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Thin-film passivation by atomic layer deposition for organic field-effect transistors

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The thin-film passivation of organic field-effect transistors (OFETs) using AlO_x films grown by atomic layer deposition was investigated. A high-quality AlO_x passivation layer was deposited on OFETs at 90 °C using trimethylaluminum and water. Despite the low deposition temperature, the 50-nm-thick AlO_x passivation layers exhibited a low water-vapor-transmission-rate value of 0.0434 g/m²/day. In addition, the mobility of the AlO_x -passivated OFETs was only slightly below that of the unpassivated devices (i.e., within 9%). Unlike unpassivated devices, the electric performance of the passivated OFETs remained almost unchanged after 2 months as a result of the excellent barrier properties of the passivation layer. © 2008 American Institute of Physics.

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As organic field-effect transistors (OFETs) are integrated into commercial circuit products, their stability and reliability become increasingly important issues. Because of the instability of the organic materials against atmospheric H_2O and O_2 , the long-term stability of OFETs is limited.^{1–8} Previous studies have shown that H_2O molecules may degrade the pentacene FET performance by interacting with pentacene species and forming traps at the grain boundaries, thereby reducing the mobility and the on current.^{5–8} Therefore, to improve the stability of OFETs, it is necessary to develop high-quality, thin passivation layers with a low water vapor transmission rate (WVTR) and excellent barrier properties. Although Han *et al.*⁹ have reported the long-term stability of OFETs passivated by double-layer polymer films composed of a lower cross-linked polyvinyl alcohol (PVA) layer and an upper photosensitive acryl layer, such transistors have their own problems. One of them is the high permeation of water through the polymer film due to the loosely packed structure of the polymer chain and the hydroxyl group in the PVA film. Therefore, inorganic passivation films, such as oxides and nitrides, are strongly required. However, most deposition techniques for obtaining inorganic films are based on plasma or high thermal energies, which are harmful to organic materials. Deposition techniques for preparing highly moisture-resistive films at low temperatures without using plasma are very important. In this study, we investigated the passivation of pentacene FETs with thin AlO_x films prepared by atomic layer deposition (ALD) to achieve long-term stability of the pentacene transistors. ALD is a well-known process for growing thin and pinhole-free films at low temperatures and producing excellent gas-diffusion barriers for organic materials. Park *et al.*¹⁰ reported excellent barrier properties of a nanometer-thick AlO_x film deposited by means of ALD. The authors found that the film was suitable for preparing the encapsulation layer of organic light-

emitting diodes. In this study, we fabricated pentacene FETs passivated by AlO_x films deposited through ALD and investigated the long-term stability and aging effects of the new devices in term of their electrical properties.

The inset of Fig. 1(a) shows the cross section of the pentacene FET used in this study. The gate dielectric is composed of two layers: a lower anodized Al_2O_3 layer with a high dielectric constant and an upper polyimide layer whose thermal stability is sufficient to withstand the passivation process. The Al_2O_3 layer (130-nm-thick) was constructed by anodizing the surface of the Al gate to 100 V at a constant current density of 0.3 mA/cm² and a temperature of 25 °C in a 0.1M ammonium pentaborate octahydrate electrolyte solution. A 3 wt % solution of polyamic acid in *N*-methyl-pyrrolidone was spin coated on the anodized Al_2O_3 layer at 5000 rpm for 120 s and then baked in a nitrogen-purged furnace at 200 and 250 °C (for 60 min) for imidization. Pentacene was deposited at a rate of 0.3 Å/s, at a pressure of 10⁻⁶ Torr, until its thickness reached 50 nm, with the substrate being maintained at room temperature. The fabrication of a pentacene FET with top-contact geometry was completed by evaporating gold through a shadow mask to define the source and drain electrodes. The channel length (L) and width (W) are 100 and 1500 μm, respectively.

