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Hye Jung Suk [a], Mi Hye Yi [a] & Taek Ahn [b]
[a] Advanced Materials Division, Korea Research Institute of Chemical Technology, Yuseong-gu, Daejeon, Korea
[b] Department of Chemistry, Kyungsung University, Nam-gu, Busan, Korea
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Thermally Crosslinked Polyvinyl Alcohol (PVA) Layers for the Passivation of Pentacene Thin-Film Transistors

HYE JUNG SUK,[1] MI HYE YI,[1,*] AND TAEK AHN[2,*]

[1]Advanced Materials Division, Korea Research Institute of Chemical Technology, Yuseong-gu, Daejeon, Korea
[2]Department of Chemistry, Kyungsung University, Nam-gu, Busan, Korea

We report a new crosslinked polyvinyl alcohol (PVA) layer to protect organic thin-film transistors (OTFTs) using the glutaraldehyde (GA) as a crosslinking agent. After thermal crosslinking reaction of PVA with GA, the water contact angle was increased from 9.8° to 55.1° as more hydrophobic state. This clearly means that hydroxyl group of PVA surface was disappeared by the crosslinking reaction. Thermally crosslinked PVA/GA was successfully adapted as solution processable passivation layer for pentacene TFT. In case of well known photo-crosslinked PVA/ammonium dichromate (ADC) passivation, extremely large initial performance drop (almost 52% mobility drop) was observed after passivation. PVA/GA passivation, however, only 3.8% initial mobility drop was found after passivation process. In addition, pentacene TFT with PVA/GA passivation layer exhibited very stable TFT operation with almost no field effect mobility drop or threshold voltage shift up to 1100 h.

Keywords Organic thin-film transistor; passivation; polyvinyl alcohol (PVA)

Introduction

Organic thin-film transistors (OTFTs) have been demonstrated as promising candidates for flexible displays, smart cards, memory, and sensors due to light weight, low-cost processing, and mechanical flexibility [1–3]. All components of a TFT such as semiconductors, gate insulators, and even electrodes are being replaced by organic materials. However, to realize a real array device such as an active matrix display using OTFT, the passivation of OTFT is the most important process, especially by solution-processable materials for low-cost devices. The performance of OTFTs degrades significantly in air, therefore, the passivation of the OTFT is necessary to elongate its lifetime by protecting the organic active layer form environmental moisture and oxygen [4,5]. 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 [6]. 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 to protect pentacene TFT, which is used as a backplane in active matrix liquid crystal displays [7]. Han et al.

*Corresponding authors' contact details: Tel.: 82-51-663-4632; Fax: 82-51-628-4628. E-mail: mhyi@krict.re.kr; taekahn@ks.ac.kr

reported the passivation material using a PVA/photoacryl double layer for pentacene TFT [8]. Recently, Lee et al. reported multi-passivation layers with PVA/PVA/photoacryl for pentacene TFT to drive AMOLED [9]. 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 [4]. 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 could absorb moisture.

In this paper, we introduce thermally crosslinked PVA using glutaraldehyde (GA) as a crosslinking agent [10] for the passivation layer of organic thin-film transistors. The chemical structure and surface morphology of PVA/GA layer were investigated by FT-IR and AFM, etc. The electrical properties and lifetime of the pentacene TFTs with a crosslinked PVA/GA passivation layer were systematically studied.

Experiments

1. 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 and photo crosslinking agent of PVA, glutaraldehyde (GA, 25% aqueous solution) 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.

2. Crosslinking and Passivation Process of PVA with Glutaraldehyde (GA)

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 8.3 wt% of glutaraldehyde (GA) or 3.0 wt% of ammonium dichromate (ADC) to PVA was added to PVA solution. Homogeneous PVA/GA or PVA/ADC solution was prepared and pentacene TFT devices were passivated using PVA/GA or PVA/ADC solution by the spin-coating method at a spin speed of 1000 rpm. PVA/GA coated pentacene TFT devices were heated at 100°C for PVA

crosslinking for 20 min. In case of PVA/ADC, the spin-coated films were annealed at 100°C for 2 min and exposed to 365 nm UV light for photo-crosslinking with 90 mJ/cm^2 exposure dose. And further thermal annealing for about 20 min was done for PVA/ADC passivated devices for equal thermal treatment condition compared with PVA/GA passivated devices. The final film thickness of the passivation layer was 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.

