Orientation control of pentacene molecules and transport anisotropy of the thin film transistors by photoaligned polyimide film

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The authors report preferential in-plane molecular orientation and charge transport anisotropy in pentacene thin film transistors achieved by using a photoaligned polyimide film with large in-plane anisotropy. Polarized infrared absorption spectra indicated that the molecular plane normal of the pentacene preferentially aligned along the average orientation direction of the underlying polyimide backbone structure. Atomic force microscope images showed that the alignment of the polyimide backbone structure significantly modiﬁed the pentacene growth process and remarkably increased the grain size. The charge carrier mobility along the polyimide alignment direction was about twice of that perpendicular to it. © 2007 American Institute of Physics. [DOI: 10.1063/1.2711776]

Owing to the advantages of low cost, flexibility, low-temperature and large area processing, etc., organic thin film transistors (OTFTs) have received worldwide interest for more than a decade. Since the charge transport in organic semiconductors is closely related to their crystallinity and grain size, the present mainstream of work in advancing the performance of polycrystalline OTFTs is to improve the film morphology and crystallinity. Since the charge transport in organic semiconductors is determined by the π orbital overlap of the conjugated molecules, the carrier mobility of the OTFTs should be substantially enhanced if the molecules can be aligned so as to increase the π orbital overlap along the current flow direction. Mechanical alignment methods, such as rubbing and friction transfer, were tried to orient pentacene, which is the most widely investigated small molecule semiconductor due to its high mobility and stability. Comparatively, photoalignment is much more attractive for OTFT application because of its potential capability for alignment patterning, which is indispensable for densely integrating OTFTs with an aligned active layer. Photoalignment also avoids the many drawbacks caused by mechanical contact, such as sample contamination and generation of static charge and scratches. Despite these advantages, only limited research of using photoaligned substrates to achieve transport anisotropy in pentacene TFTs, such as polymer films aligned by photodecomposition and photoinduced cross linking, has been reported so far. Besides, the molecular orientation of the pentacene films seems still unclear.

In this study, we adopted a different photoalignment method that uses a polymeric acid containing azobenzene in the backbone structure (Azo-PAA) to induce preferential orientation of pentacene molecules. The orientation of the Azo-PAA backbone is achieved via random rotation of azobenzene accompanied by its angular selective photoisomerization cycles. By thermally imidizing the photoaligned Azo-PAA film, we can obtain a stable polyimide (PI) film with excellent capability for aligning liquid crystal (LC) molecules.

Azo-PAA films were spun coated onto highly doped n-type Si wafers with a 300-nm-thick SiO2 layer, and then irradiated with linearly polarized light (LP-L) of wavelength 340–500 nm at normal incidence. The LP-L exposure was 320 J/cm2. Then the photoaligned Azo-PAA was thermally converted into Azo-PI, whose molecular structure is shown in the inset of Fig. 1(a). The thickness of the Azo-PI films was 11 nm. 30-nm-thick pentacene (as received from Aldrich Chemical) films were deposited on the Azo-PI films at room temperature by vacuum sublimation with a deposition rate of ~0.3 nm/min at ~10−5 Pa. The film thickness was monitored by a quartz crystal microbalance. 10-nm-thick interdigitated source and drain electrodes were formed on the pentacene film by thermal evaporation of gold through a shadow mask. The channel length (L) and channel width (W) are 0.08 and 140 mm, respectively. To determine the mole

![Graphical abstract: Color online. (a) Polarized IR spectra of the photoaligned Azo-PI film. The inset illustrates the molecular structure of the Azo-PI. (b) Polarized IR spectra of the pentacene film deposited on the top of the photoaligned Azo-PI film. The inset shows the definition of the molecular axis of pentacene.](image-url)
lar orientation of the Azo-PI and pentacene films, polarized IR absorption spectra were measured at normal incidence in a transmission geometry. Since IR light does not pass through highly doped Si wafers, low doped ones with identical SiO₂ thickness and surface roughness were used for the IR measurement. The morphology of the films was inspected by a JEOL JSPM-5200 atomic force microscope (AFM). Highly accurate and reproducible x-ray diffraction (XRD) patterns were obtained by a Rigaku Ultima III diffractometer. Keithley 487 picoammeter/voltage source units were used for electrical characterization.

