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Effects of Moisture on Pentacene Field-Effect Transistors with Polyvinylpyrrolidone Gate Insulator

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We report the effects of moisture on the electrical characteristics of pentacene field-effect transistors (FETs) with the polyvinylpyrrolidone (PVPy) gate insulator. For the condition of relative humidity below 40%, the pentacene FET exhibited a stable operation without a shift in the threshold voltage upon a gate voltage sweep direction. With increasing the relative humidity above 50%, the threshold voltage shifted critically toward the positive direction, accompanied by significant degradations in the field-effect mobility and the subthreshold slope. These moisture-induced characteristic degradations could be substantially recovered by the low-temperature annealing process under a base pressure of 2×10^{-3} *Torr.*

Keywords Field-effect transistor; moisture; pentacene; stability

Introduction

Organic field-effect transistors (OFETs) have received much interest due to their advantages such as low-cost manufacture and compatibility with flexible substrates [1]. Intensive researches into OFETs have developed materials and processing techniques, thereby achieving encouraging electrical performances comparable to or even surpassing those of amorphous silicon transistors [2,3]. And pioneering works demonstrated a wide range of applications, for example as the driving elements of flexible displays, radio-frequency identification tags and various sensors [4–6]. Now the reliablity issue of OFETs must be of primary importance for these devices to be useful in electronic appliances. Nevertheless, there are still fundamental problems with the electrical and enviromental stability of OFETs. For example,

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OFETs suffer from critical shortcomings in device performances when exposed to ambient air, which are significantly accelerated by water vapor adsorption. In particular, gate-insulator materials play an important role on the operational stability of OFETs, Therefore, the electrcial and environmental stability issues of these devices should be interpreted by the nature of gate-insulator materials.

Polyvinylpyrrolidone (PVPy) is a unique polymer which provides remarkable properties such as good initial tack, transparency, chemical and biological inertness, very low toxicity as well as cross-linkable flexibility [7]. Therefore we believe that PVPy is inherently suitable for a gate insulator in OFETs. However, there are few reports on the characteristics of PVPy and its applications to organic electronic devices. In this work, we have utilized PVPy as a new gate insulator for OFETs and investigated the electrical characteristics of OFETs with varying the relative humidity. These results are discussed.

Experimental

Pentacene FETs with a top-contact source/drain structure were fabricated. For the bottom gate electrode, about 1500-Å-thick Al layer was deposited on a precleaned glass substrate through the first metal shadow mask. Then, as a gate dielectric, PVPy (Aldrich, Mw $\sim$ 29,000, 4 wt% dissolved in anhydrous ethanol) was formed by spin-coating and baked at 100°C for 40 min in a vacuum dry oven followed by pro-curing at 60°C for 20 min. The thickness of PVPy layer was about 3500 Å by optimizing the spinning speed and its duration. After completing the curing processes, a 600-Å-thick pentacene layer, as an organic semiconductor, was thermally evaporated through the second shadow mask. Pentacene (Tokyo Kasei Kogyo Co. Ltd.) was used without further purification and deposited at a rate of 1.0 Å/s. And 400-Å-thick source and drain electrodes on the top of the pentacene film were thermally evaporated through the third shadow mask with a channel length (L) of 90 μm and width (W) of 300 μm. All evaporation processes were carried out under a base pressure of about 1.6×10^{-6} Torr.

The crystallinity of the pentacene film was studied by XRD (DMAX 2500, Rigaku) with monochromatic Cu Kα ($\lambda = 1.54$ Å) and its surface morphology was examined under AFM (XE-150, PSIA Inc.) using the contact mode. Dielectric property of PVPy and electrical characteristics of OFETs were measured at room temperature in air using impedance analyzer (HP 4192LF, Agilent Technologies) and semiconductor analyzer (EL 421C, Elecs Co.), respectively.

Results and Discussion

The device for capacitance measurement consists of PVPy layer sandwiched between Al and Au electrodes and the dielectric constant was calculated by the Eq. (1),

$$C = \frac{\varepsilon_0 \varepsilon_r}{d} A \tag{1}$$

where C is the measured capacitance, ε_0 is the permittivity of free space, ε_r is the relative dielectric constant of an insulator, A is the area of the capacitor, and d is the insulator thickness [8]. Figure 1 shows the dielectric constants as a function of the applied frequency, in which the inset shows the molecular structure of PVPy.

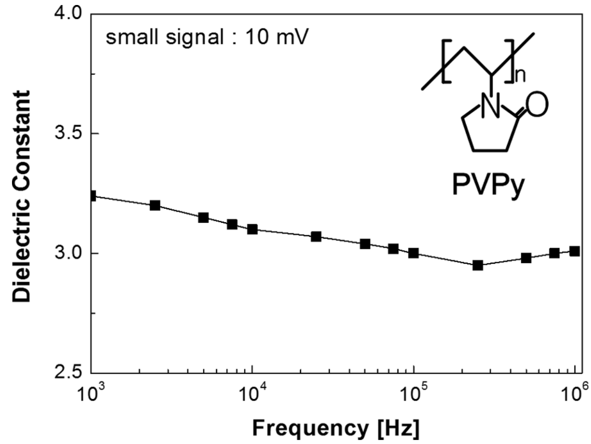


Figure 1. Calculated dielectric constants of the PVPy film at various frequencies. The inset shows the molecular structure of PVPy.

