Letter

Plasma polymerized methyl methacrylate gate dielectric for organic thin-film transistors

Jae-Sung Lim, Paik-Kyun Shin*, Boong-Joo Lee, Sunwoo Lee

Department of Electrical Engineering, Inha University/Regional Innovation Center for Environmental Technology of Thermal Plasma (RIC-ETTP), #253 Yonghyun-dong, Nam-gu, Incheon Metropolitan City 402-751, South Korea

Department of Electronic Engineering, Namseoul University, 21 Maeju-ri, Seonghwan-eup, Cheonan-City, Choongnam 330-707, South Korea

Department of Electrical Information, INHA Technical College, #253 Yonghyun-dong, Nam-gu, Incheon Metropolitan City 402–752, South Korea

A pentacene-based organic thin-film transistor (OTFT) device with plasma polymerized methyl methacrylate (ppMMA) dielectric film was fabricated. The ppMMA showed a higher dielectric constant of 3.86 than that of conventionally processed PMMA and a MIS capacitor with the ppMMA revealed negligible hysteresis in $C-V$ curves. The OTFT device with the ppMMA dielectric showed a field-effect mobility of $0.08 \pm 0.02 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ in the saturation region, a lower threshold voltage of $-3 \pm 0.15 \text{ V}$, a sub-threshold slope of $0.959 \pm 0.05 \text{ V/decade}$, an on/off current ratio ($I_{on}/I_{off}$) of $1.0 \times 10^4 \pm 0.10$, and a lower operating voltage of $-10 \text{ V}$.

© 2010 Elsevier B.V. All rights reserved.

Recently, more and more works have been emerged on organic thin-film transistors (OTFTs), because it might pave the way for various promising applications such as low-cost radio frequency transponder, bio sensor, pixel driver transistors for flat panel displays, as well as general flexible electronics. Early OTFT studies focused mainly on organic semiconductor materials, of which performance should be at least close to that of a-Si as active channel layer for conventional TFTs. Presently, pentacene seems to be one of the best choices as a low-molecule organic semiconductor for OTFTs [1,2]. Similar to conventional TFTs, gate dielectrics play a key role in the device performance of OTFTs. Because it forms interfaces with the organic semiconductor layer, crystallinity and electrical properties like field-effect mobility are often affected. Furthermore, operating voltage of the OTFT is decided by thickness and permittivity of the gate dielectric material. Although several conventional inorganic insulators (oxides, nitrides, etc.) could also be implemented to an OTFT, various organic polymer insulators are presently studied because it might match well with organic semiconductors from the viewpoint of interface characteristics as well as process compatibility [3–6]. Organic polymer insulators can be prepared by various solution process but they might cause possibly overall degradation of the device performance. A dry process for polymer insulator could be a solution to avoid such problem. Plasma polymerization technique would be an alternative to prepare the polymer gate dielectric because plasma polymerized polymers show excellent coating adhesion, chemical/mechanical/thermal stability, high barrier effect, and pinhole-free formability [7–9].

In this study, plasma polymerized methyl methacrylate (ppMMA) dielectric thin films were deposited and used as a gate dielectric of a bottom-gated top-contact type OTFT with Au/pentacene/ppMMA/ITO configuration. Film composition, surface morphology, and electrical properties of the ppMMA were investigated and their effect on the OTFT performance was studied.

ITO-coated glasses (Samsung Corning Co.) were used as substrates, where ITO was 150 nm-thick and had a sheet
The substrates were ultrasonically cleaned in acetone, ethanol and de-ionized water, by which most of the ITO surface organic contaminants were removed. The surface of ITO gate electrode was then treated in an Ar plasma prior to depositions of the insulating layer. A radio frequency (r.f.) capacitively-coupled plasma (CCP) with a pressure of 0.1 Torr, Ar flow rate of 10 sccm, and r.f. main power of 100 W was used for surface treatment of the ITO gate electrode. Without breaking vacuum after the plasma surface treatment, plasma polymerized methyl methacrylate (ppMMA) insulting layer was then deposited, where a MMA monomer (Sigma–Aldrich Co.) was used. Plasma polymerization of the ppMMA dielectric layers was done again using the r.f. CCP equipment. Details of the plasma polymerization equipment were described elsewhere [10]. The ppMMA was deposited under following experimental condition: main power of 200 W, bias power of 20 W, system pressure of 0.5 Torr, Ar flow rate of 30 sccm, and deposition time of 10 min. The thickness of the ppMMA film was measured by field emission-scanning electron microscope (FE-SEM; Hitachi, S-4300) and found to be about 100 nm. A 60 nm-thick-pentacene (Sigma–Aldrich Co.) active channel layer, and 100 nm-thick-Au source/drain electrodes layer were then deposited using thermal evaporation technique. The Au source/drain electrodes were patterned on pentacene layer through a shadow mask. The OTFT devices had inverted staggered structures of Au/pentacene/ppMMA/ITO.

