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Novel Method of Pentacene Alignment Using Photoaligned Polyimide and Its Application in Thin-Film Transistors

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Pentacene films with submicron thickness, deposited by molecular beam deposition, were fabricated and characterized using X-ray diffraction, atomic force microscopy, and Raman spectroscopy. Organic thin-film transistors (OTFTs) were fabricated on a p-type silicon substrate, using an active layer of highly ordered small pentacene molecules grown at room temperature. Pentacene film was aligned using the photoaligned polyimide method, which is usually employed to align liquid crystals. Improved field-effect mobility, in the range 0.4–0.75 cm²/V·s, was obtained in pentacene-based OTFTs with photoaligned polyimide layers on which the pentacene molecules were aligned parallel to the direction of the transport of the carriers. The mobility was improved when the current flowed parallel or perpendicular to the orientation of the pentacene films with anisotropic ratios of 2.7–8.3. The thin-film structures of pentacene on the photoaligned polyimide surface depend on the dose of UV light that irradiates on the polyimide surface. X-ray analyses reveal that the structure of the highly ordered pentacene films includes only a single “thin-film phase”, generated by optimizing the energy of irradiation of the photoaligned polyimide. However, the poorly aligned films include two phases: a “single-crystal phase” and a “thin-film phase”.

Introduction

Recently, organic semiconductors have drawn much attention as they have been proven to be favorable candidates for fabricating thin-film transistors (TFTs) and various electronic and optoelectronic devices. The performance of organic TFTs (OTFTs), characterized by parameters such as field-effect mobility, modulated on/off ratio, and threshold voltage, depends partly on the molecular structure and morphology of the films of such organic materials. The degree of molecular ordering and crystalline orientation of organic thin films have been found to markedly influence the performance of OTFT devices. The efficiency of transport of charge carriers, electrons or holes, is generally thought to increase with the ordering of the molecular chain or the crystalline orientation.

Various methods, including mechanical stretching, liquid crystalline self-organization, and rubbing, have been proposed recently for obtaining organic films with superior orientation. Orientation-controlled organic thin films have a strong potential to enhance mobility and exhibit specific properties, including optical and electrical anisotropy. Anisotropic mobility is effective in isolating an OTFT device from its neighboring components and thus reduces the effect of cross-talk in logic circuits or pixel switching elements in displays.

Pentacene, a fused-ring polycyclic aromatic hydrocarbon, is a very promising material for application in OTFTs because it has excellent field-effect mobility, favorable semiconducting behavior, and good environmental stability. This work presents a photoalignment method—a nonrubbing alignment method—to align pentacene molecules by a photoaligned polyimide (PAPI) layer which is formed by photodegradation alignment

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mechanisms. The so-called photoalignment method, which produces an axis of orientation—whose direction can be easily controlled—on the surface of the polymer (polyimide) in an LC cell upon irradiation by polarized ultraviolet (UV) light, has recently been reported. LC in an illuminated region has been shown to be oriented perpendicular to the direction of the irradiating polarized UV light. Such photoalignment has potential in aligning various liquid crystals, especially for creating multiple domains. This technique does not have many of the drawbacks of traditional rubbing for aligning LCs, including contamination of the sample, generation of static charge, and scratching. Pentacene is a rigid rodlike molecule, similar to the core structure of an LC so surface-induced ordering can also be applied to pentacene molecules. Although Swiggers et al. had previously applied LC photoalignment techniques to pentacene OTFTs, their work not particularly successful. Furthermore, no suitable process is available for patterning the pentacene layer and isolating a particular device from its surroundings. Photoalignment provides a superior method for isolating the devices using multidomain photoalignment in which anisotropy of electrical characteristics is supposed to prevent the effect of cross-talk in OTFT devices.

In this study, a PAPI layer was used to control the orientation of pentacene to generate films with strong anisotropic field-effect mobility. The electrical characteristics and morphologies of these pentacene films were investigated in context. X-ray and Raman spectroscopy revealed that the pentacene films grown on the PAPI surface irradiated with the optimal dose of UV light exhibited only a single phase and good molecular orientation. Pentacene-based OTFT devices, in which pentacene was aligned by an anisotropic photoaligned layer and the alignment was parallel to the direction of the current flow, showed enhanced field-effect mobility and anisotropic mobility ratios of 2.7–8.3. The present results are the first to demonstrate that the photoalignment method is useful in preparing highly ordered organic semiconductor films with anisotropic electrical and optical characteristics.

