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Studies on poly(methyl methacrylate) dielectric layer for field effect transistor: Influence of polymer tacticity

Ji Hoon Park [a], D.K. Hwang [b], Jiyoul Lee [b], Seongil Im [b], Eugene Kim [a,*]

[a] Department of Information Display Engineering, Hongik University, Seoul, 121-791, Republic of Korea
[b] Institute of Physics and Applied Physics, Yonsei University, Seoul, 120-749, Republic of Korea

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Abstract

Electrical properties of three kinds of poly(methyl methacrylate) (PMMA) with different tacticity, i.e. isotactic(*i*), syndiotactic(*s*), and atatic(*a*), were investigated for the application in field effect transistor. Metal-insulator-silicon structures were fabricated via spin coating PMMA on heavily doped p-type silicon (p^+-Si) followed by evaporating gold electrode. The electrical characteristics were remarkably improved by heat-treatment at temperatures 40 K above glass transition temperatures of PMMAs. Among the three PMMA isomers, *i*-PMMA was observed to possess the highest dielectric strength (1.1 MV/cm) with the lowest leakage current density, but also the lowest dielectric constant (k=2.5). Top-contact thin film transistors fabricated with the configuration of NiO_x/pentacene/*i*-PMMA/p^+-Si, where the NiO_x being used as a source/drain electrode, displayed relatively a decent field effect mobility of 0.042 cm^2/V-s which is not that low with such a low dielectric capacitor as thick *i*-PMMA film.

Keywords: Gate insulator; Tacticity; Field effect transistor; Poly(methyl methacrylate); Organic field effect transistor; Electrical properties and measurements

1. Introduction

Organic thin film transistors (OTFT) have attracted attentions due to their apparent advantages over inorganic thin film transistors in terms of mechanical flexibility, light weight, and low processing cost [1]. OTFT manufactured using pentacene as channel layer has been acknowledged as one of the most promising examples and the performance has been remarkably improved for the last decade [2,3]. Although the characteristic properties of pentacene TFTs such as field effect mobility, on/off current ratio, and threshold voltage were reported to be comparable to those of amorphous Si TFTs, there has not been enough progress on organic dielectric materials suitable for reliable OTFT [4,5]. Polymeric materials used for gate dielectric have been limited to poly(methyl methacrylate) (PMMA), poly-4-vinylphenol, and polyimides in most of studies [4–8], and there still remains large room for improving their properties.

PMMA is categorized into three species with respect to its tacticity, i.e. isotactic(*i*-), sydiotactic(*s*-), and atatic(*a*-), depending on the way that pendant methacrylate groups are arranged along the backbone chain of a polymer (Fig. 1), which led to different tertiary structures. Among three PMMAs only *a*-PMMA has been used as dielectric materials, and electrical characteristics of thin films made of other isomers have not been reported. We here begin with measuring dielectric strength and capacitance (dielectric constant) of thin films made of various PMMAs as cast and annealed above glass transition temperatures (T_g). Heat-treatment would facilitate the rearrangement of the polymer chains, which reduces the vacant volume present within the amorphous chains and helps chains to be packed close to each other [9]. It was observed that electrical properties of *i*-PMMA were superior to other PMMA isomers and these could be greatly improved by the heat-treatment. Secondly, top-contact thin film transistors with the configuration of NiO_x/pentacene/*i*-PMMA/p^+-Si, where NiO_x was used as a source and drain electrodes and heavily doped

* Corresponding author. Present address: Department of Applied Science, Hongik University, Mapo-ku, Sangsoo-dong 72-1, Seoul 121-791, Republic of Korea.
E-mail address: ekim@hongik.ac.kr (E. Kim).

