

# Preparation and Characterization of Plasma Polymerized Methyl Methacrylate Thin Films as Gate Dielectric for Organic Thin Film Transistor

Wei Ao\*, Jae-Sung Lim\* and Paik-Kyun Shin<sup>†</sup>

**Abstract** – Plasma polymerized methyl methacrylate (ppMMA) thin films were deposited by plasma polymerization technique with different plasma powers and subsequently thermally treated at temperatures of 60 to 150 °C. To find a better ppMMA preparation technique for application to organic thin film transistor (OTFT) as dielectric layer, the chemical composition, surface morphology, and electrical properties of ppMMA were investigated. The effect of ppMMA thin-film preparation conditions on the resulting thin film properties were discussed, specifically O-H site content in the ppMMA, dielectric constant, leakage current density, and hysteresis.

**Keywords:** Plasma polymerized methyl methacrylate (ppMMA), Organic thin film transistor (OTFT), Dielectric layer, Hysteresis

## 1. Introduction

Organic thin film transistors (OTFTs), deemed as the future of organic electronics, have been widely studied over the last decades [1]. However, the property of the insulator layer of OTFTs should be studied further for overall device performance improvement. One of the keys for improving the OTFT device performance is the use of high dielectric constant material.

Poly(methyl methacrylate) (PMMA) has been successfully used as gate dielectric in OTFTs with pentacene employed as semiconductor layer [2]. The combination meets the demands of high-performance OTFTs [3–5]. In particular, insulator property is very important for OTFT performance. Polymeric materials used for gate dielectric have been limited to PMMA and Poly(vinyl acetate) (PVAc) in most research, although there are numerous alternatives for improving the device performance [6]. OTFTs using *p*-type pentacene as active layer which rendered highest mobility have been acknowledged [7]. PMMA, acting as insulator layer material, can be easily hydrolyzed and can very well be recomposed. Therefore, contact with pentacene can be effectively conglomerated. Plasma polymerization process has been confirmed to be suitable in obtaining high-quality insulator layer with low surface energy, high dielectric constant, and less electron traps [8]. However, hydroxyl bonds are frequently incorporated in the deposition process of plasma polymerization, leading to hysteresis effect [9]. Various plasma polymerized insulator thin films have been

studied for application in organic electronic devices including plasma polymerized vinyl acetic acid and plasma polymerized allylamine [10] as well as plasma polymerized thiophene [11]. In addition, we have investigated plasma polymerized styrene and plasma polymerized vinyl acetate for application in OTFTs as gate insulator.

In the present paper, we propose a method to decrease the O-H bond caused by the hydroxyl bonds by post-deposition temperature treatment. In the deposition of plasma polymerized methyl methacrylate (ppMMA) using inductively coupled plasma (ICP) source, a transparent polyethylene terephthalate (PET) substrate was utilized in consideration of its applications to flexible displays. Thermal expansion coefficient between the flexible PET and the TFT layers is different. Thus, to reduce the thermal stress induced, the organic gate insulator can be used [12].

To find a better preparation condition for the ppMMA for application in OTFT as gate dielectric, the plasma power and post-deposition thermal treatment temperature were varied. The chemical composition and surface morphology of ppMMA thin films were investigated. Electrical property investigations of ppMMA were also carried out. The effect of ppMMA thin film preparation conditions on the resulting thin-film properties was discussed.

## 2. Experimental

### 2.1 Insulator layer deposition by plasma polymerization

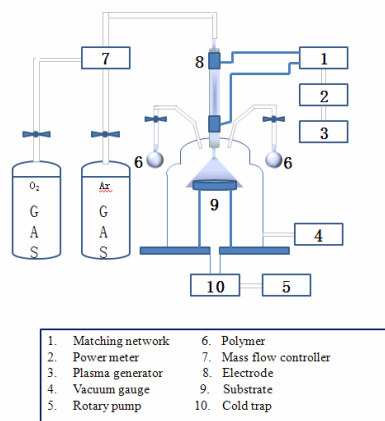
The substrates used in the present paper were indium tin oxide (ITO)-coated PET with surface resistivity of 45 Ω/□.

