij lage datasnelheid en kleine stroomsterktes kan tolereren, zodat de relatief slechte geleidbaarheid van organische materialen geen probleem wordt. Massaproductie zou de kosten genoeg kunnen verlagen, zodat bijvoorbeeld de identificatiechips op basis van een compleet organische schakelingen haalbare alternatieven kunnen worden
voor de traditionele streepjescodes die in winkels en magazijncontroles worden gebruikt. Deze nieuwe kaartjes hebben de mogelijkheid om veel meer informatie op te kunnen slaan dan de huidige passieve kaartjes en ze hoeven dan niet meer handmatig gescand te worden zoals bij de optische streepjescodes.

Wat de materialen betreft is pentacene, een bekend organische halfgeleider, algemeen erkend als een prototype in het onderzoek van dunne-laaggroei van organische kristallen en de gerelateerde fysica van elektronische apparaten. In het verleden waren er onderzoeken geweest die gewijzigd waren aan de verbetering van de kwaliteit van pentacene dunne lagen om de prestatie van de apparaten te verbeteren.

In dit proefschrift presenteren we een reeks van fundamentele onderzoeken aan pentacene dunne-laaggroei op SiO$_x$ gericht op het begrijpen van het groeimechanisme ervan door middel van oppervlakte morfologieanalyse. Het nieuwe aspect van ons onderzoek is dat wij een onconventionele techniek gebruikten voor de organische groei van dunne laag: supersonic molecular beam deposition (SuMBD). Dit is een relatief nieuwe methode voor het groeien van dunne lagen pentacene in vergelijking met het meer algemeen gebruikte organic molecular beam deposition (OMBD). In hoofdstuk 2 hebben we uitvoerig het werkprincipe en het verschil met OMBD beschreven. Het belangrijkste karakteriseringsinstrument in ons onderzoek aan pentacene dunne laag morfologie was de atomic force microscopy. Dit hebben we gebruikt in zowel de tapping mode om hoogte beelden te krijgen als in de contact scanning mode om de transverse shear microscopy uit te voeren.

In de gepresenteerde resultaten in hoofdstuk 3 hebben we aangetoond dat de kinetische energie ($E_k$) van de impinging moleculen de cruciale factor is die de oppervlakmorfologie en de kristalliniteit van de pentacene submonolaag overheerst. De groei met verschillende $E_k$ leidt tot verschillende moleculaire oppervlaktediffusivity, zoals blijkt uit de variatie in de eilandendichtheid en de verspreiding van de grootte. Met toenemende $E_k$ neemt de dichtheid van het eiland toe en de grootte van het eiland af zodat de grootte van het eiland gelijker wordt en er een versnippedere structuur van moleculaire eilanden ontstaat, die een indicatie geeft van gecorreleerde eilandgroei. Een minder fractale eilandstructuur is waargenomen in de SuMBD groei, wat eiland randdiffusie aanduidt die wordt geïnterpreteerd door het diffusion mediated groeimechanisme. Een ander belangrijke parameter voor de beschrijving van de groei is de kritische kerngrootte, dat wil zeggen één minder dan het aantal moleculen
dat nodig is voor het vormen van het kleinste eiland dat stabiel is. Door gebruik te maken van de algemene scaling functie is een overgang van de kritische kerngrootte van 3 tot 2 gevonden als $E_k > 5-6$ eV en dit resultaat verklaart het verschil in de dichtheid van het eiland van de samples die gegroeid zijn met hoge en lage $E_k$. Bovendien begint de eiland-eiland eenwording eerder in het geval voor de groei met hogere $E_k$ en het produceert een veel grotere uniformiteit en minder defecte monolaag dan depositie met een lage $E_k$. Dit blijkt uit het onderzoek van de kristalliniteit van de eerste pentacene monolayer met transverse shear microscopy: als pentacene botst tegen het siliconoxideoppervlak met een kinetische energie van 6,4 eV, bestaat de monolaag uit grote één-kristal korrels (spanning ~ 10 µm) met een vlakke oppervlak en zeer weinig korrelgrenzen, daarom heeft het een veel betere kwaliteit dan lagen geproduceerd door OMBD, die doorgaans een polykristallijnstructuur met veel kleine korrels (~ 1-2 µm) en een hoge concentratie van korrelgrenzen hebben.