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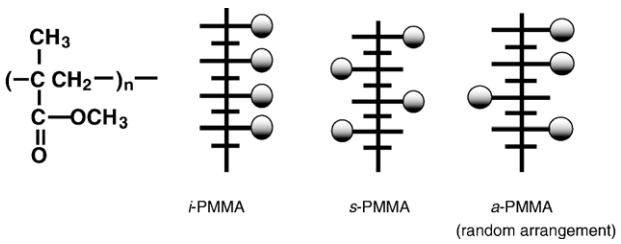

Fig. 1. Repeating unit of PMMA polymer and the schematic views of PMMAs with different tacticity: isotactic, syndiotactic and atatic PMMA, respectively. Shaded circles represent methacrylate groups.

p-type silicon(p^+-Si) was used as gate electrode, were fabricated. NiO_x was chosen since it has recently been shown to be a promising electrode material for pentacene-based transparent TFTs due to its good sheet resistance (~60 Ω/□) and work function that was well matched to that of pentacene [10].

2. Experimental details

i-PMMA and *s*-PMMA were purchased from Polyscience, and *a*-PMMA were from Pressure Chemical, and were used without further purification. The characteristics of these molecules are listed in Table 1. Each PMMA was dissolved into anisole solvent and then stirred over 6 h. The PMMA gate dielectric layers were deposited on p^+-Si substrate (0.01–0.02 Ω cm) by spin coating from solutions at appropriate concentrations. (6.3 wt.%, 13 wt.%, and 10.5 wt.% for *i*-PMMA, *s*-PMMA, and *a*-PMMA, respectively) The solutions were spun at 3000 rpm for 40 s to form uniform films. Prior to spin coating, the substrates were ultrasonically cleaned in chloroform, methanol, and de-ionized water in that order. The wafers were then dipped into buffered oxide etchant ($HF:H_2O$=1:6) to remove native oxide. Thicknesses of the films were determined to be ~640 nm by surface profilometry. To study the effect of heat-treatment, half of PMMA thin films were heat-treated at temperatures 40 K above T_g (100 °C, 170 °C and 160 °C for *i*-PMMA, *s*-PMMA, and *a*-PMMA, respectively) for 1 h in vacuum oven and the others were dried in vacuum desiccator. A 1 h annealing time was chosen to allow enough time for the polymer to relax to the equilibrium and to avoid possible degradation of the films during excessively long annealing. It was verified that larger annealing time did not change the thickness of the film any further. Gold electrode was then evaporated on the PMMA films at a base pressure of about 7×10^{-4} Pa for the measurement of dielectric strength and capacitance. Inset of Fig. 2(a) shows the schematic of our metal-insulator-semiconductor (MIS) structure prepared for the measurements of current density–electric field (J–E) and capacitance–frequency (C–f) characteristics.

Table 1
Molecular characteristics of PMMAs

	% Tacticity	Number average molecular weights (Mn)	Polydispersity indices (Mw/Mn)	Glass transition temperature (°C)
i-PMMA	98	118,000	1.32	60
s-PMMA	>79	133,000	1.16	130
a-PMMA	n.a.	160,000	1.06	120

% Tacticity of *a*-PMMA is not available.

