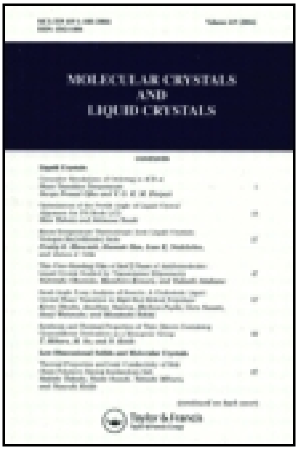

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GROWTH CONDITIONS EFFECTS ON MORPHOLOGY AND TRANSPORT PROPERTIES OF PENTACENE THIN FILMS

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GROWTH CONDITIONS EFFECTS ON MORPHOLOGY AND TRANSPORT PROPERTIES OF PENTACENE THIN FILMS

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Pentacene thin films were prepared by vacuum evaporation on SiO_2/Si (100) and glass substrates with various growth conditions. X-ray diffraction, atomic force microscopy, and electrical conductivity measurements were employed to characterize the various properties of the films. Two distinct crystalline phases were observed with the 001 spacing of 15.0Å (thin film phase) and 14.0Å (single crystal phase), respectively. The single crystal phase appeared over a critical thickness of the thin film phase, and the critical thickness was strongly dependent on growth conditions: increasing the substrate temperature decreased the critical thickness. The substrate temperature enhanced the electrical conductivity of the films parallel to the substrate surface, although the substrate temperature induces the single crystal phase. On the other hand, gaps generated between grains degraded conductivity at a too high substrate temperature. The maximum conductivity of 2.0×10^{-7}S/cm was gained at a substrate temperature of 40°C.

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Keywords: atomic force microscopy; electrical conductivity; morphology; pentacene; X-ray diffraction

1. INTRODUCTION

Organic semiconductors have been widely studied over the two last decades for their potential applications as Thin Film Transistors (TFTs), Light-Emitting Diodes (LEDs), and photovoltaic cells. [1–5] The field effect mobility has been impressively increased year by year by improving the fabrication processes or applying a new organic material as an active layer. Organic Thin Film Transistors (OTFTs) made from pentacene thin films led to a charge carrier mobility of 2.1 cm (2/Vs, which is comparable to that obtained for amorphous silicon. [6] On the other hand, the characteristics of OTFTs are drastically affected by the morphology and structure of organic thin films, which are very quite sensitive to growth conditions such as substrate-surface temperature. [7–10] Thus it is very important to control the growth parameters during growth of organic thin films.

In this work, we report on the role of the growth conditions on structure and morphology of pentacene vacuum deposition thin films by X-ray diffraction (XRD) and Atomic Force Microscopy (AFM). We also study that the growth conditions affect electrical transport characteristics of these films.

2. EXPERIMENTAL

Pentacene was purchased commercially (98%, Tokyo Kasei Co., Ltd.) and used without further purification. The polycrystalline pentacene films were thermally deposited on SiO_2/Si (100) substrates (thermally oxidized, about 500 Å) and glass substrates at a base pressure of about 4×10^{-4} Pa. The growth rate (R) and film thickness were monitored by a thickness and rate monitor (CRTM-6000, ULVAC) placed near the substrate holder. The substrate temperature was directly controlled by Digital Programming Regulator (KP1000, CHINO) with overshoot value $<1°C$ and accuracy of $\pm 0.2°C$.

The XRD analysis was performed on a diffractometer (Rint 2200 V, RIGAKU Co., Ltd.) with graphite monochromatized CuK_α radiation ($\lambda = 1.54$ Å). The morphology of the films was examined by AFM (SPA 500, Seiko Instruments Co., Ltd.); the cantilevers were used in the tapping mode and had a length of 90 μm and a force constant of 0.12 N/m. The grain size and the RMS roughness were obtained by using the AFM instrument for each individual scan (10 μm × 10 μm).

For conductivity measurements, a 200 nm thick Au layer was thermally evaporated onto naked glass substrates by using a shadow mask.

