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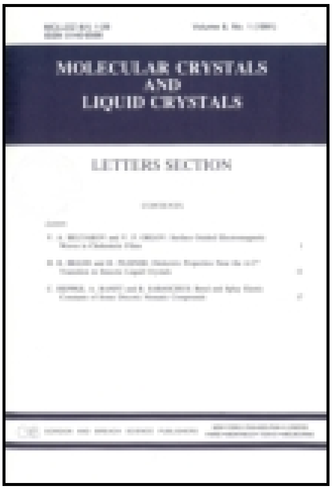

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Novel Crosslinked PVA Without Photoinitiator for Organic Passivation Layers of Pentacene Thin-Film Transistors

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We report a new polyvinyl alcohol (PVA)-tetraethoxysilane (TEOS) hybrid layer to protect an organic thin-film transistor (OTFT). PVA/TEOS hybrid thin film was successfully fabricated through hydrolysis and condensation mechanism. The surface roughness of PVA/TEOS film was measured by atomic force miscroscophy (AFM) and it showed a good surface roughness with a root-mean-squae value of about 0.23 nm. Thermally crosslinked PVA with TEOS was successfully adaped as a solution processable passivation layer for pentacene TFT. In case of well known photo-crosslinked PVA/ammonium dichromater (ADC) passivation, extremely large initial performance drop (almost 52% mobility drop) was observed after passivation. PVA/TEOS hybrid passiavtion, however, no significant initial performance drop was found after passivation process. In addition, pentacene TFT with PVA/TEOS passivation layer exhibited very stable TFT operation with almost no field mobility drop or threshold voltage shift up to 980 h.

Keywords Polyvinyl alcohol (PVA); passivation; organic thin-film transistor

Introduction

Organic thin-film transistors (OTFTs) show promise as the critical components for low-cost, flexible electronics with various applications including smart cards, electronic identification tags, and active matrix displays [1–10]. Although the performance of OTFTs has improved remarkably during the last decade, the degradation of electrical performance in ambient air is a significant problem to realize commercial devices based on OTFTs. Therefore, the passivation of the OTFTs is necessary to elongate its lifetime by protecting the organic active layer from the adsorption of oxygen and moisture in ambient air [11–15]. Several passivation approaches for OTFT using organic materials have been reported. Researchers from IBM have reported the passivation of pentacene TFT with parylene, which is based on the vacuum deposition method [16]. Unfortunately there are few reports for solution-processed passivation of OTFT, because the solvent for organic passivation can damage OTFT devices such as organic semiconductors. Sheraw and Jackson *et al*. have reported water-based PVA

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to protect pentacene TFT, which is used as a backplane in active matrix liquid crystal displays [17]. Han *et al.* reported the passivation material using a PVA/photoacryl double layer for pentacene TFT [18]. Recently, Lee *et al.* reported multi-passivation layers with PVA/PVA/photoacryl for pentacene TFT to drive AMOLED [19]. Until now, solution-processable organic materials for OTFT passivation (as the first passivation layer in contact with the organic semiconductor layer) has been water-based polyvinyl alcohol (PVA), because only polar solvent like water do not damage organic semiconductor layers due to the large differences of surface energy. Usually, the ammonium dichromate ($NH_4Cr_2O_{7,}$ ADC) was used as a photosensitizer for PVA crosslinking reaction [17]. However, there are several problems should be solved. (a) The photosensitizer could be an impurity in passivation layer, (b) UV irradiation for the initiation of crosslinking reaction could damage organic semiconductor, (c) Cr^{6+} ion released during the reaction is extremely harmful to the environment, and (d) after the crosslinking reaction, hydroxyl group of PVA still remains, this still can absorb the moisture.

In this paper, we introduce thermally crosslinked PVA with TEOS for the passivation layer of an organic thin-film transistor. The chemical structure and surface morphology of PVA/TEOS hybrid layer were investigated by FT-IR and AFM, etc. The electrical properties and lifetime of the pentacene TFTs with a PVA/TEOS passivation layer were systematically studied.