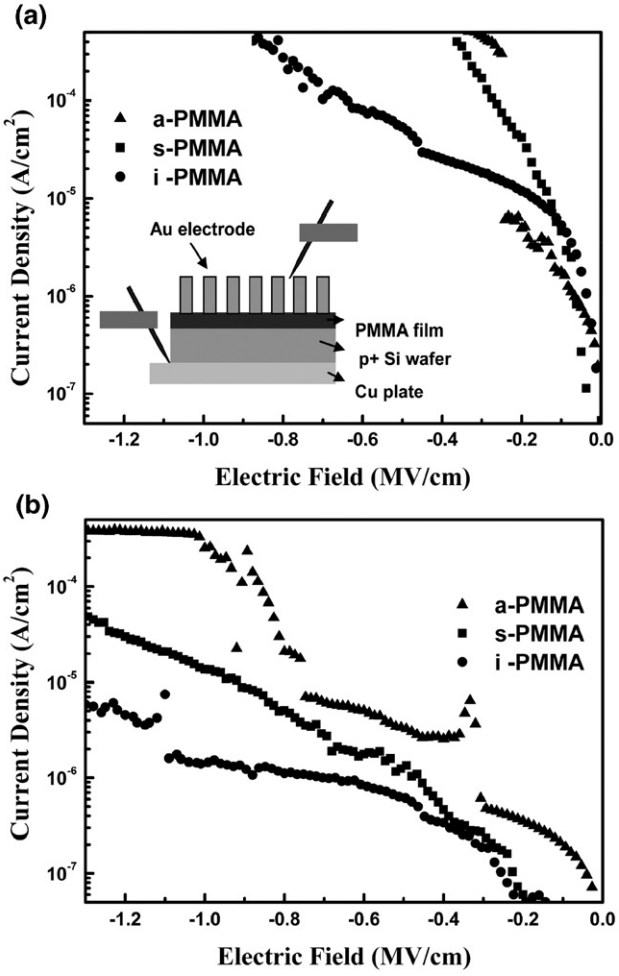

Fig. 2. Current density–electric field characteristics of PMMA with different tacticity: (a) without heat-treatment, and (b) after heat-treatment at $T=T_g+40$ K for 1 h. Schematic view inside shows our MIS structure for J–E measurements.

For TFT device fabrication (inset in Fig. 4), channels and source/drain electrodes were sequentially patterned on PMMA film through shadow masks at room temperature by thermal evaporation in vacuum chamber where base pressure was 1.3×10^{-4} Pa. The thermal deposition rate was fixed to 1 Å/s for the evaporation of pentacene (Aldrich Chem. Co., ~99% purity) and to 30 Å/s for the evaporation of NiO powder (99.97% purity) [10]. The thicknesses of pentacene and NiO_x films were 50 and 100 nm, respectively, as monitored by a quartz crystal oscillator and confirmed by ellipsometry. The nominal channel length and width were 90 and 500 μm, respectively.

All current–voltage (I–V) relations for MIS and OTFT structures were performed using semiconductor parameter analyzer (Agilent 4155C). I–V characteristics for MIS structures were converted into J–E relation after taking the thickness of dielectric layer into account. The C–f measurements were also made with impedance analyzer (HP 4192A) in the dark. All the

Table 2
Dielectric properties and thicknesses of PMMA films with different tacticity

	Film thickness (nm):	Dielectric strength (MV/cm)	Capacitance (nF/cm^2)	Dielectric constant
i-PMMA	570 (640)	1.1	3.9 (4.0)	2.5 (2.9)
s-PMMA	600 (640)	0.6	4.3 (4.1)	2.9 (3.0)
a-PMMA	600 (640)	0.3	4.1 (4.1)	2.8 (3.0)

The values in parenthesis are the ones obtained without heat-treatment.
Dielectric strength defined as the electric field where current density begins to exceed 2×10^{-6} A/cm^2.

measurements were carried out in air ambient and room temperature conditions.

3. Results and discussions

Fig. 2 exhibits the J–E characteristics of PMMAs with different tacticity, before and after heat-treatment. After spin coating, the polymer molecules exist in nonequilibrium conformation extended toward the surface and radial direction of spinning, and surplus free volume should also be left over due to abrupt evaporation of solvent. While polymer molecules are not mobile enough for conformational transitions below T_g, heat-treatment above T_g facilitates relaxation toward equilibrium conformation to fill up that free volume [9]. Thickness reduction of about 6% for *s*-PMMA and *a*-PMMA films, and 11% for *i*-PMMA were observed (Table 2). Larger volume reduction in case of *i*-PMMA is attributed to the better packing of polymer chains associated with crystallization [11]. Because the electric field in voids is higher than the average field in the dielectric film, the dielectric strength of the PMMA films with some residual voids is expected to be less than that of the continuous solid films without voids. As shown in Fig. 2(a) and (b), PMMAs without heat-treatment, show leakage current that is too high to be used for dielectric in TFT while with the treatment significantly improved J–E characteristics were achieved. Dielectric strength defined as the electric field where current density begins to exceed 2×10^{-6} A/cm^2 were listed in Table 2. Among the three PMMAs, *i*-PMMA appeared to have the most superior J–E characteristics.

