Organic Passivation Material-Polyvinyl Alcohol (PVA)/Layered Silicate Nanocomposite-for Organic Thin Film Transistor

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Abstract

We have synthesized novel organic passivation materials to protect organic thin film transistors (OTFTs) from H_2O and O_2 using polyvinyl alcohol (PVA)/layered silicate (SWN) nano composite system. Up to 3 wt% of layered silicate to PVA, very homogeneous nanocomposite solution was prepared.

1. Introduction

Organic thin-film transistors (OTFTs) have been demonstrated as promising candidates for flexible displays, smart cards, memory and sensors. These applications with organic electronics offer many advantages, such as light weight, low cost processing, and mechanical flexibility [1~4]. On the other hand, organic devices also have some significant shortcomings, such as relative low mobility and performance degradation due to moisture (H_2O) and oxygen (O_2) [5,6]. Most of researches have been focused on the mobility improvement and now the mobility of OTFT is almost the same as that of amorphous silicon thin-film transistor (TFT) or even higher. However to realize the real array device such as active matrix display, the passivation of OTFT is the most important process, especially by solution processable materials for all organic devices. Unfortunately there are not so many candidates for organic passivation because organic passivation solution can damage the OTFT device such as organic semiconductor. Most frequently used organic material for OTFT passivation is polyvinyl alcohol (PVA) in water to be safe to organic semiconductor layer by the effect of large difference of surface energy [7]. In our works, we have tried the modification of PVA passivation layer by nanocomposite approach with synthetic smectite clays to improve the barrier property of PVA layer to oxygen and moisture.

2. Experimental

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) was also obtained from the same company and used as received. The geometry of the pentacene OTFTs investigated in our postfabrication thermal annealing 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, which was cleaned using the general cleaning process for electronic applications: sonication in detergent, acetone, isopropyl alcohol and deionized water in that order, for 20 min at room temperature, and then drying in a convection oven. HMDS was spin coated with a spinning speed of 3000 rpm on top of the SiO_2 insulator to improve the properties of the interface between SiO_2 and the pentacene organic semiconductor. The baking conditions were 120 ^{o}C for 10 min. 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 $1x10^{-6}$ torr. The evaporation rate of the pentacene was 1 Å/s and the substrate temperature was maintained at 90 ^{o}C during deposition. The pentacene OTFTs were then completed by thermally evaporating 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.

Polyvinyl alcohol was purchased from Aldrich Chemical Co. and used without purification. Polyvinyl alcohol (PVA) solution was prepared as 10 wt% concentration in DI water and filtered by 0.45 um pore size membrane filter and then hydrophilic layered silicate (SWN: synthetic smectite) (3 wt%) was added to PVA solution. Homogeneous and transparent PVA/SWN nanocompostie solution was prepared and OTFT device was passivated using PVA/SWN solution by spin coating method at spinning speed of 1000 rpm. Passivated OTFT devices were annealed at 50 ^{o}C and 100 ^{o}C for 10 min at each temperature, then DI water was removed in vacuum oven at 50 ^{o}C for 6 hrs. Final film thickness of passivation layer was measured as about 1.0 µm.

3. Results and discussion

Before investigating electrical properties of passivated OTFT devices, we first checked film forming property, surface roughness, uniformity of PVA/SWN nanocomposite solution. All these properties were compared with well known PVA passivation layer. Coating property of PVA/SWN solution and surface smoothness of passivation film were investigated by AFM measurement. Figure 1 show the AFM images of PVA only and PVA/SWN passsivation film on pentacene. In both cases, surface roughness is about 1.1 nm and there were no big differences in film forming property

