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Photocurable Polyimide Gate Insulator for Pentacene Thin-Film Transistor With Excellent Chemical Resistance by Low Temperature Processing

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We introduce a photo-curable polyimide-based gate insulator for organic thin-film transistors (OTFTs) that allows low-temperature and solution-based processing and provide low leakage current density and high field-effect mobility in devices. Organic gate insulator (PI-TTE) was prepared from a blend of 75.2 wt% hydroxyl group containing polyimide (PI) and 23.8 wt% trimethylolpropane triglycidyl ether as the crosslinker, 0.5 wt% benzoyl peroxide, and 0.5 wt% triphenylsulfonium triflate as the photoacid generator (PAG). PI-TTE showed extremely low leakage current density as 2.33×10^{-10} *A/cm*^{2} *at 3.3 MV/cm and exhibited a very stable capacitance (96.74 pF/mm*^{2}*) and it is unchangeable up to 600 hrs. Pentacene TFT using PI-TTE as a gate dielectric showed a field effect mobility as 0.203 cm*^{2}*/Vs and an on/off ratio of* 1.55×10^5 *with almost no hysteresis.*

Keywords Gate insulator; OTFT; polyimide

Introduction

Flexible organic electronics devices containing organic thin-film transistor (OTFT) have received much attention of late due to the potential of this technology in smart cards, radio frequency identification (RFID) tags, nonvolatile memories, sensors, and driver circuits in flexible display [1–4]. The significant advantage of using organic materials in electronic devices is the possibility of fabricating mechanically flexible devices on flexible substrates. To realize flexible organic electronics, not only

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the organic semiconductor but also the solution processable gate insulator is very important [5–7]. To form a well-defined interface between the organic semiconductor and the gate insulator during solution processing, the gate insulator should not be soluble in the solvent used to dissolve the organic semiconductor. Although thermal curing can be used to prepare insoluble organic gate insulators, a high temperature process is still necessary to complete the chemical crosslinking, and this process distorts the plastic substrate [8].

In this paper, we report a new photo-curable organic gate insulator (PI-TTE) based on a hydroxyl containing polyimide (PI) and a triglycidyl ether derivative as the crosslinker for OTFTs that allow a low-temperature and solution-based processing and provides excellent insulating and chemical resistance. Hydroxyl group containing PI was successfully synthesized with simple one-step condensation polymerization of monomers 2,2-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 3,3′-dihydroxy-4,4′-diaminobiphenyl. The synthesized soluble aromatic PI was further reacted with trimethylolpropane triglycidyl ether for crosslinking as film state. The insulating property, chemical resistance and pentacene TFT device as gate insulator of the prepared photocured polyimide-based insulator (PI-TTE) were investigated.

Experiments

Materials and Measurements

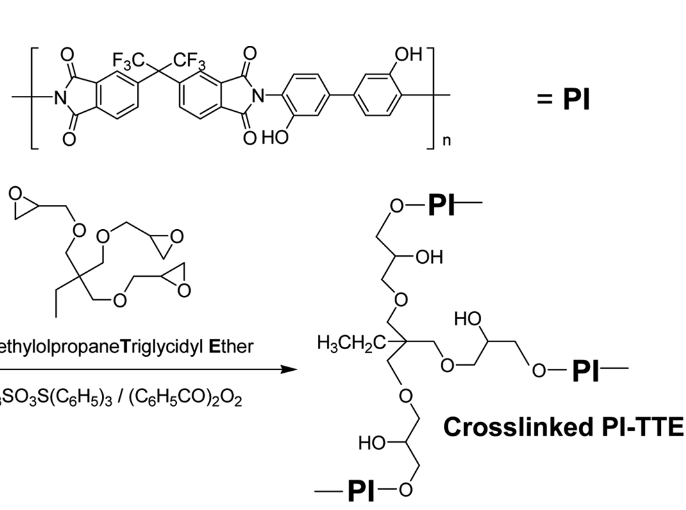
2,2-Bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 3,3′-dihydroxy-4,4′-diaminobiphenyl were purchased from TCI Chemical Co. (Japan). Trimethylolpropane triglycidyl ether, benzoyl peroxide (BPO), triphenylsulfonium triflate, pentacene were obtained from Aldrich Chemical Co. and used without any further purification. The thickness of the insulator films were determined with an alpha-step (KLA-Tencor α-step DC 50) surface profiler. All atomic force microscopy (AFM) images of the polymer surfaces were obtained with a Digital Instrument Nanoscope IV operating in tapping mode in air using a low-force imaging technique (a small tip-sample contact area), which is useful in the high-resolution imaging of polymers. The surface tension was calculated from the contact angles of water and diiodomethane on the polymer films, which were determined with a PHOENIX 450 contact angle analyzer. The output (I_{ds} vs. V_{ds}) and transfer (I_{ds} vs. V_{gs}) characteristics of the OTFT devices were measured with an Agilent E5272 semiconductor analyzer. The capacitance was measured with a HP4294A LCR meter. All these electrical measurements were carried out in air without any encapsulation.

