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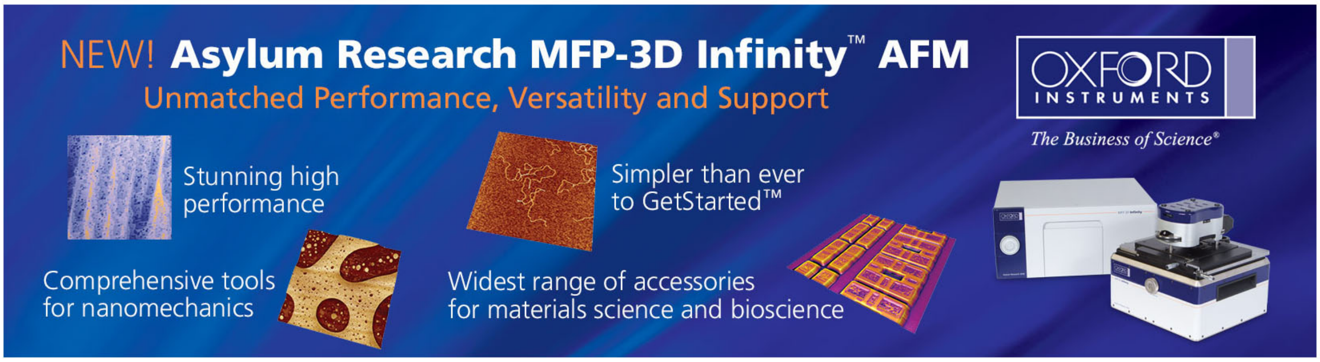

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Hall-effect mobility of pentacene films prepared by the thermal evaporating method with different substrate temperature

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We studied the Hall-effect mobility of pentacene films prepared by the thermal evaporating method with different substrate temperature. A crossover from coherent bandlike charge transport with mobilities up to several tens of cm^2/V-s at low temperature to an incoherent hopping motion at high temperature is observed. The carrier mobilities of pentacene exhibit a hopping-to-band transition around room temperature. An exhibition of high mobility of pentacene films prepared with substrate temperature of 90 °C is attributed to the increased spacing between molecules. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4733293]

Recently, organic thin film transistors (OTFTs) have become of great interest for several electronic applications, such as active-matrix flat panel displays, electronic paper, and chemical sensors, replacing the traditional inorganic-based thin film transistors.[1] Among the organic semiconductors considered for use as active materials in OTFTs, pentacene is the most widely used and studied because of its outstanding mobility. The performance of pentacene-based OTFTs is mainly determined by its carrier mobility, which is influenced by the electron-phonon coupling, crystallinity, and intermolecular bonding nature.[2–4] Thus, there is clear need for a better understanding of the conduction processes in pentacene. Charge transport in organic semiconductors has been extensively studied.[5–7] Huang and Lin found that oxygen plasma treatment may lead to an increase in the mobility, resulting from the incorporation of oxygen and the passivation of the defects in the grain-boundary region.[8] The discrepancy in mobility extracted from transfer and output characteristics of OTFTs was studied by Lin *et al.*[9] Ruiz *et al.* have reviewed recent experimental and theoretical work exploring the influence of growth parameters on the structure and morphology of vacuum-deposited pentacene films.[10] The effect of annealing temperature on the mobility of the pentacene film was investigated by Kang *et al.*[11] In addition, Sekitani *et al.*[12] and Takamatsu *et al.*[13] performed Hall effect measurements using polycrystalline pentacene-based transistors under applied gate-voltage biases. Here, we investigated the effect of substrate temperature on the Hall-effect mobility (μ) of pentacene films prepared by the thermal evaporating method. Understanding the effect is of great technological importance since it affects the OTFT performance. In this study, we found that the Hall-effect mobility increases with increasing substrate temperature reaching a maximum at substrate temperature of 90 °C, and then decreases with further increasing of substrate temperature beyond that point. Our results indicate that the enhanced mobility is due to the increased spacing between molecules.