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The substrates were cleaned by sonication disposal, washed with isopropyl alcohol and de-ionized water alternately in each step for 5 min, dried by N<sub>2</sub> gas at 120 °C for 10 min, and finally moved into a vacuum. Fig. 1 shows a schematic of 13.56 MHz radio-frequency (rf) plasma generator (AUTO ELECTRIC, ST-1000) used for plasma polymerization deposition with an impedance matching box (load coupler; AUTO ELECTRIC, LC-1000). In addition, rf power meter (Collins 30K-3) was connected to measure electric discharge power. A vacuum gauge (973 gauge controller) was used to detect the vacuum. Furthermore, cold trap with liquid nitrogen was installed to protect the rotary pump from the attack of methyl methacrylate (MMA) monomer [13]. The ppMMA thin films were deposited under the following experimental conditions: 100, 150, and 200 W of plasma power; 0.1 torr of system pressure; bias voltage of 3 V; and deposition time of 10 min. While Ar gas was introduced into the reaction tube (15 sccm) to generate ICP, MMA monomer was introduced into the Ar plasma. Subsequently, the ppMMA insulator layer was deposited.



**Fig. 1.** Schematic diagram of the plasma-polymerization equipment

## 2.2 Post-deposition thermal treatment of ppMMA

It is highly possible that moisture and oxygen gas will not be exhausted fully from the vacuum in the reaction chamber. Thus, O–H bonds would exist on the surface of the plasma polymerized polymer thin films. In addition, the dielectric property of plasma polymerized thin films might be possibly deteriorated by the O–H bonds. Due to these, we carried out post-deposition thermal treatment for the plasma polymerized thin films on a hotplate. The investigation of thermo gravimetric analysis (TGA) weight loss for ppMMA [14] has shown that the ppMMA begins to melt at 180 °C. Therefore, the temperatures for the post-deposition thermal treatment were set as 60, 90, 120, and 150 °C.

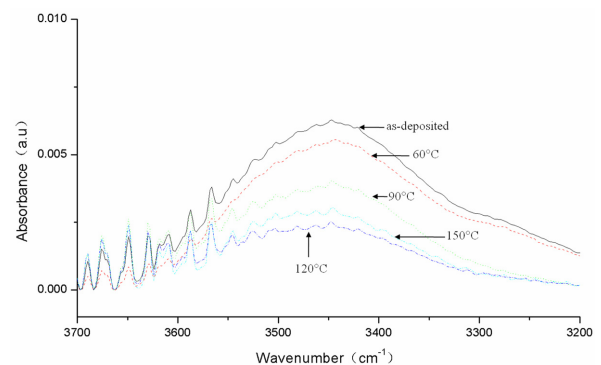
## 2.3 Characterization of the ppMMA thin films

The composition of ppMMA thin films was investigated by Fourier transform infrared spectroscopy (FT-IR) (*Bruker Optics, Vertex 80v*). The surface morphology of the ppMMA thin films was investigated by atomic force microscopy (AFM) (*Digital Instrument, Nanoscope Multimode Iva*). The thickness of ppMMA was obtained by field emission scanning electronic microscopy (FE-SEM) (*Hitachi, S-430*). The electrical properties of ppMMA thin films were investigated by current-voltage (*I-V*) (*Keithley 236 Source Measurement Unit*) and capacitance-voltage (*C-V*) (*Keithley 590 CV Analyzer*) analyses. For the *I-V* and *C-V* analyses, we prepared a metal-insulator-metal (MIM) structure of Al/ppMMA/Al and a metal-insulator-semiconductor (MIS) structure of ITO/ppMMA/pentacene/Au. For the *p*-type semiconducting layer, an 80 nm thick pentacene thin film was prepared by vacuum thermal evaporation process. Subsequently, 100 nm thick aluminum and gold thin films to be used as electric contact were prepared using the same process.