**Experimental Section**

Quartz and heavily doped p-type Si (111) wafers with a doping concentration of $5 \times 10^{15}$ cm$^{-3}$ were used as the substrates. A 1000-Å PAPI (Nissan RN-1349) layer was deposited by spin coating directly onto quartz or a 2500-Å substrate. A 1000-Å PAPI (Nissan RN-1349) layer was used to analyze the electrical properties of pentacene OTFTs. Understanding how the beam spot was around 1 μm and attained using 50 × 100 × 100 × 100 objective microscope lenses. The scattering geometry was selected to be $y(x, y)$ or $y(x, y)$, where the first symbol stands for the direction of propagation of the incident laser beam, the terms in parentheses specify the polarization of the incident beam and that of the scattered radiation, respectively, and the final symbol represents the direction of propagation of the scattered radiation. Raman measurements were made using a Jobin Yvon U1000 single-crystal graphite monochromator. The power of about 0.6 mW so the surface of the pentacene films was not damaged. This procedure was used to carefully examine the spatial variation of the Raman profile. This approach effectively probes the alignment of the pentacene molecule in the lattice phonon region.

Pentacene in OTFT devices behaved as a p-type semiconductor. Typically, the drain current, $I_D$, was measured and plotted against the drain voltage, $V_D$, at various gate voltages, $V_G$. When the gate electrode is biased negatively with respect to the source electrode, which is grounded, pentacene OTFTs operate in the accumulation mode and the accumulated charges are holes. Bottom contact thin-film transistors were used to analyze the electrical properties of pentacene OTFTs. The drain-source current, $I_D$, versus the drain-source voltage, $V_D$, curves were obtained in air by scanning gate-source voltage, $V_G$, using a HP4155C semiconductor parameter analyzer.

**Results and Discussion**

Figure 1 shows the reflective X-ray diffraction patterns of pentacene films grown on anisotropic PAPI surfaces irradiated with various doses of polarized UV light. The samples prepared on quartz substrates were measured at room temperature in ambient air. The XRD spectra of the pentacene grown on PAPI surfaces included four major reflections, but pentacene grown on the SiO$_2$ surface yielded only three weak reflection peaks. Obviously, the pentacene grown on a PAPI surface had a better crystalline quality than that grown on the SiO$_2$ surface. In Figure 1, the presence of only...
ingly, the polarized UV doses from 10 X-ray diffraction peaks of the single-crystal phase were single-crystal phase ranged from 5.97 to 6.20°. The crystals in the film were oriented with their planes parallel to the substrate. Previous studies of the growth of pentacene films have demonstrated that the pentacene molecules initially lie flat on the surface,18 growing layer-by-layer.19 Typical θ–2θ patterns of pentacene include two distinct crystalline phases, called “thin-film phase” and “single-crystal phase”, with corresponding d_{00l}-spacings of 15.4 Å and 14.5 Å, respectively.20 Among the samples irradiated with various doses of UV, three irradiated at 10, 12, and 15 J/cm2 included only one phase and gave a sharp first-order diffraction peak at 5.72° corresponding to a lattice spacing of 15.4 Å. The observed similarities among these three samples are attributable to the presence of the highly oriented pentacene thin-film phase, (00l). The other UV dose conditions yielded pentacene films that comprised two phases—the thin-film phase and the single-crystal phase, (00l'),—but the peak position of the single-crystal phase ranged from 5.97 to 6.20°. The X-ray diffraction peaks of the single-crystal phase were much weaker than those of the thin-film phase. Accordingly, the polarized UV doses from 10–15 J/cm2 were suitable for preparing pentacene films with improved molecular ordering. The crystalline parameters of the pentacene films, prepared at various UV doses, were determined. The crystalline parameters, such as the size of the crystalline domain and the degree of structural disorder, were calculated from the half-width of the diffraction peaks. The long axis of the pentacene molecule was aligned normal to the anisotropic PAPI alignment layer, so the overlying pentacene grain was preferably oriented in-plane. When PAPI absorbs polarized UV light, the weakest bonds in the polyimide parallel to the surface to form a layered structure. According to paracrystal theory,21 the average crystalline domain size measured perpendicular to the (00l) planes and the degree of structural disorder, g_{II}, are related by the following formula:

\[
(\delta s)_{o}^{2} = (\delta s)_{c}^{2} + (\delta s)_{II}^{2} = \frac{1}{L_{hkl}^{2}} + \frac{4\delta \theta_{II}^{4} m^{4}}{\lambda s_{hkl}^{2}} \tag{1}
\]

where

\[
(\delta s)_{o} = \frac{2 \cos \theta \delta \theta}{\lambda} \tag{2}
\]

Figure 1. X-ray diffraction patterns of pentacene films deposited on photoaligned polyimide surfaces irradiated at various doses of UV light. The top pattern represents the pentacene film grown directly on an SiO2 surface.

is the overall broadening, excluding instrumental broadening; \(\lambda\) represents the X-ray wavelength; \(\theta\) is the diffraction angle and \(\delta \theta\) is in radians; (\(\delta s)_{c}\) specifies the broadening associated with the size of the crystalline domain; (\(\delta s)_{II}\) measures the broadening due to lattice distortions of the second kind; \(m\) is the order of the diffraction, and \(\delta s_{hkl}\) is the average spacing between (hkl) planes. The square of (\(\delta s)_{o}\) is plotted versus the fourth power of the order of diffraction (\(m^{4}\)) of each peak from the pentacene films grown on PAPI surfaces that had been irradiated with various doses of UV. Hence, \(L_{hkl}\) and \(g_{II}\) of peaks of the thin-film phase are calculated from the intercept on the ordinate axis and the slope of the straight line determined by the least-squares method and fitted according to eq 1, as depicted in Figure 2. The small structural disorder and the large crystalline domain size arose simultaneously at UV doses between 10 and 15 J/cm2. Over such a range of UV doses, the crystalline disorders of the three samples are all below 1%, and the sizes of the crystal domains are approximately 300 Å. This result indicates that the pentacene films deposited on the PAPI surface at a UV dose between 10 and 15 J/cm² comprised large crystals and exhibited strong ordering. In contrast, the size of the crystalline domain and the degree of structural disorder of pentacene grown on the surface of SiO2 were 112 Å and 2.42%, respectively. Therefore, irradiating a PAPI alignment layer with an appropriate dose of UV could dramatically increase the structural ordering of the pentacene molecules.

Figure 3a displays an atomic force microscope (AFM) image of a pentacene film grown on the anisotropic PAPI surface irradiated with 12 J/cm² UV light. The pentacene film was highly oriented as the grains grew perpendicular to the polarization of the UV irradiation on the PAPI layer. Normal illumination with polarized light induced surface anisotropy in the PAPI alignment layer, so the overlying pentacene grain was preferably oriented in-plane. When PAPI absorbs polarized UV light, the weakest bonds in the polyimide parallel to the surface.
polarization of the incident UV beam are broken to generate free radicals.\textsuperscript{11–13} The probability of UV absorption, and hence, of breaking of main-chain bonds, is greater for main-chains aligned parallel to the direction of polarization of the UV light. Accordingly, the distribution of unbroken polymer main-chains is more likely to become anisotropic perpendicular to the direction of polarization of the UV light. This degradation mechanism broke chain A in the PAPI, which was parallel to the polarization of the UV light, and left chain B to achieve photoalignment as shown in Figure 4. The remaining chain B in the polyimide, which was perpendicular to the polarization of the UV light, induced alignment and oriented the overlying pentacene molecules. As shown in Figure 3a, the grains in the pentacene film are aligned perpendicular to the polarization of the normally incident UV light. The mean width of the pentacene grains parallel to the polarization of the UV beam exceeded 1 μm and each grain was continuous along the direction perpendicular to the polarization of the irradiation. For comparison, Figure 3b provides an AFM image of the surface of a pentacene film grown directly on the SiO\textsubscript{2} surface without a PAPI alignment layer. The deposited pentacene film contains small grains (with an average size of under 0.5 μm) with very little ordering. Evidently, the PAPI layer promotes molecular orientation.