Polymerization of Polyimide and Thin Film Fabrication of PI-TTE. In a 250 mL of three-neck flask containing 120 mL *N*-methyl-2-pyrrolidone (NMP), 2,2-bis-(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (13.3 g, 30 mmol), 3,3′-dihydroxy-4,4′-diaminobiphenyl (6.5 g, 30 mmol) and isoquinoline as a catalyst were dissolved by using a mechanical stirrer. The mixture was slowly heated to 70°C over 2 h with an oil bath and maintained that temperature for 2 h. The reaction temperature was increased to 200°C over a 2 h period and then the reaction mixture was refluxed. When the solution viscosity reached to 2,700 cps, the reaction was stopped by removing the oil bath and cooling the solution to room temperature. The hydroxyl group containing polyimide (PI) was precipitated by adding reaction mixture dropwise to the ice-cooled excess methanol/DI water co-solvent. The precipitate was filtered, washed with methanol and dried under vacuum to give 96% of hydroxyl containing polyimide. $M_n = 90{,}100$ g/mol (PDI = 1.7). ^{1}H-NMR (δ, DMSO-d_6) 7.19–8.23 (broad m, Aromatic H, 12H), 10.08 (s, hydroxyl H, 2H). FT-IR (cm^{-1}, KBr pellet) 1722 (C=O ketone), 1505 (C=C aromatic), 1383 (C-N).

The thin film as an organic insulator was prepared from a blend of 75.2 wt% hydroxyl group containing PI and 23.8 wt% trimethylolpropane triglycidyl ether (TTE) as the crosslinker, 0.5 wt% benzoyl peroxide, and 0.5 wt% triphenylsulfonium triflate as the photoacid generator (PAG). After spin-casting from a 10 wt% solution of the PI-TTE in γ-butyrolactone, the film was firstly soft-baked to remove the residual solvent on a hot plate at 100°C for 5 min, then exposed to a 5.0 J/cm^2 UV light to promote cross-linking in the film via a reaction involving the epoxy groups. Finally the film was baked at 160°C for an additional 30 min to harden the film.

Results and Discussion

The chemical structure of hydroxyl containing PI and crosslinked PI-TTE are presented in Scheme 1. With UV irradiation, network formation occurs by the photoinduced acid-catalyzed reaction between hydroxyl containing PI and the epoxy-containing crosslinker. The hydroxyl groups in PI can open the rings of the epoxy moieties to produce a product containing new hydroxyl groups, resulting in a cascade ring-opening reaction and finally the cured PI-TTE. Although the majority of a crosslinking reaction done by PAG occur between the epoxy crosslinker and the PI, BPO was added to enhance network formation by the oxy radical mechanism. These epoxy thermoset plastics bond exceptionally well to a wide range of materials and are highly moisture resistant. The PI-TTE insulator film showed excellent chemical resistance to common organic solvents (toluene, NMP, and γ-butyrolactone, etc), metal or oxide etchants based on acids, and photoresist stripper mainly composed of bases. This means that the PI-TTE is sufficiently chemically robust for use in photolithography and wet etching processes.



