

Real time monitoring of ordering in pentacene films during growth by using in-situ infrared spectroscopy



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ARTICLE INFO

Article history:

Received 5 December 2016

Received in revised form

26 March 2017

Accepted 2 April 2017

Available online 3 April 2017

Keywords:

Pentacene

Organic thin film growth

Structural ordering

Fourier transform infrared spectroscopy

ABSTRACT

By employing the *in-situ* Fourier transform infrared (FTIR) spectroscopy and curve-fitting, we studied the evolution in the ordering of vacuum-deposited pentacene films. In the FTIR spectra, the thin film and bulk phases appeared at 903.2 cm^{-1} and 907.2 cm^{-1} , respectively. The misoriented phase was also observed at 904.4 cm^{-1} . The position and the intensity of each phase varied with the film thickness as well as the growth temperature. The results indicated that most of pentacene molecules formed initially the thin film phase until the bulk and misoriented phases began to form at the increased thickness. Our study suggests that FTIR spectroscopy is an effective tool to monitor in real time the ordering of organic films for quality control.

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For the last two decades or so, tremendous efforts have been given to improve the performance of organic thin film transistors (OTFTs), which strongly depends on the crystalline orientation and molecular ordering [1,2]. For example, the carrier transport of pentacene, which is considered a prominent material for OTFTs, is most efficient in crystals with overlapped π - π orbital aligned parallel to the surface of the gate dielectric [3]. The growth at the early stage plays a crucial role in the accumulation of further deposited molecules. Conventional X-ray diffraction technique is not adequate for studying the growth at early stage, so techniques such as glancing incidence X-ray diffraction (GIXRD) [4] and cross-sectional transmission electron microscopy (TEM) [5] have been adopted. GIXRD, however, requires high power X-ray, which can damage the film. The sample slicing for cross-sectional TEM is a destructible technique. Fourier transform infrared (FTIR) spectroscopy is a non-destructible and sensitive technique, which can provide information on the structural ordering at the early stage of thin film growth because the characteristic band of infrared (IR) absorption spectrum is formed by superposition of crystalline and amorphous phases [6,7]. FTIR measurements of pentacene films have been reported [8–10], but correlation of the spectrum with

the structure is still unclear. Here, we report our study of *in-situ* FTIR spectroscopy to determine the crystalline and amorphous phases of vacuum-deposited pentacene films, and propose that FTIR spectroscopy is an effective tool to estimate in real time the ordering of organic thin films.

Vacuum-deposited pentacene films usually contain polycrystalline crystallites and amorphous phase [11]. X-ray diffraction of polycrystalline pentacene films reveals that crystallites consist of both thin film phase and bulk phase with interlayer spacing d of 15.4 Å and 14.5 Å, respectively. The structure of pentacene films depends on the deposition temperature and evolves with the thickness [3]. Past studies suggested that the thin film phase nucleates on the substrate initially and the nucleation of bulk phase increases obviously beyond a certain thickness t_c (~100 nm) [12]. The value of t_c is known to decrease with increasing deposition temperature [12,13]. We deposited the pentacene on the substrate at 29 °C and 65 °C and studied the evolution of thin film and bulk phases by analyzing *in-situ* FTIR absorption spectra.

We used pieces of undoped Si wafer as the substrate. The wafer was 500 μm thick and polished in both sides. The wafer surface was covered with native oxide and the IR-transparency was about 40%. Pentacene was deposited by thermal evaporation on the 1.5×1.5 cm substrate. The vacuum pressure during deposition was 10^{-7} torr, and the pentacene deposition rate as measured by a crystal thickness monitor was 1.2–1.3 Å/s. The infrared spectrometer (FTLA2000-104 manufactured by ABB, Canada) was mounted

