Study on the structure and morphology of vacuum-evaporated pentacene as a function of the evaporation condition

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Abstract

In order to reach the 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 condition. Here, we report the structure and morphology of thermal evaporated pentacene thin film by AFM, SEM, and XRD as a function of the evaporation rate and substrate temperature. These results play a key role in determining the electric performance of organic thin film transistor devices.

1. 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 and weight reduction.[1],[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, such as Si, Ge, and GaAs, which have charge carrier mobility of three or more orders of magnitude higher.[3] 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, 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 and deposition rate under quasi-equilibrium condition, 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 obtain maximum-sized single crystal domains in which several crystalline grains are uniformly oriented. Maximum-sized single crystal domains play a key role in determining the field effect mobility of OTFTs. If the pentacene thin film obtained the maximum-sized single crystal domains 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, deposition rate. Moreover, according to our optimized experimental data, we saw the pentacene thin film obtained the maximum-sized single crystal domains.

2. Experiments

2.1 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 by varying several substrates. A Bare

corning glass 1737 oxidized corning glass using PECVD, heavily doped bare Si-wafer, thermally oxidized Si-wafer, and the corning glass with spin-coated PMMA are used as substrates. The thin pentacene films are obtained by thermal evaporation in a high-vacuum environment with typical background pressures of 2×10^{-6} Torr. (See Fig. 2.1.1) The material is loaded in an alumna 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. The deposition rate is monitored by quartz oscillators. A shutter allows adjusting the evaporation rate to the desired value before the actual deposition of the thin pentacene film. 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.
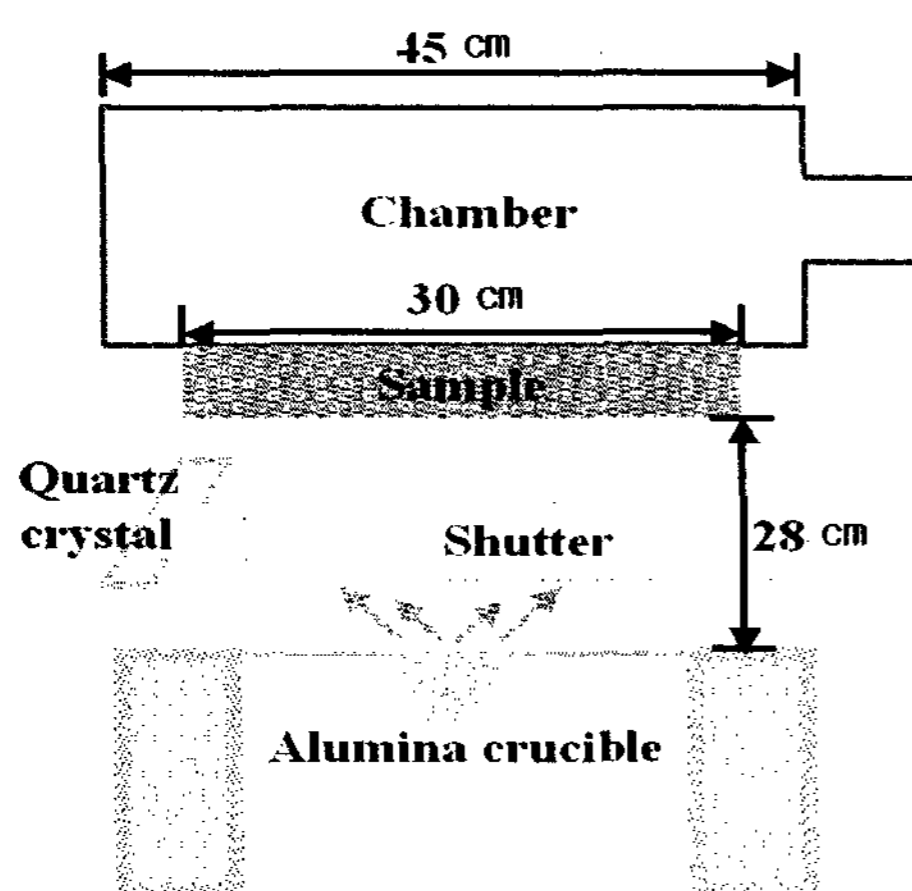

Figure 2.1.1. Experimental vacuum evaporation setup

3.   Result and discussion

3.1   Structure of evaporated pentacene

Upon deposition of thin pentacene films of 1500 Å thickness at several substrate, we analyze an increase of two commonly observed diffraction peaks in θ-2θ XRD scans.