A 70 nm thick pentacene (Luminescence Technology Corp., Hsinchu, Taiwan) layer was deposited on the glass substrates by vacuum thermal evaporation and the evaporation rate was 0.5 Å/s (as monitored by a quartz crystal microbalance after thickness calibration with atomic force microscopy measurements). The substrate temperature was fixed at 30, 50, 70, 90, and 110 °C, respectively. Gundlach *et al.*[14] pointed out that ordered films are obtained for depositions at low to moderate rates (1–5 Å/s) onto substrates held at temperatures from 20 °C to 120 °C. The pentacene films were deposited on glass substrates for the conductivity measurements, since insulating substrates are needed for such measurements. The glass samples were cleaned in chemical cleaning solutions of acetone and methanol, rinsed with de-ionized water, and blow-dried with N_2. Then, the electrodes were fabricated by depositing Au metal on the pentacene layer through a shadow mask. The carrier mobility of pentacene was measured by the Van der Pauw method at four point contact configuration.

Figure 1 shows the substrate-temperature dependence of the mobility of pentacene films at room temperature. The pentacene samples prepared with different substrate temperature show p-type behavior. We found that the carrier mobility increases with increasing substrate temperature reaching a maximum at substrate temperature of 90 °C, and then decreases with further increasing of substrate temperature beyond that point. To obtain the carrier mobility as a function of measurement temperature (T), the Van der Pauw–Hall measurements (Ecopia HMS-5000) were performed in the temperature range of 200–340 K. The magnetic field of 0.55 T was applied. The pentacene samples prepared with different substrate temperature show p-type behavior. The values of the carrier mobility for pentacene samples can be obtained from variable temperature Hall measurements, as shown in Fig. 2. The carrier mobilities are strong measurement-temperature-dependent from 200–340 K for pentacene samples prepared with different substrate temperature. Early models suggested that thermally activated small polaron hopping describes the motion of carriers through an organic crystal.[15] Seo *et al.* suggested that charge transport in pentacene occurs by an activated-transport process in the temperature range of 40–300 K.[16] Our measurements showed a significant

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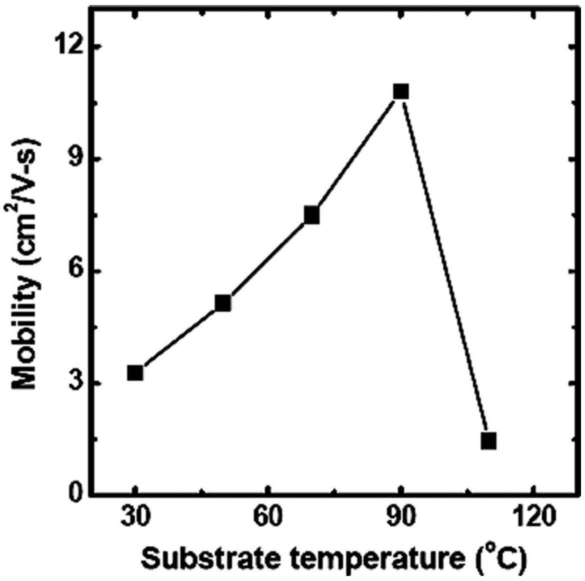

FIG. 1. The room-temperature mobility as a function of substrate temperature.

different from that reported, which cannot be explained with activation hopping. It cannot explain the sign reversal of the bulk mobility versus temperature derivative ($\partial\mu/\partial T < 0$).

Coropceanu *et al.* presented an overview of polaron models that have been reported to describe the charge transport mechanisms in organic materials.[5] According to polaron models, the total mobility can be expressed to a good approximation as a sum of two contributions:[5,17]

$$\mu = \mu_{tun} + \mu_{hop}, \tag{1}$$

$$\mu_{hop} = \frac{ea^2t^2}{k_BT\hbar^2\omega_o}\left[\frac{\pi}{g^2\mathrm{csch}\left(\frac{\hbar\omega_o}{2k_BT}\right)}\right]^{0.5} \times \exp\left[-2g^2\tanh\left(\frac{\hbar\omega_o}{4k_BT}\right)\right], \tag{2}$$