Figure 1(a) shows polarized IR absorption spectra of the photoaligned Azo-PI film, where $A_\parallel$ and $A_\perp$ are the absorbance for the IR light polarized parallel and perpendicular to the polarization direction of the LP-L, respectively. Three strong absorption bands were observed at 1370, 1503, and 1726 cm⁻¹, which are assigned to the C—N stretching vibration of the (CO)₂N bond, the phenyl C—C stretching vibration, and the C═O asymmetric stretching vibration, respectively.¹⁰ The 1370 and 1503 cm⁻¹ bands are polarized along the Azo-PI backbone, while the polarization direction of the 1726 cm⁻¹ band is perpendicular to the Azo-PI backbone. From the polarization dependence of $A_\parallel < A_\perp$ for the 1370 and 1503 cm⁻¹ bands and $A_\parallel > A_\perp$ for the 1726 cm⁻¹ band, we see that the Azo-PI backbone is oriented on average perpendicular to the polarization direction of the LP-L. The dichroic ratio $A_\parallel / A_\perp > 6$ of the 1370 and 1503 cm⁻¹ bands indicates a high degree of alignment of the Azo-PI backbone structure.

Figure 1(b) shows the polarized IR absorption spectra of the pentacene film deposited on the photoaligned Azo-PI film, which were obtained by subtracting those of the underlying Azo-PI film shown in Fig. 1(a) from those of the whole sample. Here, we denote the molecular axis of pentacene as X, Y, and Z as illustrated in the inset of Fig. 1(b). The two bands at 905 and 955 cm⁻¹ are assigned to the C—N stretching vibrations for the (CO)₂N bond, the phenyl C—C stretching vibration, and the C═O asymmetric stretching vibration, respectively.¹⁰ The 905 cm⁻¹ band is perpendicular to the Azo-PI backbone, and the 955 cm⁻¹ band is parallel to the surface, the much smaller absorbance ratio of 0.015 indicates that the long molecular axis is oriented along the surface normal.

To check the charge transport anisotropy, two OTFTs with channel length (current flow) direction parallel (||) and perpendicular (⊥) to the polarization direction of the LP-L were fabricated on simultaneously deposited two pentacene films. Their electrical characteristics are shown in Fig. 2. A much higher $I_{\parallel \parallel}$ than $I_{\parallel \perp}$ was observed as a consequence of the π orbital overlap enhancement in the perpendicular direction due to the preferential alignment of the pentacene aromatic ring. Mobilities of $\mu_\parallel = 1.94 \times 10^{-3}$ cm² V⁻¹ s⁻¹ and $\mu_\perp = 9.6 \times 10^{-4}$ cm² V⁻¹ s⁻¹ were derived from the transfer curves by using the equation $I_D = W/2L[\mu C/(V_G - V_T)]^2$, where $I_D$, $C$, $V_G$, and $V_T$ represent drain current, insulator capacitance, gate voltage, and threshold voltage, respectively. This indicates a mobility anisotropy ratio $\mu_\perp / \mu_\parallel$ of 2. A rollover appears in the high $V_G$ region of Fig. 2(a). Similar rollover was previously reported on stress biased samples. It may be explained by charge trapping or charge collecting at the contacts.¹⁶ Since rollover was never observed for OTFTs prepared on the same SiO₂ but without Azo-PI layer,¹⁷ it may be primarily ascribed to the double insulator structure used here, though the detailed reason is still unclear. The relatively low mobility of the samples should be partly ascribed to the rollover as well as the unpurified pentacene used. Besides, relatively thin Au electrodes (~10 nm) were used to prevent pentacene film damage during the Au deposition. This may also affect the mobility.

The morphologies of the pentacene films on photoaligned (the OTFT sample) and untreated Azo-PI films are shown in Figs. 3(a) and 3(b), respectively. The pentacene films consist of dendritic grains. Figure 3(c) shows the height profile of a grain, revealing a layered structure with a step height of ~1.6 nm. The XRD pattern in Fig. 3(d) discloses a “thin film phase” with a (001) periodicity of 1.55 nm. These features are similar to pentacene films on the SiO₂ surface.¹⁷ Interestingly, a large number of line-shaped islands preferentially aligned to the Azo-PI alignment direction are present on the top of the dendritic grains on the photoaligned Azo-PI surface, while on the untreated Azo-PI surface, these islands are rarely seen and irregularly arranged. The linear islands seem to be amorphous since a layered packing could
not be discerned from the AFM images. Their appearance may affect the actual thickness of the effective charge-transporting layers (the dendritic grains). This may be another cause of the low mobility, since the mobility increases with film thickness in the range of 0–30 nm. Furthermore, both the grain size and the XRD intensity of the films on the photoaligned Azo-PI surface are greatly improved compared to those on the nonaligned one. These indicate that the alignment of the Azo-PI backbone significantly affects the growth process of the pentacene film. Moreover, it should be noted that elongation of the grain shape, as reported previously, is observed along the black arrow shown in (a). (d) XRD patterns of the films.

FIG. 3. (Color online) (a) AFM image of the pentacene film on photoaligned Azo-PI surface. The white arrow indicates the Azo-PI alignment direction, which is perpendicular to the polarization direction of the LP-L. (b) AFM image of the pentacene film on nonaligned Azo-PI surface. (c) Height profile along the black arrow shown in (a).