## 3. Results and Discussions

### 3.1 Chemical composition of the ppMMA

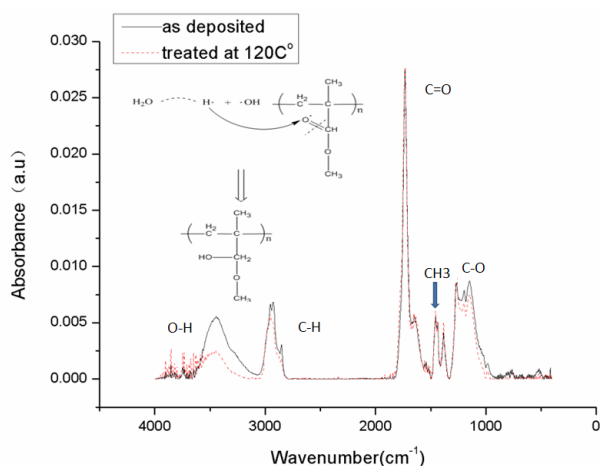
Attenuated total reflectance FT-IR spectra investigation was carried out for the single-layer plasma poly(methyl methacrylate) [15]. Fig. 2 shows the FT-IR spectra of bare and thermally treated ppMMAs, where peaks for O–H stretches at 3,400 cm<sup>-1</sup> are illustrated. The bare ppMMA sample shows high composition in the O–H sites, whereas the thermally treated ppMMA thin films show reduced O–H stretches at 3,400 cm<sup>-1</sup>, indicating that the O–H sites could be removed by post-deposition thermal treatment. Among the thermally treated ppMMA thin films, the one treated at 120 °C reveals the smallest O–H site content. Focusing on the O–H stretches at 3400 cm<sup>-1</sup>, the vacuum



**Fig. 2.** O–H peaks in the FT-IR spectra for ppMMA thin films prepared with plasma power of 200 W and subsequently thermally treated at 60, 90, 120, and 150 °C

produced during plasma polymerization of the MMA seemed not high enough to exhaust  $O_2$  and  $H_2O$  gases effectively. After the post-deposition thermal treatment, the O-H bands in ppMMA were reduced, although their thickness showed no obvious change. The O-H stretches decreased sharply after thermal treatment at  $90\text{ }^\circ\text{C}$  and reveal a minimum value for ppMMA treated at  $120\text{ }^\circ\text{C}$ , probably because the glass transition temperature in ppMMA was from  $85$  to  $165\text{ }^\circ\text{C}$ . When the thermal treatment temperature was higher than  $100\text{ }^\circ\text{C}$ , water vapor dissipated, although no breakage in the chemical bonds in ppMMA was observed.

Fig. 3 shows the comparison of the chemical composition between ppMMA thermally treated at  $120\text{ }^\circ\text{C}$  on a hotplate and that of the as-deposited ppMMA. Both ppMMA thin films reveal similar spectra except for the peak at  $3,400\text{ cm}^{-1}$ . This indicates that the post-deposition thermal treatment resulted only in the removal of O-H sites from ppMMA. The strong bands at  $1,100\text{ cm}^{-1}$  and near  $1,380\text{ cm}^{-1}$  correspond to the C-O stretch and  $CH_3$  stretches, respectively. Additionally, the C=O and CH stretches at  $1,700\text{ cm}^{-1}$  and  $2,900\text{ cm}^{-1}$  are evident. In the glass transition region between  $85$  and  $165\text{ }^\circ\text{C}$ , ppMMA space structure angle merely changed, and the C=O bond did not break in the case of the treatment with less than  $120\text{ }^\circ\text{C}$ , as shown in Fig. 3.