Experiments

Materials and TFT Device Fabrication

Pentacene (98% purity) was selected as the active layer in this study and was purchased from Aldrich Chemical Co. and used without any further purification. 1,1,1,3,3,3-Hexamethyldisilazane (HMDS, 99.9% purity) and polyvinyl alcohol (PVA) were also obtained from the same company and used as received. As thermal crosslinking agent of PVA, tetraethoxysilane $Si(OC_2H_5)_4$ (TEOS, >99%) and ammonium dichromate (ADC) were used. The geometry of the pentacene OTFTs in the passivation study was the top-contact structure. Each OTFT device contained a heavily doped n-type Si wafer as a gate electrode with a 60-nm-thick, thermally grown SiO_2 layer as a gate insulator. To improve the properties of the interface between SiO_2 and the pentacene organic semiconductor, HMDS was spin-coated on top of the SiO_2 insulator with a spinning speed of 3000 rpm. A 60-nm-thick layer of pentacene was deposited on top of the HMDS-treated SiO_2 through a shadow mask by thermal evaporation at a pressure of 10^{-6} torr. The evaporation rate of the pentacene was 1Å/s, and the substrate temperature was maintained at 90°C during deposition. The pentacene OTFTs were then completed by thermally evaporating a 60-nm-thick source and drain gold electrodes on top of the pentacene layer through a shadow mask with a channel length (L) of 50 μm and a width (W) of 1000 μm.

Crosslinking and Passivation Process of PVA with TEOS

Polyvinyl alcohol (PVA) solution was prepared in 10 wt% concentration in DI water and filtered by a 0.45 μm pore size membrane filter, and then some amount of 1M HCl solution was added to adjust pH as about 2.0. Under steady stirring, 0.94 g (10 mol% to PVA) of TEOS was gently added to previously prepared PVA acid solution at room temperature. For comparison, the PVA/ADC passivation layer was also prepared. To same prepared PVA solution, 3.0 wt% of ammonium dichromate (ADC) to PVA was added. Homogeneous PVA/TEOS and PVA/ADC solution were prepared and pentacene TFT devices were passivated using PVA/TEOS or PVA/ADC solution by the spin-coating method at a spin speed of 1000 rpm. A PVA/TEOS coated pentacene TFT device was heated for 2 min at 50°C and for 60 min at 100°C to complete the PVA and TEOS crosslinking reaction. In case of PVA/ADC passivation, a spin-coated film was annealed 2 min at 50 °C and for 2 min at 100°C and exposed to 365 nm UV light for photo-crosslinking with 90 mJ/cm^2 exposure dose. And further thermal annealing for 60 min was down for a PVA/ADC passivated device for almost equal thermal treatment condition compared with a PVA/TEOS passivated device. The final film thickness of the passivation layers of each device was adjusted as about 0.5 μm. After the passivation process, devices were stored in a humidity chamber to maintain constant humidity and temperature as 60% and 20°C, respectively.

Characterizations

The thickness of each pentacene, PVA/TEOS, and PVA/ADC film was determined using an alpha-step (KLA-Tencor α-step DC 50) surface profiler. Atomic force microscopy (AFM) images were obtained with a Digital Instrument Nanoscope IV operating in tapping mode in air. The FT-IR spectrum was obtained with a Bio-Rad Digilab Division FTS-165 spectrometer after dispersing the sample in KBr. The contact angles of water on the polymer films were determined with a PEONIX 300 contact angle analyzer. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCA-LAB 200R X-ray photoelectron spectrometer with a monochromatic Al Kα source. The electrical performance of output (I_{ds} vs. V_{ds}) and transfer (I_{ds} vs. V_{gs}) of the OTFTs were measured using an Agilent E5272 semiconductor parameter analyzer. All electrical measurements of the devices were carried out in air.

Results and Discussion

A schematic cross-sectional view of the passivated pentacene TFT device with top contact configuration is shown in Figure 1(a); Figure 1(b) is a schematic representation of the crosslinking reaction between PVA and tetraethoxysilane (TEOS). Chemical structures of PVA/TEOS and pure PVA films were investigated by FT-IR spectrum (now shown here). Major vibration bands (Si-O-Si, $\nu = 1089$ and 445 cm^{-1}; Si-OH, $\nu = 952$ cm^{-1}) associated with TEOS reactions of hydrolysis and condensation added to PVA polymer solution [20]. Also, in the frequency range from 3000 to 3700 cm^{-1}, mainly related to hydroxyl groups, a broader band was noted for PVA/TEOS hybrid spectrum compared to pure PVA. Such result is believed to be due to the TEOS sol-gel reactions that have altered PVA chains tridimensional structure. By introducing of Si-OH and Si-O-Si through hydrolysis and condensation reactions of TEOS has modified PVA semi-crystalline structure. Before investigating electrical properties of PVA/TEOS passivated TFT devices, we also checked the surface roughness of PVA/TEOS passivation layer. Surface roughness is important property of the passivation layer, because subsequent processes are applied on top of the passivation layer when preparing a real array device [21]. The surface roughnesses were investigated by AFM measurement and compared with PVA/ammonium dichromate (ADC) passivation layer. AFM images of PVA/ADC and PVA/TEOS films on top of 60-nm-thick pentacene were compared as shown in Figure 2. In both cases, the surface roughness was