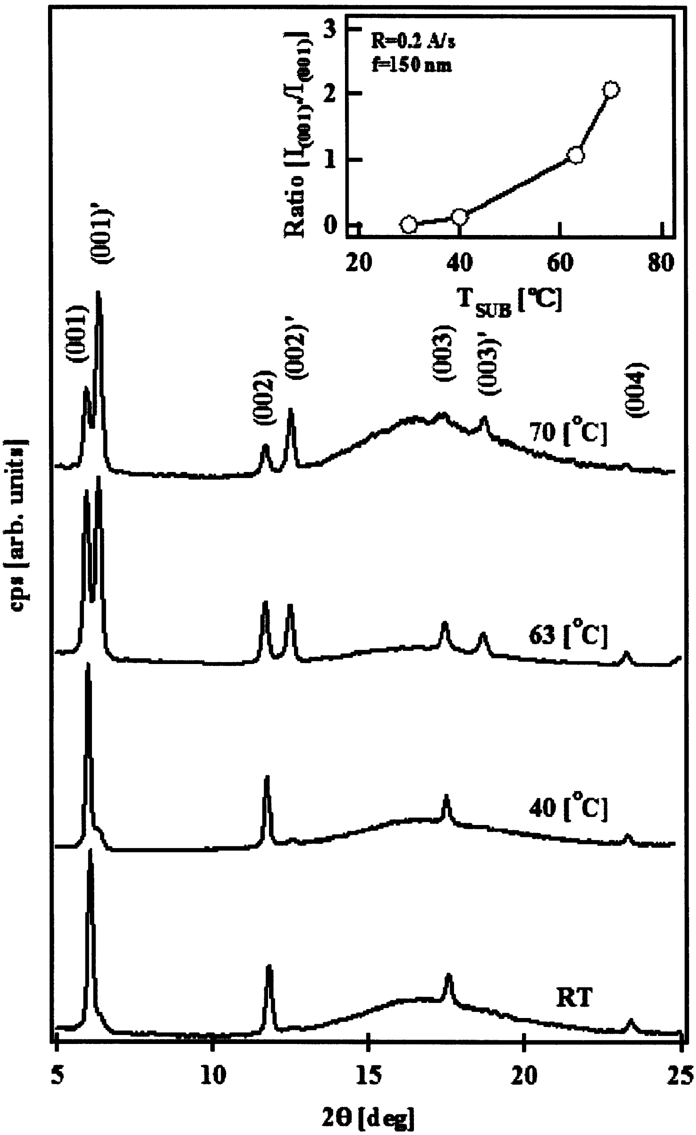

FIGURE 1 XRD spectra of pentacene films with thickness of 150 nm deposited on SiO_2/Si (100) substrates with R = 0.2 Å/s and substrate temperatures of RT (25), 40, 63 and 70°C, respectively. The inset shows the ratio of the intensity of the first order diffraction peak of phase 2 relative to that of phase 1 as a function of substrate temperature.

Au electrodes with two parallel stripes were spaced at $W = 2$ mm and $L = 40$ μm. Pentacene thin films of 100 nm were deposited at several substrate temperatures from RT to 70°C ($R = 0.2$ Å/s). Current-voltage characteristics were measured between two Au stripes opposite each other by using a two channel voltage current source/monitor system (R6245, ADVANTEST).

3. RESULTS AND DISCUSSIONS

3.1. X-ray Diffraction Analysis

Figure 1 shows XRD spectra of pentacene thin films of 150 nm deposited at several substrate temperatures between RT and 70°C ($R = 0.2$ Å/s) on SiO_2/Si (100) substrates. Films deposited at RT consist entirely of the thin

