Transistors based on ordered organic semiconductors
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Chapter 3

Identification of the morphology of the thin film phases of vacuum evaporated pentacene on SiO$_2$ substrates

We identify, using Atomic Force Microscopy and $\theta$-2$\theta$ X-Ray Diffraction techniques, the morphology of the two crystallographic phases commonly observed in vacuum-evaporated pentacene thin films on SiO$_2$ substrates used for thin film transistor applications. One phase, a substrate-induced thin film phase, forms directly onto the SiO$_2$ substrate and constitutes a layer of strongly faceted grains with a step height between terraces of 15.5 Å. Above a critical thickness of this thin film phase, lamellar structures are found in increasing fraction when the film thickness is increased. These structures are identified as the second phase, with a vertical periodicity of 14.5 Å, corresponding to the pentacene triclinic bulk phase. Furthermore, we find maximum sized single crystal domains ($\sim$15 μm in diameter), consisting of several micrometer-sized uniformly oriented grains of the thin film phase, at a substrate temperature of 80 °C and a deposition rate of 0.08 nm/s.
3.1 Introduction

Thin film transistors (TFTs) based on organic material as active layer have recently received considerable interest. Organic based TFTs offer advantages compared to traditional amorphous silicon transistors, like mechanical flexibility and weight reduction. [1,2] Also the organic TFT is a powerful experimental tool to investigate the charge carrier transport properties of organic materials, including the density of states distribution, charge carrier mobility and stability.

Pentacene is an interesting semiconducting organic material for use in TFTs. Its extremely high mobility [3] (1.5 cm$^2$V$^{-1}$s$^{-1}$) makes this material competitive with the standard amorphous silicon technology, and the highly crystalline structure of the thin films allows pentacene TFTs to serve as a model system [4] for charge transport studies. Recently, Nelson et. al. [5] made a first attempt to explain temperature dependent measurements of the charge carrier mobility in terms of a fundamental transport mechanism. However, large sample-to-sample variations, which were ascribed to traps and/or contact effects, excluded a clear interpretation of the data. Besides these effects, also the thin film morphology and the molecular crystal structure are crucial parameters in determining the TFT characteristics.

From X-Ray Diffraction (XRD) studies, it is known that pentacene thin films fabricated by vacuum evaporation [1,6–8] or pulsed laser deposition (PLD) [9,10] typically consist of two crystallographic phases. Next to pentacene, also oligo-phenyl based thin films show these two crystallographic phases. [11–13] The morphology of the active region of a pentacene TFT will therefore be an average of these two crystalline phases in different proportions. The electrical behaviour of pentacene TFTs is a combination of the conduction properties of both phases, which complicates the analysis of the obtained data. Ideally, the pentacene TFT should consist of a singly-phased layer. This requires a thorough study of the pentacene thin film morphology and its crystal structure as a function of the evaporation parameters.

In this chapter we experimentally identify the morphology of the two crystallographic phases of vacuum-evaporated pentacene thin films on SiO$_2$ substrates. We have fabricated several thin films with varying substrate temperatures and with varying film thicknesses. The films are studied by means of Atomic Force Microscopy (AFM) and XRD techniques. Finally, we
optimize the thin film morphology to obtain maximum-sized single crystal domains in which several crystalline grains are uniformly oriented.

3.2 Morphology and structure of pentacene thin films

3.2.1 Experimental conditions

As-received pentacene, obtained from Aldrich Chemical Corporation, is used without additional purification (in Section 3.2.5 the morphology changes are discussed when using purified pentacene). Highly doped Si-wafers, thermally oxidized in a dry atmosphere (SiO$_2$ thickness about 170 nm) are used as substrates. The thin films are obtained by thermal evaporation ($\sim$ 240 °C) in a high-vacuum environment with typical background pressures of $10^{-7}$ mbar. The deposition rate is monitored by an Intellemetrix IL 400 quartz oscillator and the substrate temperature is measured by chromel-alumel thermocouples.

3.2.2 Thin-film structure at various substrate temperatures

Upon deposition of pentacene thin films of 100 nm thickness at several constant substrate temperatures between 20 °C to 120 °C, we observe an increase in the ratio between the two commonly observed first order diffraction peaks in $\theta$-2$\theta$ XRD scans (see Fig. 3.1).

