Magnetic-field-induced enhancement of crystallinity and field-effect mobilities in phthalocyanine thin films

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Magnetic-field-induced enhancement of crystallinity and field-effect mobilities in phthalocyanine thin films

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Organic semiconductor thin films were fabricated by thermal deposition of free-base and metal phthalocyanines under a static magnetic field. A vertical magnetic field enhanced the crystallinity of the edge-on orientation of the phthalocyanine discs, whereas a horizontal magnetic field had a minimal effect on the crystallinity. The major factor for the orientation change is attributed to the diamagnetic anisotropies of $\pi$-electrons in the phthalocyanine macrocycles. Field-effect transistors of phthalocyanine films fabricated under a vertical magnetic field exhibited better hole mobilities and on-current values with smaller threshold voltages than those of phthalocyanine films fabricated without a magnetic field. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4816244]

Control of molecular orientation with better crystallinity is important for enhancing the performance of organic semiconducting devices such as organic field-effect transistors (OFETs) and organic solar cells (OSCs). For efficient charge carrier transport, parallel alignment of $\pi$-stacked columns of discotic molecules to a substrate surface with high crystallinity is appropriate for OFETs, whereas homeotropic columnar orientation is preferred for OSCs. Several methods for improving the crystallinity of organic thin films have been proposed, such as thermal heating of the substrate during deposition, thermal- or solvent-annealing after thin-film fabrication, and surface treatment of the substrate. However, applying external fields during the thin-film fabrication process might make it possible to control both the orientation and crystallinity of thin films with ease over large areas without a time-consuming and complicated fabrication process. In particular, the use of a magnetic field is a powerful technique for controlling the orientation of various kinds of materials such as carbon nanotubes and liquid crystalline (LC) mesogens. In case of fluidic materials such as LCs and materials in viscous media, a magnetic field is efficient for aligning the materials. However, for solid organic materials without fluidic media, orientation control using a magnetic field is very rare. Furthermore, generation of a strong magnetic field requires large and expensive equipment such as electromagnets and superconducting magnets. Thus, molecules capable of responding to small magnetic fields are required for a simple fabrication process. In this study, we report how the magnetic field affects the orientation and crystallinity of thin films of discotic phthalocyanine (Pc) molecules (Figure 1(a)), by utilizing small permanent magnets with sub-Tesla magnetic flux density. We initially anticipated that a horizontal magnetic field ($H_{//}$, Figure 1(b)) may induce in-plane alignment of $\pi$-stacked Pc columns, which would lead to in-plane anisotropic charge carrier transport. However, no such effect was observed for thin films fabricated under $H_{//}$. In contrast, we found that a vertical magnetic field ($H_{\perp}$, Figure 1(c)) can enhance crystallinity of the edge-on orientation of Pc molecules, which results in better OFET properties in comparison with thin films fabricated without a magnetic field.

By applying an external magnetic field, a molecule having a magnetic anisotropy $\Delta K (= K_\perp - K_{//})$, where $K_\perp$ and $K_{//}$ are molecular principal susceptibilities perpendicular and parallel to the symmetry axis of the molecule, respectively) is subject to a torque $N$ expressed as follows:

$$N = I_\alpha = - m \Delta KB^2 \sin \theta,$$

where $I$, $\alpha$, $m$, $B$, and $\theta$ denote moment of inertia, angular acceleration, mass of molecule, magnetic flux density, and angle between molecular symmetry axis and magnetic flux, respectively. When a molecule orients its magnetization easy axis along the direction of the magnetic field, the molecule is stabilized by the free energy gain ($\Delta U$) described as follows:

$$\Delta U = -(1/2)\Delta KB^2.$$
Based on these magnetic anisotropy data, we fabricated CuPc, NiPc, and H$_2$Pc thin films under a static magnetic field using neodymium–iron–boron (Nd–Fe–B) permanent magnets. The square-shaped magnets with 4.0 cm on a side and 1.5 cm in thick were placed in a vacuum evaporation chamber in such a way that the magnetic field was applied parallel (H//) or perpendicular (H?) to the substrate (Figures 1(b) and 1(c), respectively). The magnetic flux density at the substrate surface was 0.35 T for each configuration. The distance between substrate and evaporation source is 20 cm. Prior to the thin-film fabrication, the powder samples of CuPc, NiPc, and H$_2$Pc, purchased from Aldrich Co. Ltd., were purified twice by thermal sublimation in vacuum. The evaporation rate, substrate temperature, and vacuum level were 0.2 Å s$^{-1}$, 25 °C, and 5.0 × 10$^{-4}$ Pa, respectively, and the film thicknesses were fixed at 50 nm.