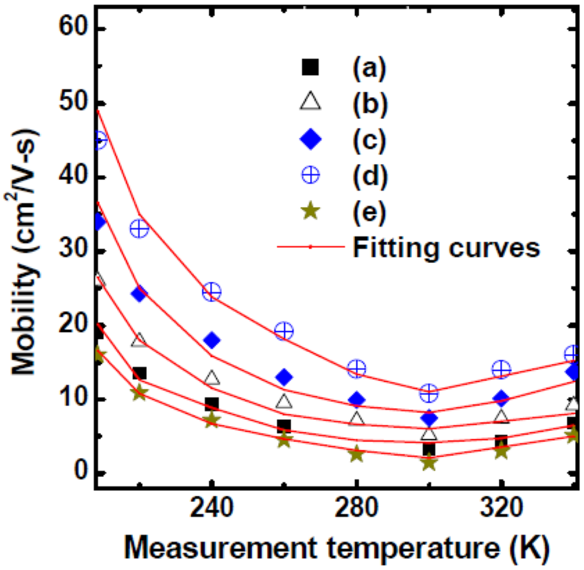

FIG. 2. The Hall-effect mobility as a function of measurement temperature [pentacene films prepared with substrate temperature of (a) 30 °C, (b) 50 °C, (c) 70 °C, (d) 90 °C and (e) 110 °C].

$$\mu_{tun} = \frac{ea^2\omega_o}{k_BT}\left[\frac{g^2\mathrm{csch}\left(\frac{\hbar\omega_o}{2k_BT}\right)}{\pi}\right]^{0.5} \times \exp\left[-2g^2\mathrm{csch}\left(\frac{\hbar\omega_o}{2k_BT}\right)\right], \tag{3}$$

where g is a coupling constant, $\hbar\omega_o$ is the phonon energy, a denotes the spacing between molecules, t is the transfer integral, k_B is Boltzmann's constant, and e is the electron charge. The hopping mobility (μ_{hop}) can be obtained from Eq. (2). The tunneling mobility (μ_{tun}) can be obtained from Eq. (3). Here, the first term of Eq. (1) is due to electron tunneling (coherent electron transfer) and dominates transport at low temperatures; the second term of Eq. (1) is related to hopping motion (incoherent electron transfer) and becomes dominant at higher temperatures. For strong local electron-phonon couplings ($g^2 \gg 1$), two distinct temperature regimes occur; see Fig. 18 of Ref. 5: (1) at low temperatures, the mobility is bandlike; (2) as temperature increases, the hopping term starts to dominate, and the mobility exhibits a crossover from coherent transport to an incoherent, temperature-activated transport. Figure 2 shows the carrier mobility as a function of measurement temperature and the fitting curves. To extract the charge-transport parameters, the relationship between μ and $\hbar\omega_o$ (t, a or g^2) was examined based on the equations [Eqs. (1), (2), and (3)]. We found that the reduction of $\hbar\omega_o$ may lead to suppressed (enhanced) tunneling (hopping) conduction at low (high) temperatures. Upon t, tunneling conduction at low temperatures is not affected. However, hopping conduction at higher temperatures is sensitive to the t variation. On the other hand, the increased spacing between molecules may lead to enhanced tunneling (hopping) conduction at low (high) temperatures. Based on the experimental data, the charge-transport parameters have been extracted from the equations [Eqs. (1), (2), and (3)] and compared, as demonstrated in Table I. We found that the carrier mobility increases with increasing substrate temperature reaching a maximum at substrate temperature of 90 °C, and then decreases with further increasing of substrate temperature beyond that point. A possible origin of this characteristic is discussed based on a Hall-effect analysis. For pentacene samples prepared with different substrate temperature, $g^2 = 6$ suggests that the mobility-measurement temperature characteristic is dominated by tunneling (hopping) at low (high) temperatures, owing to strong electron-phonon couplings. Figure 2 shows that the tunneling (hopping) conduction at low (high) temperatures enhances with increasing substrate temperature. We found that substrate temperature of 90 °C significantly improved the room-temperature mobility, owing to the

TABLE I. Fitting parameters and results for pentacene films prepared with different substrate temperature.

Substrate temperatures	g^2	$\hbar\omega_o$ (meV)	a (nm)	t (eV)
30 °C	6	79	2.5	0.42
50 °C	6	79	2.8	0.42
70 °C	6	79	3.3	0.42
90 °C	6	79	3.9	0.42
110 °C	6	79	2.2	0.42