For the deposited pentacene film on the corning glass 1737, two crystallographic phases are observed (see Fig. 3.1.3). 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 15.5Å. 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 14.5Å, 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 thin film phase is dependent on substrate temperature. In our experiment, above substrate temperature at 50 ℃ this phase is characterized. The pentacene triclinic bulk phase can be identified as the lamellar-like structures. This phase is very important to analysis the growth of vacuum evaporated pentacene. Because this phase is strongly attributed to the charge carrier transport property of pentacene, including the density of states distribution, charge carrier mobility and stability. This phase is absent in the room temperature thin films.
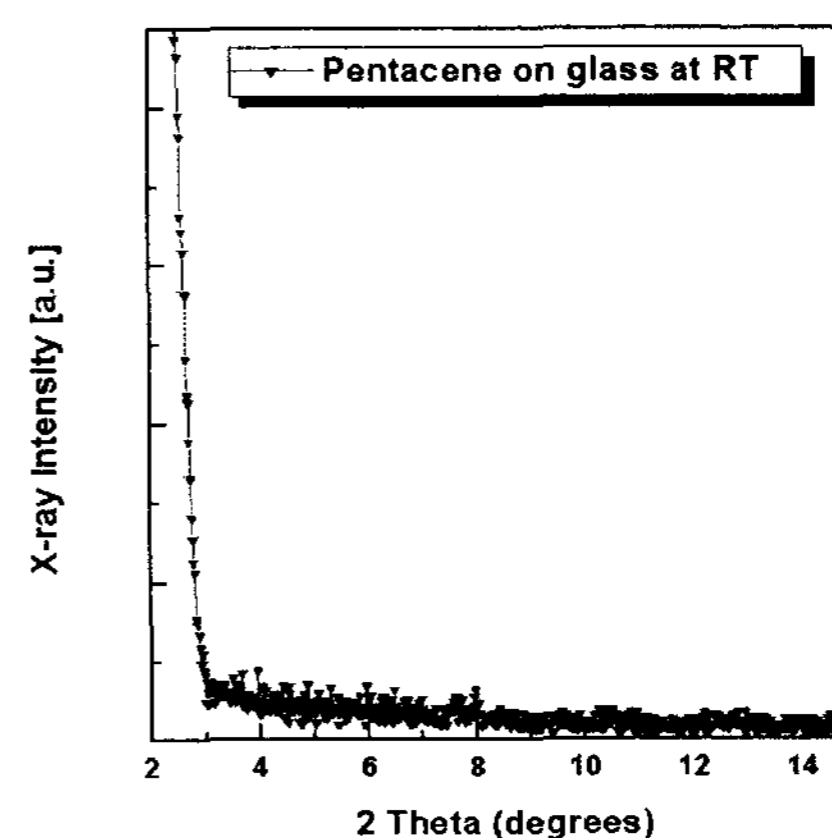