Table I. Magnetic anisotropies (in 10$^{-6}$ cm$^3$ mol$^{-1}$) of H$_3$Pc, NiPc, ZnPc, and CuPc.

|       | ΔK   | K$_{||}$ | K$_{\perp}$ | Ref. |
|-------|------|----------|-------------|------|
| H$_3$Pc | 610  | -751     | -141        | 19   |
| NiPc  | 505  | -565     | -60         | 19   |
| ZnPc  | 647  | -851     | -204        | 19   |
| CuPc  | 644  | No data  | No data     | 20   |

Figure 2(a) shows out-of-plane X-ray diffraction (XRD) patterns of CuPc thin films on glass substrates under no magnetic field (no H), H//, and H?. A diffraction peak assigned as a-CuPc (200) was observed at 2θ of 6.8° (d = 12.8 Å) for all the magnetic field conditions, indicating that CuPc molecules are deposited with an edge-on orientation. However, the diffraction intensity was obviously different: The sample fabricated under H? displayed 1.5-times stronger diffraction intensity than that fabricated under no H and H//. A similar tendency was observed for the diamagnetic NiPc and H$_2$Pc thin films (Figures 2(b) and 2(c), respectively), where H? resulted in 1.4–1.5-times stronger intensity of the (200) diffraction peaks in comparison with no H and H//. These observations clearly indicate that the crystallinity of the edge-on orientation of Pcs is enhanced by a vertical magnetic field. It is worth noting that the effect of H? was observed when CuPc was deposited on an Au-coated substrate. CuPc tends to align with a face-on orientation on metal surfaces.$^{22,23}$

![FIG. 1. (a) Molecular structure of metal phthalocyanine, its D$_{4h}$ symmetry axis, and the directions of molecular principal susceptibilities, K$_{||}$ and K$_{\perp}$, (b) and (c) Schematic illustrations of the experimental setups for thermal deposition of Pcs under horizontal (b) and vertical (c) magnetic fields (H$_{||}$ and H$_{\perp}$, respectively).](image)

![FIG. 2. Out-of-plane XRD patterns of (a) CuPc, (b) NiPc, and (c) H$_2$Pc thin films on glass substrates, and (d) CuPc thin films on a Au (10 nm)/glass substrate fabricated under no H (black), H// (blue), and H? (red). (e) In-plane XRD pattern by grazing incidence X-ray beam of CuPc thin film on a glass substrate fabricated under H//. Inset shows ψ-angle dependency of the diffraction intensity at 2θ = 6.8°. (f) Polar plots of absorbance at 622 nm, recorded upon rotation of a polarizer every 10°, for CuPc thin films fabricated under no H (black) and H// (blue). AFM images of CuPc thin films on glass substrates fabricated under (g) no H and (h) H?. The average grain size and rms roughness are 48 nm and 0.79 nm, respectively, for no H and 55 nm and 0.75 nm, respectively, for H?.](image)
However, $H_{\perp}$ partly changed the orientation of CuPc to an edge-on orientation (Figure 2(d)).

The Pc discs tend to align parallel to the magnetic field as a result of the diamagnetic anisotropies of the Pc discs. As shown in Figure 3(a), $H_{\perp}$ induces a rotational motion of Pc discs toward the upstanding direction, leading to the enhanced crystallinity of the edge-on orientation of Pcs. On the other hand, $H_{\parallel}$ imparts in-plane rotational torque to the Pc disc (Figure 3(b)). Initially, we expected that $H_{\parallel}$ would result in a parallel alignment of $\pi$-stacked Pc columns by the in-plane rotation. However, the magnetic field used in this study was not strong enough to rotate the Pc discs toward the in-plane direction. In fact, in-plane XRD analysis of the CuPc thin film fabricated under $H_{\parallel}$ showed $\phi$-angle dependencies of the (200) diffraction intensity, but it was negligibly small (Figure 2(e)). Furthermore, polar plots of the absorbance at 622 nm in the polarized absorption spectra of the CuPc thin film fabricated under $H_{\parallel}$ displayed nearly complete semicircles, similar to that of the CuPc thin film fabricated under no $H$ (Figure 2(f)). It is worth noting that, from atomic force microscopy (AFM) images, minimal morphological differences were observed between the CuPc thin films prepared under no $H$ Figure 2(g) and those prepared under $H_{\parallel}$ Figure 2(h). This result clearly indicates that the crystallinity in each grain improves more for thin films fabricated under $H_{\parallel}$ than for thin films fabricated under no $H$.