Films deposited at room temperature consist entirely out of the thin film phase and are characterized by one set of diffraction peaks in XRD spectra with vertical periodicity of 15.5 Å (phase 1). Increasing the substrate temperature introduces a second set of diffraction peaks with vertical periodicity of 14.5 Å (phase 2), which is attributed to the pentacene triclinic bulk phase [14–16]. At a substrate temperature of 115 °C, the first order diffraction peaks of both phases are of equal magnitude.

Analysis of these films with optical polarization microscopy shows an increasing fraction of what with using AFM turns out to be lamellar-like structures (see Fig. 3.3b) at increased substrate temperatures. These structures are completely absent in the room temperature thin films. This suggests that the lamellar-like structures can be identified as being the pentacene
Figure 3.1. The inset shows a typical XRD spectrum of a vacuum-evaporated pentacene thin film (thickness 100 nm), deposited at a substrate temperature of 78 °C (rate ~0.1 nm/s) on SiO$_2$, indicating two crystallographic phases with a vertical periodicity of 15.5 Å and 14.5 Å, respectively. In the main figure, the ratio of the intensity of the first order diffraction peak of phase 2 relative to phase 1 is shown as a function of substrate temperature.

3.2.3 Morphology identification of the crystallographic phases

In order to identify both pentacene thin film phases we analyzed thin films deposited at a constant substrate temperature (87 °C) and a constant deposition rate (0.09 nm/s) with various thicknesses.

The obtained XRD spectra of these films are shown in Fig. 3.2. Again we observe a varying ratio between the diffraction peaks of both phases. With increasing film thickness, the intensity of those peaks that correspond to the bulk phase increase.

The XRD data show that the pentacene bulk phase sets in after a critical thickness of the thin film phase and that the fraction of bulk phase increases...
with the film thickness. The critical thickness of the thin film phase is strongly dependent on the substrate temperature. For a room temperature substrate, the critical film thickness is at least 100 nm (see Fig. 3.1) and it decreases with increasing substrate temperature. At a substrate temperature of 87 °C the critical film thickness is about 30 nm (see Fig. 3.2). These results indicate that the thin film phase is a substrate-induced phase and that the critical film thickness of this phase is strongly dependent on the substrate temperature.

AFM images of the films with layer thicknesses of 25 and 38 nm are shown in Fig. 3.3. The film consisting only of the thin film phase (Fig. 3.3a) shows uniformly distributed 1-2 μm-sized grains with a strong facetting behaviour. These grains have a layered structure with a mono-molecular step height of roughly 2 nm which corresponds to the vertical periodicity of 15.5 Å as observed in the XRD spectra. The facetting behaviour is observed at every separate terrace and the facets are oriented along the same crystallographic direction, indicating a preferential growth direction of the crystallite.

The facetting directions are along the [110] and the [110] unit cell directions corresponding to the herringbone directions, as observed with molecular resolved images on one terrace (see Fig. 3.4). Within the accuracy of the molecular resolved image we estimate that the a and b values of the in-plane unit cell of the thin film phase are comparable to the values known for bulk pentacene. From this we conjecture that the major difference between the thin film phase and the bulk phase is the length and orientation of the c-axis in the unit cell and the resulting different molecular packing. AFM images of films with thicknesses above the critical thickness reveal lamellar-like plates (Fig. 3.3b) with a length of 1-5 μm and typical heights of about 150-200 nm. The density of these lamellar-like structures is observed to increase with film thickness.

The commonly observed two crystallographic phases in XRD spectra [1,7] can now be identified with the corresponding morphology using the AFM and XRD measurements. The increase of the lamellar-like structures with the film thickness as observed with AFM together with the increase of phase 2 in the XRD spectra leads to the conclusion that the lamellar-like structures can be identified as pentacene bulk phase. The thin film phase is characterized by strongly faceted grains and is the first to grow onto the substrate. The critical film thickness is dependent on the substrate temperature.
Figure 3.2. XRD spectra of pentacene films with thicknesses (d) of 25 nm, 38 nm, 50 nm and 150 nm deposited at a substrate temperature of 87 °C (rate ~0.09 nm/s). At a film thickness of 150 nm, the bulk phase has become the dominant phase. This in contrast to the XRD spectrum of very thin film of 25 nm thickness, where the thin film phase is the only contribution.