Figure 3.1.1 The observed diffraction peaks in 2θ XRD scans of vacuum-deposited pentacene on glass, (thickness 150nm) at room temperature. In this figure, two crystallographic phases of 15.5 Å and 14.5 Å, respectively is absent in the room temperature.
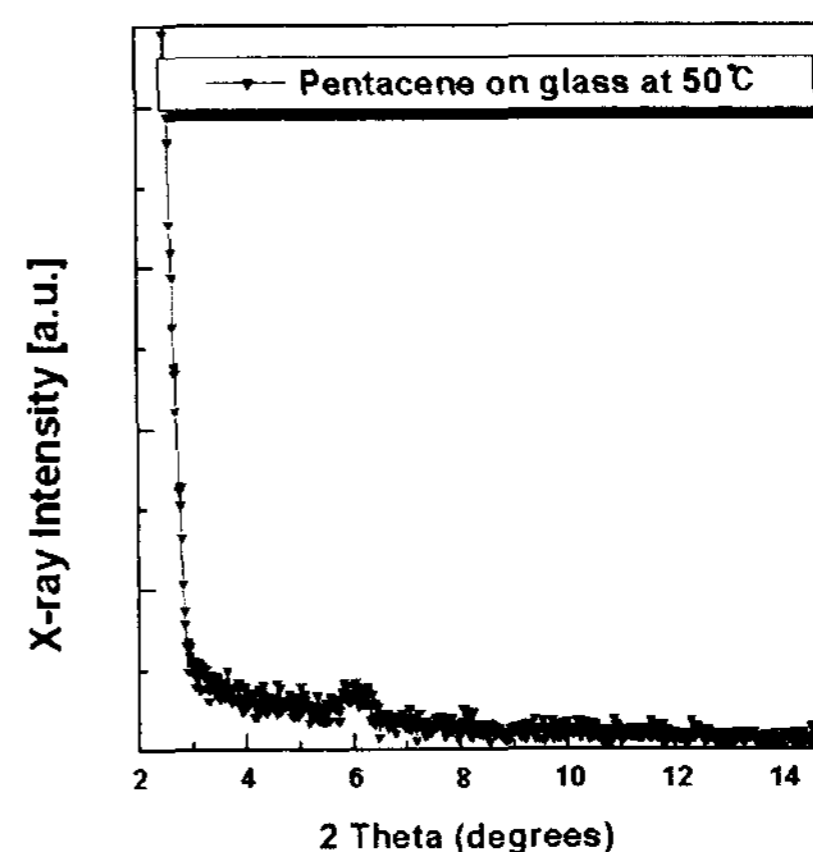

Figure 3.1.2. The observed diffraction peaks in 2θ XRD scans of vacuum-deposited pentacene on glass.

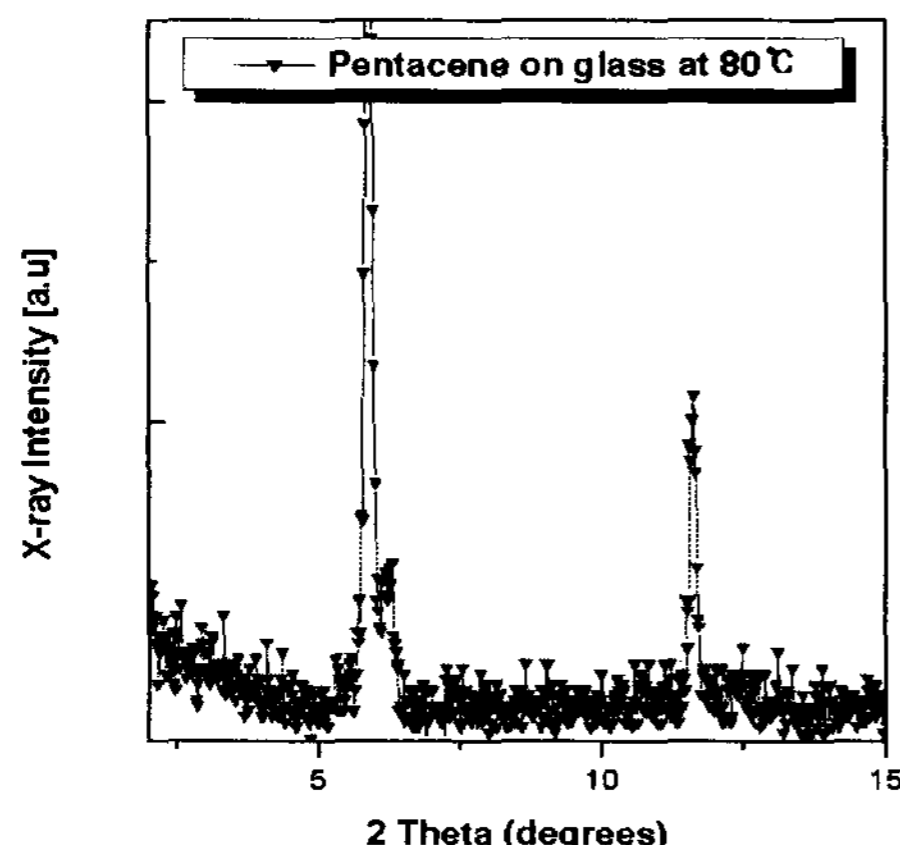(thickness 150nm) at 50℃. The surface induced thin film phase is shown in this figure. This intensity is very low.