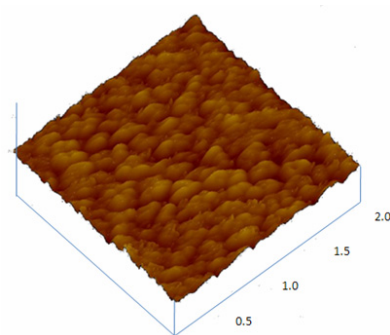


**Fig. 3.** FT-IR spectra of the as-deposited ppMMA and thermally treated ppMMA thin films prepared with plasma power of  $200\text{ W}$  and thermal treatment temperature of  $120\text{ }^\circ\text{C}$

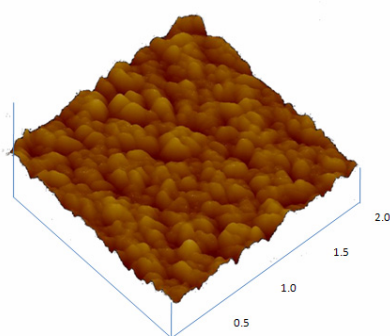
### 3.2 Surface morphology of the pentacene/ppMMA/Si

AFM is a high resolution type of scanning probe microscopy [16]. To find the better process condition of ppMMA as gate dielectric for OTFT, the surface morphology of vacuum-evaporated pentacene ( $80\text{ nm}$ ) on ppMMA/Si was investigated. Fig. 4 shows the  $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$

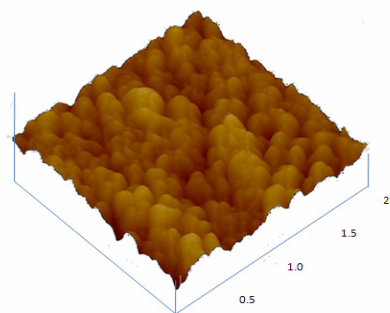
$\mu\text{m}$  AFM images of pentacene on ppMMA thin films prepared with  $100$ ,  $150$ , and  $200\text{ W}$  plasma powers. The pentacene thin film on ppMMA prepared at  $200\text{ W}$  plasma power reveals larger grain size than that deposited on the ppMMA prepared at plasma powers of  $100$  and  $150\text{ W}$ . The bigger grain size of the pentacene semiconductor would indirectly cause higher field effect mobility of the charge carrier in the resulting OTFT device. Hence, the  $200\text{ W}$  plasma power could be the better choice to obtain high-performance gate dielectric layer in OTFT devices.



(a)  $100\text{ W}$  (RMS=5.834 nm)



(b)  $150\text{ W}$  (RMS=4.401 nm)



(c)  $200\text{ W}$  (RMS=4.801 nm)

**Fig. 4.** The  $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$  AFM images of the pentacene thin films on top of ppMMA thin films prepared with different plasma powers: (a)  $100\text{ W}$ ; (b)  $150\text{ W}$ ; (c)  $200\text{ W}$

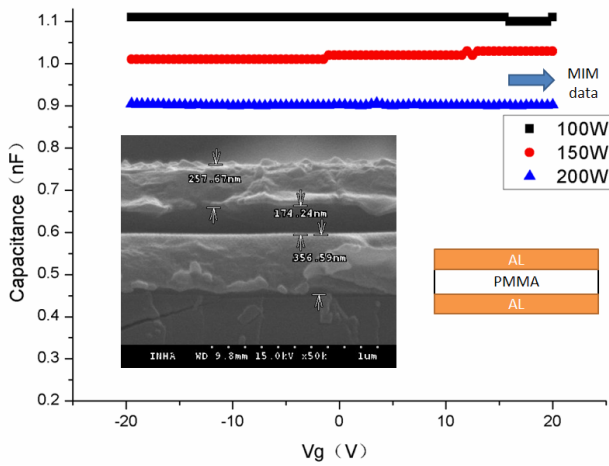
### 3.3 Electrical properties of the ppMMA

The dielectric constant  $k$  of the ppMMA was investigated using a MIM structure of Al/ppMMA/Al. Fig. 5 shows the capacitance measurements, where the cross-sectional diagram and SEM image of the MIM structure are presented.

The dielectric constant  $k$  of the ppMMA layer can be obtained using the equation

$$k = C \frac{d}{\epsilon_0 A}$$

where  $\epsilon_0$  is the permittivity in vacuum ( $8.85 \times 10^{-14} \text{ F}\cdot\text{cm}^{-1}$ ),  $d$  is the polymer thickness,  $C$  is the device capacitance, and  $A$  ( $0.04 \text{ cm}^2$ ) is the area of the insulator [14].