Scheme 1. Chemical structures of hydroxyl containing PI and crosslinked PI-TTE.

To investigate the potential of PI-TTE as a gate insulator, we firstly checked whether the leakage current density is sufficiently low and the breakdown voltages sufficiently high by testing the corresponding metal-insulator-metal (MIM) devices. The precursor PI-TTE mixture was spin coated on top of the bottom ITO electrode and then the films were soft baked, UV curing (except this step for non-crosslinked PI-TTE), and hard-baked as described in experimental section. The MIM devices were then completed by evaporating the top gold electrodes. The final thickness of a film was controlled to 300 nm. The active area of each MIM device was 50.24 mm^2. Figure 1 shows the leakage current density-electric field (*J-E*) characteristics of the PI-TTE (non-crosslinked and crosslinked) insulator film. The leakage current densities were lower than 2.33×10^{-10} A/cm^2 at 3.3 MV/cm and the breakdown electric field were larger than 3.5 MV/cm. The leakage current densities at 3.3 MV/cm are two orders of magnitudes lower than those of a plasma-grown AlO_x insulator with a phosphonic acid-based self-assembled monolayer [9]. Furthermore, these low leakage current densities and high breakdown electric fields are substantially superior to other polymer dielectrics. For example, the breakdown electric fields of crosslinked PVP and crosslinked cyanoethylated PVA are around 2.5 MV/cm, and the leakage current densities at 2.5 MV/cm are three orders of magnitude higher than that of crosslinked polyimide PI-TTE [10–11].

We also measured frequency dependent capacitance of a film of PI-TTE and calculated dielectric constant. The capacitance and dielectric constant of PI-TTE were found to be 96.7 pF/mm^2 and 3.3 at 10 kHz. In addition, we measured the capacitance of a sample stored in air over about 600 h. The capacitance of PI-TTE almost did not change even after 600 h, implying that the PI-TTE gate insulator is good resistant to moisture and other environmental conditions. Therefore, the field-effect mobility values obtained from the dielectric constant 3.3 for PI-TTE can be assumed to be very reliable [7].

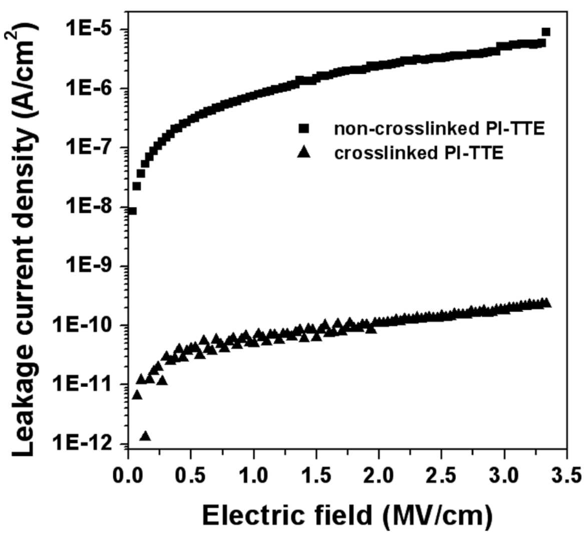


Figure 1. Leakage current density-electric field (*J-E*) characteristics of non-crosslinked and crosslinked PI-TTE.

