Stable Encapsulated Organic TFT With a Spin-Coated Poly(4-Vinylphenol-Co-Methyl Methacrylate) Dielectric

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***Abstract*—The influences of encapsulation on the hysteresis and the gate-bias-stress effects (both positive and negative gate bias stresses) of pentacene organic thin-film transistors (OTFTs) with poly(4-vinylphenol) and poly(4-vinylphenol-co-methyl methacrylate) (PVP-PMMA) gate dielectrics are investigated. The encapsulation and the use of less polar gate dielectrics like PVP-PMMA copolymers are both important to suppress moisture adsorption and to obtain a stable pentacene OTFT. Compared to the air-stable OTFT with a fluoropolymer dielectric, the stable encapsulated OTFT with a PVP-PMMA dielectric is a low-cost promising candidate for mass production consideration.**

***Index Terms*—Bias stress, pentacene, poly(4-vinylphenol-co-methyl methacrylate) (PVP-PMMA), reliability, thin-film transistor.**

I. Introduction

ORGANIC thin-film transistors (OTFTs) are attracting intensive attention for their potential applications in flexible low-cost electronic circuits due to their advantages, such as lightweight, low cost, and flexibility [1]–[5]. Polymer gate dielectrics are the most promising candidates to be used in OTFTs because of their solution processability and low process temperature [3]–[10]. Among the family of polymer gate dielectrics, poly(4-vinylphenol) (PVP) has been reported most frequently because of its high device performance [3]–[6]. However, the remaining hydroxyl groups ($-$OH groups) in PVP dielectric films easily attract water to cause slow polarization, severe hysteresis [3]–[5], and considerable threshold voltage shifts (ΔV_T) during gate bias stress [6], [7]. Recently, amorphous fluoropolymer has been proposed to serve as the gate dielectric to fabricate air-stable OTFTs [7], [8]. The hysteresis and the bias stress effects (BSEs) are eliminated because the fluoropolymer contains no $-$OH groups and is highly water repellent. However, adding fluorine element into polymer significantly increases the material cost. To develop a low-cost polymer gate dielectric for a stable OTFT, poly(4-vinylphenol-co-methyl methacrylate) (PVP-PMMA) is reported to successfully fabricate hysteresis-free pentacene OTFTs [9], [10]. The methyl methacryl moiety in PMMA is less polar than the phenol moiety in PVP, and the insertion of methyl methacryl groups into the PVP polymer backbone suppresses water adsorption on the dielectric and reduces the number of free $-$OH groups. However, the BSEs for pentacene OTFT using PVP-PMMA have never been discussed. Moreover, encapsulation methods like depositing encapsulation layers or sealing devices with cavity-formed encapsulation glass are reported to effectively isolate devices from air [1], [11]. Since the instability due to $-$OH groups is strongly related to water adsorption, it is important to study the influences of encapsulation on hysteresis and on BSEs.

In this letter, we fabricate pentacene OTFTs using PVP and PVP-PMMA as gate dielectrics. We investigate the hysteresis, the positive gate BSEs, and the negative gate BSEs of the devices when devices are exposed to air or sealed with cavity-formed encapsulation glass. An excellent stability for encapsulated pentacene OTFT with a PVP-PMMA gate dielectric is demonstrated. After a gate bias stress of 10 000 s, a small ΔV_T below 0.5 V is obtained.

II. Experimental

A 50-nm-thick aluminum metal is evaporated through the shadow mask onto the glass substrate to form the metal gate. Four-hundred-nanometer-thick PVP (Aldrich, $Mw \sim 20\,000$) and PVP-PMMA (Aldrich) are spin coated on substrates. For the PVP dielectric, poly(melamine-co-formaldehyde) (PMF) is utilized as a cross-linking agent, and the propylene glycol monomethyl ether acetate is used as the solvent. The weight ratio between PVP and PMF is 11:4, and the film is baked at 200 °C for 1 h. For PVP-PMMA, no cross-link agent is added, the N, N-dimethylformamide is used as the solvent, and the baking condition is 150 °C for 1 h. Then, unpurified pentacene obtained from Aldrich was evaporated through a shadow mask onto the dielectric with a deposition rate of 0.5 Å/s at room temperature. After the formation of a 50-nm-thick pentacene, 70-nm-thick gold was deposited through the shadow mask to form source/drain contacts. The device channel width and length are 1000 and 200 μm, respectively. The encapsulation was performed by sealing devices with cavity-formed encapsulation glass in the glove box, which is filled with nitrogen and ultralow water and oxygen concentrations ($H_2O < 0.1$ ppm and $O_2 < 0.1$ ppm). The devices were first put into a vacuum chamber (pumped down to 1×10^{-6} torr) that was linked to

