Ultraviolet-Light-Induced Growth of 6,13-Bis(triisopropylsilylethynyl)pentacene Spherulites

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ABSTRACT: Spin-cast small $\pi$-conjugated molecules exhibit poor molecular order because of rapid evaporation of the solvent, resulting in low charge-carrier mobility. Herein, we present simple ultraviolet (UV) exposure methods as a versatile post-treatment for inducing the growth of crystalline spherulites of 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-PEN). The UV exposure effectively transformed the amorphous state into a crystalline phase in the solid films. UV exposure of the TIPS-PEN films spin-cast using toluene with a high boiling point improved the intermolecular interaction within only a few minutes, which enhanced charge-carrier transport in organic transistors prepared using these films. The presence of residual solvent facilitated the mobilization of TIPS-PEN molecules, enabling their reorganization. Furthermore, UV exposure of the patterned specific regions in TIPS-PEN films reduced the off-state currents in the organic transistors prepared using the films.

1. INTRODUCTION

Organic $\pi$-conjugated molecules have attracted considerable attention because they are inexpensive, processed using simple methods, mechanically flexible, and lightweight. Among small organic semiconductors used to form an active layer, 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-PEN) has numerous advantages including excellent electrical performance and compatibility with various solution processing methods because of its high solubility in organic solvents. Its superior electrical properties stem mainly from the high regularity of its molecular arrangement. The substituted group in TIPS-PEN hampers the herringbone packing of pentacene molecules, which leads to a strong cofacial $\pi-\pi$ interaction. However, solution-processed TIPS-PEN exhibits low charge-carrier transport, indicating the presence of defects in its in-plane structure. In particular, conventional spin-cast TIPS-PEN films cannot exhibit a crystal growth behavior because of the high solvent evaporation rate, resulting in interfacial charge trapping and a decrease of the field-effect mobility. Extensive efforts have been devoted to enhance the charge transport in TIPS-PEN films. To ensure that TIPS-PEN films exhibit superior electrical properties, post-treatment methods that induce interchain $\pi-\pi$ stacking interactions of molecules are essential. Thermal,12-14 and solvent vapor15-18 annealing are representative post-treatment methods for fabricating crystalline films. However, thermal treatment is an unsuitable method for multilayered devices because it causes interfacial instability as a consequence of the different coefficients of thermal expansion of the layer materials. In addition, solvent vapor annealing can dissolve or dewet the cast films and requires a processing time greater than 30 min. Simple UV light exposure for a conjugated polymer has recently been reported to induce the formation of ordered chains. Brief UV exposure has been shown to promote the ordered formation of conjugated polymers, which in turn enhances charge-carrier transport. Thus, the development of a simple approach to enhance the crystallinity of small $\pi$-conjugated molecules could strongly affect the organic transistor field. Herein, we present simple UV exposure methods as a versatile post-treatment for improving the structural order of TIPS-PEN films. UV irradiation as a post-treatment process may be more convenient than other post-treatment methods because it requires only a few minutes and does not cause dewetting or interfacial instability. Reducing the post-treatment processing time enables high-throughput processing of highly crystalline organic films because of the mild processing conditions compared with those of other post-treatment methods. The structural changes and the electrical characteristics of TIPS-PEN films exposed to UV light were characterized as a function of the UV exposure time, wavelength, and the solvents used. Furthermore, we improved the crystallinity of specific regions of TIPS-PEN semi-
conductive films by selectively exposing the films to UV light using a patterned mask. The crystalline patterned TIPS-PEN film was found to exist only in the channel region of the device array, leaving the unexposed film in a lower-crystalline or amorphous state to minimize leakage currents between devices.22

2. EXPERIMENTAL SECTION

2.1. Preparation of the TIPS-PEN Films and Organic Field-Effect Transistors. The TIPS-PEN used as a semiconductor material was purchased from Sigma-Aldrich and was dissolved in chloroform and toluene at a concentration of 10 mg·mL\(^{-1}\). The organic field-effect transistors (OFETs) were fabricated as top-contact bottom-gate type, and a highly n-doped Si wafer with a 300 nm-thick layer of SiO\(_2\) was used for the gate electrode and the insulator (capacitance = 10.8 nF·cm\(^{-2}\)). The substrates were washed sequentially with acetone and ethanol for 30 min per sequence using an ultrasonicator and then dried in a N\(_2\) stream. The previously prepared TIPS-PEN solutions were spin-coated onto a Si wafer at 1200 rpm for 30 s. After the spin-coating process, the TIPS-PEN thin films were promptly exposed to UV light with a wavelength of 254 nm (265 \(\mu\)W/cm\(^2\)) or 365 nm (350 \(\mu\)W/cm\(^2\)) in a dark room under ambient atmospheric conditions. The UV light was produced using a UV lamp (VILBER, VL-4.LC, 4 W), and the exposures were conducted for various times (0−7 min) at room temperature. The UV-exposed TIPS-PEN films were dried overnight in a vacuum oven to remove residual solvent in the films. Source and drain electrodes were formed on the TIPS-PEN films by evaporating Au using a shadow mask. The crystalline patterned TIPS-PEN thin films were characterized by polarized optical microscopy (SmartLab, Rigaku). The thickness of the spin-coated TIPS-PEN films was measured using an ellipsometer (J. A. Woollam Co.). The electrical performance of the OFETs was assessed using an Ultratech system (PerkinElmer). The field-effect mobility and on–off ratio were determined from output and transfer curves in the saturation regime. A total of 30−40 devices were tested, and the measurement values related to their device performance under a given set of experimental conditions were averaged.