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outside the growth chamber in such a way that each of two windows (made of ZnSe) on the chamber faced the infrared source and the detector. The pentacene deposition and the FTIR measurement were performed simultaneously. After each 10 nm deposition until the film became 180 nm thick, the IR-absorption spectrum was recorded with an accumulation of 50 scans at a resolution 4 cm^{-1} , of which the result is depicted in Fig. 1. The resolution of the spectra shown in Fig. 1 is low, as one notices, but we like to stress that this was not caused by the poor resolution of our spectrometer but rather due to the limit set by the internal interference of the infrared light passing through the Si substrate. In other words, when we increased the spectrometer resolution to 1 cm^{-1} , a strong modulation appeared in the spectra due to the optical interference (not shown here). Since the thin film phase of pentacene is known to form on SiO_2 substrate [12], we wanted to use the present substrate. We thus tried to filter out the high frequency modulation from the spectra obtained with 1 cm^{-1} resolution, but the output was the same as those obtained with 4 cm^{-1} resolution. We also measured the spectra after taking out the grown films on other FTIR spectrometers, but the modulation was unavoidable. As an additional check, we compared the FTIR spectra of pentacene powder obtained with 1 cm^{-1} and 4 cm^{-1} resolution respectively and found that the two spectra were similar in overall shape except in some little details and the exact peak position. Therefore, we argue that, although the resolution of the spectra shown in Fig. 1 are not high enough to show detail, they are adequate to meet our purpose, which is a rough estimate of the quality during the pentacene films were forming but not a detailed analysis of the grown films.

Fig. 1(a) and (b) show the thickness-dependent FTIR spectra of pentacene films deposited at $29\text{ }^\circ\text{C}$ and $65\text{ }^\circ\text{C}$, respectively. In the spectra of $29\text{ }^\circ\text{C}$ deposition, the peak appears at 902.6 cm^{-1} initially, but shifts to 904.5 cm^{-1} when the film becomes about 90 nm thick. The 904.5 cm^{-1} peak is reported to originate from the C-H out-of-plane vibration mode as calculated by the Gaussian'98 program for the B3LYP/6-31G(d,p) level with a scale factor of 0.9613 [14]. In the spectra of $65\text{ }^\circ\text{C}$ deposition, the peak appears at 902.6 cm^{-1} initially, but shifts to 904.5 cm^{-1} when the film thickness exceeded about 30 nm. A shoulder at 906.5 cm^{-1} also begins to show up from 30 nm thickness.

To investigate the origin of the peak evolution revealed in Fig. 1, we prepared separate samples of 20 and 60 nm thick at $29\text{ }^\circ\text{C}$ and $65\text{ }^\circ\text{C}$, respectively, and performed FTIR and X-ray diffraction (XRD) measurements outside the growth chamber. The result is displayed in Fig. 2, from which one can notice that each of the four FTIR spectra reveals a similar structure of the corresponding spectrum depicted in Fig. 1. In the case of $29\text{ }^\circ\text{C}$ growth, the FTIR spectra (Fig. 2(a)) show a peak at 902.6 cm^{-1} for both 20 nm and 60 nm

thick films with a hint of shoulder at 904.5 cm^{-1} . The corresponding XRD spectra depicted in Fig. 2(b) reveal a (001') peak near $2\theta = 5.82^\circ$, which has been attributed to the pentacene crystalline thin film phase [15–17]. There may be a very weak (001) peak near $2\theta = 6.18^\circ$ for the 60 nm film, which is known to originate from the pentacene bulk crystalline phase [18]. On the otherhand, the FTIR spectra of the $65\text{ }^\circ\text{C}$ growth show the peak at 902.6 cm^{-1} initially for the 20 nm thick film but the peak shifts to 904.5 cm^{-1} for the 60 nm thick film. The corresponding XRD spectra reveal the thin film phase at $2\theta = 5.82^\circ$ and $2\theta = 6.18^\circ$, with the intensity of the latter far surpassing the former with the increased thickness.

