

Organic thin-film transistors with reduced photosensitivity

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Abstract

Organic thin-film transistors with a minimal threshold voltage shift and a more stable photocurrent under illuminated conditions can be made by embedding titanium dioxide (TiO₂) nanoparticles into a polymer dielectric layer. While the studies of pentacene morphology using atomic force microscopy and X-ray diffraction have shown similar results before and after embedding the TiO₂ into the dielectric layer, it has been found that the presence of TiO₂ nanoparticles is essential. The reduced photosensitivity can be attributed to the recombination centers induced by the TiO₂ nanoparticles and this can enhance substantially the recombination process of the electrons trapped in the channel.

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1. Introduction

Currently, there is increased interest in thin-film transistors made of organic materials due to their great potential applications in low-cost and flexible electronics, such as smart cards, radio-frequency identification (RFID) tags and paper-like displays [1–6]. A level of performance by organic thin film transistors (OTFTs) comparable to that of amorphous silicon (a-Si) has been achieved. For example, a field-effect mobility higher than 1 cm²/V s and with several orders of on–off ratio has been demonstrated for OTFTs based on pentacene. While the

intrinsic properties of organic semiconductors and the device physics of OTFTs have been studied extensively, their reliability and photoresponse levels have not received much attention until recently [7–12]. Moreover, methods to lower photosensitivity and to improve device stability have received considerably less attention.

On the other hand, the photosensitivity of OTFTs is a critical issue for driving applications in displays, such as liquid-crystal displays (LCDs) [12]. For instance, pentacene has high level of photo absorption in the visible range, which is due to its high oscillator strength and low energy between its highest occupied molecular orbital (HOMO) and its lowest unoccupied molecular orbital (LUMO): around 1.7 eV. Therefore, light from backlight modules may pass through the OTFTs and cause

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a serious threshold voltage (V_{th}) shift [12]. As a result, OTFTs usually cannot be turned off effectively when the gate bias is set at zero under illumination [10–12]. In this work, one method to reduce photosensitivity and to enhance device stability has been reported. To put it simply, by blending the polymer dielectrics with titanium dioxide (TiO_2) nanoparticles, the V_{th} shift is minimized and the output current becomes more stable under white light illumination. This improvement can be attributed to the recombination centers induced by the TiO_2 nanoparticles. Moreover, by reducing the photosensitivity, the pentacene-based OTFTs has the potential to drive the circuits without a noticeable V_{th} shift and with no light shield. Finally, the device reported in this work will greatly facilitate the making of more reliable transparent organic electronics: an area which has received much attention recently [13,14].

2. Experimental

Titanium oxide with a rutile structure ($k = 114$) was used as the high-dielectric component in the nanocomposite dielectrics [15,16]. The device structure is shown in Fig. 1a. Poly-4-vinylphenol (PVP) and poly(melamine-co-formaldehyde) methylated were dissolved in propylene glycol monomethyl ether acetate (PGMEA), blended with TiO_2 nanoparticles, whose surface was further modified with organosiloxane to enhance their solubility (Ishihara Sangyo Kaisha LTD., Japan) [16]. The solution was then spin-coated onto the indium-tin-oxide (ITO) patterned glass substrates and ITO was used as the gate electrodes. The resulting film was further thermally annealed to 200 °C. Then, the thermally evaporated pentacene was used as the semiconducting layer for the OTFTs. Next, gold was thermally

evaporated as the source and drain electrodes. The channel length (L) and width (W) of the devices were 100 and 2000 μm , respectively. To suppress the degradation of the on-off ratio after adding the nanoparticles, the insulator was further over-coated with a very thin-layer of poly(α -methylstyrene) (P α MS) by spin-coating from a diluted toluene solution (0.1 wt%). Due to the robustness of the cross-linked polymers, the underlayer was not affected by this process [16]. The film thickness and roughness were measured using a DI 3100 series atomic force microscope (AFM). The current-voltage (I - V) characteristics of the OTFTs were measured with a HP 4156A semiconductor parameter analyzer. The illumination light source was a standard Hg lamp. All measurements were performed under the atmosphere.

3. Results and discussion

The transfer characteristics of the devices before and after the modification of the P α MS are shown in Fig. 2a. The extracted mobility of the PVP device following the conventional field effect transistor model is $0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The threshold voltage and subthreshold slope are 0.5 V and 2.9 V/decade, respectively. Initially, the on-off ratio was about 1.0×10^4 , but after the addition of a thin layer of the low- κ material, P α MS, the subthreshold swing became smaller, the on-off ratio was improved by one order; while the mobility was almost unchanged.

