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Solution-processed 6,13-bis(triisopropylsilylethynyl) (TIPS) pentacene thin-film transistors with a polymer dielectric on a flexible substrate

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Abstract
The authors report the fabrication of solution-processed 6,13-bis(triisopropylsilylethynyl) (TIPS) pentacene thin-film transistors with a cross-linked poly-4-vinylphenol (PVP) dielectric on a polyethersulphone (PES) substrate. The device exhibited useful electrical characteristics, including a saturation field effect mobility of 2.08×10^{-2} cm^2 V^{-1} s^{-1}, a current on/off ratio of 10^5, a threshold voltage of -2 V and an excellent subthreshold slope of 0.86 V/dec. It was demonstrated that the significant improvement in the subthreshold slope of TIPS-pentacene TFTs could be attributed to a decreased carrier trap density at the PVP/TIPS-pentacene film interface. Furthermore, a 1,2,3,4-tetrahydronaphthalene (Tetralin) solvent used in this study had a high boiling point, which had a positive effect on the morphology and the molecular ordering of the TIPS-pentacene film.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Organic thin-film transistors (OTFTs) have been widely investigated due to their potential for organic electronics, including radio frequency identification (RFID) tags, solar cells, smart cards and flexible displays [1, 2]. The device performance of OTFTs based on organic semiconductors (OSCs) such as pentacene is comparable to that of hydrogenated amorphous silicon thin-film transistors (a-Si:H TFTs). In order to utilize their compatibility with flexible substrates and low-cost fabrication approaches using printing technologies such as the ink-jet and roll-to-roll process, developments of high-performance solution-processed OSCs are required. Generally, the pentacene film can be fabricated with an expensive vacuum evaporation process due to its limited solubility in organic solvents [3]. To overcome this drawback, many researchers have made an effort to obtain soluble pentacene. Afzali *et al* reported the film preparation of a pentacene precursor that can be deposited by a spin-coating method and then converted to pentacene by heating or illumination of UV light [4, 5]. However, pentacene film formation by this precursor method requires a multi-step synthesis with a low purity and a relatively high-temperature conversion process (>200 °C). A functionalized pentacene, 6,13-bis(triisopropylsilylethynyl) (TIPS) pentacene, is a promising candidate because it has sufficient solubility in common organic solvents. In addition, the bulky functionalized groups in TIPS-pentacene help to disrupt the face-to-edge herringbone structure in unmodified pentacene, which leads to a predominant cofacial π-stacking structure, thereby efficiently maximizing a π-orbital overlap [6, 7]. The 1,2,3,4-tetrahydronaphthalene (Tetralin) solvent used in this study is a hydrocarbon having a chemical formula of $C_{10}H_{12}$. It has been reported that the use of an appropriate solvent with a high boiling point had a positive effect on the film morphology, the molecular ordering of the OSCs and the corresponding electrical properties [8]. The boiling point of Tetralin is 207 °C, which is higher than the boiling point of commonly used organic solvents such as chlorobenzene (132 °C), anisole (155 °C) and toluene (111 °C).

In our previous research, we reported on the fabrication of solution-processed OTFTs with TIPS-pentacene as the OSC and siloxane-based spin-on glass (SOG) as the inorganic gate dielectric [9]. However, the device performance was inferior and the substrate was a rigid silicon wafer ruling out its use in solution-processing techniques based on low-cost polymeric substrates. The use of an organic gate dielectric is likely to be an important element in organic electronics. Among the various organic gate dielectrics, a cross-linked poly-4-vinylphenol (PVP) is receiving considerable attention [10–13]. In this paper, we report on the fabrication and the characterization of high-performance OTFTs with TIPS-pentacene as a solution-processed OSC, the PVP polymer as a gate dielectric and polyethersulphone (PES) as a flexible substrate.