Next we deposited pentacene on top of the non-crosslinked PI-TTE and crosslinked PI-TTE films and studied the surface morphology of the pentacene films deposited on the gate dielectrics using atomic force microscopy (AFM). Although non-crosslinked and crosslinked PI-TTE have similarly pinhole-free surfaces and low root-mean-square (RMS) surface roughness (6.1–6.7 Å), pentacene film on these dielectrics have somewhat different morphologies, as shown in Figure 2. The grain size of the pentacene film on the crosslinked PI-TTE film (2.5 ~ 3.5 μm) is larger than that on the non-crosslinked PI-TTE film (0.5 ~ 1.5 μm). The reduction of the surface polarity of hydroxyl containing PI as a result of the reaction its hydroxyl groups with trimethylolpropane triglycidyl ether (TTE) improves pentacene crystal growth on its surface, because the surface energy fluctuations that are present when there are a large number of polar groups on the PI surface prevent surface diffusion of the pentacene molecules and considerably increase the nucleation density [12].

We fabricated pentacene transistors in the top-contact geometry using the crosslinked PI-TTE gate dielectrics. Indium tin oxide (ITO) coated glass was used as the substrate and the ITO was patterned as 2 mm wide stripes to produce the gate electrode. PI-TTEs were spin-coated on top of the gate electrodes as gate insulators and films were soft baked, UV curing, and hard-baked as same manner in MIM device fabrication. The final thicknesses of gate dielectrics were adjusted to about 300 nm.

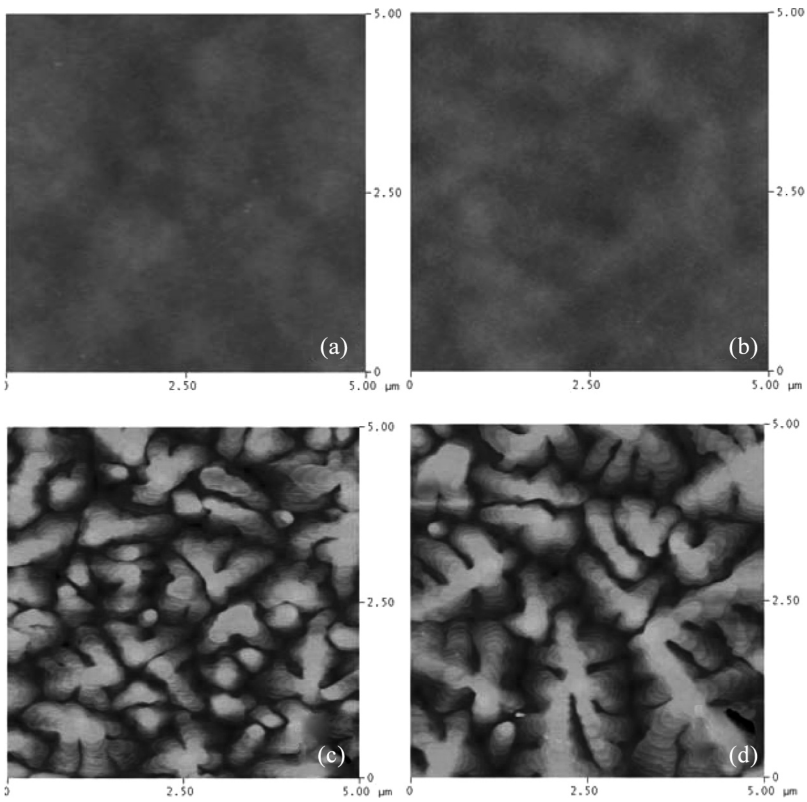
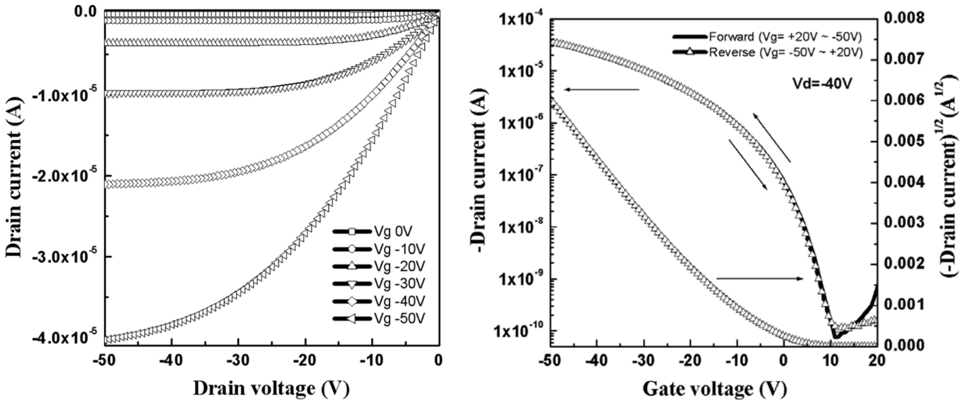