Figure 3.1.3. The observed diffraction peaks in 2θ XRD scans of vacuum-deposited pentacene on glass (thickness 150nm) at 80℃. The figure 2.2.3 shows a typical XRD spectrum of vacuum-evaporated pentacene thin film indicating two crystallographic phases of 15.5 Å and 14.5 Å, respectively.

For other substrates, two crystallographic phases as a function of other substrates are similar to the pentacene phase observed on the glass. We characterized the phases as a function of other substrates in the table 3.1.1.

Table 3.1.1. The observed phase of pentacene film by varying several substrates

	Room-temp.	50℃	80℃
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 2wt.%	No phase	1 phase	2 phase
PMMA 3wt.%	No phase	1 phase	2 phase

3.2 Morphology of evaporated pentacene

Second, we report on the increased sizes of the crystallites within the thin pentacene film by elevating a 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 thin pentacene films from 100 nm to 6μm as a function of substrate temperature (see the figure 3.2.5). The obtained crystallites are all strongly facetted that represent the equilibrium shape of these crystals.
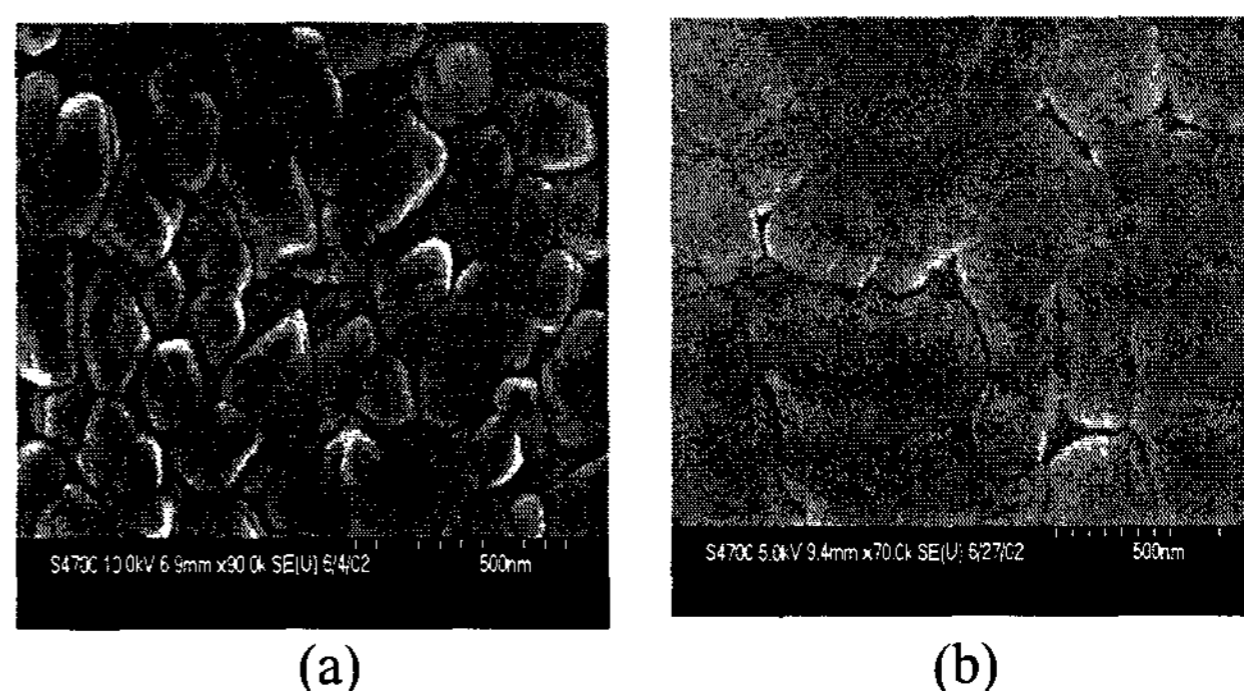