Polarized Raman spectroscopy was employed to investigate the orientation of pentacene molecules in the crystal. Raman measurements were made on the sample with a PAPI alignment layer irradiated with 12 J/cm\textsuperscript{2} UV light; X-ray analysis determined that the layer of pentacene had a maximum crystalline domain size of 300 Å and a structural disorder of 0.92%. When Raman scattering was performed with \textit{y}(x,\textit{x},\textit{y}) geometry, the polarizations of the laser beam and the collected Raman signal were parallel to the polarization of the irradiated UV light. Figure 5a shows the Raman spectrum measured in that case. The Raman peak at 1158 cm\textsuperscript{-1} corresponds to origination from the in-plane molecular vibration of pentacene as indicated in Figure 6, whereas the peak at 1155 cm\textsuperscript{-1} represents the out-of-plane vibration perpendicular to the molecular axis on both sides of the pentacene molecule.\textsuperscript{22,23} Notably, the intensity of the Raman peak at 1155 cm\textsuperscript{-1} exceeds that of the peak at 1158 cm\textsuperscript{-1} because the electric field of the
incident laser beam considerably enhances the atomic motion perpendicular to the molecular axis on both sides of the pentacene molecule. This observation implies that the axis of the molecule was aligned perpendicular to the polarizations of both the laser beam and the irradiated UV light.

Figure 5b shows the Raman spectrum measured in y(z,x) geometry: the polarizations of the laser beam and the collected Raman signal were perpendicular to the polarization of the irradiated UV light. The polarizations of the incident laser and the collected Raman signal were parallel to the axis of the pentacene molecule. The intensities of both peaks are almost the same, because the in-plane vibration of the pentacene molecule has two components in each of the x and z directions. This result revealed that the laser beam polarized along the molecular axis or perpendicular to the UV polarization did not enhance any particular atomic motion. Furthermore, Figure 5c presents the Raman spectrum of the sample without the PAPI layer measured from y(z,x)y or y(x,x)y geometry. The lack of an alignment layer prevented the features associated with in-plane and out-of-plane molecular vibrations from being resolved by varying the polarizations of the laser beam, and the peaks were much less intense than that of the sample with a PAPI layer. The pentacene molecules were again shown to be aligned perpendicular to the polarization of the UV light. Thus, the Raman spectra again established that the pentacene molecules could be aligned effectively using the photoalignment technique, and that pentacene molecules preferred to align perpendicular to the polarization of the UV light that had irradiated the PAPI layer. This result is consistent with the X-ray and AFM measurements.

The electrical characteristics of the bottom-gate OTFT devices, in which the pentacene film had been fabricated on top of a PAPI alignment layer, were measured to confirm that the pentacene molecules were well oriented. Figure 7 indicates that the drain current (I_D) as a function of drain-source voltage (V_{DS}) at several values of gate-source voltage (V_{GS}), for a pentacene OTFT that has a PAPI alignment layer aligned parallel to the flow of current. A saturation field-effect mobility of 0.4\text{ cm}^2\text{V}^{-1}\text{s}^{-1} was determined; the threshold voltage was around \(-1\text{ V}\), and the modulated on/off current ratio was approximately \(10^5\). The OTFT had poor field-effect mobility in the control sample (in which the pentacene layer was deposited directly on top of the silicon dioxide without the photoalignment layer). The mobility of the control sample was typically about 0.03 cm²/V·s, with a saturation current of only 10 μA at V_G = \(-100\text{ V}\) (as shown in Figure 8), and a threshold voltage of around \(-20\text{ V}\).

Moreover, when pentacene is oriented perpendicular to the direction of the flow of current, the device exhibited a low saturation current and the field-effect mobility ranged from 0.09 to 0.15 cm²/V·s. Notably, the flow of current favors transport parallel to the alignment. The anisotropic ratio of the field-effect mobility of carriers transported parallel to the direction of alignment to those transported perpendicular to the direction of alignment, \(\mu_//\mu_\perp\), is in the range 2.7–8.3.