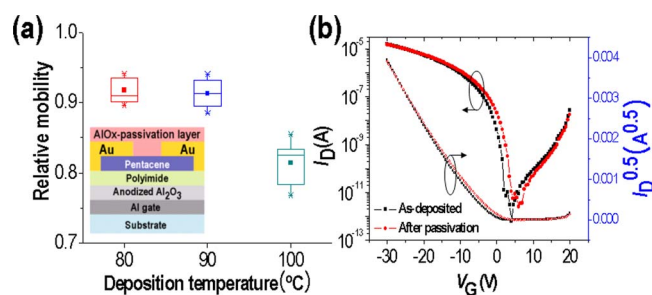


FIG. 1. (Color online) (a) Variations in the mobility after passivation at deposition temperatures of 80, 90, and 100 °C, (b) Transfer curves before/after AlO_x passivation at 90 °C. The inset shows the schematic structure of an AlO_x -passivated pentacene FET.

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Passivation on the pentacene FET was achieved by means of an AlO_x layer grown in an ALD reactor using nitrogen as carrier gas. Trimethylaluminum (TMA) and H_2O were used as precursors, supplying Al and O, respectively. The sequence of pulses for a one-cycle deposition of AlO_x is TMA (0.5 s)/ N_2 (0.8 s)/ H_2O (0.5 s)/ N_2 (2.5 s).¹⁰ All the charge mobilities were calculated in the saturation regime.

Figure 1(a) shows the mobility reduction after passivation of the pentacene FETs with AlO_x as a function of the deposition temperature. The mobility of pentacene FETs passivated at 100 °C was about 18% below that of the nonpassivated transistors. On the other hand, the mobility of the devices passivated at 80 and 90 °C decreased by about 9%. This result indicates that passivation at a temperature equal to (or lower than) 90 °C would not induce considerable deterioration of the pentacene FETs. In addition, Park *et al.*¹⁰ reported that the barrier properties of AlO_x increase with increasing film thickness and deposition temperature. In this study, high-quality barrier properties—with a WVTR value of 0.0434 g/m² day at 38 °C for an active area of 50 cm²—were obtained for 50-nm-thick AlO_x -coated poly-ether sulfone (PES) films deposited at 90 °C in an ALD reactor, whereas the unpassivated PES films exhibited a higher WVTR value (i.e., 92.8 g/m² day at 38 °C for an active area of 5 cm²). These results imply that 50-nm-thick AlO_x films deposited at 90 °C can show excellent barrier properties, not only for protection against water vapor but also for minimizing damage to the device.

Figure 1(b) shows the transfer-characteristic curves of the pentacene devices before and after passivation at 90 °C. As can be seen, the electrical characteristics of the transistors were degraded by the passivation process. The field-effect mobility (μ) decreased from 0.42 to 0.38 cm²/V s and the threshold voltage (V_T) shifted from -5.7 to -4.7 V. Ferrari *et al.*¹¹ had already reported such a small degradation, which originated from the deformation of the organic layer due to the penetration of TMA and H_2O into the devices during the passivation process.

To estimate the stability and lifetime of the pentacene FETs in ambient air with a relative humidity (RH) of 25%, the devices were kept (either passivated or not) in dark conditions. Figures 2(c) and 2(d) show the relative mobilities and threshold-voltage shifts of pentacene FETs with/without passivation layers exposed to ambient air for 60 days. Figures 2(e) and 2(f) show the transfer characteristics of devices without and with a passivation layer. As shown in Fig. 2(b), the on current of the unpassivated devices increases temporarily during the first 5 days due to an increase of the capacitance (from 13.3 to 14.6 nF/cm²), which results from the absorption of H_2O into the hygroscopic polyimide dielectrics [Fig. 2(a)].

