Pentacene TFT With Reduced Threshold Voltage Using PMMA-co-MAA/Sol-Gel-Derived TiO$_2$ Composite Insulator

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Abstract—We report improvements in the characteristics of pentacene thin-film transistors (TFTs) achieved by using a poly(methylmethacrylate-co-methacrylic acid) (PMMA-co-MAA)/sol-gel-derived TiO$_2$ composite insulator. The gate-leakage current of TFTs containing this insulator is comparable to that of devices composed of bare PMMA-co-MAA. The reduction in the threshold voltage is the most pronounced improvement observed herein (compared to the variations of other characteristic parameters). This can be explained by the negative surface potential of the sol-gel-derived TiO$_2$ film.

Index Terms—Insulator, organic thin-film transistors (TFTs) (OTFTs), sol-gel, TiO$_2$.

I. INTRODUCTION

ORGANIC thin-film transistors (TFTs) (OTFTs) are envisaged to pave the way for flexible and rugged electronics because of their simple and low-temperature processability [1], [2]. Recently, there is a large range of discussion on the significance of gate-insulator materials for high-performance OTFTs [3], [4]. Gate-insulator materials are required to be solution processable for low-cost manufacturing and should also provide a high capacitance to enable low-voltage operation. The confluence of these two requirements has stimulated research into organic/inorganic composite insulators. Previous studies have led to the development of polymer/TiO$_2$ nanoparticle composite insulators [5], [6], but high gate-leakage currents caused an increase in the OFF-state current (exceeding 10$^{-8}$ A) and a decrease in the on/off ratio (to 10$^3$). This behavior arises from the nonuniform dispersion of nanoparticles. One way to circumvent these drawbacks is to apply a sol-gel process. In this letter, we investigated the characteristics of a poly(methylmethacrylate-co-methacrylic acid) (PMMA-co-MAA)/sol-gel-derived TiO$_2$ composite film, as well as the performance of pentacene TFTs, wherein these films were used as insulator layers. In contrast to most previous studies, which emphasize only the high-dielectric-constant properties of inorganic components, this letter demonstrates the surface-potential effects of a composite insulator, formed by means of a sol-gel process, on the device performance.

II. EXPERIMENTS

The sol-gel precursor solution was prepared by blending 4 wt% PMMA-co-MAA (Aldrich Chemical Company), dissolved in chloroform, with titanium tetraisoproxide [(TTIP); Aldrich Chemical Company] as a TiO$_2$ precursor. The composition ratio was controlled to be about 15:1 (PMMA-co-MAA:TTIP). To fabricate OTFTs, a 50-nm-thick Al gate electrode was thermally deposited onto a glass substrate using a first shadow mask. Different gate insulators were formed by spin coating in a glove box in which the relative humidity was kept below about 30%. It is noteworthy that solvent elimination was carried out under a base pressure of about 2 × 10$^{-3}$ torr at room temperature to avoid phase segregation in the sol-gel-derived TiO$_2$ film. The resulting thickness of the bare PMMA-co-MAA film was about 1250–1300 nm, whereas that of the composite film was 1800–1900 nm. The thickness of the PMMA-co-MAA film was about 1250–1300 nm, whereas that of the composite film was 1800–1900 nm. Pentacene (Tokyo Chemical Industry Company; used without further purification) was thermally evaporated through a second shadow mask onto the insulator-coated substrate at a rate of 0.1 nm/s, up to a thickness of 60 nm. Top-contact OTFTs were constructed by depositing 50-nm-thick Au source/drain electrodes using a third shadow mask. The channel length and width were 90 and 200 μm, respectively.

III. RESULTS AND DISCUSSION

Fig. 1(a) shows a cross-sectional scanning electron microscopy (SEM) image of the composite film, which exhibits a bilayer structure, with a top-layer thickness of about 600 nm and a bottom-layer thickness of 1200–1300 nm. The distribution of Ti atoms in the composite film was analyzed using its depth profile, which was obtained by means of Auger electron spectroscopy measurements. Fig. 1(b) shows that Ti atoms are present to a depth of about 550–600 nm from the surface of
the composite film, which indicates that sol-gel-derived TiO$_2$ mainly distributes on the top layer, whereas the bottom layer consists of PMMA-co-MAA. In detail, Ti atoms are uniformly distributed to a depth of about 360 nm, but the Ti content decreases gradually, which suggests that sol-gel-derived TiO$_2$ is mixed with PMMA-co-MAA in the range between 360 and 600 nm from the surface of the top layer. These results presumably arise from the hydrolysis of TTIP in contact with exterior moisture to form TiO$_2$, because the hydrolysis process occurs from the top–down. The capacitance-versus-frequency (C–F) characteristics of both insulator films are shown in Fig. 1(c). The capacitance value for the composite insulator is larger than that for the bare PMMA-co-MAA insulator.

