

Structure and Morphology of Vacuum-Evaporated Pentacene as a Function of the Substrate Temperature

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In order to reach high quality of organic thin films such as high mobility for device applications, it is strongly desirable to study the growth properties of pentacene film as a function of evaporation conditions. Here, we report the structure and morphology of thermal evaporated pentacene thin film by Atomic Force Microscope (AFM), Scanning Electron Microscope (SEM), and X-ray diffractometry (XRD) as a function of the evaporation rate and substrate temperature. These results play a key role in determining the electrical performance of organic thin film transistor devices.

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I. INTRODUCTION

Organic thin film transistors (OTFTs) based on pentacene as active layer have recently received considerable interest. Organic TFTs offer advantages compared to traditional field-effect transistors, like mechanical flexibility [1] and weight reduction [2]. But, because of the relatively low mobility of organic TFTs, they cannot rival the performance of field-effect transistors based on single crystalline inorganic semiconductors [3], such as Si, Ge, and GaAs, which have charge carrier mobility [4] of three or more orders of magnitude higher [5]. To make organic TFTs with high mobility, it is very important to grow pentacene with a molecular crystal structure and morphology. Substrate temperature, deposition rate [6], and base pressure are crucial conditions that can influence the molecular crystal structure and morphology of pentacene.

In this work, we have grown pentacene with varying substrate temperature or deposition rate under quasi-equilibrium conditions, *i.e.*, close to solid-vapor (S-V) phase transition. We characterized the pentacene thin films by means of XRD, AFM, and SEM image spectra as a function of the substrate temperature during the evaporation process, in order to obtain a highly ordered layered structure of the pentacene thin films. Finally, we optimized the evaporation conditions to ob-

tain maximum-sized single crystal domains in which several crystalline grains are uniformly oriented. Maximum-sized single crystal domains and their uniform orientation play a key role in determining the field effect mobility of OTFTs [7]. If the pentacene thin film obtained between the maximum-sized single crystal domains and its uniform orientation is defined in the channel, the high mobility of pentacene thin film will be obtained.

Our experimental data show that the morphology of vacuum-evaporated pentacene thin film is strongly dependent on the used evaporation conditions such as substrate temperature and deposition rate. Moreover, according to our optimized experimental data, we saw pentacene thin film having the maximum-sized single crystal domains.

II. EXPERIMENTAL

1. High-vacuum evaporation setup

As-received pentacene is used without additional purification. First, in order to find an ordered layered structure of the thin pentacene films, we observed the thermally vacuum-deposited pentacene varying the substrates. A bare Corning glass 1737, Plasma-Enhanced Chemical Vapor Deposition (PECVD)-oxidized Corning glass, heavily doped bare silicon wafer, thermally oxidized Si-wafer, and the Corning glass with spin-coated

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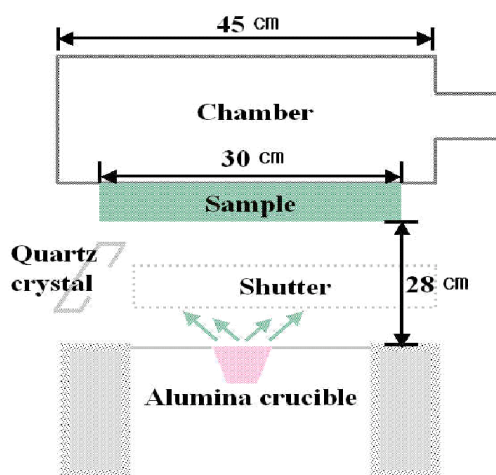


Fig. 1. Experimental vacuum evaporation setup.

poly (methyl methacrylate) (PMMA) are used as substrates. The thin pentacene films are obtained by thermal evaporation in a high-vacuum environment with a typical background pressure of 2×10^{-6} Torr (Figure 1). The material is loaded in an alumina crucible, which is resistively heated. The temperature of the sample holder can be controlled in a large temperature range by resistive heating elements and water-cooling. The temperatures of the substrate are monitored by chromel-alumel thermocouples. An Intellemetrix IL 400 quartz oscillator monitors the deposition rate. A shutter allows adjusting the evaporation rate to the desired value before the actual deposition of the pentacene thin film. Also, during the deposition of this film, the deposition rate was kept