2. Experimental details

Figures 1(*a*) and (*b*) exhibit the molecular structures of TIPS-pentacene and PVP, respectively. As shown in the cross-sectional SEM image of figure 1(*c*). the OTFTs with an inverted staggered (bottom-gate and top-contact) configuration were fabricated on a 150 nm thick indium-tin oxide (ITO, sheet resistance ~10.0 ohm/sq) gate electrode, which was sputtered on a 100 μm thick PES substrate. A 750 nm thick cross-linked PVP film served as a gate dielectric. To prepare a PVP solution, the PVP powder (Sigma-Aldrich, Mw ~20 000) was mixed with 13 wt% of propylene glycol monomethyl ether acetate (PGMEA) and then we added the cross-linking agent, poly melamine-co-formaldehyde methylated (Sigma-Aldrich, Mw ~511), to the PVP solution with a ratio of 1:20. To form a PVP dielectric film, the PVP solution was coated on the PES substrate with an ITO electrode and a curing process was conducted at 200 °C for 10 min on a hot plate to enforce the cross-linking of the PVP polymer. For the active layer, a 200–800 nm thick TIPS-pentacene film was deposited on the PVP dielectric by drop casting from a 4 wt% and 8 wt% solution with the Tetralin solvent. We employed the drop-casting technology for forming the TIPS-pentacene film because the drop-casted TIPS-pentacene film showed large grains and a high degree of molecular ordering [7]. Finally, the 200 nm thick Au source and drain electrodes were evaporated through a shadow mask to minimize the contact resistance between the TIPS-pentacene film and the Au electrodes and to create the corresponding efficient carrier injection. For a comparison, we also fabricated TIPS-pentacene TFTs with a 250 nm thick thermally grown silicon dioxide (SiO_2) as a gate dielectric and a highly doped p-type silicon wafer (resistivity: <0.005 ohm cm) as a rigid substrate. The surface morphology and the structural property of the TIPS-pentacene film on the PES substrate with the PVP dielectric were studied with atomic force microscopy (AFM, XE-100) and x-ray diffraction (XRD, D/max 2200 V) spectroscopy in the symmetric reflection coupled θ–2θ arrangement with a

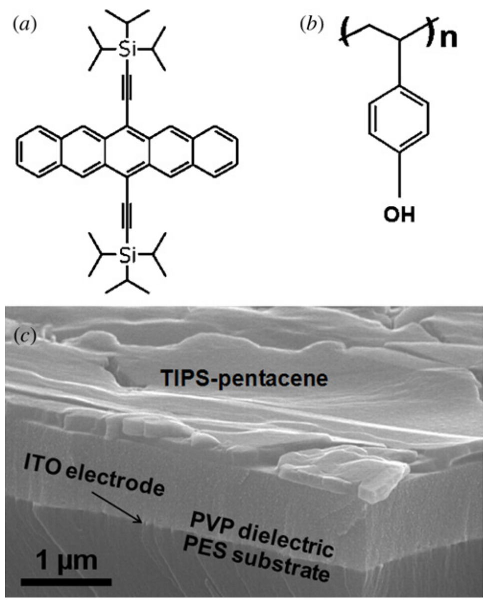

Figure 1. The molecular structures of (*a*) TIPS-pentacene, (*b*) PVP and (*c*) the cross-sectional SEM image of TIPS-pentacene TFTs with an inverted staggered (bottom-gate and top-contact) configuration.