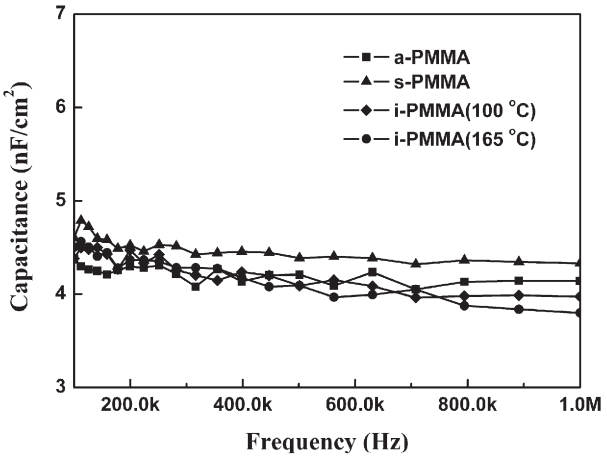

Fig. 3. Capacitance–frequency characteristics of PMMA with different tacticity after heat-treatment at $T=T_g+40$ K for 1 h. The data for *i*-PMMA annealed at 165 °C for 1 h are also shown.

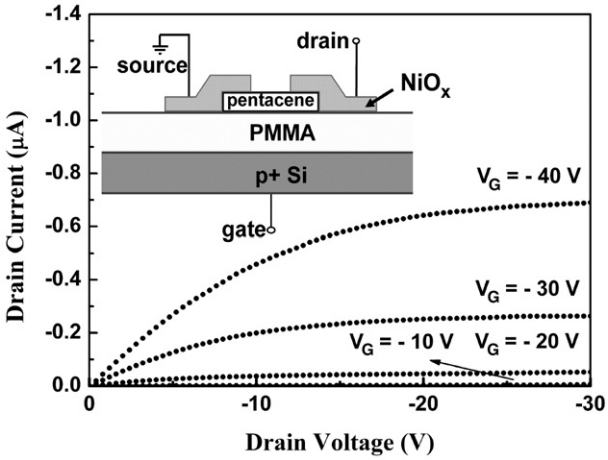

Fig. 4. Drain current–drain voltage characteristics of NiO_x(100 nm)/pentacene (50 nm)/*i*-PMMA(570 nm, heat-treated)/heavily doped p^+-Si transistor devices.

Fig. 3 displays the C–f characteristics of PMMA films after heat-treatment. The capacitance data hardly varied with frequency, while relatively unstable capacitance patterns were observed for the films without heat-treatment, which reflect that the presence of more free volume facilitates various dielectric relaxations [12]. Given the capacitance (measured at 1 MHz), film thickness, and electrode area, we calculated dielectric constant as also summarized in Table 2. According to the table, dielectric constant becomes smaller after heat-treatment, and particularly significant reduction (from 2.9 to 2.5) was observed in the dielectric constant of *i*-PMMA. It is likely that the compact packing of molecules, due to the heat-treatment, may hinder the chain rotation of ester groups that are responsible for dipole moment to be aligned under the applied bias. We also annealed *i*-PMMA at 165 °C which is above melting point of *i*-PMMA. In this case, the thickness of *i*-PMMA film was maintained to be almost identical to that of *i*-PMMA film that was annealed at $T=T_g+40$ K. We have also measured the contact angle of the droplets of de-ionized water on all PMMA