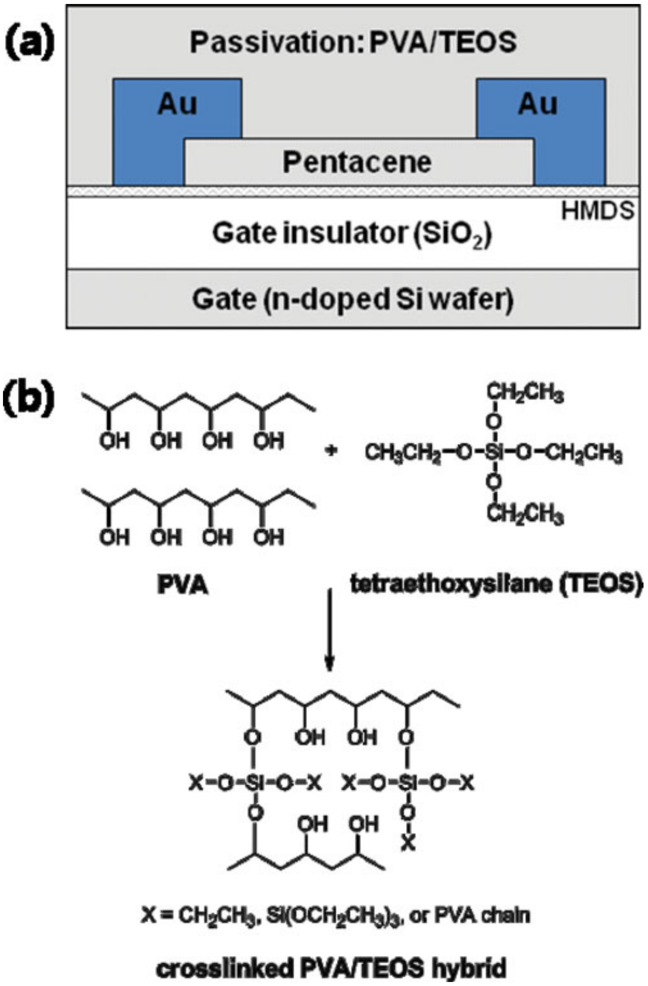

Figure 1. (a) Schematic (a) cross-sections of the PVA/tetraethoxysilane (TEOS) passivated pentacene thin-film transistor and (b) representation of PVA crosslinking reaction with TEOS.

about less than 0.50 nm (PVA/ADC: 0.347 nm, PVA/TEOS: 0.233 nm). About 0.233 nm of surface roughness of PVA/TEOS layer is quite acceptable for subsequent processes. The surface atomic composition of PVA/TEOS passivation layer was also studied by means of XPS measurements. Small but apparent Si 2p (99.7 eV) peak in the spectrum of PVA/TEOS film clearly confirmed the presence of network of PVA and TEOS. Figure 3 shows transfer characteristics of pentacene TFTs in a deposited state; transfer characteristics were also measured after PVA/ADC and PVA/TEOS passivation. All pentacene TFT devices showed a similar mobility, 0.25–0.27 cm^2/Vs, in the pentacene deposited state (before passivation). There are significant performance changes, however, after passivation. We found a substantial on-current drop after PVA/ADC passivation as shown in Figure 3(a). In case of pentacene TFT with the PVA/TEOS passivation layer (Figure 3(b)), however, there was almost no current drop and even a slightly increased [18, 22]. The performance

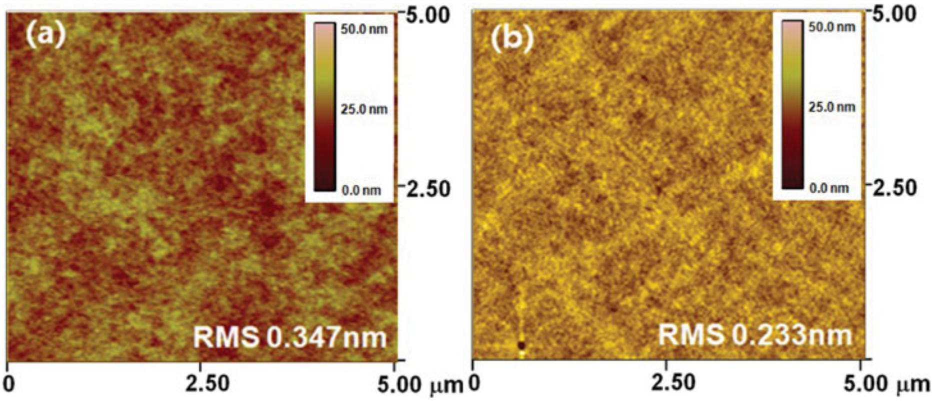

Figure 2. Atomic force microscopy images (5 μm x 5 μm) of (a) PVA/ADC and (b) PVA/TEOS films on 60-nm-thick pentacene film.

