Preparation of PMMA-co-MMA/TiO$_2$ Composite Film by Sol-Gel Process and Its Application to OTFTs as a Gate Insulator

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Abstract

In this study, nanocomposite layer composed of PMMA-co-MMA and TiO$_2$ was prepared by sol-gel process using TTIP as a precursor and was utilized as a gate insulator of OTFTs. The composite insulator provides the lower threshold voltage and the enhanced sub threshold slope of OTFTs mainly due to its higher dielectric constant than that of the bare PMMA-co-MMA. Consequently, it is demonstrated that the sol-gel process can open an interesting direction for the fabrication of high-performance OTFTs, and contribute for OTFTs to be feasible for real applications.

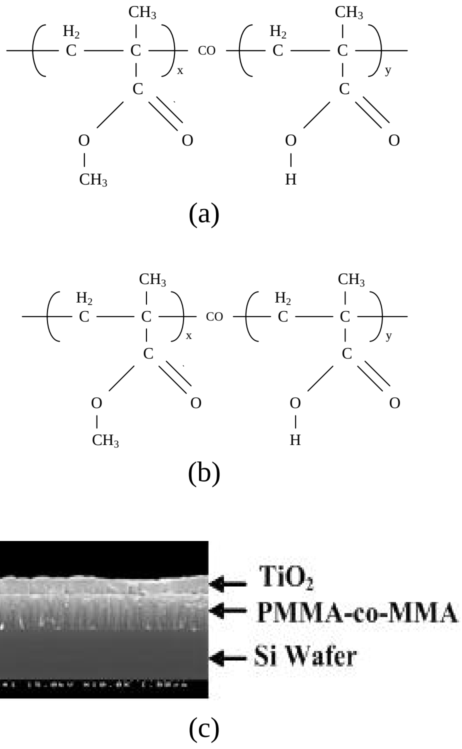
1. Introduction

Organic thin-film transistors (OTFTs) have been the focus of intense research efforts at least since 1980s[1,2]. The motive of attentions in organic electronics is mainly originated from that organic semiconductors can offer a unique combination of properties: the conductivity of these materials can be tuned by chemical or electrochemical manipulation; they are low density, bendable and easily processed. Additionally, they are compatible with flexible substrates and suitable for large area coverage, where low cost of manufacturing is required. In order to fully enjoy the advantages of OTFTs, namely, mechanical flexibility and low-cost feature for flexible electronics, it is necessary to develop polymeric gate dielectric materials. Recently, OTFTs with solution-processable polymer gate insulators have been reported and some of them show excellent electronic properties close to those with inorganic gate insulators[3,4]. However, in spite of eye-opening progress in the performance of OTFTs with polymeric gate insulators, high threshold voltage due to low dielectric properties of polymeric insulators is one of subjects to be solved.

Previously, *Cui et al.* have reported that a self-assembled SiO$_2$ nanoparticle thin film as a gate insulator provided large field-effect mobility and low threshold voltage under low operating voltages[5]. And we have also reported that organic-inorganic composites which consisted of polyvinylacetate (PVAc) and clays, or poly(4-vinylphenol) (PVP) and titanium dioxide (TiO$_2$) particles, could improve the performance of OTFTs by modifying the dielectric properties of polymers[6,7]. But it was very difficult to disperse inorganic particles uniformly into polymer solution and aggregated clusters in the composite film even deteriorated device performance.

2. Experimental Details

For the preparation of sol-gel precursor solution, PMMA-co-MMA (Aldrich) was dissolved in chloroform without further purification and TTIP (Aldrich) was mixed with PMMA-co-MMA solution. The composition ratio of sol-gel precursor solution by weight percentage is approximately 15 : 1 (PMMA-co-MMA solution : TTIP). The molecular structures of PMMA-co-MMA and TTIP are shown in figure 1 (a) and (b). For the OTFT fabrication, a 50-nm-thick Al gate electrode was thermally evaporated on a glass substrate using the first shadow mask. Two different gate insulators, such as a 740-nm-thick PMMA-co-MMA layer and a 1140-nm-thick composite layer, were formed by spin-coating followed by solvent degassing at a pressure of about 2×10^{-3} Torr for 30 min. The elimination of solvent was carried out at room temperature because a phase-segregation of TiO$_2$ film could occur by heat. And, for the composite film, it was observed that TiO$_2$ film was immediately formed at the surface of PMMA-co-MMA layer by the hydrolysis reaction or process after spin-coating. Figure 1 (c) shows the cross-sectional image of the composite film. Pentacene was thermally evaporated through the second mask onto the gate insulator at a rate of 1.0 Å/s and to be about 60 nm thick. Subsequently, a 50-nm-thick Au layer was thermally evaporated through the third mask for the source and drain contacts. All the deposition processes were carried out at a base pressure of about 1.6×10^{-6} Torr. The channel length and width of OTFTs are 90 μm and 300 μm, respectively.