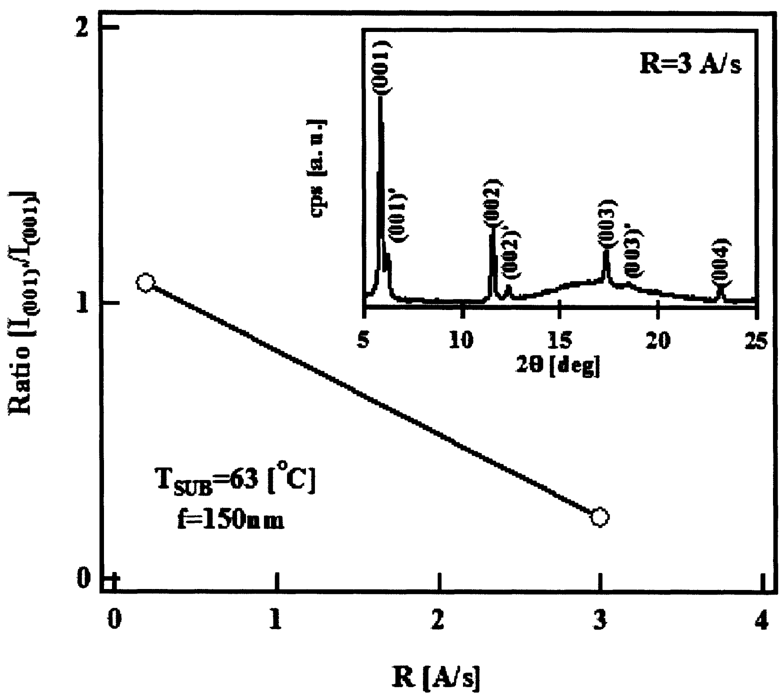

FIGURE 2 The ratio of the intensity of the first order diffraction peak of phase 2 relative to phase 1 is shown as a function of growth rate when the films of 150 nm were deposited at a substrate temperature of 63°C on SiO_2/Si (100) substrates. The inset shows XRD spectra of the films of 150 nm deposited at R = 3.0 Å/s.

film phase (phase 1) and are characterized by one set of diffraction peaks with d_{001} spacing of 15.0 Å. Increasing substrate temperature introduces another set of diffraction peaks with $d_{001'}$ spacing of 14.0 Å, which is attributed to the single crystal phase (phase 2). The spacings of the two phases are slightly different from those of the reported 'thin film phase' (15.4 Å) and 'bulk crystal phase' (14.5 Å) due to polymorphism in pentacene. [11] The ratio of the intensity of the first order diffraction peak of the phase 2 relative to that of the phase 1 is increased with increasing substrate temperature (see the inset of Fig. 1). At a substrate temperature of 60°C, the first order diffraction peaks of both phases are of an equal magnitude.

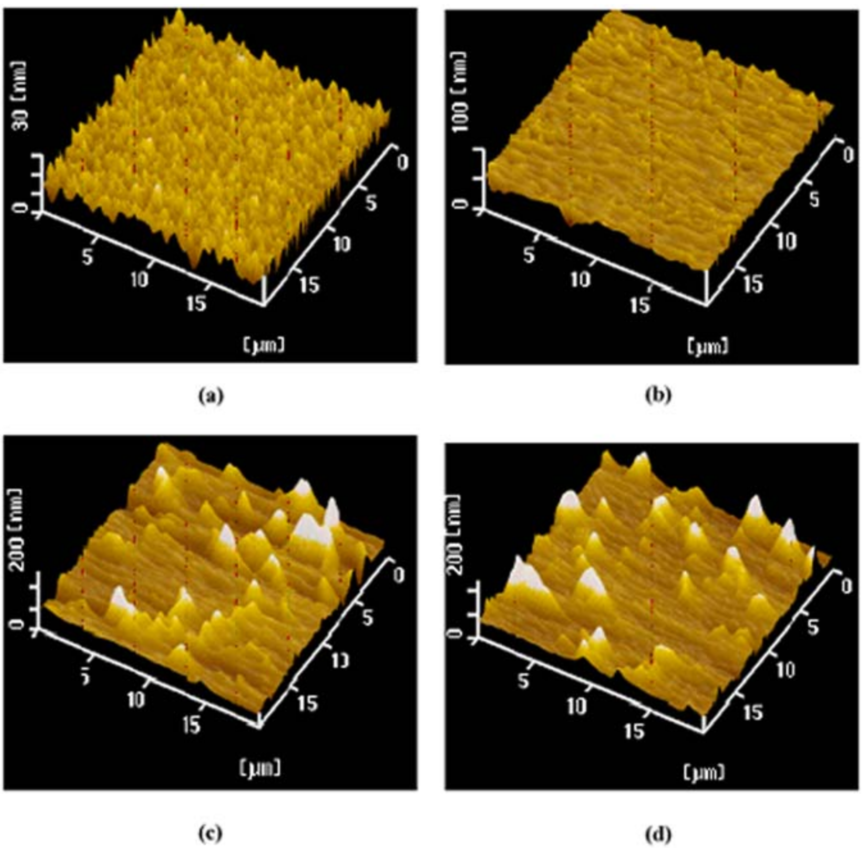

FIGURE 3 AFM images of pentacene thin films deposited on SiO_2/Si (100) substrates with the following conditions: (a) RT, 0.2 Å/s, 150 nm; (b) 63°C, 0.2 Å/s, 45 nm; (c) 63°C, 0.2 Å/s, 150 nm; (d) 63°C, 3.0 Å/s, 150 nm. (See COLOR PLATES I–IV)

Figure 2 shows the growth rate dependence of the ratio of the intensity of the first order diffraction peak of the phase 2 relative to that of the phase 1, where pentacene thin films of 150 nm were deposited at a substrate temperature of 63°C on SiO_2/Si substrates. From the result, the critical thickness of the phase 1 is also affected by the growth rate.