Film composition, surface morphology, and electrical properties of the ppMMA were investigated using Fourier transform infrared spectroscopy (FTIR; Bruker Optics, Vertex 80v) in vacuum, contact angle measurements (Erma Inc.), X-ray diffraction (XRD; Rigaku, D/Max 2200V/PC), atomic force microscope (AFM; Digital instrument, Nanoscope Mutimode IVa) and capacitance–voltage analysis (C–V, Keithley 590), respectively. For investigating performance of the OTFTs, current–voltage (I–V) characteristics according to applied voltage change were measured by a source measurement unit (Keithley 236) combined with another source measurement unit (Keithley 2400).

**Fig. 1a** shows FTIR spectrum for the ppMMA thin film. The FTIR spectra of the ppMMA and conventional spin-coated poly methyl methacrylate (PMMA) are consistent with similarly processed materials in Ref. [7], which identifies chemical similarities and dissimilarities of the two materials. Functional groups such as C–O, C==O, and CH are observed. The ppMMA thin film exhibits strong bands at 1730 cm\(^{-1}\) corresponding to the poly dimethylketene-like vinyl ester structure. Additionally, the C==C and CH stretches at 1460 and 1386 cm\(^{-1}\) are also evident. In the ppMMA, plasma polymer was formed in a cross-linked 3D network which is typical in plasma polymerization. This is indicated by the differences between the characteristic absorption peaks of ppMMA and solution processed PMMA, suggesting significant amount of fragmentation and rearrangement in the plasma deposition process. Inset in the Fig. 1a is AFM image of the surface of ppMMA gate dielectric. The surface roughness of a 100 nm-thick-ppMMA on ITO-coated glass was characterized and showed good root mean square roughness of about 0.24 nm. Fig. 1b shows a cross-sectional SEM image of the OTFT device. The surface energy of the ppMMA dielectric was about 45 mJ/m\(^2\), which was similar to that of pentacene (42–48 mJ/m\(^2\)), which suggests that it might be possible to develop more efficient OTFTs channel by matching the surface energy of the ppMMA dielectric and the pentacene [11,12].

**Fig. 2** shows the reflective XRD patterns and AFM image of 60 nm-thick-pentacene layer grown on ppMMA dielectric. XRD and AFM experiments were performed in order to investigate the effects of the surface properties of the gate dielectric on the surface morphology of pentacene. The structure of pentacene layer was elucidated by XRD in reflection mode at 20 kV, 20 mA and Cu K\(\alpha\) radiation \((\lambda = 1.5406 \text{ Å})\) with a coupled \((\theta–2\theta)\) scans configuration. The corresponding XRD pattern contains a series of sharp (0 0 k) peaks indicating that the pentacene film is highly ordered. The first peak at 5.7\(^{\circ}\) (the thin-film phase) corresponds to a lattice parameter of 15.6 Å. The AFM images of pentacene layer on ppMMA reveal a dendritic structure.
with a grain size of \( \sim 1 \mu m \). The data suggest a robust and pinhole-free ppMMA film, where the growth morphology of pentacene was similar to those prepared on other polymer substrates [13].