(a)   (b)

Figure 3.2.1. SEM image of a 150nm 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℃ with a deposition rate ~0.5 Å /s.
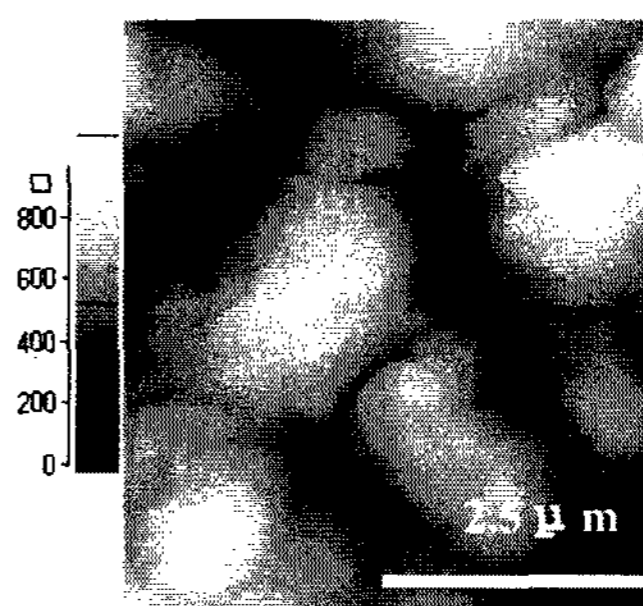

Figure 3.2.2. AFM image of image of a 150nm thin film of vacuum evaporated pentacene on glass at a substrate temperature of 80℃ with a deposition rate ~0.5 Å /s

The figure 3.2.1 and 3.2.2 represent the different grain size. The grain size of 250nm, 850nm, respectively in the figure 3.2.1 (a) and (b) is observed.

But, raising the substrate of 80℃(see the figure 3.2.2), a large number of crystallites with diameters of about 2.5μm are formed due to enhancement of diffusion length of the molecules along the substrate, and re-evaporation of the molecules from substrate.
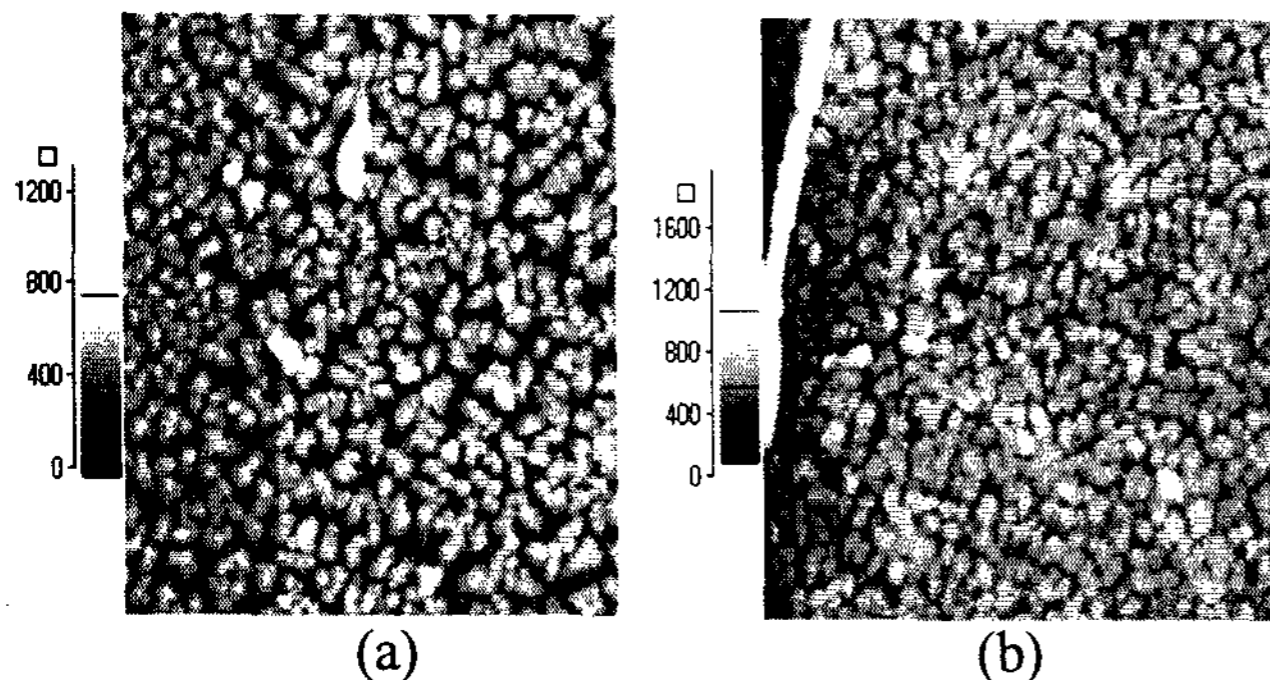