3.2. AFM Analysis

Figure 3 shows AFM images of pentacene thin films deposited on SiO_2/Si substrates with various growth conditions. Figure 3(a) shows that the film of 150 nm deposited at RT ($R = 0.2$ Å/s) consists of small grains of approximately 150 ~ 500 nm in size with high density which appear to coalesce to form clusters approximately 1 ~ 2 μm in size. As seen in Figure 3(b) the film of 45 nm deposited at a substrate temperature of 63°C ($R = 0.2$ Å/s) consisting only of the phase 1 shows uniformly distributed 2 ~ 4 μm size grains

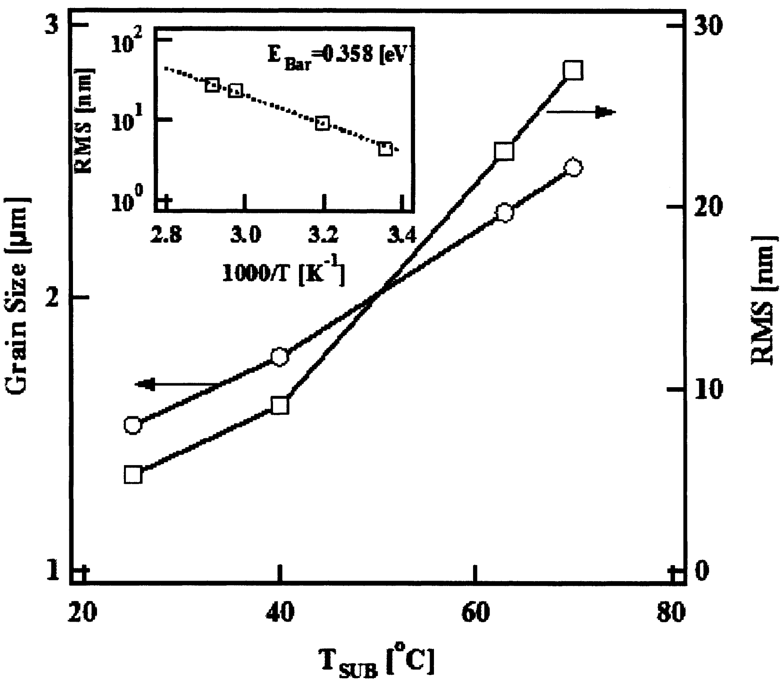

FIGURE 4 The RMS and grain size are shown as a function of substrate temperature of pentacene thin films of 150 nm deposited at R = 0.2 Å/s on SiO_2/Si (100) substrates. The inset shows the RMS amplitude (σ) vs inverse temperature (1000/T) with a linear fit yielding the activation barrier of $E_{Bar} = 0.358$ eV.

with a strong faceting behavior. In Figure 3(c) and Figure 3(d), the films of 150 nm deposited at a substrate temperature of 63°C ($R = 0.2$ Å/s and 3.0 Å/s, respectively) over the critical thickness reveal lamellar-like plates with a length of 1 ~ 5 μm and a typical height of about 80 to 200 nm (the phase 2). Comparing Fig. 3 (c) with Figure 3 (b) and Figure 3 (d), it is observed that the density of these lamellar-like structures increases with the film thickness and decreases with the growth rate.

Figure 4 shows the RMS and grain size increase with increasing the substrate temperature of SiO_2/Si substrates, and the RMS roughness amplitude (σ) increases closely following an Arrhenius behavior as $\sigma \propto \exp(-E_{Bar}/k_BT)$ with the activation energy $E_{Bar} = 0.358\,eV$ and K_B is the Boltzmann constant in the inset of Figure 4 [12].

Furthermore, Figure 5 shows the substrate temperature dependence of the grain size and the RMS of pentacene thin films of 150 nm deposited at several substrate temperatures between RT and 70°C (R = 0.2 Å/s) on glass substrates. Increasing the substrate temperature, both the grain size and the RMS increase, but the grain size is smaller than that of the films deposited on SiO_2/Si substrates (see Fig. 4). The latter result may originate from a larger surface roughness of glass substrates, which trends to grow films with a high density of small grains.

