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Enhancement of grain size and crystallinity of thin layers of pentacene grown under magnetic field

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ABSTRACT

Field-effect mobilities (μ) of pentacene films, prepared by a thermal deposition under a magnetic field (*H*-field), were largely enhanced, in comparison with that prepared without an *H*-field. Under a perpendicular *H*-field with respect to the substrate surface, the crystallinity of the edge-on pentacene orientation is enhanced, resulting in the 9-fold enhancement of μ. Furthermore, under parallel *H*-field with respect to the substrate surface, μ of the pentacene films were 23-fold greater than that prepared without the *H*-field. The surface morphology studies by atomic force microscopy of the ultra thin films of pentacene clarified that the grain size of the pentacene at the interface with the substrate is larger for films under parallel *H*-field than that prepared without an *H*-field. The simple and effective method for enhancing the semiconducting properties of the organic thin films gives high technological impact in its application to organic electronics.

1. Introduction

Organic semiconductors attract an increasing attention due to their peculiar advantages, such as light-weight, flexible, simple and large area fabrication process, and so on. One of the important points noted for the practical use of organic semiconductors is the increase in charge carrier mobility. In addition to the development of new π-conjugated molecules, an important challenge faced in obtaining superior semiconductor properties is the arrangement of molecules with high crystallinity [1,2]. General methods for increasing crystallinity include the control of deposition rate and substrate temperature, post-annealing, and modification of the substrate surface [3–10]. Meanwhile, if an external field, such as the electric and magnetic fields, can enhance the orientation and crystallinity of the organic thin films, the semiconducting properties will be much more effectively enhanced [11–15].

In this context, we recently reported that the thermal deposition of metal phthalocyanine (MPc), under a magnetic field (*H*-field), can effectively enhance the edge-on crystallinity of the MPc molecules, being twice as large as the field-effect hole mobility (μ) as that prepared without an *H*-field [16]. The MPc disk possesses a large diamagnetic anisotropy due to the π-conjugated electrons [17], and the perpendicular *H*-field induces a rotational torque to the MPc disk toward the upstanding direction. In the present study, we apply this technique to a fabrication of pentacene thin films, and investigate whether an *H*-field affect the morphology and crystallinity. We found that, similar to the case of the MPc, a perpendicular *H*-field enhances the edge-on orientation of the pentacene molecules, leading to a 9-fold enhancement of μ. Furthermore, a parallel *H*-field also enhances μ by more than 20 times, which can be attributed to the increase in the grain size of the pentacene at the interface with the substrate.

2. Experiments

Powder sample of pentacene was purchased from Aldrich Co Ltd., and purified twice by thermal sublimation under a reduced pressure ($<10^{-3}$ Pa). Thin films of pentacene were fabricated without an *H*-field or under an *H*-field with neodymium-iron-boron (Nd–Fe–B) permanent magnets [16]. The square-shaped magnets with 4.0 cm on a side and 3.0 cm in thickness were placed in a vacuum evaporation chamber (Sanyu Electron model SVC-700TMSG), in such a way that the *H*-field was applied vertically ($H_{\perp}$) or horizontally ($H_{//}$) to the substrate (Fig. 1). The magnetic flux density at the substrate surface was 0.5 T for each configuration. The distance between the substrate and the evaporation source is 20 cm with the evaporation rate, substrate temperature, and vacuum level at 0.2 Å s^{-1}, 25 °C, and 1.0×10^{-3} Pa, respectively. Pentacene with a film thickness (t) of 15 nm were

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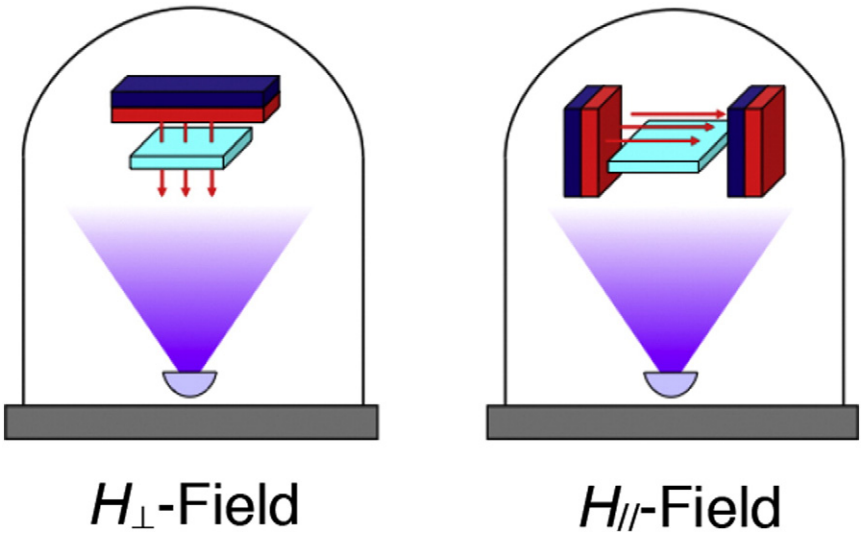