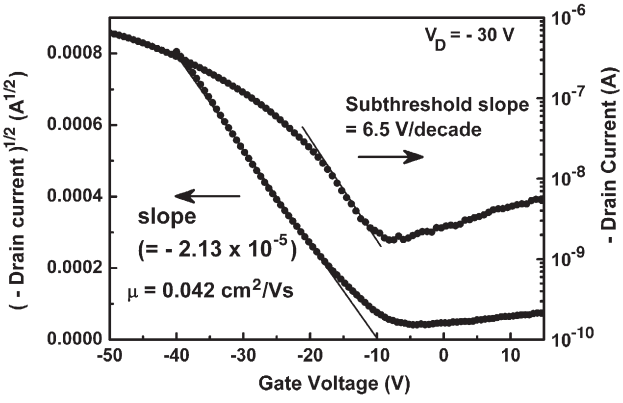

Fig. 5. $\sqrt{-I_D}$–V_G and $\mathrm{Log}_{10}(-I_D)$–V_G characteristics of NiO_x(100 nm)/pentacene (50 nm)/*i*-PMMA(570 nm, heat-treated)/heavily doped p^+-Si transistor devices under saturation regime ($V_D=-30$ V).

films. Regardless of tacticity and heat-treatment, an identical contact angle close to 65° was observed, which means that the surface energy difference among all the PMMAs is not conceivable.

Figs. 4 and 5 demonstrate the drain current–drain voltage (I_D–V_D) and the drain current–the gate voltage (I_D–V_G) curves, respectively, for our TFT device that consists of NiO_x(100 nm)/pentacene(50 nm)/*i*-PMMA(570 nm, heat-treated)/p^+-Si. We selected only *i*-PMMA as the TFT dielectric layer because of its low leakage current (as demonstrated in Fig. 2(b)). The results obtained using conventional *a*-PMMA can be found elsewhere [13,14]. Well-saturated output characteristics with increasing drain voltage were observed in Fig. 4. According to $\sqrt{I_D}$–V_G curve of Fig. 5, threshold voltage was observed at −10 V which is significantly smaller than the values reported elsewhere (−15 V [13] and −27.5 V [14].) for pentacene TFTs using *a*-PMMA and Au as gate dielectric and source/drain electrode, respectively. This means that carrier trapping at the interfaces between pentacene and heat-treated *i*-PMMA layer in our device is more or less restricted [14]. Field effect mobility could be extracted from square root of absolute values of drain current versus gate voltage curve. Our TFT exhibited mobility of 0.042 cm^2/V-s which is larger than or comparable to the values reported elsewhere [13,14]. As charge carrier transport occurs within a few monolayer of pentacene layer, the difference in microstructure at the interface between *i*-PMMA dielectric and pentacene might have influenced the hole transport [13]. The current modulation (I_{on}/I_{off}) was less than 10^3 under a drain saturation condition of V_D=−30 V, which is due to the large leakage current. Further improvement would be needed for *i*-PMMA to be utilized for high performance organic transistor. The experimental results reported hitherto show that *i*-PMMA possesses the interesting dielectric properties and is judged to be useful candidate as gate insulator material for organic TFT.

4. Conclusions

We have investigated the electrical properties of three kinds of PMMA with different tacticity for the application in field effect transistor. As heat-treatment of PMMAs at $T=T_g+40$ K greatly improved dielectric characteristics, among the three PMMAs isomers, *i*-PMMA displayed the highest dielectric strength (1.1 MV/cm) with the lowest leakage current density but also the lowest dielectric constant (k=2.5). We fabricated pentacene-based TFT that consists of thermally evaporated NiO_x, spin-coated and then heat-treated *i*-PMMA, and p^+-Si for the source-drain electrodes, gate dielectric, and gate electrode, respectively. Our TFT exhibited a field effect mobility as large as 0.042 cm^2/Vs which is not that low with such a low dielectric capacitor as 570 nm-thick *i*-PMMA film. Low threshold voltage of −10 V were also observed. We conclude that *i*-PMMA among three isomers showed the best dielectric properties and may be a promising gate insulator for pentacene TFT.

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