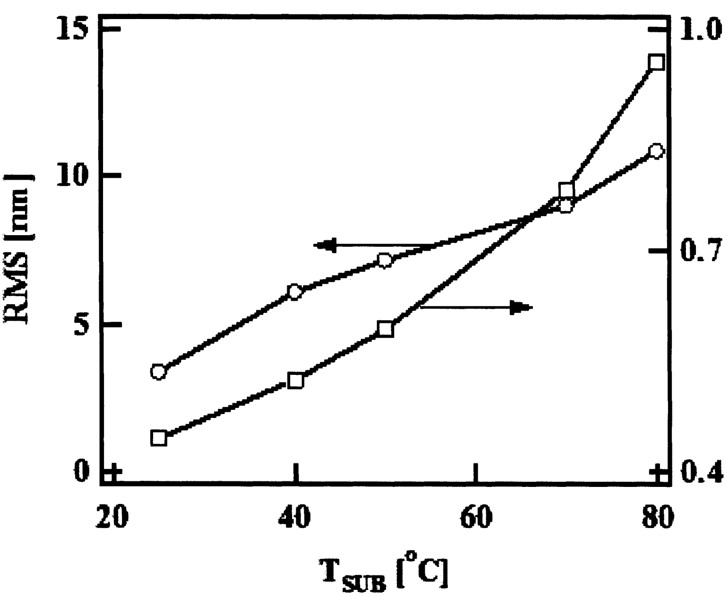

FIGURE 5 The substrate temperature dependence of the RMS and grain size of pentacene thin films of 150 nm deposited at $R = 0.2$ Å/s on glass substrates.

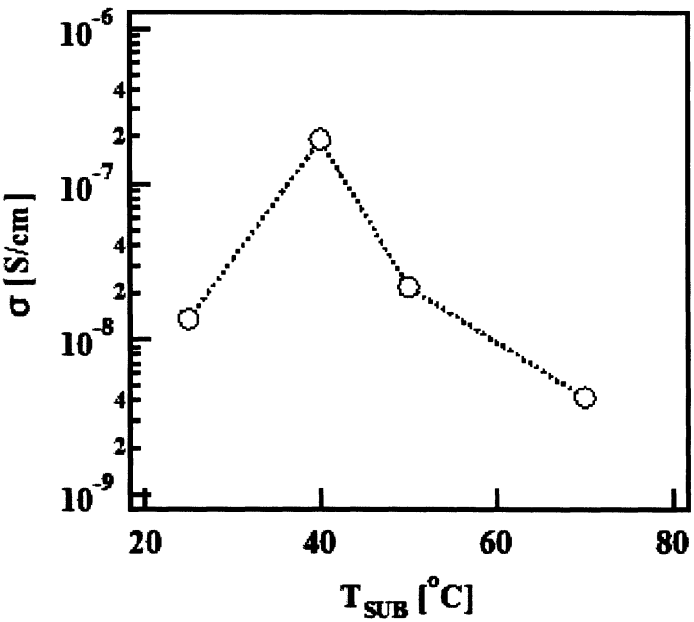

FIGURE 6 The electrical conductivity of pentacene thin films of 100 nm deposited at $R = 0.2$ Å/s on glass substrates is shown as a function of substrate temperature.

3.3. Transport Measurements

Figure 6 shows electrical conductivity of the pentacene thin films as a function of the substrate temperature. As seen in Figure 6, increasing in grain size due to a high substrate temperature improves electrical transport characteristics, although the high substrate temperature induces the phase 2. On the other hand, gaps generated between grains degrade conductivity at a too high substrate temperature. An optimum substrate temperature of 40°C gains the maximum conductivity of 2.0×10^{-7} S/cm.

4. CONCLUSIONS

We have described a detailed characterization of the morphology and electrical properties of pentacene thin films grown by vacuum evaporation on SiO_2/Si and glass substrates with various growth conditions. We have observed two distinct crystalline phases with the 001 plane spacing of 15.0 Å (thin film phase) and 14.0 Å (single crystal phase), respectively. The single crystal phase appeared over a critical thickness of the thin film phase, and the critical thickness was strongly dependent on growth conditions. Increasing the substrate temperature decreased the critical thickness and higher growth rate increases the critical thickness. On the other hand, it was found that gaps generate between grains degraded conductivity at a too high substrate temperature. The maximum conductivity of 2.0×10^{-7} S/cm was gained at a substrate temperature of 40°C.

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