Figure 2. AFM images (5 μm × 5 μm) of the gate insulators of non-crosslinked PI-TTE (a) and crosslinked PI-TTE (b), and pentacene deposited on non-crosslinked PI-TTE (c) and crosslinked PI-TTE (d).



(a) (b)

Figure 3. Output (a) and transfer (b) characteristics of pentacene TFT with crosslinked PI-TTE as gate insulator measured in ambient air.

A 60 nm thick layer of pentacene was deposited on top of the gate insulator through a shadow mask by using thermal evaporation at a pressure of 1×10^{-6} torr. The pentacene TFTs were then completed by using thermal evaporation to add 50 nm thick source and drain gold electrodes on top of the pentacene layer, creating transistors with a channel length (L) and a width (W) of 50 and 1000 μm respectively. The output (I_{ds} vs. V_{ds}) and transfer (I_{ds} vs. V_{gs}) characteristics of the pentacene TFTs with PI-TTE are shown in Figure 3 (a) and (b). The device with crosslinked PI-TTE exhibits typical p-type characteristics with clear transitions from linear to saturation behavior in output curve. The transfer characteristics of crosslinked PI-TTE device also show a steep current increase in the subthreshold region and low leakage current as about 2.5×10^{-10} A. The filed-effect mobility was calculated in the saturation regime from the linear fit of the square root of the drain current ($I_d^{0.5}$) versus gate voltage (V_g) by using equation $I_d = (C_i W/2L)\mu(V_g\text{-}V_{th})^2$, where C_i is the capacitance of the crosslinked PI-TTE, and μ is the field-effect mobility. The mobility was calculated to be 0.203 cm^2/Vs with a C_i of 99.1 pF/mm^2. Pentacene TFT had a V_{th} of -2.8 V, and on/off current ratio of 1.55×10^5, and a subthreshold swing of 2.5 V/decade when V_g was swept from +20 V to −50 V as a drain voltage (V_d) of −40 V. The leakage current of the crosslinked PI-TTE device was improved by about more than four order of magnitude, 2.5×10^{-10} A, compared to 6.05×10^{-6} A for OTFT with non-crosslinked PI-TTE, threshold voltage and also subthreshold swing were also greatly enhanced. In addition, TFT device with crosslinked PI-TTE did not show any hysteresis despite the operation in ambient air. Since the polyimide-based photocurable PI-TTE gate dielectrics have good aspects, such as good chemical resistance and very stable capacitance, and furthermore the device using the gate insulator gives a high TFT performance without hysteresis, the PI-TTE is promising for the fabrication of low-cost and high performance TFT arrays.

Conclusion

In this paper, we have introduced a photo-curable polyimide-based gate dielectric that is chemically robust for common organic solvents, etchants and strippers.

The photocuring capability of the gate insulator makes the film insoluble at low temperature, so that reliable fabrication of OTFTs on plastic substrates is possible. The extremely low leakage current density as 2.33×10^{-10} A/cm^2 at 3.3 MV/cm and a stable capacitance up to 600 h implying that the PI-TTE gate insulator is good resistant to moisture and other environmental conditions. In addition, pentacene TFT devices fabricated using the PI-TTE did not show any hysteresis with a high field-effect mobility of 0.203 cm^2/Vs. We propose that solution-processable and photo-curable organic gate insulators of polyimide-based type could be a promising material for flexible electronics and display backplanes.

Acknowledgment

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