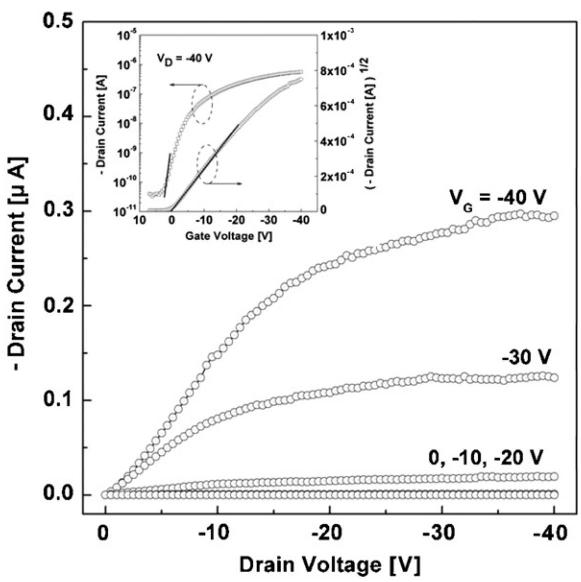

Figure 2. Output characteristics (I_D–V_D) for an OTFT with a TIPS-pentacene film deposited on a silicon wafer substrate by drop casting from an 8 wt% TIPS-pentacene solution with Tetralin. The inset shows the transfer characteristics ($\log_{10}(-I_D)$–V_G (squares) and $\sqrt{-I_D}$–V_G (circles)) in the saturation regime at a drain voltage (V_D) of −40 V.

Cu Kα_1 radiation ($\lambda_{K\alpha 1} = 1.54$ Å) x-ray source. All current–voltage (*I*–*V*) characteristics of our OTFTs were measured by a semiconductor characterization system (Keithley SCS 4200) in a dark box.

3. Results and discussions

Figure 2 shows a typical output characteristics (I_D–V_D) for an OTFT with an OSC active channel deposited on a

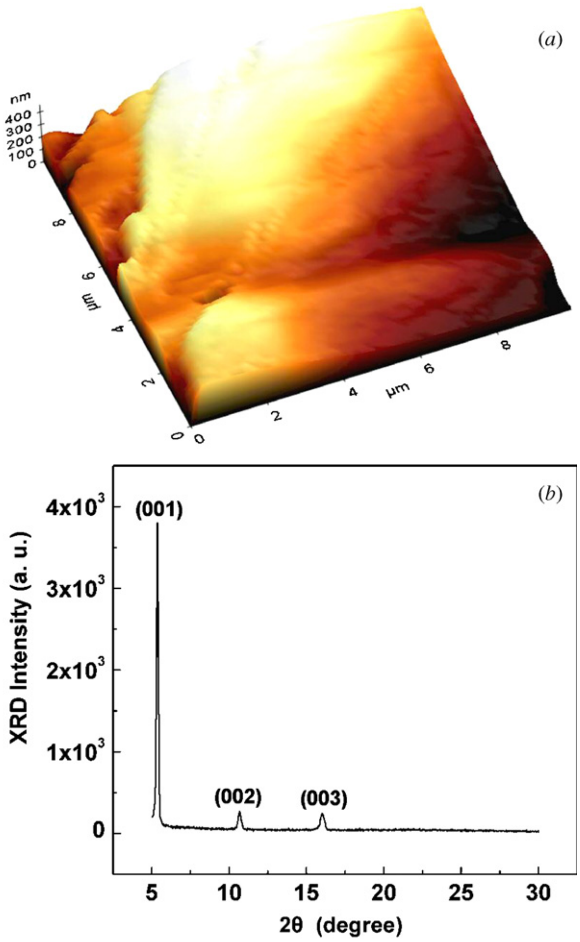

Figure 3. (*a*) The AFM image and (*b*) the XRD spectra for the TIPS-pentacene film deposited on a PVP dielectric by drop casting from a 4 wt% TIPS-pentacene solution with Tetralin. The AFM image is $10 \times 10\ \mu m^2$.