3. Characterization

The thickness of each pentacene and PVA/GA 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. 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 Fig. 1(a); Fig. 1(b) is a schematic representation of the crosslinking reaction between PVA and glutaraldehyde (GA). Chemical structures of PVA/GA and pure PVA films were investigated by FT-IR spectrum as shown in Fig. 2. The relative increase of the C=O band of PVA/GA at 1740 cm^{-1} indicates that the aldehyde groups of GA did

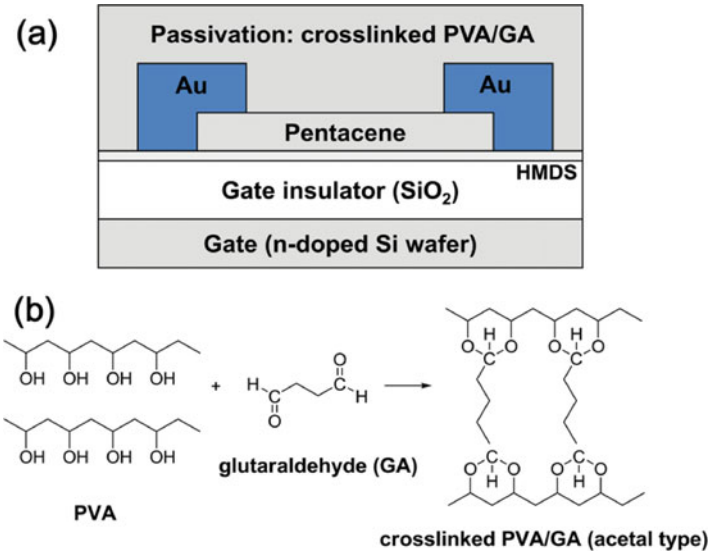

Figure 1. Schematic (a) cross-sections of the PVA/glutaraldehyde (GA) passivated pentacene thin-film transistor and (b) representation of PVA crosslinking reaction with GA.

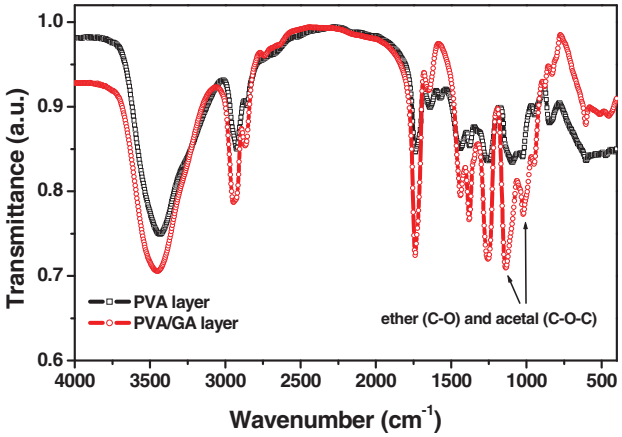

Figure 2. FT-IR spectra of pure PVA and PVA/GA.

not completely react with O-H groups of PVA chain. In addition, a broader absorption band (from $\nu = 1013$ to 1128 cm^{-1}) was found, which can be attributed to the ether (C-O) and the acetal ring (C-O-C) bands formed by the crosslinking reaction of PVA with GA (Fig. 1(b)). Therefore, it can be assumed that GA has acted as chemical crosslinker among PVA polymer chains. Before investigating electrical properties of PVA/GA passivated TFT devices, we also checked the surface roughness of PVA/GA 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. The surface roughnesses were investigated by AFM measurement and compared with PVA/ammonium dichromate (ADC) passivation layer. AFM images of PVA/ADC and PVA/GA films on top of 60-nm-thick pentacene were compared. Figure 3 shows, in both cases, the surface roughness was about less than 0.50 nm (PVA/ADC: 0.46 nm, PVA/GA: 0.45 nm). About 0.45 nm of surface roughness of PVA/GA layer is quite acceptable for subsequent processes. Figure 4 shows images of the water contact angle on the pure PVA and crosslinked PVA/GA layer. As can