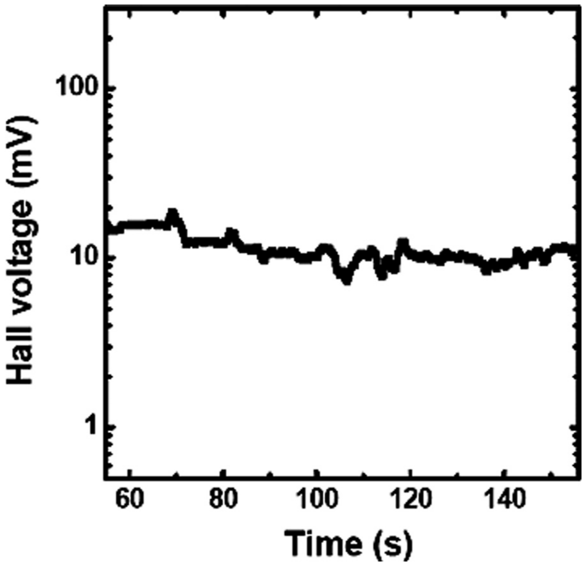

FIG. 3. The Hall voltage-time curve of pentacene films prepared with substrate temperature of 90 °C at B = 0.55 T.

increased spacing between molecules (Table I). It corresponds to a thermodynamically stable structure during the growth of the thin pentacene film.[18] The room-temperature mobility of pentacene films prepared with substrate temperature of 110 °C is lower than that of pentacene films prepared with substrate temperature of 90 °C. This is because of the reduced spacing between molecules (Table I). Jurchescu *et al.* found that the temperature dependence of the mobility is consistent with the band model for charge transport in pentacene, with the interaction of the delocalized carriers with the phonons, the main scattering process.[4]

To evaluate the Hall-effect mobility, we measured the time-dependent Hall voltage (V_H). The voltage induced by the magnetic field was referred to as V_H. The V_H measurement of pentacene films prepared with substrate temperature of 90 °C using the Van der Pauw geometry was performed at room temperature, while the magnetic field (B = 0 or 0.55 T) was applied and a constant voltage (V_C) of 20 V was applied to the electrodes located along the diagonal. V_H at B = 0.55 T could be evaluated by subtracting the voltage at B = 0 T. Figure 3 shows V_H induced between electrodes perpendicular to the induced current by V_C of 20 V as a function of time at room temperature. The V_H-time curves were measured using a Keithley Model-4200-SCS semiconductor characterization system. We found that the average V_H value is 12 mV. The Hall-effect mobility is evaluated from the equation $\mu = V_H/BV_C$ and its value was about 11 cm^2/V s. Sekitani *et al.* measured the carrier mobility of pentacene field-effect transistors (FETs) using the Van der Pauw geometry under applied gate-voltage biases of −40 V.[12] The Hall-effect mobility was calculated to be 0.4 cm^2/V s.[12] In this study, the Hall-effect mobility was measured by the Van der Pauw method without the application of a gate voltage. The application of a gate voltage of −40 V may lead to the accumulation of holes in the channel of pentacene FETs. In addition, their FETs were annealed at 140 °C for 12 h.[12] Guo *et al.* found that only low temperature annealing at 45 °C for 2 h caused improved mobility of pentacene-based OTFTs compared to the value before annealing, while annealing with temperature >50 °C decreased the mobility.[19] In one dimension systems, Coropceanu *et al.* suggested that the increased spacing between molecules may lead to increased diffusion coefficient (decreased effective mass of the charge carriers), thus increasing μ_{hop} (μ_{tun}).[5] In addition, the carrier mobilities of pentacene exhibit a hopping-to-band transition around room temperature (Fig. 2). An exhibition of high room-temperature mobility of pentacene films prepared with substrate temperature of 90 °C may be due to a combined effect of the increased spacing between molecules, hopping transport and band conductions. In Ref. 20, thermally evaporated pentacene exhibited the high mobility of 5.5 cm^2/V s. The carrier mobility as high as ∼35 cm^2/V s was reported at room temperature with an ultrapure pentacene crystal.[4] According to the time-of-flight measurements, the polymeric insulations can have intrinsic carrier mobility ranging from 1 to 10 cm^2/V s.[7]

In summary, we have discussed the measurement-temperature dependence of the Hall-effect mobility of pentacene films prepared by the thermal evaporating method with different substrate temperature. It is shown that the carrier mobility increases with increasing substrate temperature reaching a maximum at substrate temperature of 90 °C, and then decreases with further increasing of substrate temperature beyond that point. The measurement temperature dependence of the Hall-effect mobility in pentacene implies that the μ-T characteristic is dominated by tunneling (hopping) at low (high) temperatures. The carrier mobilities of pentacene exhibit a hopping-to-band transition around room temperature. Our results indicate that the enhanced mobility is due to the increased spacing between molecules.

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