Fig. 2(a) shows the X-ray diffraction (XRD) peaks for the pentacene films grown on the different types of insulators. All the diffraction peaks correspond to the pentacene films grown on the different types of insulators. The capacitance value for the composite gate insulator is larger than that of bare PMMA-co-MAA is only 1.3 nm.

Fig. 3 shows the transfer characteristics of OTFTs, fabricated using different gate insulators, operating at a drain voltage ($V_D$) of $-40$ V. The field-effect mobility was calculated in the saturation region, and the threshold voltage was extracted from a plot of the square root of the drain current ($I_D$) versus the gate voltage ($V_G$) by extrapolation to $I_D = 0$. The OTFT containing the composite insulator exhibited a field-effect mobility of $0.13 \text{ cm}^2/\text{V} \cdot \text{s}$ and a threshold voltage of $-8.1$ V with a sub-threshold swing of 1.9 V/decade. These characteristics are superior to those (i.e., $0.11 \text{ cm}^2/\text{V} \cdot \text{s}$, $-12.8$ V, and 2.1 V/decade, respectively) of the device composed of the bare PMMA-co-MAA insulator. It should be mentioned that a lower threshold voltage was obtained in the composite gate insulator even with thicker physical thickness. Further improvements in the device performance are also expected by reducing the thickness of the composite gate insulator below 200–300 nm and modifying its surface roughness. In particular, noteworthy is the on/off ratio of about $10^5$ for both TFTs, which can be attributed to the comparable gate-leakage currents ($I_G$), shown in the inset of Fig. 3. Considering that the previous studies on organic/inorganic composite insulators have suffered from serious $I_G$ problems [5], [6], our composite insulator (prepared by means of a sol-gel process) could be a promising material for OTFT applications.

Note that the threshold voltage change was the most remarkable variation observed among the studied device parameters. Since the threshold voltage represents the gate voltage beyond the flatband, just starting to form a conducting channel, the flatband voltage ($V_{FB}$) is an important parameter to interpret the significant reduction in the threshold voltage. The flatband voltage is related to the number of fixed charges ($Q_{fi}$) at the interface between the pentacene and insulating layers, as shown in

$$V_{FB} = \Phi_{MS} - \frac{Q_{fi}}{\varepsilon_0 \varepsilon_r} d$$

where $\Phi_{MS}$ is the work-function difference between the gate metal and the semiconductor, and $d$ and $\varepsilon_r$ are the thickness and
dielectric constant of the gate insulator, respectively [7]. Fig. 4 shows the dependence of the flatband voltage on the dielectric thickness for metal–insulator–semiconductor (MIS) capacitors. The curve of the MIS capacitor containing the composite insulator has a positive slope, whereas that of the capacitor containing the bare PMMA-co-MAA insulator exhibits a negative slope. Equation (1) then represents the existence of negative charges at the interface between the pentacene layer and the sol-gel-derived TiO$_2$ film. To elucidate the origin of such negative charges, we measured the electrokinetic potential of sol-gel-derived TiO$_2$ using the electrophoretic light scattering technique, which is based on the scattering of light from particles that move in liquid under the influence of an applied electric field. The inset in Fig. 4 indicates a negative electrokinetic potential, which is an inherent property of the sol-gel-derived TiO$_2$. Consequently, it can be stated that the negative potential of the sol-gel-derived TiO$_2$ film generates a built-in electric field which has an analogous effect to that of a negative gate bias, resulting in a shift of the flatband voltage to more positive values so that the threshold voltage change can be more pronounced. These results suggest that proper optimization of the composite insulator, formed by means of a sol-gel process, can be extended to control the threshold voltage, as well as the flatband condition in OTFTs.

IV. CONCLUSION

Improvements in the performance of pentacene TFTs have been achieved by using a PMMA-co-MAA/sol-gel-derived TiO$_2$ composite insulator, without augmenting the gate-leakage current. Importantly, we found a significant reduction in the threshold voltage, which was strongly related to the negative surface potential of the sol-gel-derived TiO$_2$ film. These results provide useful information on the operation of OTFTs containing sol-gel-derived composite insulators and are promising for the further development of low-voltage OTFTs with high performance.

REFERENCES