Table 1 compares the results obtained herein with data extracted from the literature on studies of OTFT devices, for pentacene aligned using various methods. The anisotropic ratio of the field-effect mobility obtained herein slightly exceeds that obtained by Swiggers et al.⁷ using a rubbing method, but was less than that found by Chen et al.⁶ The data herein show a significant improvement in field effect mobility over that of samples without an alignment layer. Swiggers et al. also used the photoalignment method to align pentacene, but they...
obtained data that revealed poor optical anisotropic characteristics and provided no results of tests on OTFT devices. In this work, irradiation UV light at various energies was used to generate variously aligned layers. The initial results indicate that the order of the alignment depends on the energy density of irradiation. Weaker irradiation yields less well-oriented pentacene films. X-ray analysis revealed that poorly aligned films include two coexisting phases: the single-crystal phase and the thin-film phase. Dimitrakopoulos et al. found that the mixed-phase pentacene film has relatively poor transport properties. Swiggers et al. may have obtained poorly photoaligned pentacene films because they used inadequate energetic irradiation to generate an orientation axis along which pentacene molecules could be aligned.

Conclusions

In summary, the method of photoalignment has successfully generated pentacene OTFTs with anisotropic electrical characteristics and enhanced carrier mobility. This is the first study of the anisotropic electrical characteristics of OTFT devices based on pentacene alignment using photoalignment technology. Anisotropic electrical properties support circuit design, for example, in isolating adjacent components without requiring a large spatial separation or a patterned organic semiconductor layer. In most organic semiconducting films, such as pentacene, organic active layers deposited over the entire substrate are normally conducting, and a suitable means of patterning the active layer to isolate the devices from each other is often lacking. These problems can be solved by fabricating multiple alignment domains in the organic semiconducting film using the photoalignment method. We expect that further optimization of the photoalignment conditions in OTFT devices would increase anisotropy of electrical characteristics and may improve the devices for use in circuit applications.

The structure of highly ordered thin films of pentacene was studied by X-ray diffraction, atomic force microscopy, and polarized micro-Raman spectroscopy. The structure of a pentacene thin film, consisting only of the thin-film phase, was developed by controlling the dose of UV light in the photoalignment process. The AFM and Raman measurements obtained herein provide direct evidence of the mechanism of the alignment of pentacene molecules. The photoalignment layers were found to induce a preferred direction, perpendicular to the electric field of the UV light, along which the pentacene grains were aligned. Polarized Raman spectroscopy is a very powerful technique for probing the structure of a pentacene film, as it has the advantages of fast and noncontactive measurements, high sensitivity, and the ability to monitor physical modifications in the micron range. Further work is in progress to evaluate the effects of alignment on other molecules.

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Table 1. Comparison of Anisotropic Electrical Characteristic of OTFT Based on Aligned Pentacene by Using Different Alignment Methods

| reference | alignment method | $\mu_{||}$ | $\mu_{\perp}$ | $\mu_{||}/\mu_{\perp}$ | mobility anisotropy ratio$^b$ | times of enhanced mobility$^c$ |
|-----------|----------------|-----------|-----------|----------------|----------------|----------------|
| this work | photoalignment | 0.03      | 0.4–0.75  | 0.99–0.015     | 2.7–8.3       | 13.33–25      |
| Chen et al.$^d$ | rubbing | 0.15      | 0.24–0.25 | no activity    | $>400$        | 1.6–1.67      |
| Swiggers et al.$^e$ | photoalignment | 0.007     | 0.02      | 0.008         | 2.5           | 2.86          |

$^a$ $\mu_{\text{non}}$ is the field-effect mobility of the samples without alignment layer. $\mu_{||}$ and $\mu_{\perp}$ are the field-effect mobility parallel to and perpendicular to aligning direction, respectively. $^b$ Calculated from the ratio of $\mu_{||}$ to $\mu_{\perp}$. $^c$ Calculated from the ratio of $\mu_{||}$ to $\mu_{\text{non}}$. $^d$ Ref 6. $^e$ Ref 7. $^f$ The value is the optical anisotropy characteristic and dichroic ratio.