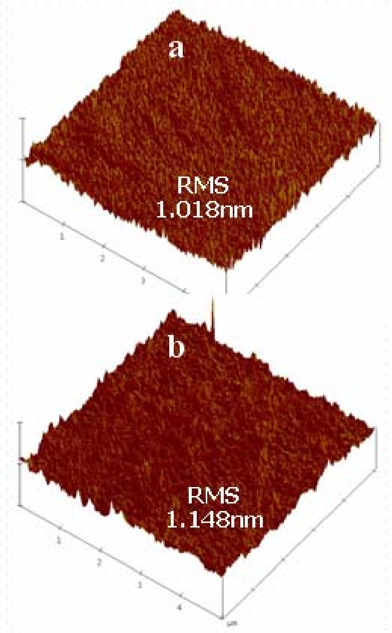

Fig. 1. AFM images of (a) PVA and (b) PVA/layered silicate film on pentacene.

Figure 2 show the TEM images of PVA (a) and PVA/SWN (b). We observed layered silicate (SWN) is well distributed in PVA. SWN is known having a dimension with about 300 nm width, but in TEM images, average width of SWN is below 300 nm. This means that layered silicate (SWN) is not positioned parallel to substrate. Above 3 wt% layered silicate, we didn’t get the homogeneous PVA/SWN nanocomposite solution.

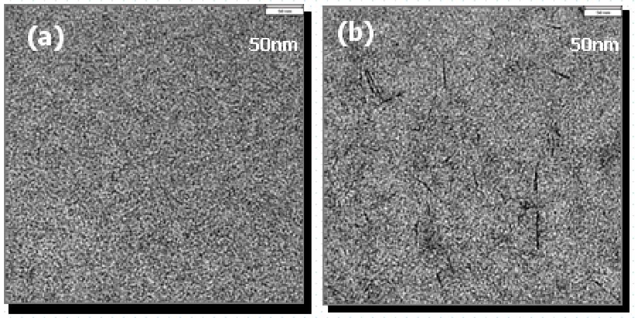

Fig. 2. TEM images of (a) PVA and (b) PVA/layered silicate film.

To evaluate passivation property of PVA/layered silicate nanocomposite, first we have prepared three pentacene OTFT devices. One is pentacene only deposited device and others are pentacene OTFTs with PVA and PVA/SWN nanocomposite passivation layer, respectively. Clearly, there are performance differences of each devices, so we selected specific devices that show similar TFT performances as first pentacene deposited state. After passivation, we stored OTFT devices at ambient air. Figure 3 and 4 show transfer and output curves of pentacene OTFTs as deposited state and also transfer and output characteristics were measured after PVA passivation and PVA/SWN nanocomposite passivation. All pentacene OTFT devices showed almost similar mobilities as 0.35 ~ 0.37 cm^{2}/Vs as deposited state (before passivation). But there are significant performance changes after passivation. Normally, optimal state of pentacene is damaged by H_2O based PVA passivation in many other reports, so there should be large initial performance drop after passivation. We found also on substantial on-current drop after PVA passivation. However, in the case of PVA/layered silicate passivated pentacene OTFT, there was almost no on current drop and even slightly increased. We measured transfer characteristics of three OTFT devices (without passivation, PVA passivation, PVA/layered silicate passivation) as time.