In the case of the unpassivated devices exposed to ambient air for 2 months, the mobility sharply decreased from 0.40 to 0.10 cm²/V s, whereas the subthreshold swing (SS) increased from 0.9 to 3.6 V/decade and the threshold voltage shifted from -5.7 to -0.9 V. The activation energy (E_A) increased markedly with time (from 52.1 to 86.2 meV) after 30 days of exposure to ambient air without passivation [Fig. 3(a)]. These results indicate that in the presence of air, O_2 and H_2O penetrate into the pentacene film, thus inducing many localized trap states at the pentacene and pentacene/dielectric interface and hindering charge transport.³⁻⁸

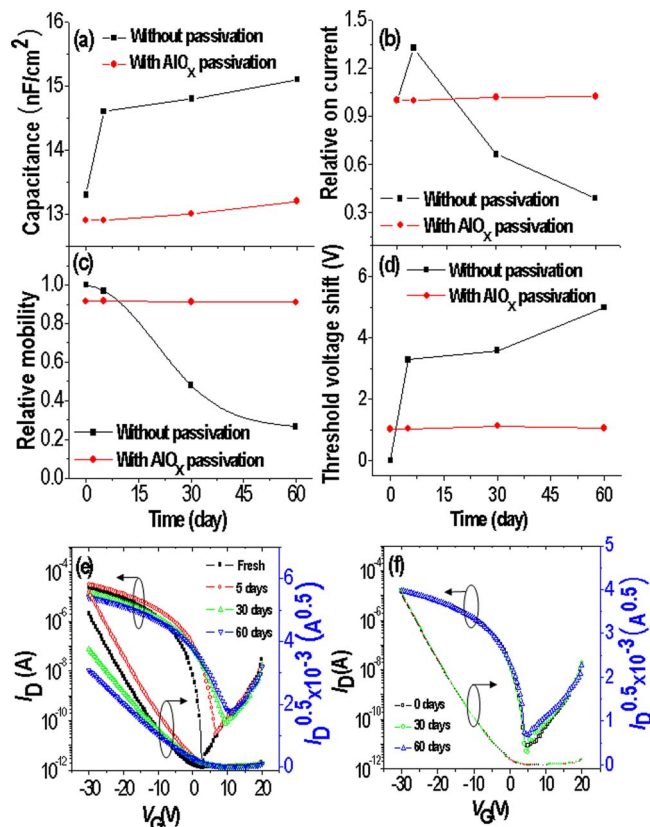


FIG. 2. (Color online) Time dependence of the electrical characteristics of pentacene FETs in air (RH=25%): (a) Capacitance, (b) relative on-current, (c) relative mobility, (d) threshold-voltage shift, (e) transfer characteristics of unpassivated devices, and (f) transfer characteristics of an AlO_x (50-nm-thick) passivated device in air.

On the other hand, the passivated devices did not exhibit any notable deterioration in their transfer curves after 2 months [Fig. 2(f)]. Also, unlike the unpassivated devices, their capacitance remained almost the same after this time [Fig. 2(a)]. In case of passivated device, the E_A slightly increased after passivation (from 52.1 to 60.0 meV) due to a deformation of the organic layer caused by the penetration of TMA and H_2O into the organic FET devices during the process. Despite this small increase, the overall value of E_A hardly changed after 30 days in ambient air (RH=25%). These results suggest that the AlO_x layer deposited by ALD prevents the penetration of H_2O and O_2 from air into both the organic semiconductor and the polymer gate dielectric, thus providing long-term stability to the pentacene FETs.

To clarify the origin of the atmospheric degradation of pentacene FETs, the effects of oxygen and humidity on the temperature-dependent behavior of the mobility were investigated for unpassivated devices in dark conditions. As shown in Fig. 3(b), the E_A of unpassivated devices exposed to dry O_2 gas (99.999%) at 1 atm under dark conditions is only slightly enhanced (by up to 57 meV, i.e., <10%) and changes only slightly with increasing exposure time. Jurcescu *et al.*³ suggested that oxygen species that have penetrated into the pentacene crystal may increase the number of holes near the valence band due to the formation of a reversible charge-transfer complex (*p*-doping) between pentacene and electronegative oxygen. In contrast, oxygen species that have diffused to the grain boundaries change pentacene into pentacene-quinone by oxidation under the influence of light