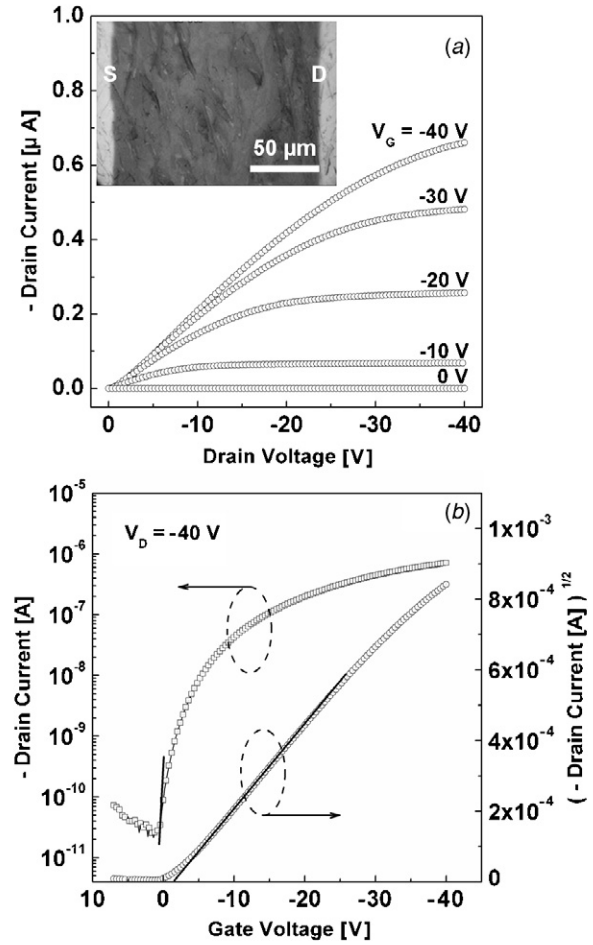

Figure 4. (*a*) The output characteristics (I_D–V_D) for an OTFT with a TIPS-pentacene film deposited on a PVP dielectric on a PES substrate by drop casting from a 4 wt% TIPS-pentacene solution with Tetralin. The gate voltage (V_G) ranges from 0 V to −40 V in 10 V steps. The inset shows the optical image of the TIPS-pentacene film between the source and drain electrodes. (*b*) The transfer characteristics ($\log_{10}(-I_D)$–V_G (square) and $\sqrt{-I_D}$–V_G (circle)) were obtained at a drain voltage (V_D) of −40 V.

silicon wafer substrate by drop casting from a 8 wt% TIPS-pentacene solution with Tetralin. The inset figure shows the transfer characteristics ($\log_{10}(-I_D)$–V_G and $\sqrt{-I_D}$–V_G) in the saturation regime at a V_D of −40 V. The gate voltage (V_G) was swept from 0 V to −40 V. The curves exhibited the typical p-type transistor behavior in an accumulation mode. The electrical characteristics of OTFTs were determined from the $\log_{10}(-I_D)$–V_G and $\sqrt{-I_D}$–V_G curves in the inset. This device displayed electrical characteristics including a saturation field effect mobility (μ_{sat}) of 1.99×10^{-2} cm^2 V^{-1} s^{-1}, a subthreshold slope (SS) of 2.12 V/dec, a current on/off ratio of 10^5 and a threshold voltage (V_{th}) of 0.5 V. Without any modification of the dielectric and the electrode surface, the electrical characteristics of the device showed encouraging performance [14].

Figure 3 shows that the AFM image and the XRD spectra explain the surface morphology and structural property of the TIPS-pentacene film deposited on the PVP dielectric by drop casting from a 4 wt% TIPS-pentacene solution. The AFM image in figure 3(*a*) demonstrated that the large crystals of TIPS-pentacene film with a surface roughness (root mean square) of 92.38 nm were grown directly on the PVP surface. The bright area in the image indicates that the molecular growth is inclined in the perpendicular direction. As shown in figure 3(*b*), the XRD spectra exhibited a series of (0 0 *l*) diffraction peaks, indicating a well-organized molecular structure that coincided with a high degree of molecular ordering for a solution-deposited OSC film. The sharp peak was observed at 5.36° corresponded to a layer-by-layer separation of 16.2 Å, which was nearly consistent with the result obtained in an investigation by Anthony *et al* [15]. The OSC film formation and the device performance are strictly influenced by the surface energy and the surface roughness of the dielectric film [16–18]. So, the interface property between the TIPS-pentacene and the dielectric film is very important. Because the triisopropylsilyl functionalized groups of the TIPS-pentacene are hydrophobic, the TIPS-pentacene film was well formed on the PVP dielectric that has hydrophobic (low surface energy of 34 mJ m^{-2}) and flat (surface roughness of 0.58 nm) surface properties.