(a)

(b)

(c)

Figure 1. The molecular structures of (a) PMMA-co-MMA and (b) TTIP and the cross-section SEM image of (c) the PMMA-co-MMA/TiO$_2$ composite film (The resulting TiO$_2$ film is thought to be an anatase crystalline form.).

3. Results and Discussion

MIM (Al/insulator/Au) capacitors were fabricated to investigate the dielectric properties of the bare PMMA-co-MMA and the composite insulators, and the experimental capacitance *vs.* frequency plots are shown in figure 2. It is evident that the capacitance of the capacitor with the composite insulator is larger than that with the bare PMMA-co-MMA. The calculated dielectric constant of the composite insulator was about 9.4 at 100 kHz, while that of the bare PMMA-co-MMA was calculated about 4.0, which is attributed to the dielectric property of TiO$_2$ film ($\varepsilon_r \approx 30$). And OTFTs with the composite insulator can operate at relatively lower voltages than the devices with the bare PMMA-co-MMA.

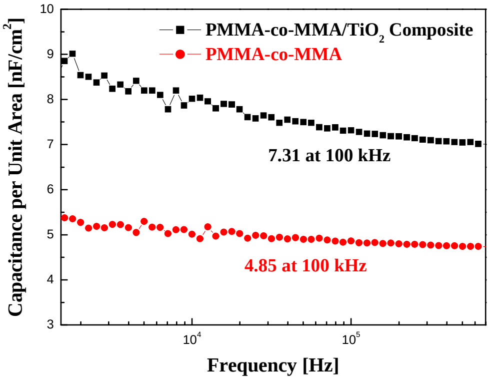


Figure 2. The capacitance-frequency plots of MIM capacitors with two different insulators.

Typical output and transfer characteristics of OTFTs with different gate insulators are shown in figure 3. For the output characteristic measurements, the drain current (I_D) of the fabricated OTFTs, where the drain-source voltage (V_D) was swept from 0 to - 40 V with the sweep step of -0.5 V at the gate-source voltage (V_G) of -30 V. And for the transfer characteristic measurements, the V_G was swept from 10 to - 40 V with the sweep step of - 0.5 V at the V_D of -30 V, and from the curve of the square root of I_D versus V_G, field effect mobility (μ_{eff}) in the saturation region is estimated using eq. (1):

$$I_{D,sat} = \frac{W\mu_{eff}C_i}{2L}(V_G - V_T)^2 \qquad (1)$$

where C_i is the capacitance of the gate insulator per unit area, V_T is the threshold voltage[8]. In accordance with our expectations, it is clearly observed that the composite insulator led to increased saturation current, and lower threshold voltage and subthreshold slope of OTFTs due to its high dielectric constant. However, the gate leakage current of OTFTs with the composite insulator is larger than that of OTFTs with PMMA-co-MMA. It is thought that the large gate leakage current hindered drain current from further increasing in the high gate (or drain) voltage region for transfer (or output) characteristics. Comparisons of parameters of two devices are listed in Table I.

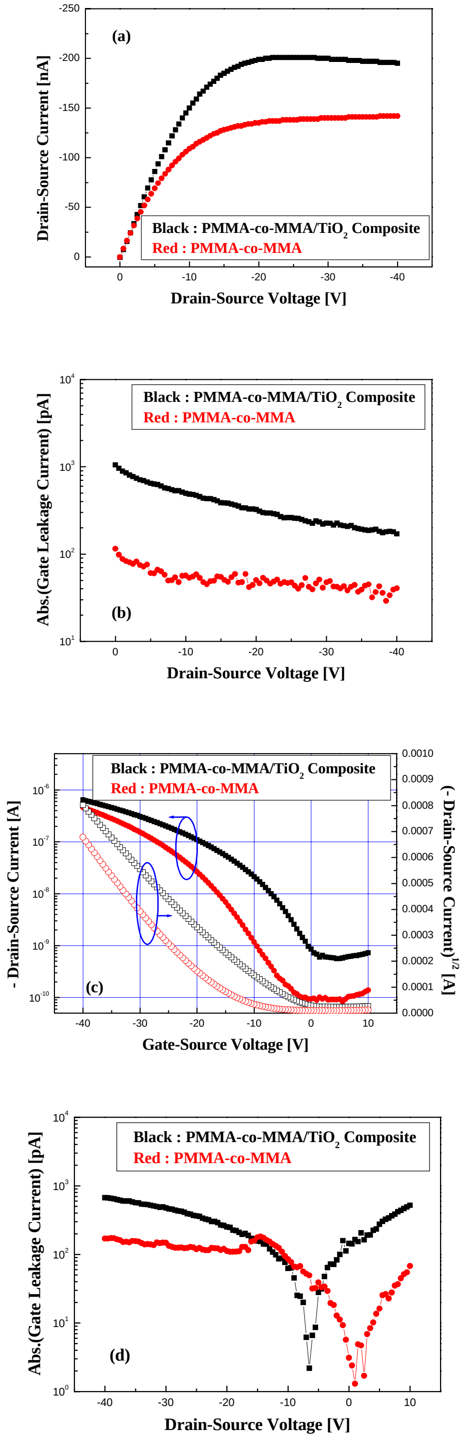


Figure 3. The electrical characteristics of OTFTs: (a) output characteristics (@ V_G = -30 V) and (b) the concomitant gate leakage current; (c) transfer characteristics (@ V_D = -30 V) and (d) the concomitant gate leakage current.