(a)   (b)

Figure 3.2.3. AFM image of a 150nm thin film of vacuum evaporated pentacene on PECVD oxide at a substrate temperature of (a) room temperature with a deposition rate ~0.5 Å /s and (b) 50℃ with a deposition rate ~0.5 Å /s.
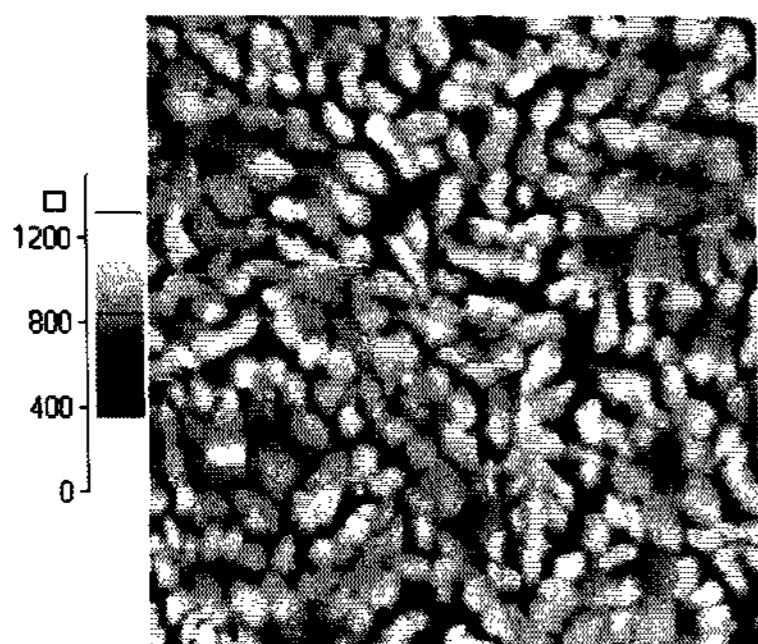

Figure 3.2.4. AFM image of image of a 150nm thin film of vacuum evaporated pentacene on PECVD oxide at a substrate temperature of 80℃ with a deposition rate ~0.5 Å /s

The figure 3.2.3 (a),(b), and 3.2.4 show that on varying substrate temperature from room-temperature to 80℃, the individual grain sizes can be drastically improved from 250nm(figure 3.2.3.a) to 6μm(figure 3.2.4) depending on the evaporation condition such as substrate temperature.