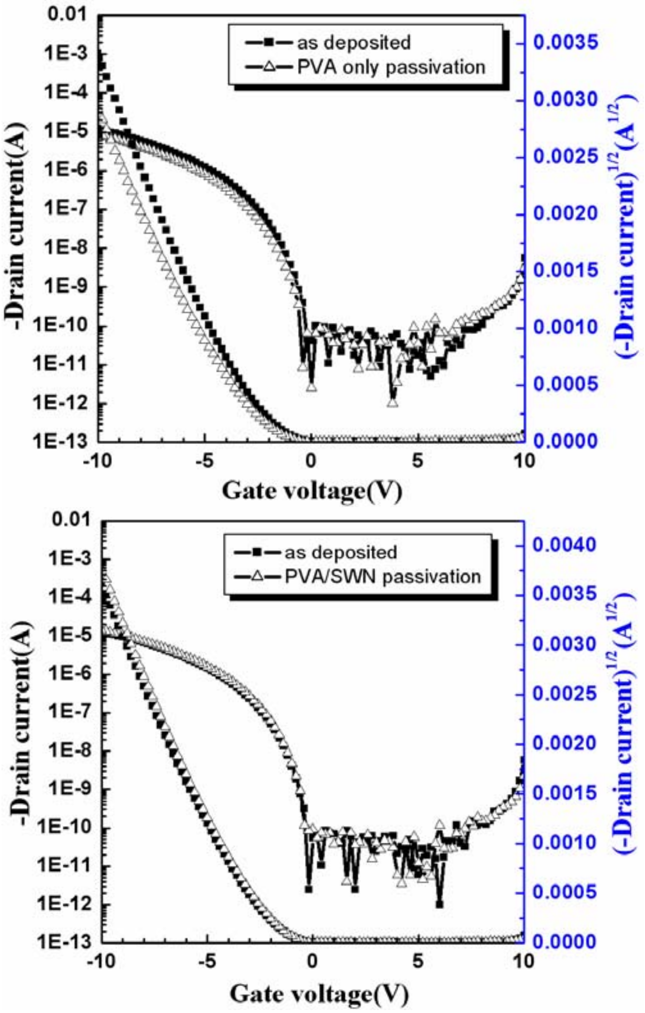

Fig. 3. Transfer characteristics (I_{ds} vs V_{gs} and $I_{ds}^{1/2}$ vs V_{gs}) of pentacene OTFT as deposited state, with PVA and with PVA/layered silicate passivation.

The performance parameters of OTFT devices with and without passivation were extracted from transfer the characteristics curves (for drain current vs gate voltage, I_{ds} vs V_{gs}) shown in Figure 3. The field effect carrier mobility (μ) was extracted from a plot of $I_{ds}^{1/2}$ versus V_{gs} in the saturation regime based on the following equation:

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

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 passivation, mobility was decreased from 0.35 cm^2/Vs to 0.27 cm^2/Vs. It is almost 25 % performance drop compared to as deposited state device.

In the case of non-passivated device, there is also mobility drop from 0.36 cm^2/Vs to 0.31 cm^2/Vs, it just came from the degradation of device in air as time goes by. Pentacene OTFT device passivated with PVA/SWN nanocomposite exhibited slight performance improvement after passivation. In other reports also, several results show that on- and off-currents were sometimes increased slightly [7,8]. They explained that this can be happened by the doping effect induced by oxygen in ambient air or PVA solution. However, in our case, off current was nearly unchanged after passivation, only on current level was slightly increased from OTFT device passivated with PVA/SWN.