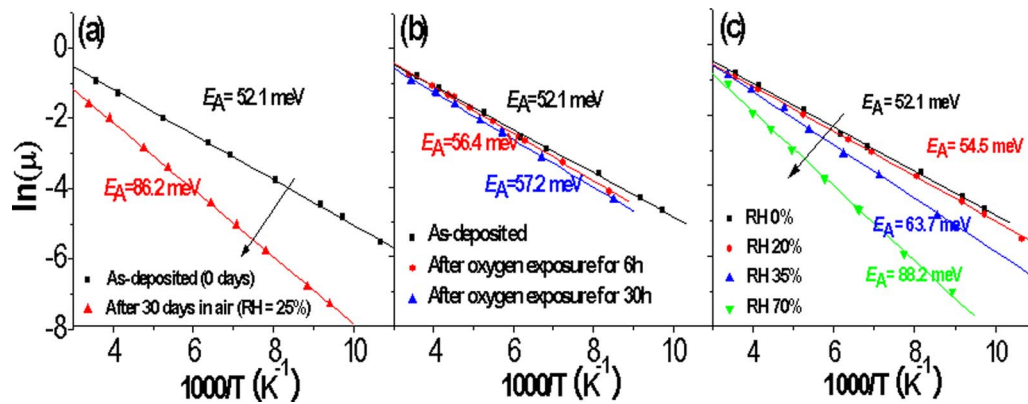


FIG. 3. (Color online) Temperature-dependent mobility and activation energy (E_A) of pentacene FETs: (a) unpassivated devices exposed to air for 0 and 30 days (RH=25%), (b) unpassivated devices exposed to oxygen for 0, 6, and 30 h (RH=0%), and (c) unpassivated devices exposed to humidity for 6 h (at RH=0%, 20%, 35%, and 70%).

or thermal energy.⁴ The quinones do not contribute to the accumulation of holes, but hinder charge transport. However, the pentacene FETs examined herein under dark conditions did not exhibit any notable effects of oxygen on the E_A after 30 h of exposure. This insensitivity to oxygen exposure might be attributed to the high density of grain boundaries in the channel and the mild condition without light or high thermal energy.⁹ Contrarily, the E_A of the pentacene devices did change significantly upon exposure to humidity after 6 h. As shown in Fig. 3(c), the value of E_A increased slightly (within 5%) in air with low RH (of 20%) and then increased abruptly to 88.2 meV in air with high RH (of 70%). This value is similar to that of a sample aged for 30 days in air with RH=25% [Fig. 3(a)]. While in the case of OFETs exposed to dry oxygen gas or ambient air with low RH (i.e., below 20%) no significant changes (less than 10%) were observed in the E_A for 6 h, the E_A of aged devices in ambient air with high RH (i.e., above 70%) did increase markedly. This rapid and remarkable change of the E_A upon varying the humidity indicates that the major factor causing atmospheric degradation of the devices is the H_2O present in the dark atmosphere. The absorbed H_2O molecules rapidly induce trap states in the channel, which results in a reduction of the mobility and a decrease of the on current.

In summary, we have fabricated pentacene FETs, passivated with 50-nm-thick AlO_x films, which exhibit a WVTR value of $0.0434 \text{ g/m}^2 \text{ day}$. By applying a plasma-free ALD process at low temperatures, the mobility of the passivated devices could be preserved at more than 90% of that of the corresponding unpassivated devices, and no significant degradation of the electrical characteristics was observed after 2 months. On the other hand, the mobility of the unpassi-

vated devices did decrease markedly (down to 25% of the initial value) after this time, with the electrical characteristics of these transistors being significantly degraded in ambient air. Water molecules absorbed in the pentacene film or at the pentacene/dielectric interface rapidly induce trap states, resulting in a reduction of the mobility and a degradation of the electrical characteristics.

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