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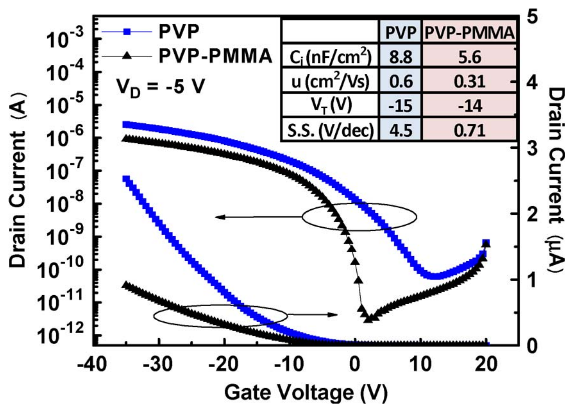


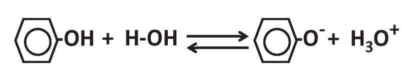
Fig. 1. Initial transfer characteristics of pentacene OTFTs with PVP and PVP-PMMA dielectrics. The typical parameters are listed in the inset.

the glove box to reduce the water absorption. Then, devices are packed by the cavity-formed encapsulation glass. The glass substrate and the encapsulation glass are sealed by ultraviolet (UV) binder. The UV binder was exposed to UV light for 1 min, and the devices were shielded from the UV light by capping a simple metal mask during the UV exposure process. The devices were measured at room temperature. The threshold voltage was extracted using the linear region equation, and the mobility was calculated from the maximum transconductance in the linear region [2].

III. Results and Discussion

The initial (unencapsulated) transfer characteristics for pentacene OTFTs with PVP and PVP-PMMA dielectrics measured in air are shown in Fig. 1. The gate capacitances per unit area, the field-effect mobilities, the threshold voltages, and the subthreshold swings of these two devices are listed in the inset in Fig. 1. Normal output characteristics of these two devices without the contact issue are obtained (not shown). Similar to the results reported in [9], OTFTs with the PVP-PMMA dielectric exhibit better subthreshold swing and lower off current because of the reduced water adsorption and the suppressed slow polarization in the dielectric. In this letter, the surface roughness obtained form the atomic force images is 0.52 nm for the PVP dielectric and is 0.56 nm for the PVP-PMMA dielectric. The dielectric leakage current obtained from the metal–insulator–metal structure at an electric field of 1 MV/cm is 1.7×10^{-8} A/cm^2 for PVP and is 2.8×10^{-8} A/cm^2 for PVP-PMMA.

The hysteresis behaviors measured without and with encapsulation for devices with PVP and PVP-PMMA dielectrics are shown in Fig. 2(a) and (b), respectively. For OTFT with the PVP dielectric exposed to air, an obvious *clockwise* hysteresis loop is observed. This loop direction is usually explained by the slow polarization due to polar molecules and mobile ions in the PVP layer [4], [5]. When OTFT with the PVP dielectric is encapsulated, hysteresis is eliminated. It has been reported that the hysteresis is strongly related to water [4], [5]. When devices are encapsulated in nitrogen environment right after the deposition of source and drain electrodes, the devices are well stored in a dry environment. It is also interesting to note that the field-effect mobility and the off current of encapsulated OTFT with the PVP dielectric are smaller than those of the unencapsulated ones. Specifically, for OTFT with the PVP dielectric, mobility drops from 0.6 to 0.125 $\mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s}$ after encapsulation. It is proposed that the electron trapping or the negatively charged hydroxyl groups in PVP help to accumulate holes and thus increase the effective field-effect mobility [3]. The hydroxyl groups also exhibit a deprotonation process when reacting with water [12]. In our study, the reduced mobility and the decreased off current for encapsulated devices can be explained by the following reaction [12]:



(1)

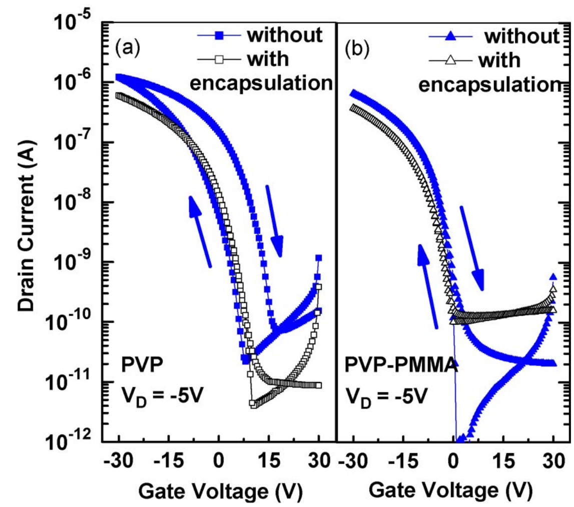


Fig. 2. Hysteresis for pentacene OTFTs with (a) PVP and (b) PVP-PMMA dielectrics before and after encapsulation.

When OTFTs with the PVP dielectric are encapsulated in dry environment, (1) reacts to the left direction, and the negative-charged hydroxyl groups decrease. As a result, the field-effect mobility and the off current decrease. For devices with the PVP-PMMA dielectric, as shown in Fig. 2(b), no hysteresis is observed when devices are measured with and without encapsulation. The field-effect mobilities for unencapsulated and encapsulated OTFTs with the PVP-PMMA dielectric are 0.31 and 0.235 $\mathrm{cm}^2/\mathrm{V} \cdot \mathrm{s}$, respectively.