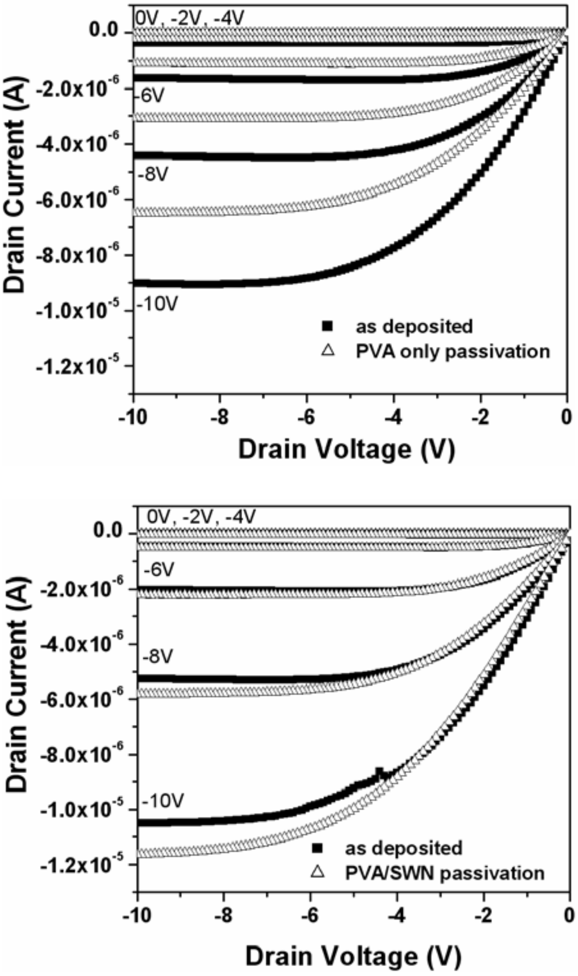

Fig. 4. Output characteristics (for drain current vs. drain voltage, I_{ds} vs V_{ds}) of OTFTs with and without passivation

Figure 5 show the mobility changes of pentacene OTFT device as time going of without passivation, PVA passivtaion and PVA/SWN nanocomposite passivation. Even up to 80 hrs in ambient air, there is no mobility drop as compared to as pentacene deposited state.

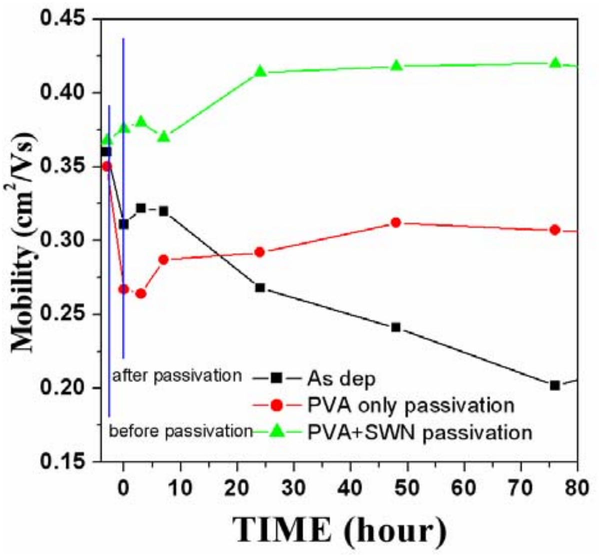

Fig. 5. Mobility changes of pentacene OTFTs with and without organic passivation.

Non-passivated pentacene device usually affected from O_2 and H_2O. Although pentacene is highly hydrophobic, H_2O molecules can easily diffuse in the crevices between the pentacene grains and interact with the trapped carriers by altering the electric field at the grain boundaries. Therefore, mobility of accumulated charges in the transistor channel decreases (in Figure 5, As dep.), which in turn reduces also the saturation current. Meanwhile, when the transistor is in the off state, that means with zero gate voltage, trapped H_2O increased the conductivity between source and drain. In the case of passivated pentacene device with PVA/SWN nanocomposite, on/off current ratio and field-effect mobility remained almost constant and even slightly increased up to 80 hrs. One possible explanation is that layered silicate in PVA nanocomposite acts as barrier toward H_2O and O_2. And also fabrication and thermal annealing processs of passivation layer to remove the solvent of H_2O are also important for long term stability of OTFT device. Further deep investigation of the effect of PVA/layered silicate passivation is under progressing.

4. Summary

We have synthesized novel organic passivation materials to protect organic thin film transistors (OTFTs) from H_2O and O_2 using Polyvinyl alcohol (PVA)/layered silicate (SWN) nano composite system. Up to 3 wt% of layered silicate to PVA, very homogeneous nanocomposite solution was prepared. Pentacene OTFT device showed no significant initial performance drop after passivation with PVA/layered silicate nanocomposite and even mobility was slightly improved. But PVA only passivated OTFT device showed 25 % of field effect mobility drop after passivation. PVA/layered silicate nanocomposite also formed smooth film layer by spin coating method with surface roughness below 1.1 nm. We propose layered silicate containing PVA nanocomposite film can be used as good organic passivation layer in OTFT.

5. References

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