**Fig. 5.** Capacitance of the MIM structures of Au/ppMMA/Au with ppMMA prepared by different plasma powers of 100, 150, and 200 W

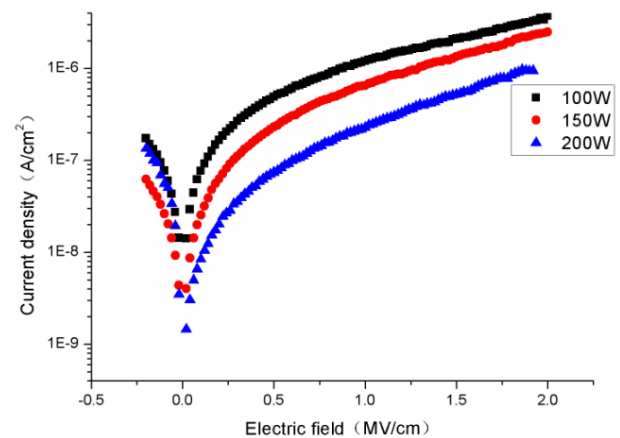
Table 1 provides the capacitance measurement results and calculated dielectric constants of ppMMA. All the ppMMA thin films reveal fairly large dielectric constant  $k$  values of over 5.6, and their values are similar to each other, independent of the plasma power of the ppMMA polymerization deposition. Hence, from the viewpoint of dielectric constant, all the plasma powers proposed in the present study are suitable for obtaining a good insulator for OTFT fabrication.

**Table 1.** Dielectric constant ( $k$ ) for the ppMMA thin films prepared by various plasma powers

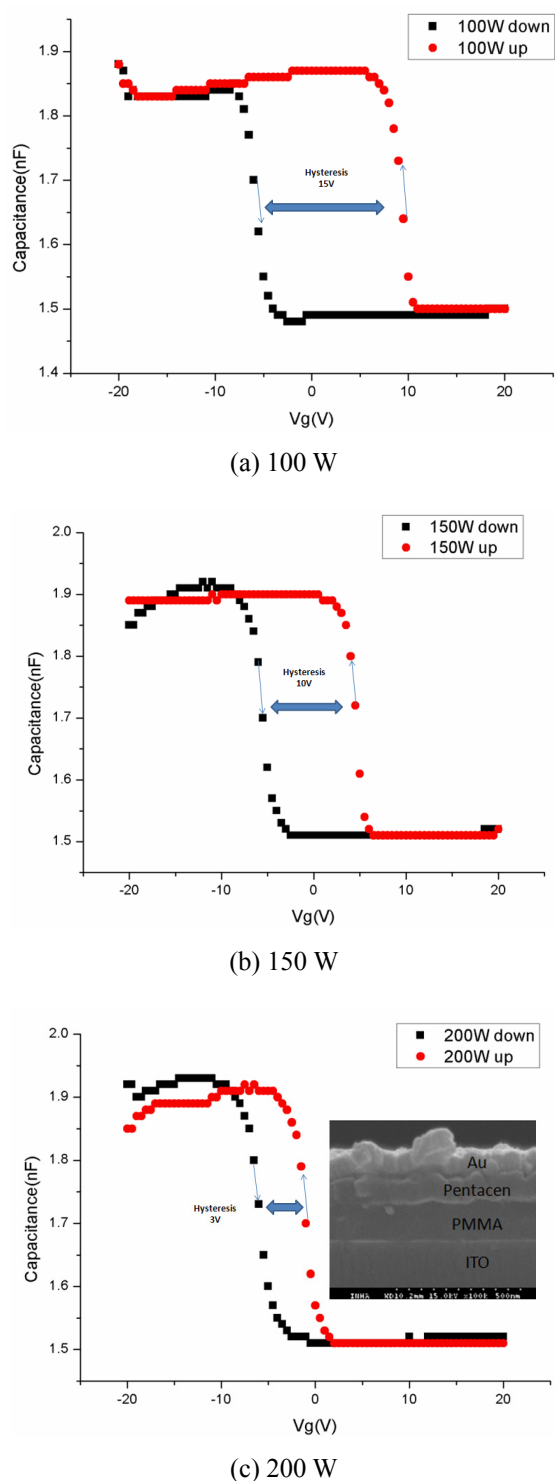
Power	$A$ [ $\text{cm}^2$ ]	$d$ [nm]	$C$ [nF]	$k$
100W	0.04	180	1.1	5.60
150W	0.04	200	1.0	5.65
200W	0.04	220	0.9	5.60