parameters of all pentacene TFT devices were extracted from transfer characteristics (for drain current vs. gate voltage, I_{ds} vs. V_{gs}) shown in Figure 3. The field effect mobility (μ) was extracted from a plot of $I_{ds}{}^{1/2}$ vs. V_{gs} in the saturation regime based on the following equation:

$$\mathrm{I}_{ds} = \frac{WC_i}{2L}\mu\left(V_{gs} - V_T\right)^2 \tag{1}$$

where C_i and V_T are the capacitance per unit area of the gate SiO_2 layer and the threshold voltage, respectively. After PVA/ADC passivation, mobility decreased from 0.27 cm^2/Vs to 0.13 cm^2/Vs. This is almost a 52% drop in performance compared to the pentacene deposited device. Passivation experiments were conducted on four pentacene TFT devices including 12 TFT channels (one device has three TFT channels in our device structure) and we observed always initial performance drop between 50~60% as compared with the performance of as pentacene deposited state. UV irradiation for PVA/ADC passivation can cause the damage to organic semiconductor and TFT performance. However, the pentacene OTFT devices passivated with the PVA/TEOS exhibited no mobility drop and even a slight improvement in field effect mobility after passivation from 0.25 cm^2/Vs to 0.26 cm^2/Vs. We always got similar results as performance improvement between 0% and 5% compared with as pentacene deposited state. It is unclear, however, why this mobility improvement occurred. In some reports, however, on-and off-current sometimes increased slightly. Those reports explained that this increase occurred because of the doping effect induced by oxygen in ambient air or PVA solution. In our case, however, off current nearly unchanged after passivation; as depicted in Figure 3(b), passivation increased (slightly) only the on-current level. To check the lifetime of the pentacene TFT devices with PVA/TEOS passivation, the field effect mobilities of PVA/TEOS passivated pentacene TFT devices were measured for nearly 980 h (the real measurement data) as shown in Figure 4. In our previous study, usually without passivation layers, pentacene TFT showed a significant drop in mobility with time, device failure occurred at about 290 h [21]. PVA/TEOS passivated pentacene TFT, however, did not any significant mobility drops and the other performance parameters of pentacene TFTs with PVA/TEOS passivation were almost unchanged up to 980 h. There are no limitations for additional processes like double or triple passivation layers