3.2.4 Optimization of single crystal domains of the thin film phase

The size of the grains of the thin film phase (Fig. 3.3a) is strongly dependent on the evaporation parameters. Both an increase in substrate temperature
3.2 Morphology and structure of pentacene thin films

Figure 3.3. AFM images of pentacene thin films at deposited film thicknesses of (a) 25 nm showing faceted terrace-like thin layers of the pentacene thin film phase and (b) 38 nm showing lamellar-like structures (white portions), which is attributed to the pentacene bulk phase; the background morphology is thin-film phase ordered.

(20 to 115 °C) and a decrease of the deposition rate at a constant temperature yields an increase in the size of the individual grains (1-2μm) and an increase in size of the single crystal domains. In these domains, several grains are uniformly oriented with the same azimuthal orientation with respect to the substrate plane, as determined with optical polarization microscopy techniques [17]. The size of the single crystal domains is maximal (∼15 μm in diameter) at a substrate temperature of 80 °C and a deposition rate, just above the critical desorption rate, of 0.08 nm/s.

3.2.5 Morphology of purified pentacene thin films

The pentacene material used in the following experiments is based on the raw material received from Aldrich Chemical Corporation which was additionally purified by a vacuum sublimation process [18]. With this material thin films were made at substrate temperatures of 88°C using evaporation rates of ∼0.12 nm/s. A typical AFM image of such a thin film is shown in Fig. 3.5. Again, the thin film consists of two different morphologies with each its characteristic structure. Next to dendritic like crystals of about 1 to
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Figure 3.4. AFM images of (a) individual terraces of the pentacene thin film phase with (b) a scan zoomed in on one terrace with molecular resolution showing the a and b axis of unit cell with $a = 6.1 \pm 1 \text{ Å}$ and $b = 7.9 \pm 1 \text{ Å}$. (c) These scans indicate that the facet directions are along the [1 1 0] and the [1 1 0] directions of the unit cell.

2 $\mu$m in diameter we observe circularly shaped crystals with a clear layered structure and showing strong facetting behaviour (see Fig. 3.5(b)). These circularly shaped crystals can grow to sizes up to 5-10 $\mu$m in diameter. The fraction of dendrite-like and circular crystals is seen to be critically dependent on the used substrate temperature and possibly on the evaporation rate. At lower substrate temperatures (between 80 and 88°C) the number of dendrite-like crystals increases and the size of the circular crystals decreases. Additional XRD experiments have to be carried out in order to establish the crystal structure of both types of thin-film morphologies. Based on the previous experiments shown in this chapter, it is likely that the dendrite-like structures correspond to the pentacene bulk phase and the circular shaped crystals with the clear layered structure to the thin-film phase. However, more detailed experiments are needed to make conclusive statements. In Chapter 5 we discuss the effects of the purity of the pentacene material on the TFT performance.
Figure 3.5. AFM images of a 50 nm thin film of purified pentacene deposited at a substrate temperature of 88°C with a deposition rate \( \sim 0.12 \text{ nm/s} \). The thin-film morphology consists of dendrite like crystals and crystals with circular shapes (a). The circularly shaped crystals clearly show a layered structure with facetting of each terrace (b).
3.3 Discussion and conclusions

The experimental data show that the morphology of vacuum evaporated pentacene thin films is strongly dependent on the used evaporation parameters and the film thickness. The large sample-to-sample variations observed in the results presented by Nelson et al. [5] can therefore possibly be attributed partly to differences in film morphology, in addition to the reported traps and/or contact effects. We believe that the obtained record mobilities [3] of the double (stacked) layer TFTs of 1.5 cm²V⁻¹s⁻¹ are likely to consist solely of the thin film phase, making this phase the high mobility phase of pentacene. Ideally, one would like to use these singly-phased pentacene transistors in order to study the fundamental transport properties.

In this chapter we have experimentally identified the morphology of the two crystallographic phases known to exist in vacuum evaporated pentacene thin films on SiO₂ substrates. We have shown that a thin film phase forms directly onto the SiO₂, constituting a substrate-induced layer of faceted grains with a vertical periodicity of 15.5 Å. Above a critical film thickness, which is dependent on substrate temperature, lamellar-like structures are found with increasing fraction as a function of the film thickness. These structures are identified as the second phase, and are attributed to the pentacene triclinic bulk phase with a vertical periodicity of 14.5 Å. We have maximized the size of the single crystal domains (~15 μm in diameter) of the thin film morphology, using a substrate temperature of 80 °C and a deposition rate of 0.08 nm/s.

References

References

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