Fig. 1. Schematic illustrations of the experimental set up for thermal deposition of pentacene under vertical ($H_{\perp}$, left) and horizontal ($H_{//}$, right) magnetic fields.

thermally deposited on 1,1,1,3,3,3-hexamethyldisilazane (HDMS)-treated SiO_2 (200 nm)/p-Si substrate. Au electrodes (50 nm) were deposited onto the pentacene films to construct top-contact bottom-gate field-effect transistor (FET) devices with a channel width and length of 0.75 mm and 50 μm, respectively [18,19]. FET properties were measured at 25 °C in a Nagase model GRAIL10-Helips-4-HT high-vacuum prober system, using a Keithley model SCS-4200 semiconductor parameter analyzer. Out-of-plane and in-plane X-ray diffraction (XRD) patterns were recorded at 25 °C on RIGAKU model Miniflex600 and SmartLab diffractometers, respectively, with a Cu$K\alpha$ radiation source (40 kV and 15 mA). Atomic force microscopy (AFM) measurements were conducted on a SII-Nanotechnology model S-image scanning probe microscopy.

3. Results and discussion

Let K_1, K_2, and K_3 be the principal susceptibilities of pentacene [20], where K_1 and K_2 are in-plane susceptibilities and K_3 is the out-of plane susceptibility. The diamagnetic anisotropy ΔK is given by

$$\Delta K = K_3 - K_1 = 3(\chi_M - K_1) \quad (1)$$

where χ_M is the molar susceptibility of pentacene. According to reference [20], K_1 and χ_M are -114.9×10^{-6} and -205.4×10^{-6} cm^3 mol^{-1}, respectively, thereby ΔK is -271.5×10^{-6} cm^3 mol^{-1}. The negative ΔK value indicates that the molecular plane of pentacene tends to align parallel to the magnetic flux.

As shown in Fig. 2a and b, the pentacene films prepared under $H_{\perp}$- and $H_{//}$-fields exhibited much higher drain current values (I_d) than that prepared without an H-field. The I_d values of the samples prepared under $H_{\perp}$- and $H_{//}$-fields were enhanced in 7- and 11-fold, respectively, compared to that fabricated without an H-field. We measured 4–6 samples independently prepared under each condition, and found that the average μ values prepared under $H_{\perp}$- ($\mu_{H\perp}$) and $H_{//}$-fields ($\mu_{H//}$) are 0.064 and 0.162 cm^2 V^{-1} s^{-1} with standard deviations (σ) of 0.021 and 0.027 cm^2 V^{-1} s^{-1}, respectively. These values are 9.1 and 23 times greater than that prepared without the H-field ($\mu_{H=0}$ = 0.007 cm^2 V^{-1} s^{-1} with σ of 0.001 cm^2 V^{-1} s^{-1}, Table 1).

In order to investigate the effect of the H-field to the molecular orientation and crystallinity, the pentacene films with t = 3.0 nm and 15 nm were fabricated under different H-field conditions. Following the XRD patterns of the thin films, periodic diffraction peaks assigned as (001) and (002) of the pentacene crystal lattice plane were observed at 2θ of 5.5 and 11° (d = 16.1 and 8.0 Å, respectively) for all the H-field conditions (Fig. 3a and b), indicating that pentacene molecules were deposited with an edge-on orientation [21]. The intensities of the (100) diffraction peaks fabricated under the $H_{\perp}$- and $H_{//}$-fields are 2.2 and 1.8 times greater for films with t = 3 nm (Fig. 3a) and are 1.6 and 1.1 times greater for films with t = 15 nm (Fig. 3b) than that of the film

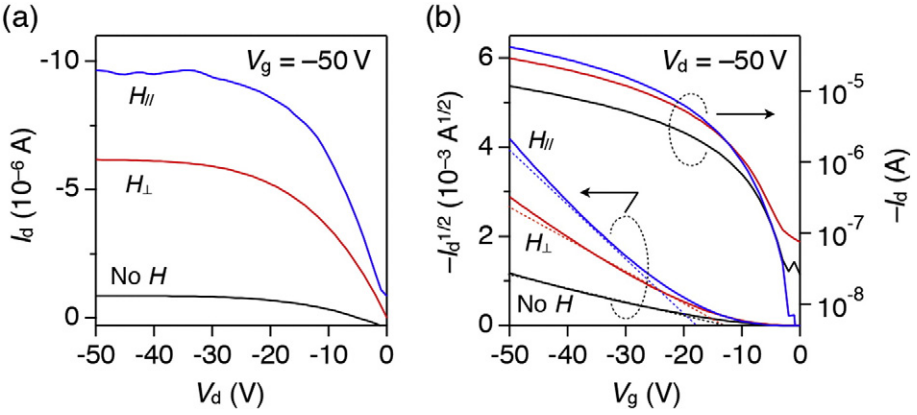

Fig. 2. (a) Output profiles of pentacene thin films fabricated without H-field (black), under $H_{\perp}$-field (red), and $H_{//}$-field (blue) with a V_g value of −50 V. (b) Transfer profiles of pentacene thin films fabricated without H-field (black), under $H_{\perp}$-field (red), and $H_{//}$-field (blue) with a V_d value of −50 V.