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Improving performance of selective-dewetting patterned organic transistors via semiconductor-dielectric blends

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ABSTRACT

The fabrication of the self-patterned OTFTs based on a blend of 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) and poly(methyl methacrylate) (PMMA) were investigated. Structural analysis revealed a well-defined TIPS-pentacene-top/PMMA-bottom bilayer structure formed in the blend film. Because the PMMA underlayer acts as a modification layer at the semiconductor/dielectric interface, the blend OTFTs exhibited over 5 times higher mobility and significantly reduced hysteresis than pristine TIPS-pentacene device. This selective wetting/dewetting process based on polymer blends allows the formation of patterned films with a self-organized modification layer and has great potential for economical processing of large-area and high-performance electronic devices.

1. Introduction

The use of solution-processed organic semiconductors for the fabrication of thin-film transistors would enable a new generation of low-cost, large area flexible electronics through high-throughput solution-deposition techniques [1–10]. These low-cost solution processes such as spin coating or casting, however, usually produce entirely covered and unpatterned semiconductor films, which may cause dramatic leakage current, and crosstalk between adjacent devices [11]. Therefore, patterning of the semiconductors is crucial for the development of large scale device arrays and complex circuits. A variety of techniques have been developed to pattern organic thin-film transistors (OTFTs) including microcontact printing, ink-jet printing, silk screen printing, laser ablation, physical stripping, photolithography, and selective wetting/dewetting [12–16]. Among these methods, selective wetting/dewetting has attracted more attention due to its high-throughput, low-cost, and simplicity [11,16,17].

Selective wetting/dewetting is a bottom-up self-organization method using a substrate with predefined surface-energy patterns. In order to facilitate the selective deposition of organic films on the channel regions, highly polar functional groups such as hydroxyls or aminos are usually introduced to the channel surface to enhance the wettability of semiconductor solutions [18]. However, such highly polar surfaces are likely to act as charge traps in the OTFT devices and remarkably deteriorate the device performance. For example, the 6,13-bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene) OTFTs patterned on a hydrophilic surface showed a maximum mobility of 0.052 $\mathrm{cm^2\,V^{-1}\,s^{-1}}$, although the solution is prepared using a solvent with optimal evaporation rate for the wetting/dewetting patterning [19]. In attempts to solve this problem, several groups have used two types of modifiers with different wettability to treat the channel regions and the periphery surface separately. For example, Minari and coworkers reported the fabrication of an OTFT array on a plastic substrate by presenting phenyl-terminated self-assembled monolayers (SAMs) at channel regions and alky-terminated SAMs covering the rest of the surface [20]. Kim and coworkers coated a hydrophobic fluoropolymer film onto silicon dioxide and then modified the channel regions with hexamethyldisilazane (HMDS) [21]. Chang et al. employed two types of SAMs to treat the silicon dioxide surfaces, with HMDS forming channel regions and octyltrichlorosilane (OTS) covering the remaining areas [22]. Although the dual-modification approach has several advantages over simple mono-modification treatment, it obviously makes the process more complicated.

Blending is a facile and effective method for tuning and optimizing the electronic and optoeletronic properties of organic electronics. Common examples include the bulk heterojunction solar cell and blends for organic light emitting diodes. The use of organic blends in OTFTs has brought about significantly improved

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features including device performance, material cost, mechanical properties, and environmental stability [23–30]. Small-molecule organic semiconductors show high crystallinity, high field-effect mobility, and high stability but often have poor solution processability [31–33]. The integration of small molecules within polymeric matrices may provide a means of enhancing device uniformity while preserving the intrinsically high mobility associated with small molecule. Moreover, several groups have reported significantly improved electrical properties for blend semiconductors in OTFTs when compared with those of neat small molecules [34–40]. In this work, we report a wetting/dewetting process based on polymer blends for the fabrication of patterned OTFTs. Through the formation of vertically phase-separated bilayers, a modification layer simultaneously forms at the semiconductor/dielectric interface in the wetting/dewetting process.

2. Experimental

2.1. Materials

6,13-Bis(triisopropylsilylethynyl) pentacene (TIPS-pentacene), Poly(methyl methacrylate) (PMMA, $\mathrm{Mw} = 996\,\mathrm{kg\,mol^{-1}}$), (1H,1H,2H,2H-heptadecafluorodecyl) trichlorosilane (HFDS), 1,2-dichlorobenzene were purchased from Aldrich Chemical Co. All materials were used as received without further purification.

2.2. Patterning of semiconductor films via wetting/dewetting process

The Si/SiO_2 substrates were cleaned in piranha solution, washed with distilled water, and stored in a vacuum oven prior to use. The surface-energy patterning was performed as follows. First, a HFDS SAM was formed onto the surface by vapor phase reaction in a vacuum desiccator for 2 h to provide a uniform hydrophobic surface. The water contact angle on the HFDS treated surface was 130°. The HFDS groups were then removed from the regions of channels to render the surface hydrophilic by exposure to UV-ozone through a shadow mask. The pristine TIPS-pentacene and TIPS-pentacene/PMMA (50/50, w/w) were dissolved in 1,2-dichlorobenzene solution (2 wt%) and then spin-coated (2000 rmp, 60 s) onto the surface-patterned substrates, thus selectively coating the channel regions with organic semiconductor layers. The above procedures were all processed in ambient conditions.