Table 1. The properties of the fabricated OTFTs according to the gate insulators.

	PMMA-co-MMA	Composite
V_T	-16.5 V	-7.1 V
S.S.	6.5 V/decade	5.5 V/decade
I_{on}/I_{off}	5.2×10^3	1.2×10^3
μ_{eff}	0.09 cm^2/Vs	0.05 cm^2/Vs

According to AFM images, it is thought that relatively rough surface of the composite insulator might be the main cause of the large gate leakage current, compared to that of the bare PMMA-co-MMA. The root-mean-squre roughness for the composite insulator is measured about 1.36 nm and 2.03 nm for the bare PMMA-co-MMA. And it is also observed that the growth of pentacene molecules was affected by the gate insulator, which resulted in different grain sizes in pentacene film according to the gate insulators. The smaller grains of pentacene on the composite film than that on PMMA-co-MMA can explain the reduction in the field effect mobility for the device with the composite insulator because grain boundary deteriorates charge transport among vicinity grains.

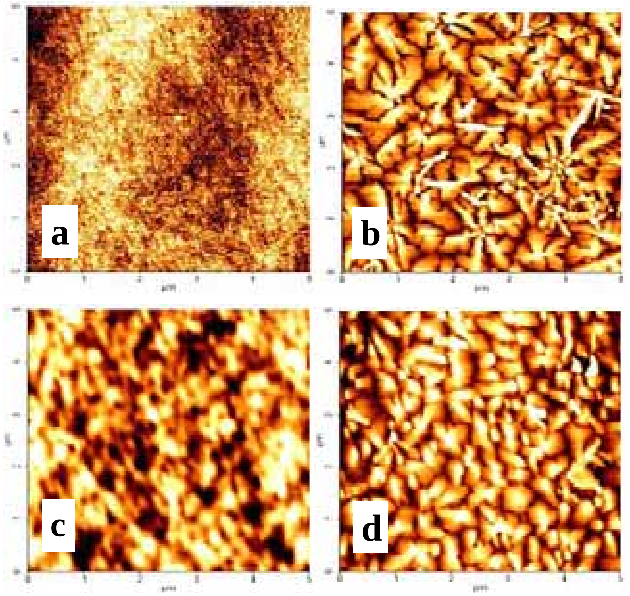


Figure 4. The AFM images: (a) the bare PMMA-co-MMA film, (b) pnetacene on the bare PMMA-co-MMA film, (c) the composite film, and (d) pentacene on the composite film.

4. Summary

OTFT is believed to be one of the key elements for future flexible electronics. However, OTFTs often suffer from high operating voltage due to the low charge carrier mobilities of organic semiconductors. Since the field-induced current is proportional to the field-induced charge density and carrier mobility, one way to overcome this problem is to use *high-k* gate insulators, which can enhance the field-induced carrier density. However, most *high-k* materials used for OTFTs so far are based on ceramics and hence are usually brittle and expensive to prepare. The poor mechanical properties of these materials make it highly challenging to be realistic in the flexible electronics. In addition, the preparation of these *high-k* materials requires a high-temperature annealing process, which is not compatible with plastic substrates. Consequently, it is necessary to develop a cheap and easy way (e.g. a solution-processable method) to fabricate gate insulators with both a high dielectric constant and a mechanical flexibility. Acceding to these demands, nanocomposite materials with *high-k* particles have been reported by some groups, but there are still critical issues associated with aggregation and uniform dispersion of nanoparticles. In this work, we have successfully achieved our purpose to develop a solution-processable insulator with *high-k* property by mixing PMMA-co-MMA with TTIP, which is easily prepared by a sol-gel process and simply forms TiO_2 film at room temperature by hydrolysis reaction. Nevertheless, there are some drawbacks in the sol-gel derived composite insulator to realize a reliable device performance; *high-k* insulators often lead to some hysteresis in the electrical characteristics and applying electric field to the gate for the device with *high-k* insulator creates dipoles within the insulator, which increase the surface disorder at the semiconductor-insulator and consequently reduce the field effect mobility due to a localization of charge carriers[9]. Currently, our investigations are focused to overcome such drawbacks of sol-gel derived composite insulators.

5. Acknowledgements

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6. References

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