As a further investigation, we also performed XRD measurement of the 180 nm thick films, of which the FTIR spectra are shown in Fig. 1(a) and (b), after taking them out of the growth chamber. The XRD spectrum of the film grown at $29\text{ }^\circ\text{C}$ shows a strong peak near $2\theta = 5.82^\circ$ (001 crystalline thin film phase) and a very weak peak near $2\theta = 6.18^\circ$ (bulk crystalline phase), as shown in Fig. 3(a). For the film deposited at $65\text{ }^\circ\text{C}$, the bulk phase is prominent with the weak thin film phase, as shown in Fig. 3(b). The intensity of the bulk phase peak of the $65\text{ }^\circ\text{C}$ sample is relatively weaker than the thick film phase peak of the $29\text{ }^\circ\text{C}$ sample, which indicates that the films deposited at the latter temperature are more ordered while the $65\text{ }^\circ\text{C}$ samples are more amorphous. Our FTIR spectra together with the XRD spectra suggest that the observed spectral dependence was caused by the structural evolution which depends on the growth temperature and the film thickness [9].

The characteristic bands of semicrystalline polymers can be interpreted as the superposition of crystalline and amorphous components [6,7]. We analyzed our FTIR spectra to differentiate the crystalline phase and the amorphous phase. Fig. 4(a) and (b) show FTIR spectra obtained from 180 nm thick pentacene films deposited at 29 and $65\text{ }^\circ\text{C}$, respectively. We fitted the spectra with the three Gaussian function curves in an attempt to resolve the crystalline and amorphous components. We associate two of the three fitted curves centered near 903.2 and 907.2 cm^{-1} with the crystalline phase of thin film and bulk, respectively [9]. We believe that the third fitting curve centered near 904.4 cm^{-1} is associated with the amorphous molecules. This conclusion is based on the comparison of the FTIR and XRD spectra of the pentacene films we deposited on the substrate cooled to $-150\text{ }^\circ\text{C}$ (not shown here). The intensity of the amorphous peak is stronger for the $65\text{ }^\circ\text{C}$ film as shown in Fig. 4, and this is consistent with the relatively weak intensity of the bulk crystalline phase revealed in the XRD spectrum of the $65\text{ }^\circ\text{C}$ film [Fig. 3(b)].

We plot in Fig. 5 the intensity evolution in real time of the thin film, bulk and amorphous phases while pentacene was being deposited at 29 and $65\text{ }^\circ\text{C}$, respectively. The intensities of the three

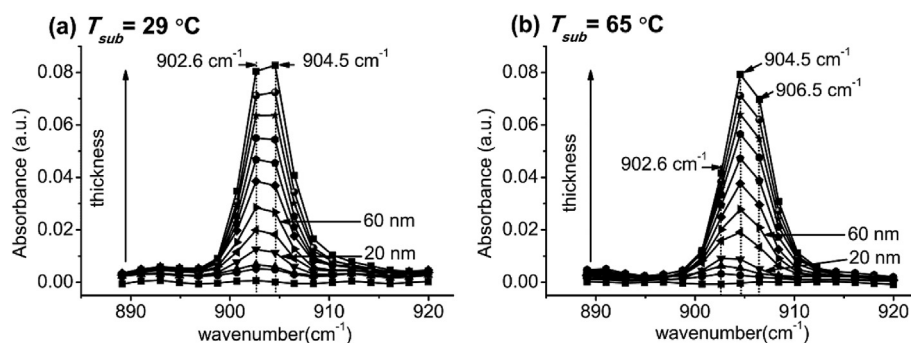


Fig. 1. FTIR absorption spectra obtained from vacuum-deposited pentacene films at the growth temperature of (a) $29\text{ }^\circ\text{C}$ and (b) $65\text{ }^\circ\text{C}$. The spectral peaks in both cases shift to a higher wavenumber with increasing thickness, but the shift occurs earlier for the $65\text{ }^\circ\text{C}$ deposition. Each spectrum in both (a) and (b) corresponds to, from the lowest to the highest, 0, 5, 10, 20, 40, 60, 80, 100, 120, 140, 160, and 180 nm thick film.

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