The controllable threshold voltages and turn-on voltages in pentacene TFTs have been demonstrated by using different organosilanes with various functional groups as the self-assembled monolayers (SAMs) on the SiO_2 insulators [17,18]. To quantify the device characteristics, the turn-on voltage (V_{to})

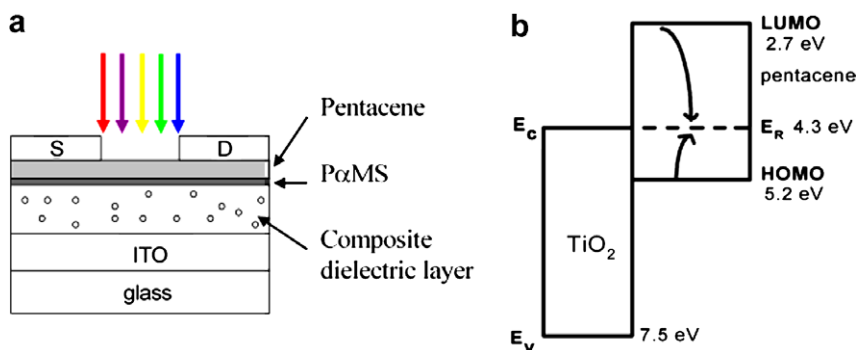


Fig. 1. (a) The device structure of the OTFTs in this study and (b) energy band diagram of pentacene and TiO_2 .

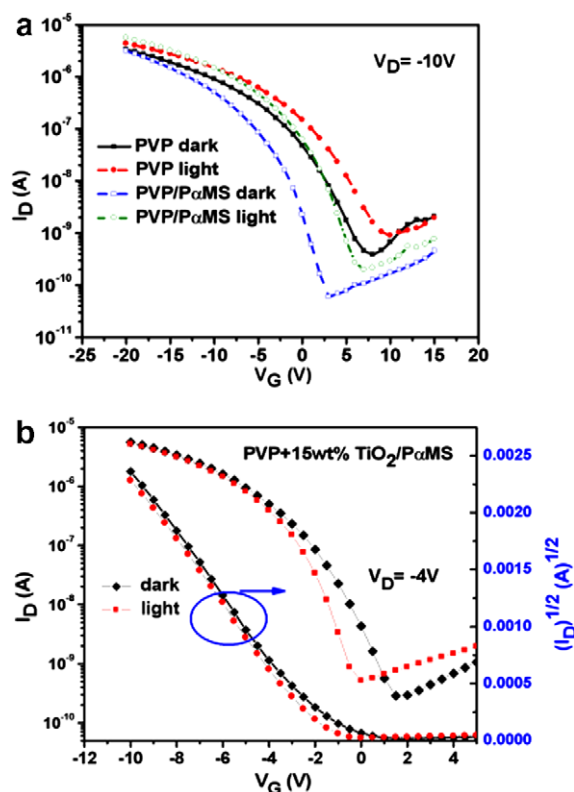


Fig. 2. Transfer curves for devices in the dark and under illumination with (a) cross-linked PVP and cross-linked PVP/P α MS double layers as the dielectric insulators and (b) PVP + 15 wt% TiO₂ as the gate insulator.

is defined as the gate voltage at which the drain current starts to increase exponentially; while the transistor is in a flat-band position [18,19]. The built-in electric field resulting from the polar SAM molecules induces mobile charges which alters the threshold voltage [17,18]. In this study, the water contact angle on the cross-linked PVP surface is 69.0°, while the angle on P α MS is 86.7°. This indicates that cross-linked PVP is much more polar than P α MS. Similarly, the high polarity of cross-linked PVP, which is attributable to its hydroxyl groups, may also explain the high surface polarization which causes the higher mobile charge density. Consequently, as shown in Fig. 2a, the V_{th} and V_{to} are more positive when compared with those of devices with a P α MS thin-film. Such phenomena suggest the presence of a dipole field at the pentacene/dielectrics interface [18]. However, after applying a low- κ P α MS onto the PVP, the V_{to} shifts from 7.5 V to 2.5 V. This change implies a lower free charge density at the interface. The non-polar properties of P α MS prevent surface polarization, thereby reduc-

ing the charge density in the conducting channel at $V_g = 0$ V.

While the device was under white illumination (10 mW/cm²), the threshold voltages and V_{to} of both the devices shifted toward the position direction, the off-current became stronger (Fig. 2a). In addition, the subthreshold swings also increased. It has been suggested that the photogenerated electron–hole pairs increase the off-state current dramatically [11,12]. However, while the holes can flow out through the drain electrode under the electrical field, the electrons may be trapped at the grain boundaries of the pentacene, and/or the insulator/pentacene interface, resulting in a positive shift in the V_{th} [11,12].