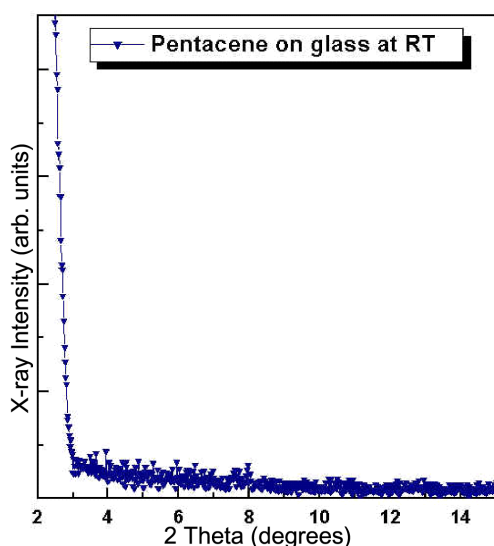


Fig. 2. The observed diffraction peaks in $\theta - 2\theta$ XRD scans of vacuum-deposited pentacene on glass, (thickness 150 nm) at room temperature. In this figure, two crystallographic phases of 15.5 Å and 14.5 Å are absent at the room temperature.

constant by controlling D.C power in order to analyze the change of this film as a function of substrate temperature. After evaporation, the substrate is slowly cooled to room temperature in order to prevent the damage of pentacene film due to the sudden phase transition.

III. RESULTS AND DISCUSSION

1. Structure of evaporated pentacene

Upon deposition of pentacene thin films of 1500 Å thickness on several substrates, we analyze an increase of two commonly observed diffraction peaks in $\theta - 2\theta$ XRD scans. For the deposited pentacene film on the Corning glass 1737 except for a substrate temperature of room temperature, two crystallographic phases are observed. One phase, a substrate-induced thin film phase, forms directly onto the 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 with increasing the fraction of the film thickness. These structures are identified as the second phase, with a vertical periodicity of 14.5 Å, corresponding to the pentacene triclinic bulk phase. The pentacene thin film phase indicates a preferential growth direction of the crystallite. This phase is characterized by strongly faceted grains and is the first to grow onto the substrate. The film thickness of the thin film phase is dependent on substrate temperature. In our experiment, this phase is characterized at substrate temperatures above 50 °C. The pentacene triclinic bulk phase can be identified as the lamellar-like structures. This phase is very important to analyze the growth of vacuum evaporated pentacene, because this phase is strongly attributed to the charge carrier transport properties of pentacene, including the density of states distribution, charge carrier mobility, and stability. This phase is absent at room temperature.

As shown in Fig. 2, where the deposition rate was kept constant by controlling D.C power, and substrate temperature is room temperature, we can find that the structure of pentacene thin film is amorphous, because two crystallographic pentacene phases are not found. But at a higher substrate temperature between 50 °C and 80 °C in Fig. 3 and 4, these phases are characterized. In the case of a substrate temperature up to 80 °C, the peak of these phases becomes large, which represents the enhancement of molecular ordering.

For other substrates, two crystallographic phases as a function of substrates are similar to the pentacene phase observed on the glass. We characterized the phases obtained on various substrates in Table 1.

2. Morphology of evaporated pentacene

Table 1. The observed phase of pentacene film, varying several substrates.

	Room-temp.	50 °C	80 °C
Glass	No phase	1 phase	2 phase
Silicon Wafer	No phase	1 phase	2 phase
PECVD Oxide	No phase	1 phase	2 phase
Thermal Oxide	No phase	1 phase	2 phase
PMMA 2 wt.%	No phase	1 phase	2 phase
PMMA 3 wt.%	No phase	1 phase	2 phase

Second, we report on the increased sizes of the crystallites within the thin pentacene film by elevating the substrate temperature and deposition rate during evaporation. At these higher substrate temperatures, the diffusion length of the molecules along the substrate is enhanced and allows for the formation of a limited number of nucleation sites in the initial stages of growth, whereafter a 3D growth of these islands sets in without formation of additional nucleation sites. Using this approach, we are able to enhance the crystallite sizes of pentacene thin films from 100 nm to 6 μm as a function of substrate temperature. The obtained crystallites are all strongly faceted, which represents the equilibrium shape of these crystals.

Figures 5 and 6 represent the different grain sizes. The grain size of 250nm and 850nm in the Figure 5(a) and (b) respectively are observed. However, raising the substrate temperature to 80 °C (Figure 6), a large number of crystallites with diameters of about 2.5 μm are formed. According to our expectation, diffusion length of molecules

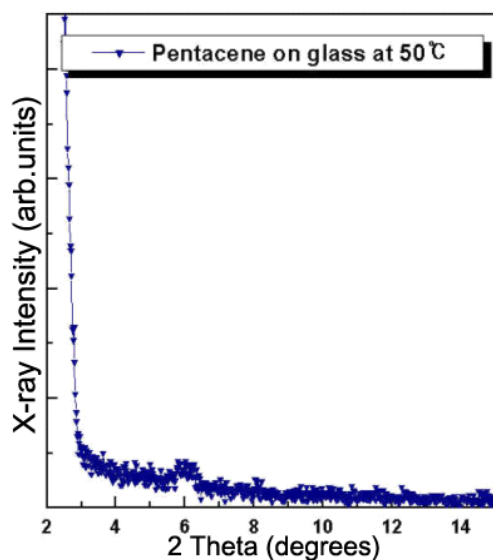


Fig. 3. The observed diffraction peaks in $\theta - 2\theta$ XRD scans of vacuum-deposited pentacene on glass (thickness 150 nm) at 50 °C. The surface induced thin film phase is shown in this figure. This intensity is very low.