Figure 4 shows the I_D–V_D output characteristics for several gate voltages and the $\log_{10}(-I_D)$–V_G and $\sqrt{-I_D}$–V_G transfer characteristics for $V_D = -40$ V for an OTFT with an OSC active channel deposited on a PVP dielectric by drop casting from a 4 wt% TIPS-pentacene solution with Tetralin. The channel width and length were 1500 μm and 150 μm, respectively. The inset (optical image) in figure 4(*a*) shows that the TIPS-pentacene film on the PVP dielectric has large grain bridges across both the source and drain electrodes, which are oriented so that carriers need not encounter several grain boundaries while traversing the channel. As shown in figure 4(*a*), there is a good saturation state at high V_D indicating a depletion region in the active layer. But, the I_D–V_D output characteristics show the saturation current limitation at high V_G and the nonlinear I_D–V_D characteristic at low V_D. This result is probably related to 'contact limitation' between the electrode and the TIPS-pentacene film [7]. From the transfer curves ($\log_{10}(-I_D)$–V_G and $\sqrt{-I_D}$–V_G) in figure 4(*b*), the electrical characteristics, such as a μ_{sat}, an on/off current ratio and a V_{th}, are extracted. The device has a μ_{sat} of 2.08×10^{-2} cm^2 V^{-1} s^{-1}, a current on/off ratio of 10^5 and a V_{th} of -2 V. Most notably, the excellent subthreshold slope (SS) was found to be 0.86 V/dec, as observed in the $\log_{10}(-I_D)$–V_G curve. The sharpness of the field effect inception is determined by the SS, which shows the trap behavior and the interface quality between the OSC and the gate dielectric. Therefore, the significant improvement in the SS could be attributed to a decreased interface trap density at the PVP/TIPS-pentacene interface. We obtain the maximum interface trap density (N_{SS}) of 6.63×10^{11} cm^{-2} eV^{-1} given by equation (1),

$$N_{\mathrm{SS}} = \left[\frac{\mathrm{SS}\,\log(e)}{kT/q} - 1\right]\frac{C_{\mathrm{area}}}{q}. \qquad (1)$$

From this result, we can explain that the fully-cured cross-linked PVP dielectric might have only a minimal density of the hydroxyl radical (OH) and internal impurities, so the remnant dipole effects become minimized and then the interfacial carrier traps could be effectively reduced [19]. Although the saturation field effect mobility of TIPS-pentacene TFTs on the PES substrate has an inferior performance compared with the performance obtained by other groups, dielectric surface modification using a self-assembled monolayer (SAM) will give rise to a considerable improvement in the electrical performance of TFTs based on solution-processed TIPS-pentacene [7]. However, the SAM treatment has some disadvantages because the SAM treatment requires a long immersion time, and the solvent may destroy the polymer dielectric and substrate. These properties are not compatible with the OTFTs' fabrication method using the polymer materials. In fact, further optimization of the device performance and development of the amelioration method which is consistent with the OTFTs' fabrication are required.

4. Conclusions

We demonstrate the solution-processed fabrication and operation of high-performance TIPS-pentacene TFTs using a spun PVP dielectric and a polymeric substrate for flexible applications. The TIPS-pentacene film on the PVP surface showed a well-organized molecular structure which coincided with the high degree of molecular ordering. A flexible OTFT using a solution process is found to have a saturation field effect mobility of 2.08×10^{-2} cm^2 V^{-1} s^{-1} and an excellent subthreshold slope of 0.86 V/dec. These performances are comparable to vacuum-deposited pentacene TFTs. It is foreseeable that high-performance flexible OTFTs with solution-processed OSCs and gate dielectrics will be fabricated by printing technologies such as the ink-jet and roll-to-roll process.

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