A change in the behavior of the devices was observed upon blending the TiO₂ nanoparticles into the gate dielectrics. Fig. 2b shows the transfer characteristics of the device in the dark and under illumination. In the dark, the threshold voltage becomes lower because of the use of an insulator with a higher dielectric constant, while the subthreshold swing also decreases to about 1 V/decade. Such phenomena are quite consistent with previous reports on OTFTs with adopted high- κ insulators [5]. Upon illumination, instead of a positive shift, the V_{to} comes closer to 0 V, the subthreshold swing becomes even better. The changes of the V_{th} and subthreshold swing are exactly *opposite* to those of the devices with PVP and PVP/P α MS (Fig. 2a) as the gate dielectrics. The electric parameters of the devices have been summarized in Table 1.

To explain the different behaviors of the devices represented in Fig. 2, several experiments have been conducted which attempt to identify the possible mechanisms involved. First, from the surface morphology analysis using an AFM, it has been shown that the morphology of pentacene is quite similar on the surfaces of both the neat cross-linked PVP and the nanocomposite with the thin P α MS film (Fig. 3) [16]. Furthermore, the X-ray diffraction patterns of the pentacene deposited on the neat cross-linked PVP, the P α MS, the nanocomposite with additional PVP, the P α MS, all reflect the so-called “thin-film” phase structure [20]. Consequently, the morphology change is not likely to be the mechanism which causes the different device behaviors upon blending the nanoparticles.

The above mentioned observation is also probably due to the processes occurring at the ITO–insulator interface. In order to determine whether the effect is due to the interface, heavy n-type doped

Table 1
Electrical parameters in this study

Device	Mobility (cm ² /V s)	Dielectric constant	Insulator thickness (nm)	Ci (nF/cm ²)	V _{th} (V)	S.S. (V/decade)	On–off ratio
PVP dark	0.10 ± 0.02	4.3 ± 0.1	290	13.1	0.5	2.9	9 × 10 ³
PVP light	0.10 ± 0.02	4.3 ± 0.1	290	13.1	4.5	3.2	4 × 10 ³
PVP/PαMS dark	0.13 ± 0.02	4.2 ± 0.1	290	12.8	−4.3	1.8	9 × 10 ⁴
PVP/PαMS light	0.14 ± 0.01	4.2 ± 0.1	290	12.8	0.2	2.1	5 × 10 ⁴
PVP/TiO ₂ /PαMS dark	0.40 ± 0.05	10.5 ± 0.3	270	34.1	−2.8	1.1	5 × 10 ⁴
PVP/TiO ₂ /PαMS light	0.40 ± 0.05	10.5 ± 0.3	270	34.1	−2.9	0.9	2 × 10 ⁴

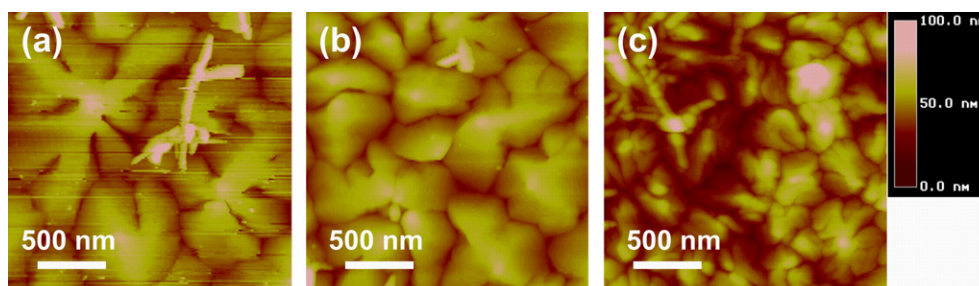


Fig. 3. AFM images of pentacene on (a) cross-linked PVP, (b) PaMS/cross-linked PVP and (c) PaMS/TiO₂ nanoparticles + cross-linked PVP.

Si and SiO₂ were used in the devices as the gate electrode and the dielectrics, respectively (Fig. 4). The SiO₂ surface was further modified with a nanocomposite (15% TiO₂ in PVP)/PαMS bi-layer. However, the device with TiO₂ exhibited similar behavior (that is, a negligible V_{th} shift), which implies that the mechanism is not relevant to the different processes of the gate electrodes. On the other hand,

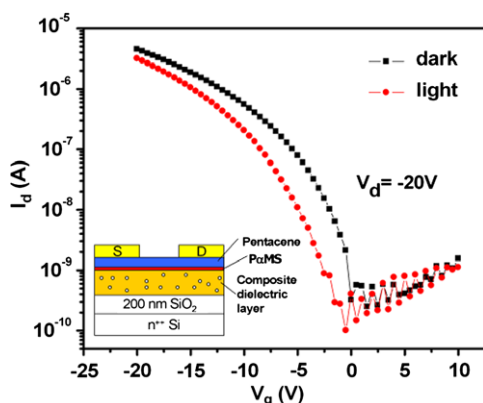


Fig. 4. Transfer characteristics of the device with n-doped Si/SiO₂ as the substrate in the dark and under illumination. The inset shows the device structure.

the present of TiO₂ nanoparticles in the gate insulator seems essential to minimize the effect of white illumination for the device.