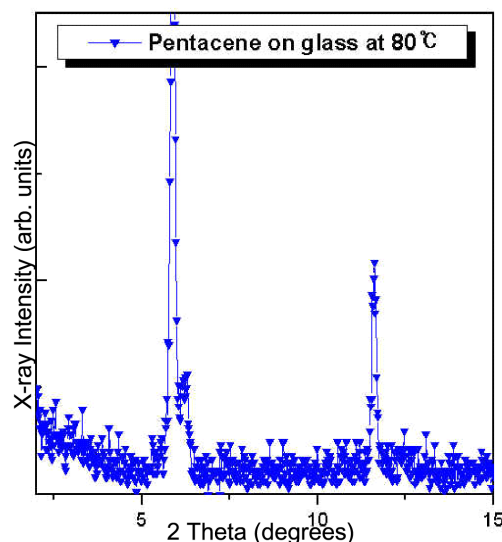


Fig. 4. The observed diffraction peaks in $\theta - 2\theta$ XRD scans of vacuum-deposited pentacene on glass (thickness 150 nm) at 80 °C. Figure 4 shows a typical XRD spectrum of vacuum-evaporated pentacene thin film indicating two crystallographic phases of 15.5 Å and 14.5 Å, respectively.

along the substrate and re-evaporation of the molecules from substrate must be enhanced.

Figures 7(a), (b), and 8 show that on varying substrate temperature from room temperature to 80 °C, the individual grain sizes can be drastically improved from 250 nm (Figure 7(a)) to 6 μm (Figure 8) depending on the evaporation conditions such as substrate temperature.

We characterized the analysis of an increase in grain size as a function of other substrates in Figure 9. As will be shown in Figure 9, the morphology of thin pentacene films on raising the temperature of the substrates is strongly dependent on the actual substrate temperature. In grain size as a function of substrate materials, we can see that at 80 °C, the grain sizes of the pentacene deposited on both thermal oxidized wafer and PECVD-oxidized glass are greater than those of other substrates. According to our expectation, the growth of pentacene

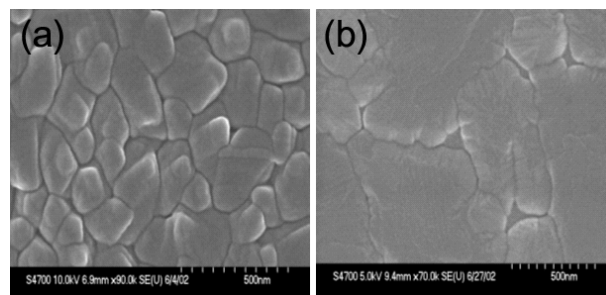


Fig. 5. SEM image of a 150 nm thin film of vacuum evaporated pentacene on glass at a substrate temperature of (a) room temperature with a deposition rate ~ 0.5 Å/s and (b) 50 °C with a deposition rate ~ 0.5 Å/s.

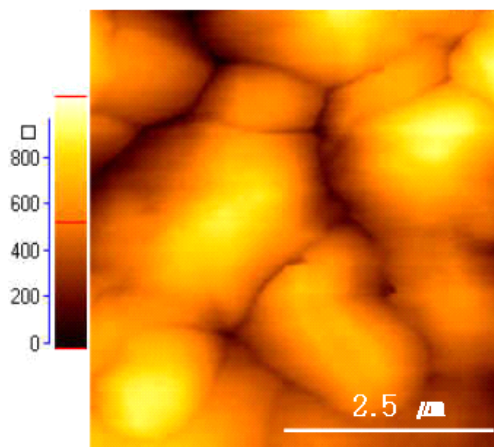


Fig. 6. AFM image of a 150 nm thin film of vacuum evaporated pentacene on glass at a substrate temperature of 80 °C with a deposition rate $\sim 0.5 \text{ \AA/s}$.