2.3. Transistor device fabrication

Heavily doped n-type Si substrates with a 300 nm thermally grown silicon dioxide were cleaned and treated as described above. Patterned semiconductor films were deposited as stated above without any post annealing. A 50 nm thick Au layer was deposited by thermal evaporation and patterned through shadow masks to form the source–drain electrodes. Channel length (L) and channel width (W) of the device are 100 and 800 μm, respectively.

2.4. Measurements

The morphologies of the blend films were characterized by polarized optical microscopy (POM, Leica DM-2500M), field-emission scanning electron microscopes (FESEM, Hitachi S-4200), and atomic force microscopy (AFM, Digital Instruments Multimode) operating in a tapping mode. The film thickness was measured using a surface profiler (XP-100, KLA-Tencor). The contact angle of the surface was determined by a video-based automatic contact angle measuring instrument (OCA15, Data Physics). UV–vis absorption spectra were measured from the film on quartz substrates by a UV–vis spectrophotometer (UV-2550, Shimadzu). The electrical characteristics of the TFT devices were measured in accumulation mode using Keithley 4200 units under ambient conditions.

3. Results and discussion

TIPS-pentacene was used as the organic semiconductor because of its high solubility in common organic solvents and high field-effect mobility. Poly(methyl methacrylate) was used as the dielectric because of its good film-forming characteristics. In order to achieve complete phase separation, 1,2-dichlorobenzene with high boiling point was chosen as the solvent. Fig. 1a schematically shows the selective wetting/dewetting patterning process for OTFTs fabrication based on TIPS-pentacene/PMMA blends. Highly doped silicon wafers with 300 nm thick thermally grown SiO_2 were cleaned and treated with (1H,1H,2H,2H-heptadecafluorodecyl) trichlorosilane (HFDS) by vapor phase reaction to provide a uniform hydrophobic surface with a water contact angle of 130°. The area that had been selected as the channel region of the OTFTs was then irradiated with ultraviolet (UV) light through a shadow mask for removal of the THFDS layer. A 2 wt% solution of TIPS-pentacene and PMMA (50/50, w/w) in 1,2-dichlorobenzene was then deposited onto the substrates by spin-coating. Due to the different wettability on the surface, the solution can only stay in the UV-treated regions. After the solvent evaporates, organic blend films formed in the desired geometry. As shown in Fig. 1b, features with size ranging from 50 to 300 μm were fabricated by this process. It should be noted that this is not the limited resolution achievable with this technique. The resolution can be further improved by using finer photomask.

To reveal the film structure, a patterned TIPS-pentacene/PMMA deposit with a diameter about 150 μm was observed using polarized optical microscopy (Fig. 2a and b). The POM images show that the selectively wetting/dewetting patterned TIPS-pentacene/PMMA blend film exhibits strong birefringence, indicating the presence of uniaxial molecular ordering. As PMMA is amorphous, it means that the TIPS-pentacene is highly crystalline in the blend films. Orthogonal solvent was used to selectively dissolve the component so as to elucidate the characteristics of the interface between TIPS-pentacene and PMMA. The substrate was immersed into cyclohexane, which dissolves TIPS-pentancene but not PMMA. The OM image (Fig. 2c) clearly shows a continuous remaining layer at the pattern region. Under the cross-polarized microscope, the remaining layer is totally dark and thus amorphous. Surface profile scanning was used to characterize the change of height profile before and after cyclohexane treatment. Fig. 3 reveals that the height at the center of the droplet is about 50 and 30 nm before and after cyclohexane treatment, indicating a 20 nm TIPS-pentacene-rich layer over a 30 nm PMMA-rich layer.

To further provide evidence to confirm the film structure, we also characterized the blend films using field-emission scanning electron microscopes (FESEM, Hitachi S-4200), and atomic force microscopy (AFM, Digital Instruments Multimode) operating in a tapping mode. The SEM image (Fig. 4a) shows that the surface of the TIPS-pentacene/PMMA blend film is covered mostly by a ribbon-like feature. AFM image (Fig. 4c) also shows a faceted shape and a step-terrace geometry, which is very similar to those observed for TIPS-pentacene single crystals, indicating the formation of a highly crystalline TIPS-pentacene layer on the surface of the blend film. In addition, step-height of the terrace is estimated to be 1.7 nm, close to1.65 nm of, the (0 0 1) d-spacing of TIPS-pentacene molecule, which reconfirms that the (0 0 1) planes are parallel to the substrate plane. After immersing the substrate into cyclohexane, the TIPS-pentacene component was selectively dissolved and the interfaces between TIPS-pentacene and PMMA layers was