2.2. Characterization. UV−vis absorption spectra were acquired using a UV−vis spectrophotometer (Lambda 365, PerkinElmer). The film surface morphologies of the TIPS-PEN films were characterized by polarized optical microscopy (POM) (Olympus BX51) and atomic force microscopy (AFM); the atomic force microscope (Bruker, Multimode 8) was operated in the tapping mode. The crystalline structures of the TIPS-PEN films were investigated by X-ray diffraction (XRD) analysis (SmartLab, Rigaku). The thickness of the spin-coated TIPS-PEN films was measured using an ellipsometer (J. A. Woollam Co.). The electrical performance of the OFETs was characterized using a semiconductor analyzer (Keithley 4200-SCS), with the devices at room temperature, under vacuum, and in a dark environment. The field-effect mobility and on-off ratio in the TIPS-PEN films were calculated from the transfer curves in the saturation regime. A total of 30−40 devices were tested, and the measurement values related to their device performance under a given set of experimental conditions were averaged.

3. RESULTS AND DISCUSSION

The influence of the UV irradiation on the crystallinity of the TIPS-PEN thin films was investigated as a function of the exposure time. Figure 1 shows the UV−vis absorption spectra of TIPS-PEN films prepared using different solvents, different UV wavelengths, and various UV exposure times. As shown in Figure 1a,b, the UV−vis absorption spectra of the TIPS-PEN film spin-cast with chloroform show only three peaks at 549, 594, and 646 nm. The UV−vis spectra of this thin film spin-cast with chloroform are similar to the spectra of TIPS-PEN in the solution state, where the molecules are well dissolved (Figure S1). These results indicate that an amorphous film was formed because the solvent evaporated before crystals could form during solidification of the thin films as a consequence of the low boiling point of the chloroform solvent. Figure 1c shows the normalized absorption intensity versus the UV exposure time for different UV wavelengths, indicating that the normalized intensity is constant irrespective of the UV wavelength and exposure time.

In the case of films spin-cast with toluene, crystalline films were formed because of the slow evaporation rate of the solvent (Figure 1d,e). The spectra of the as-prepared thin films show a peak at \(\lambda = 590 \text{ nm} \) associated with an intrachain \(\pi−\pi^*\) transition (0−2) and weak energy features at 649 and 700 nm corresponding to the second transition (0−1) and first transition (0−0), respectively.23 Compared with the absorption spectrum of TIPS-PEN in the solution state, the spectra of the TIPS-PEN films show a new absorption band (\(\sim 700 \text{ nm} \)), which is explained by a stoichiometric conversion of free molecules into single crystals. When the TIPS-PEN films were exposed to UV light, the intensity of the (0−0) transition gradually increased with increasing UV exposure time, which resulted in the color of the thin film changing from blue to dark blue (inset of Figure 1e). This phenomenon is attributed to an increase in the number of ordered aggregates involved in the interchain \(\pi−\pi\) stacking interaction.24−26 The presence of the residual solvent facilitated the mobilization of TIPS-PEN molecules for reorganization. Figure 1f shows the ratio of the intensities of the (0−0) and (0−2) transitions, \(A_{0−0}/A_{0−2}\), as a function of the UV exposure time at various UV wavelengths. Notably, the change in the \(A_{0−0}/A_{0−2}\) intensity with increasing
UV exposure time was substantially greater at the 365 nm wavelength, where the energy was weaker. When the UV exposure time was longer than 5 min, the intensity of the (0−0) transition decreased. This result indicates that the molecular order in the TIPS-PEN films decreased when the UV exposure time exceeded a certain threshold. This decrease is attributed to photo-oxidation, which occurs when organic materials are exposed to air and light. Long UV exposure times lead to the formation of peroxide radicals (•O−) or hydroxyl radicals (•OH), both of which are strong oxidizing agents and can oxidize TIPS-PEN.27,28

Figure 2 shows ex situ POM images of the TIPS-PEN films prepared with different solvents, UV wavelengths, and UV exposure times. In the case of the film spin-cast with chloroform, the results show that an amorphous thin film with few crystalline aggregates was obtained irrespective of the UV exposure time and wavelength. In the case of the film spin-cast with toluene, the results show that a crystalline thin film was produced and that the crystals of the TIPS-PEN films exposed to UV light with λ = 365 nm became large. Large spherulites with nucleation centers and grain boundaries were clearly observed in the TIPS-PEN samples exposed to 365 nm UV light, indicating that irradiation using UV light with the appropriate energy leads to the self-assembly of two-dimensional (2D) TIPS-PEN crystals. The grain size of the spherulites increased with the increasing exposure time. The TIPS-PEN film exposed to UV light for 5 min exhibited the largest 2D crystal grain size among the observed samples. Additional images corresponding to different UV exposure times are shown in the Supporting Information Figures S3,S4.