It was thought that improved crystallinity of CuPc thin films by $H_{\perp}$ may improve the charge transport properties. To address this issue, we fabricated FET devices using CuPc thin films fabricated under a magnetic field. Thus, CuPc films were deposited (film thickness: 15 nm) on a 1,1,1,3,3,3-hexamethyldisilazane (HMDS)-treated SiO$_2$ (200 nm)/p-Si substrate with and without a magnetic field, and then, the source and drain Au electrodes (50 nm) were deposited onto the CuPc thin films to construct top-contact bottom-gate FET devices with a channel width and length of 0.75 mm and 50 $\mu$m, respectively. As shown in Figure 4(a), all the CuPc films displayed an output profile characteristic of p-type FETs, where the drain current ($I_d$) was linearly enhanced and then saturated as the drain bias voltage ($V_d$) increased to a negative side under a gate bias voltage ($V_g$) of $-50$ V. Obviously, a CuPc thin film fabricated under $H_{\parallel}$ ($=0.35$ T) exhibited larger $I_d$ in comparison with that fabricated under no $H$ (Figure 4(a)). The observed $I_d$ value was further increased when $H_{\perp}$ was increased to 0.50 T, where $I_d$ was enhanced fourfold in comparison with that fabricated under no $H$ (Figure 4(a)). The field-effect mobilities ($\mu_{\text{FET}}$) for devices under $H_{\perp}$ of 0.35 T and 0.50 T were increased by 1.4 and 2.1 times, respectively, in comparison with that fabricated with no $H$ (Figure 4(d) and Table II). Furthermore, both the on-current values at $V_{th} (= -50$ V (Figure 4(b)) and the threshold voltages ($V_{th}$, Figure 4(c)) were improved for samples fabricated under $H_{\perp}$ (Table II).

Because the size of the grains was identical in the CuPc thin films prepared under no $H$ and $H_{\parallel}$ (Figures 2(g) and 2(h)), the enhanced FET properties most likely result from the modified crystallinity of each grain. According to the systematic decrease of $V_{th}$ values for the samples prepared under $H_{\perp}$, the better crystallinity of CuPc films enhanced not fabricated with no $H$ (Figure 4(d) and Table II). Table II. $\mu_{\text{FET}}, V_{th}$, and on-to-off current ratio of CuPc thin films fabricated under no $H$, $H_{\perp}$, and $H_{\parallel}$. The values are average of 3–5 samples. Numeric values in parentheses indicate standard deviations.

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<th>$H_{\parallel}$ (0.35 T)</th>
<th>$V_{th}$ (V)</th>
<th>on/off ($\times 10^4$)</th>
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<tr>
<td>No $H$</td>
<td>1.8(2)</td>
<td>19(0)</td>
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<tr>
<td>$H_{\perp}$ = 0.35 T</td>
<td>2.6(4)</td>
<td>11(1)</td>
</tr>
<tr>
<td>$H_{\perp}$ = 0.5 T</td>
<td>3.8(4)</td>
<td>2(1)</td>
</tr>
<tr>
<td>$H_{\parallel}$ 0.35 T (channel)</td>
<td>1.3(1)</td>
<td>18(1)</td>
</tr>
<tr>
<td>$H_{\parallel}$ 0.35 T (i/ channel)</td>
<td>1.6(4)</td>
<td>13(5)</td>
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only the charge carrier mobilities but also charge injection from the electrode. In contrast, the CuPc thin films fabricated under $H_{\perp}$ exhibited no clear differences in comparison with those fabricated under no $H$, irrespective of whether the channel direction was parallel or perpendicular to the magnetic field direction (Figure 4(d) and Table II). These results were consistent with the fact that in-plane anisotropy of the molecular orientation was hardly induced by $H_{\perp}$, as evidenced by in-plane XRD and polarized absorption spectroscopy results (Figures 2(e) and 2(f)). Because the magnetic field is applied only close to the substrate, we consider that $H_{\perp}$ affects the molecules on the substrate surface just after they are deposited, not during they are approaching to the substrate. It is worth noting that NiPc and H$_2$Pc also showed enhanced crystallinity when fabricated under $H_{\perp}$ (Figures 4(e) and 4(f)). However, thin films of these compounds exhibited very poor FET outputs with the order of 10$^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$. Furthermore, $H_{\perp}$ resulted in little enhancement in FET properties or even makes it worse (Figures 4(g) and 4(h)).

In summary, applying a vertical magnetic field during the fabrication process of phthalocyanine thin films can induce their edge-on orientation and enhance the film crystallinity, thus improving the charge transport properties. This simple fabrication method is quite useful and widely applicable for enhancing the performance of various kinds of organic semiconducting molecules. Molecules such as pentacene and rubrene in particular, which originally exhibit high field-effect mobilities in OFET devices, 26, 27 may be candidates for the magnetic field-induced orientation. Molecules having large paramagnetic anisotropy will be much more sensitive to magnetic fields.

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