Another critical dielectric property of the insulating layer for OTFT is the leakage current density, which is directly related to the on/off current ratio  $I_{\text{on/off}}$ . Measurement of the current density-voltage ( $J$ - $V$ ) characteristics of the MIM structure with the ppMMA insulators was conducted. Fig. 6 shows the  $J$ - $V$  characteristics of the MIM structures with the ppMMA thin films prepared with plasma powers of 100, 150, and 200 W. ppMMA reveals relatively low leakage current density of  $10^{-8} \text{ A/cm}^2$  at an electric field of 0.25 MV/cm compared with the leakage current density of  $10^{-7} \text{ A/cm}^2$  for PVP [17]. In contrast to dielectric constant, the plasma power for the plasma polymerization deposition shows obvious effect on the leakage current density of the resulting MIM device. The higher the plasma power is, the lower is the leakage current density. Therefore, a 200 W plasma power is proven to be capable of obtaining a better dielectric layer for OTFT device, and an OTFT device with the ppMMA dielectric prepared under this condition would have higher on/off current ratio  $I_{\text{on/off}}$ .

One of the main problems of the application of polymer dielectrics to OTFT device is the occurrence of hysteresis [1], which might result in instability of the OTFT device performance. Hysteresis in OTFTs is caused by two factors. One is the insufficiently cross-linked polymerization and O-H adsorption in the polymer dielectric network. The other is the presence of electron traps in semiconductor and gate dielectric [18]. In the current research, we tried to find a method to obtain the lowest O-H bonds in the ppMMA dielectric and highly cross-linked polymer network. The  $C$ - $V$  analysis on the MIS structure shown in Fig. 7 proves the effectiveness of the method. The MIS structure with ppMMA prepared with 200 W plasma power reveals a remarkably smaller hysteresis than those of the MIS structures with ppMMA prepared with plasma powers of 100 and 150 W.



**Fig. 6.** Current density-electric field measurement results for the MIM structures of Au/ppMMA/Au with ppMMA prepared by different plasma powers of 100, 150, and 200 W



**Fig. 7.** Hysteresis in the  $C$ - $V$  curve for the MIS structure of ITO/ppMMA/pentacene/Au with ppMMA prepared by different plasma powers of 100, 150, and 200 W

#### 4. Summary and Conclusion

In order to obtain better insulating layers for application to OTFT device, plasma polymerization for ppMMA thin

films and post-deposition thermal treatment were carried out. The chemical compositions and electrical properties of the ppMMA thin films were investigated, and the effect of ppMMA thin film preparation process conditions on the resulting dielectric properties were discussed. The post-deposition thermal treatment of ppMMA was proved to be effective in reducing the O-H bonds in ppMMA. Moreover, ppMMA treated at 120 °C showed the smallest O-H peaks in the FT-IR spectra, which demonstrated that ppMMA revealed the smallest O-H bond content in the polymer network. All the ppMMA thin films prepared in the current study revealed fairly large dielectric constant values of over 5.6. The ppMMA prepared with plasma power of 200 W showed the smallest leakage current density of  $10^{-8}$  A/cm<sup>2</sup> under an electric field of 0.25 MV/cm in the  $J$ - $V$  characteristics, as well as the smallest hysteresis in the  $C$ - $V$  characteristics. Therefore, we conclude that the plasma polymerization process of ppMMA with subsequent thermal treatment is a promising process technique in the preparation of a high-performance dielectric layer for OTFT device fabrication.

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