The results strongly indicate that the blending of TiO₂ nanoparticles is an important part of the mechanism. The present of TiO₂ nanoparticles probably induces the recombination of the centers in the channel. As seen in Fig. 1b, because of the conduction band of TiO₂ and/or the energy levels induced locate between the HOMO and LUMO of the pentacene, they may behave like recombination centers; thereby releasing the trapped electrons. Consequently, upon illumination, the excess electrons can be eliminated more easily and the V_{th} shift is suppressed.

Stress tests on the three different devices were also performed to further understand the effects of the TiO₂ nanoparticles. The typical stress-test results of the devices, both in the dark and under illumination, used in this study are shown in Fig. 5. For the device with a neat cross-linked PVP as an insulator, the field-induced current and/or photocurrent increased steadily over time. This result was consistent with the previous report [8,12]. It has already been indicated that the absorption of water molecules in cross-linked PVP enhances surface polarization, thus

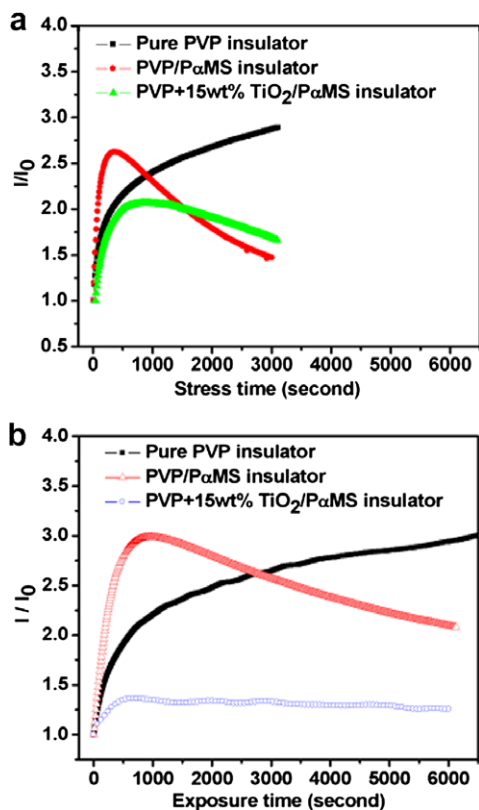


Fig. 5. The normalized time-dependent current of the devices (a) in the dark; and (b) under illumination. The devices with PVP and PVP/P α MS as the dielectric layers were biased at $V_g = -10$ V and $V_d = -10$ V; while the device with 15 wt% TiO₂ nanoparticles was measured at $V_g = -5$ V and $V_d = -4$ V.

the accumulation of extra charges increases the current and results in a positive shift of V_{th} [8]. However, after modification with P α MS, the current increased initially, but then, decreased with time. Since P α MS is non-polar, the surface polarization probably was found to be inhibited. In addition, it was also found that the hydrophobic P α MS may also retard water absorption. Consequently, after the initial sharp increase, the increase of photocurrent is relieved and the current decreases again, probably due to the natural device decay [8].

On the other hand, a more stable current was observed after the introduction of TiO₂ nanoparticles in the dark (Fig. 5a). Furthermore, upon white-light illumination, although an initial increase in photocurrent was also observed, the magnitude was much smaller (Fig. 5b). The device only exhibited a very small current decay. The more stable photocurrent may further confirm the presence of recombination centers introduced by the TiO₂

nanoparticles dispersed in the organic insulator; the latter can suppress the electron trapping. Without the recombination centers, the trapped electrons will cause a dramatic increase in current.

4. Conclusion

It has been shown that the issues of light sensitivity and V_{th} shift can be overcome by blending TiO₂ nanoparticles into the polymer dielectrics. The more stable photocurrent and minimized V_{th} shift can be attributed to the recombination centers induced by the doping of the TiO₂ nanoparticles. The energy levels deep in the energy gap and away from the HOMO and LUMO of the pentacene can serve as the recombination centers, which, in turn, can enhance substantially the recombination process in the OTFTs.

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