The dielectric constant of PVPy was about 3 at 100 kHz, which is in the range of conventional polymeric insulators, such as polystyrene, poly(vinyl acetate), etc. Insulating property of the PVPy gate insulator was also examined using the Al electrode/PVPy (3500 Å)/Al electrode structure (not shown here). The fabricated PVPy film exhibits the electric field strength of about 2 MV/cm.

The structural and morphological characteristics of pentacene film deposited onto the PVPy layer are shown in Figure 2. The XRD spectrum shows two diffraction peaks at 5.76° and 6.14° corresponding to thin film phase and triclinic bulk phase, respectively. The strongest peak near 5.76° indicates that the major component of this film is a thin film phase with an interplanar spacing of 15.3 Å, while the diffraction peak near 6.14° corresponds to the bulk phase with an interplanar

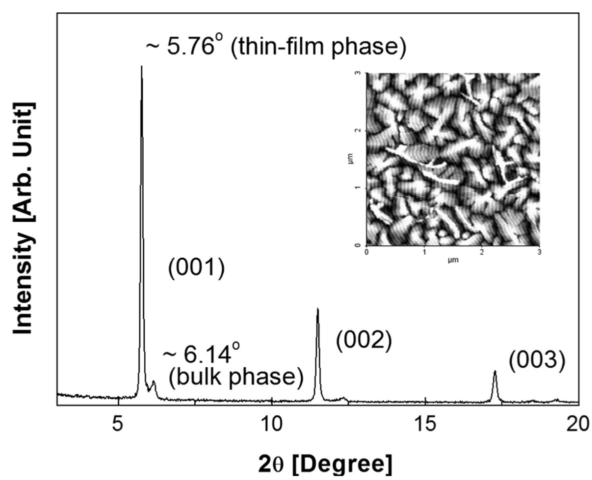


Figure 2. XRD pattern of 1200-Å-thick pentacene film on the PVPy gate insulator. The inset shows the surface of 300-Å-thick pentacene film deposited on the PVPy gate insulator characterized by AFM (3 μm × 3 μm).

spacing of 14.4 Å. This indicates that the pentacene molecules are highly ordered in perpendicular direction to the PVPy layer. Obviously, the AFM image shows that pentacene molecules tend to form well-ordered crystallites in herringbone structure as shown in the inset of Figure 2, where the grain size is measured to be 600–800 nm. Since the interaction of π-electron systems between adjacent molecules depends strongly on their stacking nature, a vertical alignment of pentacene molecules to the PVPy-coated substrate can provide a strong π-orbital overlap and increase the charge transport properties.

Figure 3 shows the drain current (I_D) versus the gate voltage (V_G) characteristics, i.e., the transfer curve, measured at the drain voltage (V_D) of -30 V under the relative humidity below 40%. The calculated field-effect mobility and the extracted threshold voltage (V_T) were 0.23 cm^2/Vs and -12.7 V, respectively. And the on/off current ratio was observed to be about 5×10^4 with a subthreshold slope of 3.2 V/decade from the inset. Of particular interest is its stable operation without a shift in the threshold voltage upon a gate voltage sweep direction. Indeed, the threshold voltage shift in this device was less than 0.1 V.

In order to investigate the effects of ambient moisture on the electrical stability of the pentacene FET with the PVPy gate insulator, typical transfer characteristics were measured with varying the relative humidity. Comparing the initial characteristics, immediately obtained after device fabrication, with those re-measured after 30 min under different relative humidity conditions, it was found that the device performance rapidly degraded following exposure to ambient moisture. Figure 4(a) shows that the degradation in field-effect mobility and subthreshold slope critically occurred with increasing the relative humidity. Furthermore, the threshold voltage pronouncedly shifted toward the positive direction upon a gate voltage sweep direction for the device exposed to the relative humidity of about 50%, as shown in Figure 4(b). From the threshold voltage shift of about 8 V, the trapped charge density at the pentacene/PVPy interface was calculated to be about 4.7×10^{11} cm^{-2}.

From the results so far achieved, we can attribute the significant degradation in the device performance to moisture penetrated into the pentacene/PVPy interface because the polar H_2O molecules can result in trapping charges, thereby generating residual charges at the interface. Similar results of the effects of moisture