The gate BSEs of unencapsulated OTFTs with PVP and PVP-PMMA dielectrics are studied by plotting the transfer characteristics of these devices after positive and negative gate bias stresses in Fig. 3(a) and (b), respectively. The positive gate bias stress is performed by applying gate bias (V_G) of 15 V for 2000 s. The negative gate bias stress is performed by applying gate bias minus the threshold voltage $(V_G - V_T)$ of -15 V for 2000 s. For unencapsulated OTFT with the PVP dielectric, both positive and negative gate bias stresses cause severe degradation on device performance. OTFT with the PVP-PMMA dielectric exhibits a better immunity to gate bias stress. However, a significant threshold voltage shift is still observed.

The bias-stress-induced ΔV_T can be effectively suppressed when devices are encapsulated. ΔV_T's of encapsulated OTFTs with PVP and PVP-PMMA dielectrics are plotted as a function

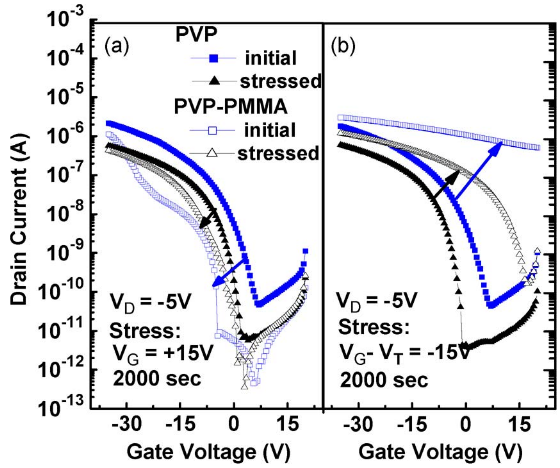


Fig. 3. Comparison of the initial and the stressed transfer characteristics of pentacene OTFTs with PVP and PVP-PMMA dielectrics when the gate-bias-stress conditions are (a) $V_G = +15$ V for 2000 s and (b) $V_G - V_T = -15$ V for 2000 s.

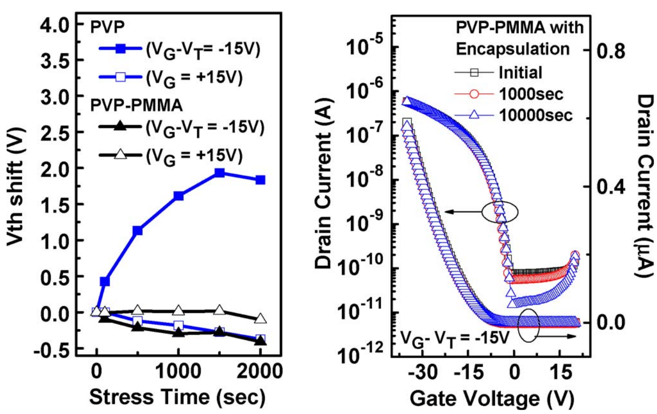


Fig. 4. (a) Threshold voltage shift as a function of stress time for encapsulated pentacene OTFTs with PVP and PVP-PMMA dielectrics. Both positive gate bias stress ($V_G = +15$ V) and negative gate bias stress ($V_G - V_T = -15$ V) are compared. (b) Initial and stressed transfer characteristics of encapsulated pentacene OTFT with PVP-PMMA dielectric. Stress condition is $V_G - V_T = -15$ V. The stress time is up to 10 000 s.

of stress time in Fig. 4(a). The suppressed BSE after encapsulation verifies that the BSE is strongly related to water and oxygen. The superior stable performance for OTFT with the PVP-PMMA dielectric indicates that the less polar dielectric effectively suppresses the water adsorption and BSE. The transfer characteristics of encapsulated OTFT with the PVP-PMMA dielectric after 10 000-s negative bias stress ($V_G - V_T = -15$ V) are plotted in Fig. 4(b). There is almost no degradation on device performance after stress. The ΔV_{th}'s after 2000- and 10 000-s negative bias stresses ($V_G - V_T = -15$ V) are 0.45 and 0.04 V, respectively. This result is comparable to the reported air-stable OTFT with a fluoropolymer dielectric [7].

IV. Conclusion

Not only the hysteresis but also the bias-stress-induced ΔV_T is sensitive to moisture. For OTFT with the PVP dielectric, encapsulation effectively suppresses the hysteresis by blocking the moisture. However, the absorbed water molecules on PVP films cause pronounced threshold voltage shift after the gate bias stress. The less polar PVP-PMMA dielectric successfully suppresses the absorption of water molecules. An encapsulated OTFT with PVP-PMMA exhibits a ΔV_T below 0.5 V after 10 000-s gate bias stress. The proposed stable device is a promising low-cost candidate to realize OTFT mass production.

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