One of the main problems of OTFT devices is the occurrence of hysteresis. Although they are very often ignored in the literature, Gu et al. [14] described hysteresis effect for MIS capacitors based on pentacene and attributed them to carrier trapping or migration of dopants [15]. Fig. 3a shows the \( C-V \) characteristics (100 kHz) of a MIS device with a 100 nm-thick ppMMA in dark at room temperature. The normalized capacitance \( C/C_{MAX} \) was ranged to be within 1.00 and 0.80 when voltage was applied from \(-20\) to \(+20 \) V. \( C-V \) characteristics in accumulation–depletion region were investigated using the MIS structure, and gate bias was swept back to check the amount of hysteresis origination from bulk or interface charge trapping. Very small hysteresis was observed in the \( C-V \) curves, which is due to low carrier trapping in MIS capacitor by non-solvent process and cross-linked polymerization deposition [16,17]. Dielectric constant \( k \) of the ppMMA layer was obtained with the following equation: [18]

\[
k = \frac{C d}{\varepsilon_0 A}
\]

where \( C \) (1.37 nF) is capacitance of the ppMMA dielectric, \( d \) and \( A \) are the ppMMA thickness (100 nm) and the dot area (0.04 cm\(^2\)), \( \varepsilon_0 \) is permittivity in vacuum \( (8.85 \times 10^{-14} \text{ F cm}^{-1}) \), respectively. According to the calculation, we obtained a higher dielectric constant \( (k = 3.86) \) for the ppMMA in an ITO–ppMMA–Au (MIM) sandwich structure, in contrast to the conventional PMMA layers \( (k = 2.5–2.9) \) in Ref. [3]. Jang et al. [4] described a correlation between device field-effect mobility and permittivity of dielectric materials. The higher field-effect mobility for dielectrics with higher dielectric constants may be due to increases the number of hole carriers at the semiconductor–dielectric interface. To investigate the potential of ppMMA as gate dielectric, we checked whether their leakage current density is sufficiently low by testing the corresponding ITO–ppMMA–Au (MIM) devices. Fig. 3b shows the current density–electric field \( (J-E) \) curve of the ppMMA insulator on ITO, and in particular the leakage behavior of the ppMMA dielectric. The ppMMA appeared to have quite a good dielectric strength of \( \sim 2 \) MV/cm based on a minimum leakage current density of \( \sim 10^{-8} \) A/cm\(^2\) even though its total thickness was only 100 nm. This might be caused by the pinhole-free ppMMA dielectric with highly cross-linked structure. Fig. 4 shows \( I-V \) characteristics of the
OTFT device with a 100 nm-thick-ppMMA layer in dark at room temperature: (a) typical output $I_D$–$V_D$ curve at applied step gate voltages ($\pm 2 \text{ V}$); (b) transfer $I_D$–$V_G$ curve at fixed $-10 \text{ V}$ drain voltage. The $I$–$V$ characteristics were measured for the OTFT device with channel length of $100 \mu\text{m}$ and channel width of $2000 \mu\text{m}$. From these data, average field-effect mobility was calculated in the saturation current regime ($V_D = -10 \text{ V}$) by equation which are derived in threshold voltage $V_{TH}$ and field-effect mobility $\mu$:

$$I_{Dsat} = \frac{W}{2L} C_i \mu (V_G - V_{TH})^2$$

where $W$ and $L$ are channel width and length, $C_i$ is capacitance per unit area of the ppMMA insulators, $V_G$ and $V_{TH}$ are gate and threshold voltage, and $\mu$ is field-effect mobility. The OTFT devices with the ppMMA insulator was found to have a field-effect mobility of $0.08 \pm 0.02 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$ in the saturation region, a lower threshold voltage of $-3 \pm 0.15 \text{ V}$, a lower sub-threshold slope of $0.959 \pm 0.05 \text{ V/decade}$, and an on/off current ratio ($I_{on}/I_{off}$) of $1.0 \times 10^4 \pm 0.10$, respectively. This combination of favorable properties demonstrated that the OTFT can be operated successfully at voltages $\sim 10 \text{ V}$.

An OTFT device with inverted staggered structure of Au/pentacene/ppMMA/ITO was fabricated. Proposed plasma polymerization method could be applied to a completely dry process for the OTFT fabrication, which offers a one-step and compatible process with conventional methods. The OTFT with the ppMMA dielectric was found to have a lower operation voltage of $-10 \text{ V}$. It was demonstrated in this report that the $100 \text{ nm}$-thick-ppMMA dielectric thin film could be used to obtain an OTFT device with favorable electrical properties and performance of the OTFT device could be significantly improved. Plasma polymerization method has the benefits of polymer gate dielectrics including potentially high capacitive coupling, and shadow mask patterning and in situ dry processing with large-area flexible substrates.

Acknowledgments

This work was supported by the Regional Innovation Center for Environmental Technology of Thermal Plasma (RIC-ETTP) at the INHA University designated by MKE (2009).

References