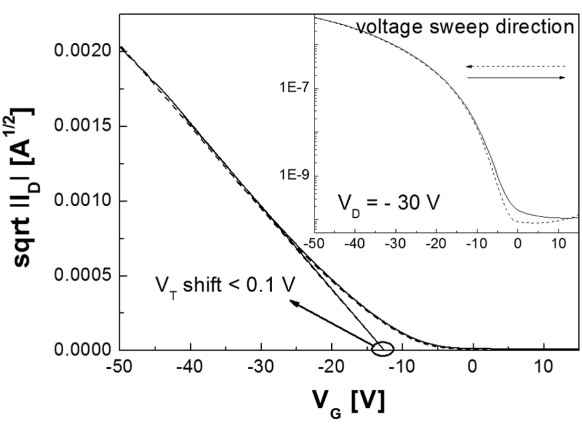
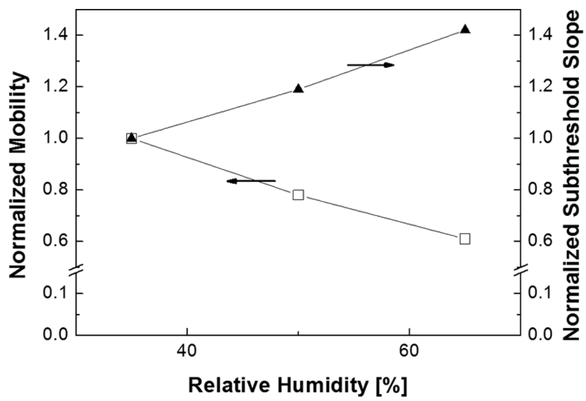
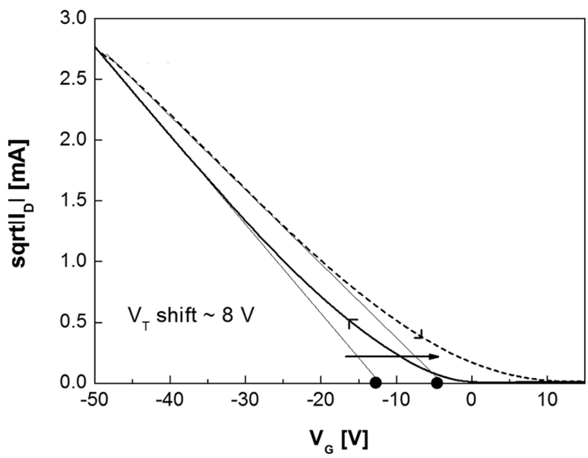


Figure 3. Transfer curve of the fabricated OFET. The inset shows $\log_{10}|I_D|$ versus V_G plot.



(a)



(b)

Figure 4. (a) Normalized field-effect mobility and subthreshold slope of the pentacene FET with the PVPy gate insulator according to the relative humidity. (b) $|I_D|^{1/2}$ versus V_G plots showing the threshold voltage shift induced by ambient moisture.

on the device performance have been also reported in literature [9]. Figure 5(a) shows the microscopic image of water droplet on the PVPy layer. Surprisingly, it is observed that the PVPy film completely absorbed water, which implies that the characteristic degradations in the pentacene FET with the PVPy gate insulator were essentially induced by the polar H_2O molecules adsorbed at the pentacene/PVPy interface and even penetrated into the PVPy layer. In order to eliminate such H_2O molecules, the degraded device was annealed at 60°C for 1 h under a base pressure of 2×10^{-3} Torr. It is found that the degraded characteristics can be substantially recovered by the simple thermal annealing, as shown in Figure 5(b), which is very likely to our previous report [10]. Consequently, these results demonstrate that the hydrophile property of a gate-insulator material plays a significant role on the environmental stability of OFETs. Further investigations on the moisture-dictated structural deformation in the pentacene film should be carried out under various temperatures.

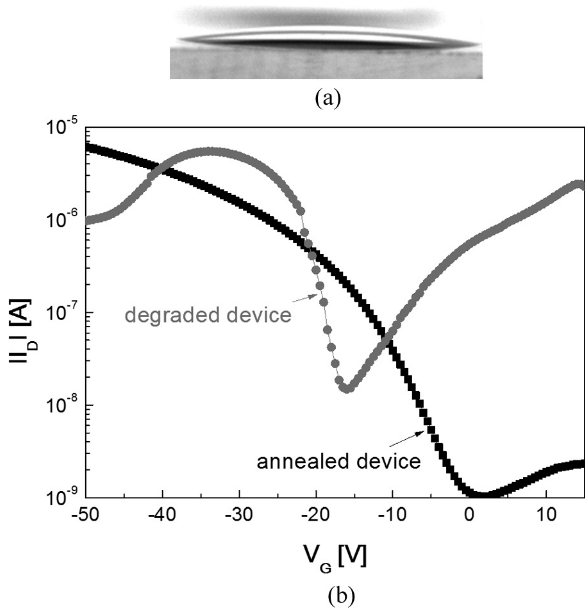


Figure 5. (a) Microscopic image of water drop on the PVPy film and (b) transfer curves of the degraded device according to the thermal annealing at 60°C.

Conclusion

In this paper, we have investigated the effects of ambient moisture on the electrical characteristics of the pentacene FET with the PVPy gate insulator. The fabricated device exhibited significant degradations in device performance with increasing the relative humidity, which could be explained by the polar H_2O molecules penetrated into the pentacene/PVPy interface and/or even into the PVPy layer. The water absorbent nature of PVPy facilitated the characteristic degradations in OFETs. We have shown that moisture-induced characteristic degradations in OFETs can be substantially recovered by the simple thermal annealing at 60°C.

Acknowledgments

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