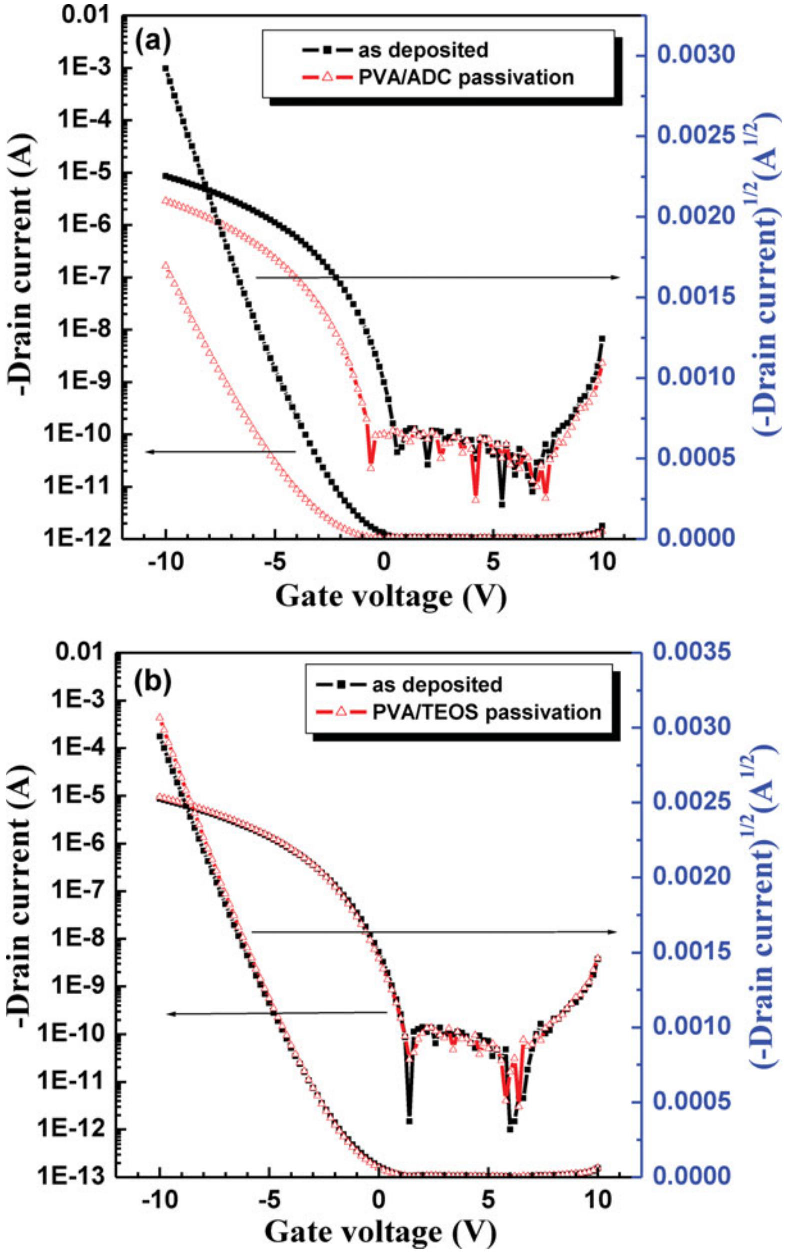

Figure 3. Transfer characteristics (for drain current vs. gate voltage, I_{ds} vs. V_{gs} and $I_{ds}{}^{1/2}$ vs. V_{gs}) of pentacene OTFTs before and after (a) PVA/ADC and (b) PVA/TEOS passivation.

on top of PVA/TEOS passivation layers with photoacryl or other materials, which further improve the barrier property and protect the OTFT device from water and oxygen. In any case, we strongly believe that a PVA/TEOS could be used as an excellent first passivation layer in contact with an organic semiconductor layer in an OTFT device without any TFT performances drop.

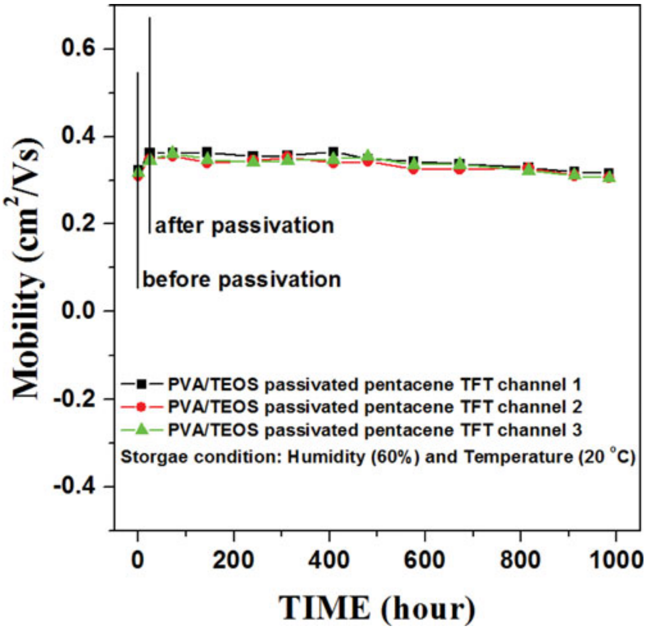

Figure 4. Field effect mobility changes up to 980 h of three PVA/TEOS passivated pentacene TFT channels.

Conclusion

We have prepared a novel solution processable hybrid material to protect organic thin-film transistor (OTFT) using a polyvinyl alcohol (PVA) and tetraethoxysilane (TEOS) as a crosslinking agent. The crosslinked structure of PVA/TEOS layer was identified by FT-IR study. The surface of PVA/TEOS passivation layer was very smooth with a root mean square (RMS) value of about 0.23 nm obtained by AMF analysis and found to be suitable for a passivation layer. A pentacene TFT device with a conventional PVA/ammonium dichromate (ADC) passivation showed almost about 52% large drop in field effect mobility after passivation. However, the pentacene TFT device showed no significant initial performance drop and even slightly improved after passivation with a PVA/TEOS passivation. In addition, pentacene TFT with PVA/TEOS passivation showed no field effect mobility changes almost up to 980 h. Compared to conventional PVA/ADC system, our PVA/TEOS hybrid material could be a better candidate as a solution processable passivation layer for OTFTs.

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