In hoofdstuk 4 zijn onze onderzoeken gerapporteerd die gericht zijn op hoe de invalshoek $\theta$ van de moleculaire bundel en de substraattemperatuur $T_s$ de groei van de submonolaag beïnvloedt. Ook hier variëren we de $E_k$ voor de botsing van de pentacene tegen het oppervlak. Wij hebben gekeken naar de interactie van de energieke pentacene met de SiOx-oppervlak door het onderzoeken van het stickingcoëfficiënt $S_0$, de grootedistributie van het eiland en de kritische kerngrootte. Met toenemende $\theta$ bij constante $E_k$ neemt $S_0$ af als gevolg van de verbeterde moleculoppervlakte verstrooiing door efficiënte omzetting van parallel naar normaal impuls. Echter, bij toenemende $\theta$ bij constante $E_k$ neemt $S_0$ ook af omdat als de botsende moleculen meer energie behouden na de eerste inelastische botsingen, de kans om verstrooid te worden uit het oppervlak groter is. Molecuul-oppervlak verstrooiing door oppervlaktefononen wordt onderdrukt bij het groeien op een lager $T_s$ (~ 200 K) bij normale frequentie zoals blijkt uit een hogere pentacene stickingcoëfficiënt ten opzichte van de depositie op kamertemperatuur (RT) in de eerste periode van het groeien. Echter, voor het groeien bij grote invalshoek van de straal lijkt de relatief lagere dichtheid van de oppervlaktefononen bij 200 K efficiënte energiedissipatie van de moleculen te belemmeren tijdens hun diffusie evenwijdig aan het oppervlak. In feite, een lagere initiële stickingcoëfficiënt is waargenomen dan in het geval bij RT. Ons onderzoek toont aan dat de nucleatiedichtheid en de grootte van het eiland bij verschillende groeiparameters sterk beïnvloed zijn door de gevolgen van de moleculaire oppervlaktediffusiviteit en de
molecuuloppervlakte verstrooiing. De kritische kerngrootte bepaald door de algemene scalingfunctie toont een sterke afhankelijkheid van de normale component van de $E_k$ en een overgang van 2 naar 3 moleculen van de kritische kerngrootte is gevonden voor de groei bij $E_k = 6,3$ eV als $\theta$ groter wordt en zich verwijdert van het normaal.

In het laatste deel van dit proefschrift hebben we geïllustreerd hoe door SuMBD gegroeide pentacenenlagen van hoge kwaliteit gebruikt kunnen worden in veldeffect transistoren (FET) met bodemcontact met de Au elektroden. We hebben het oppervlak van de Au-elektrode in de transistorstructuur gemonifieerd met een self-assembled monolayer van (perfluoro)-alkanethiols om het metalen oppervlak los te krijgen van de pentacene. Het belangrijkste resultaat van dit werk was dat er voor het eerst een hoge kwaliteit pentacene monolaag is geproduceerd op het raakvlak tussen Au en SiOx. Het overgangsgebied dat normaal gesproken waargenomen zou worden in de buurt van een kale Au elektrode en wordt gekenmerkt door geïsoleerde 3D korrels met een hoge concentratie van korrelgrenzen was compleet verwijderd in onze apparaten. De veldeffect transistoren gebouwd met dergelijke ultradunne pentacenenlagen tonen veel betere elektronische en overdrachtskenmerken.

De drie resultaten beschreven in dit proefschrift zijn samengevat:

1) we hebben aangetoond dat de kinetische energie van pentacene botsend op SiOx de oplossing factor is bij het bepalen van de oppervlakmorfologie en de kwaliteit van de gedeponeerde lagen;

2) we hebben ontdekt dat de stickingcoëfficiënt van pentacene op SiOx oppervlak sterk wordt beïnvloed door de moleculaire kinetische energie, de invalshoek van de moleculaire bundel en de gebruikte temperatuur van het substraat;

3) wij zijn er in geslaagd de hoogwaardige pentacene ultradunne lagen te produceren die toegepast kunnen worden in veldeffect transistoren met bodemcontact met de Au elektroden.

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Yu Wu, Groningen, 2008
List of publications