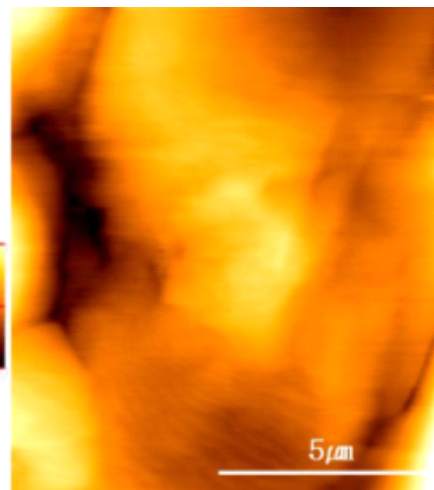


Fig. 8. AFM image of a 150 nm thin film of vacuum evaporated pentacene on PECVD oxide at a substrate temperature of 80 °C with a deposition rate $\sim 0.5 \text{ \AA/s}$.

occurs well on hydrophilic substrate.

In this figure, we can see the grain size of pentacene deposited on oxide type substrate growth is extremely large.

IV. CONCLUSION

We have studied the structure and morphology of thermally evaporated pentacene films as a function of evaporation temperature.

Generally, the growth mode of thermally evaporated pentacene thin film is described by a Volmer-Weber type of process [8] in which the nucleated islands have a 3-dimensional growth mode without the formation of an initial complete monolayer. The growth mode is described in the thermodynamic regime in which surface and interface free energies dominate the structure and morphology of the films. In the kinetic growth mode regime, which is commonly used for epitaxial growth of inorganic materials, the formed nuclei are already stable for clusters of two or more atoms and are in strong su-

persaturation with the vapour phase. In this regime, the vapour pressure of the thin pentacene films is negligible compared to the depositing flux. In the thin pentacene films with (sub) monolayer coverage, we have shown that Oswald ripening [9] is an important process determining the thin film growth. In this process the total free energy of the thin film is minimized in terms of thermodynamic arguments, large islands with low total free energy grow at the expense of less stable smaller islands.

Next to this effect, large strongly faceted crystallites are obtained using increased substrate temperatures together with an evaporation rate just above the re-evaporation rate from the substrate, which means that the molecules of the islands are in dynamic equilibrium

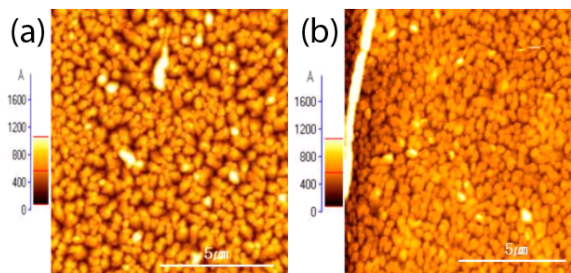


Fig. 7. AFM image of a 150 nm thin film of vacuum evaporated pentacene on PECVD oxide at a substrate temperature of (a) room temperature with a deposition rate $\sim 0.5 \text{ \AA/s}$ and (b) 50 °C with a deposition rate $\sim 0.5 \text{ \AA/s}$.

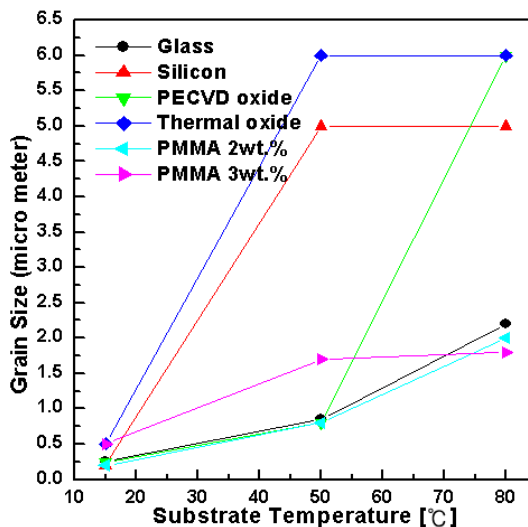


Fig. 9. The increase in grain size as a function of substrate temperature.

with the vapor phase of the source, unlike the case of the supersaturation regime in the kinetic growth process.

These aspects of growth of ordered thin pentacene films indicate that these films are grown at the thermodynamic limit in which Oswald ripening and small supersaturations are important aspects of growth.

In this study, we have experimentally identified the morphology of the thermal evaporated pentacene film with two crystallographic phases. We have shown that a thin film phase forms directly onto 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.

As a result of our experiments, we have known that the thin pentacene film strongly depended on substrate temperature, and grew well onto hydrophilic substrate better than hydrophobic substrate. In addition, we have maximized the grain size of the thin pentacene film (about 6 μm in its diameter), at a substrate temperature of 80 °C and deposition rate of 0.5 Å/s.

Maximum-sized single crystal domains play a key role in determining the field effect mobility of OTFTs. If the pentacene thin film obtained with the maximum-sized single crystal domains is defined in the channel, a high

mobility of pentacene thin film will be obtained.

So, if this growth of pentacene using our results is adapted in the fabrication of organic transistors, the electrical properties of the transistor will be highly enhanced.

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