In subsequent experiments, having determined the experimental conditions that maximize the UV effect, we prepared films using toluene solvent and 365 nm UV light. Figure 3 shows the nanoscale morphology and surface profile, as observed by AFM, of TIPS-PEN films exposed to UV light for various times. The TIPS-PEN film spin-cast with toluene shows typical dendritic features, and the crystal size and roughness of the TIPS-PEN film increase with the increasing UV exposure time. The roughness after UV exposure was increased as much as fourfold compared with that before UV exposure. The increase in the crystal size indicates that because of the UV exposure, some adjacent TIPS-PEN grains were bonded together via a recrystallization process. However, in the case of the film exposed to UV light for 7 min, the surface roughness decreased because the crystals of the TIPS-PEN degraded.

Figure 2. POM images of the TIPS-PEN films spin-cast with (a−e) chloroform and (f−j) toluene solutions and subsequently exposed to UV light with a wavelength of 254 or 365 nm for various times.

Figure 3. Tapping-mode AFM height images and surface profiles of the TIPS-PEN films spin-cast with toluene and exposed to UV light with a wavelength of 365 nm for various times: (a) 0, (b) 1, (c) 3, (d) 5, and (e) 7 min. (f) Roughness of the TIPS-PEN films as a function of the UV exposure time.

Structural changes in the TIPS-PEN films as a function of the UV exposure time were investigated by XRD along the out-of-plane direction of films exposed to UV light with a wavelength of 365 nm (Figure 4). All of the TIPS-PEN films showed a (00l) diffraction pattern in the out-of-plane direction, indicating that the TIPS-PEN molecules assembled with their side group aligned vertically on the substrate,29,30 irrespective of the UV exposure time. The intensity of the diffraction peaks of the TIPS-PEN films gradually increased with increasing UV exposure time, which means that brief UV exposure did not promote the crystallization of TIPS-PEN molecules. However, when UV light was exposed to the film for more than 5 min, the intensity of the diffraction peaks was rather reduced. We used Scherrer’s equation to calculate the mean domain size (R) of the TIPS-PEN crystals as a function of the UV exposure time. The equation is $R = K \lambda / (β \cos θ)$, where K is a shape factor, λ is the wavelength of X-rays, β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the Bragg angle.31 The FWHM gradually decreased with the increasing UV exposure time when the exposure time was 5 min or less, suggesting that the mean domain size of the TIPS-PEN molecules increased with the increasing UV exposure time. The average domain size of the TIPS-PEN molecules tended to increase gradually with increasing UV exposure time, and the largest domain size of 42.06 nm corresponded to an exposure time of 5 min. This orientation and larger domain
Figure 4. XRD patterns of the TIPS-PEN films spin-cast using a toluene solution and subsequently exposed to UV light with a wavelength of 365 nm for various times plotted on (a) linear and (b) logarithmic axes. (c) Domain size (left axis) and FWHM (right axis) of the TIPS-PEN films as a function of the UV exposure time. (d) Schematic showing molecular orientations of TIPS-PEN films with their side group aligned vertically on the substrate. The arrows indicate the (001) orientation.

Figure 5. (a) Plot of the drain current as a function of the gate voltage at a fixed drain voltage ($V_D = -40$ V) on both linear (left axis) and logarithmic (right axis) scales for as-cast TIPS-PEN films, films exposed to UV light, and films exposed to UV light after deposition of a shadow mask. (b) Average field-effect mobilities (left axis) and on–off ratio (right axis) of the OFETs based on TIPS-PEN films exposed to UV light for 5 min. (c) Schematic of the patterned UV exposure process using a shadow mask. An optical microscope image shows the patterned crystal phase of the TIPS-PEN thin films exposed to UV light after deposition of a shadow mask.

4. CONCLUSIONS

TIPS-PEN films with large spherulites were prepared by optimizing the UV exposure time, wavelength, and solvent types. The TIPS-PEN film structure, including its molecular orientation, grain size, and morphology, could be well controlled through careful selection of the solvent and UV exposure conditions. UV exposure of films effectively transformed amorphous-state films into films with a spherulite crystalline state. The amount of residual solvent is very important for TIPS-PEN reorganization. UV exposure of TIPS-PEN films spin-cast using toluene with a high boiling point was found to improve the intermolecular interaction within only a few minutes, which led to enhanced charge-carrier transport in OFETs fabricated using these films. The UV exposure of specially patterned TIPS-PEN films decreased the off-state currents in the OFETs fabricated using these films. Hence, our proposed UV exposure post-treatment method is a useful method to control the structural order and morphology of small π-conjugated molecules.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.1c03050.

UV–vis absorption spectra of TIPS-PEN solutions and films and POM images of TIPS-PEN films for various exposure times (PDF)

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Notes
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