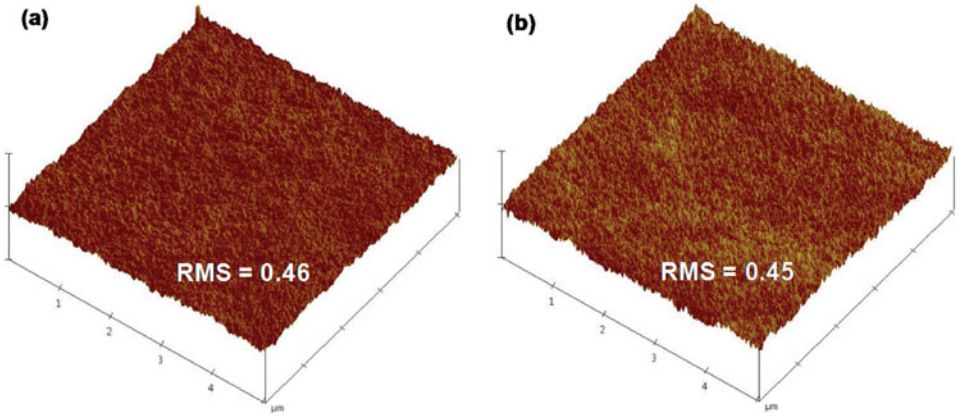

Figure 3. Atomic force microscopy 3D height images (5 μm $\times$ 5 μm) of (a) PVA/ADC and (b) PVA/GA films on 60-nm-thick pentacene film.

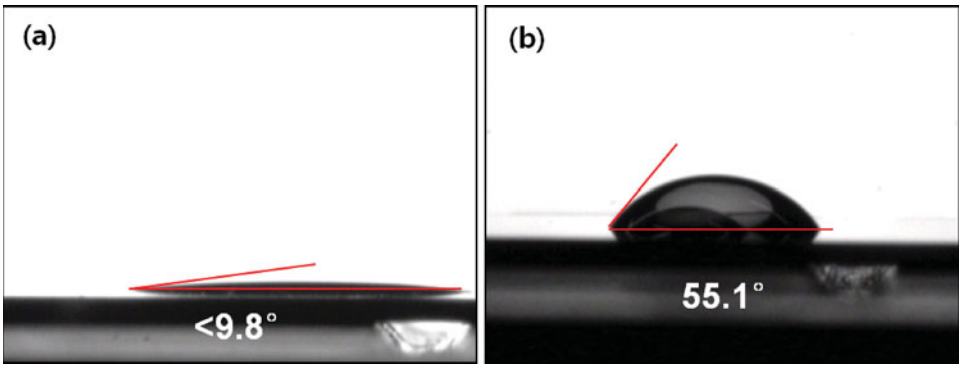

Figure 4. Optical microscopy images of a water drop on the surface of (a) pure PVA and (b) PVA/GA layer.

be seen in Fig. 4(a), water contact angle on the PVA layer is very low and is even hard to measure. The result is not unusual because PVA has a hydroxyl group in the polymer side chain and easily absorbs water. Therefore, the surface of PVA is in an extremely hydrophilic state. As is well known, water is a key factor in the degradation of OTFT devices [11.12]. Nevertheless, PVA is widely used for passivation in OTFT, at least as a 1st passivation layer in contact with the organic semiconductor layer because polar solvents like water do not damage organic semiconductor layers [13]. However, for extended lifetime of the TFT device, the surface of the passivation layer should be hydrophobic and should be densely packed. After the crosslinking reaction PVA with GA, the surface is changed into a more hydrophobic state (water contact angle: 55.1°) as shown in Fig. 4(b). It clearly means that the hydroxyl group of the pure PVA is reacted with GA and the surface of PVA layer is changed into more hydrophobic state. The contact angle of the surface of PVA/ADC film also showed somewhat hydrophobic state (water contact angle 43.2) than that of pure PVA. It is clear that the hydroxyl group still remains after crosslinking reaction between PVA and ADC, however the connections of PVA main chain by crosslinking reaction might be the reason for the change of surface hydrophobicity of PVA/ADC film.

Figure 5 shows transfer characteristics of pentacene TFTs in a deposited state; transfer characteristics were also measured after PVA/ADC and PVA/GA passivation. All pentacene TFT devices showed a similar mobility, 0.26–0.27 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 Fig. 5(a). In case of pentacene TFT with the PVA/GA passivation layer (Fig. 5(b)), however, there was almost no current drop. The performance parameters of all pentacene TFT devices were extracted from transfer characteristics (for drain current vs. gate voltage, I_{ds} vs. V_{gs}) shown in Fig. 5. 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:

$$I_{ds} = \frac{WC_i}{2L}\mu(V_{gs} - V_T)^2, \tag{1}$$

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

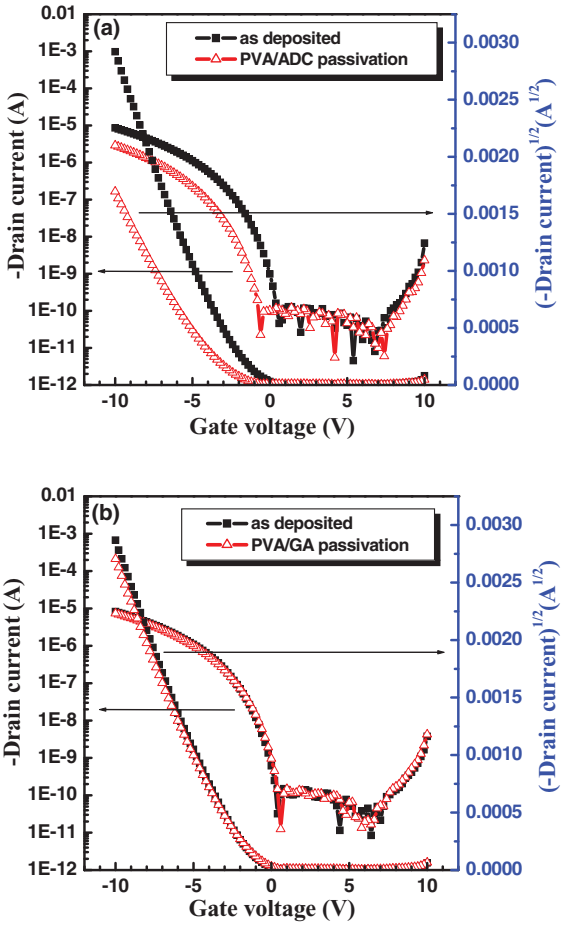

Figure 5. Transfer characteristics (for drain current vs. gate voltage, I_{ds} vs. V_{gs} and $I_{ds}^{1/2}$ vs. V_{gs}) of pentacene OTFTs before and after (a) PVA/ADC and (b) PVA/GA passivation.

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. However, the pentacene OTFT device passivated with the PVA/GA exhibited almost no mobility drop after passivation from 0.26 cm^2/Vs to 0.25 cm^2/Vs (only 3.8% mobility drop). To confirm reproducibility, we did PVA/GA passivation experiment over more than four pentacene TFTs (more than 12 channels) and we always obtained similar results as performance drops only between 0% to 4% compared with as pentacene deposited state. In case of PVA/ADC passivation, UV irradiation should be down for the photosensitization of ADC and this can cause the damage to organic semiconductor and TFT performance. In our previous passivation study [13], usually without passivation layers, pentacene TFT showed a significant drop in mobility with time, device failure occurred at about 290 h. To check the lifetime of the pentacene TFT devices with PVA/GA passivation, the field effect mobilities of four pentacene TFT devices with PVA/GA passivation were measured for nearly 1100 h (the real measurement data) as shown in Fig. 6. We did not observe any significant mobility drops and the

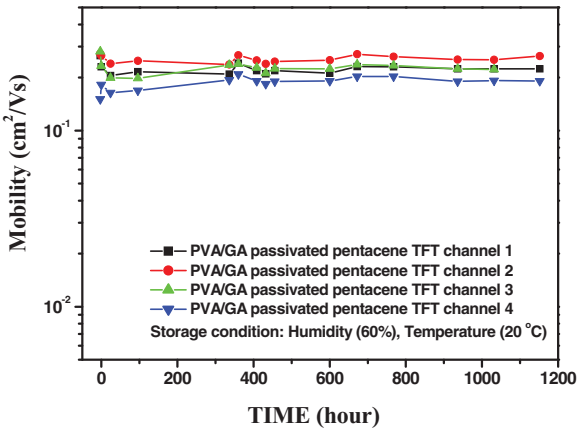

Figure 6. Field effect mobility changes up to 1100 h of four PVA/GA passivated pentacene TFT channels.

performance of pentacene TFT with PVA/GA passivation was almost maintained. There are no limitations for additional processes like double or triple passivation layers on top of PVA/GA passivation layers with photoacryl material 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/GA passivation layer could be used as a excellent first passivation layer to protect OTFT from oxygen and water.

Conclusion

We have prepared a novel organic passivation material to protect organic thin-film transistor (OTFT) using a polyvinyl alcohol (PVA) and glutaraldehyde (GA) as a crosslinking agent. The crosslinked structure of PVA/GA layer was identified by FT-IR study. A very smooth surface roughness with a root mean square (RMS) value of about 0.45 nm of the surface of PVA/GA layer was also identified by AFM 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 after passivation with a crosslinked PVA/GA material. In addition, pentacene TFT with PVA/GA passivation showed no field effect mobility changes almost up to 1100 h. In terms of environmental stability, no photosensitizer, and more hydrophobic surface compared to conventional PVA/ADC system, our PVA/GA material could be a better candidate as a solution processable passivation layer for OTFTs.

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