We characterized the analysis in increase of grain size as a function of other substrates in the figure 3.2.5. As will be shown in the figure 3.2.5, the morphology of thin pentacene film by elevating the substrates are strongly dependent on the actual substrate temperature. In grain size as function of substrate materials, we can see that at substrate temperature of 80℃, the deposited pentacene on both

thermal oxidized wafer and oxidized glass using PECVD are better than that of other substrate. According to our expectation, the growth of pentacene occurs on hydrophilic substrate well.
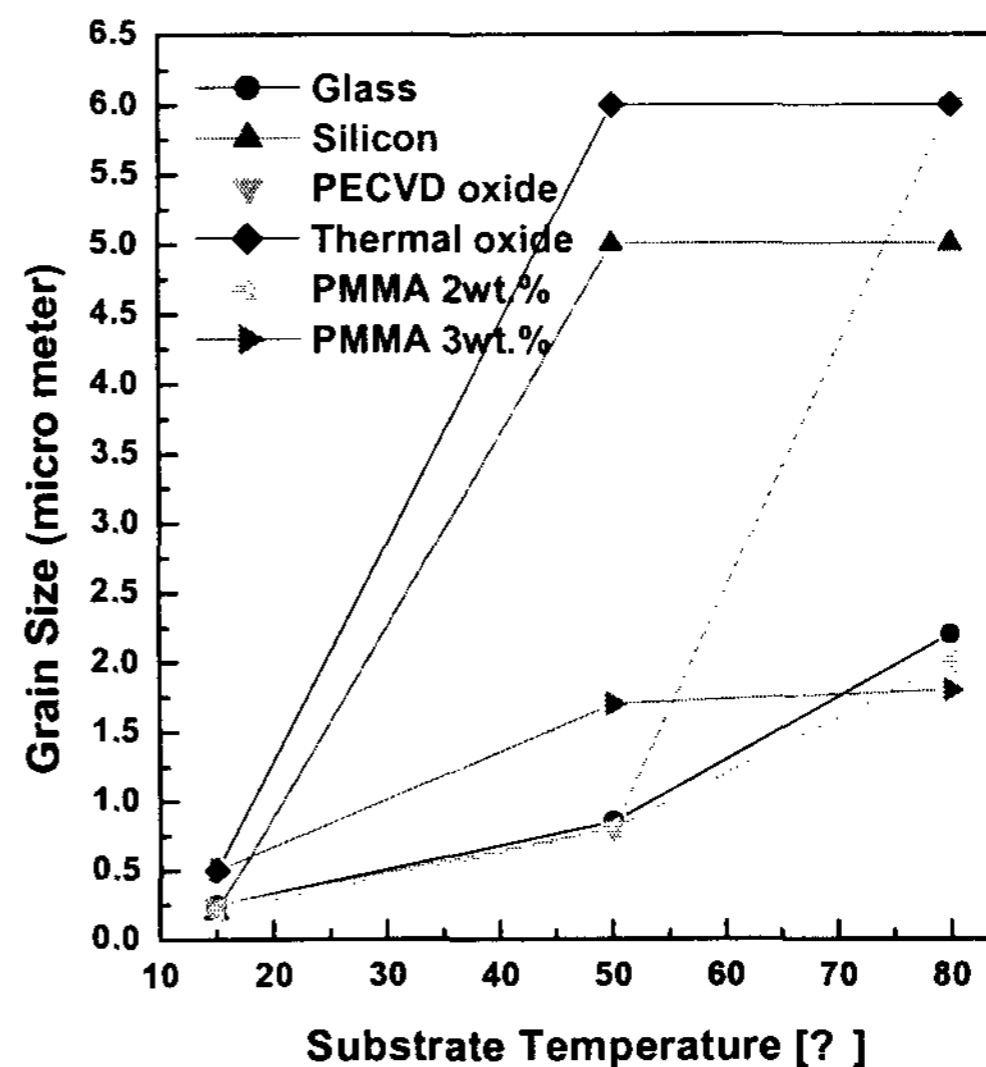

Figure 3.2.5. The increase of grain size as a function of substrate temperature

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

4.   Summary

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

Generally, The growth mode of thermally evaporated pentacene thin film is described by a Volmer-Weber type of process 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 supersaturation 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 coverages we

have shown that Oswald ripening 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 facetted 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 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 in 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 15.5Å.

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 6μm in its diameter), using a substrate temperature of 80℃ and a 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 the maximum-sized single crystal domains is defined in the channel, the high mobility of pentacene thin film will be obtained.

So, if this growth of pentacene using our result is adapted in the fabrications of organic transistor, the electric property of organic transistor will be highly enhanced.

5.   References

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