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Organic–inorganic hybrid gate dielectrics for low-voltage pentacene organic thin film transistors

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ABSTRACT

Organic thin film transistors (OTFTs) for low-voltage operation have been realized with very thin organic–inorganic hybrid gate dielectrics. Organic–inorganic hybrid thin films have good electrical properties, including high dielectric strength and low leakage current density down to 40 nm thickness. In addition, organic–inorganic hybrid thin films have smooth and hydrophobic surface. OTFTs with 40-nm-thick organic–inorganic hybrid dielectrics are operating within −5 V and exhibit a mobility of 0.3 $cm^2/(V\,s)$, a threshold voltage of −2.6 V, and a small subthreshold swing of 0.43 V/decade. In addition, OTFTs with 40-nm-thick organic–inorganic hybrid dielectrics have low hysteresis.

1. Introduction

Organic thin film transistors (OTFTs) have attracted much attention because of their processability, low cost, and flexibility. Their performance has improved impressively during the last two decades, which is comparable to that of hydrogenated amorphous silicon TFTs which are used in active matrix liquid-crystal displays [1]. The organic gate dielectrics are favored as the gate dielectrics in OTFTs due to their solution processability and flexibility which can lower process temperature and make it easy to fabricate large-area OTFTs [2,3]. However, the OTFTs with polymer gate dielectrics have a high threshold voltage due to the low capacitance of polymer gate dielectrics. To reduce the threshold voltage of OTFTs with polymer gate dielectric, it is necessary to increase the capacitance of gate dielectrics either by increasing the dielectric constant (κ) or by decreasing the thickness of gate dielectrics. However, the polymeric gate dielectrics are limited to have high capacitance since polymer materials have low κ and high leakage current densities. To increase the capacitance of solution processable dielectrics, nanocomposite dielectric layers [4] which are high κ nanoparticles embedded in polymer matrix or self assembly monolayers (SAMs) [5] are used as gate dielectrics to reduce the threshold voltage. However, a nanocomposite dielectric layer has a rough surface and a high gate leakage current to have a low on/off current ratio. In addition, it is difficult to fabricate uniform and pin-hole free SAMs.

The sol–gel derived siloxane based organic–inorganic hybrid materials (hybrimers) are nanocomposite materials in which inorganic and organic components are intimately linked at the molecular scale by a covalent bond and nano-sized oligomers are dispersed [6,7]. Since they combine the characteristics of both glass and polymers, it has low leakage current density and very smooth surface [8]. In addition, it is easy to control the physical and chemical properties of hybrimers such as dielectric constant, thermal stability, refractive index, surface roughness, and hydrophobicity by a suitable selection of precursors and optimization of processing parameters [6–9]. Furthermore, the photo-patternability of gate dielectric can be achieved by grafting photo-sensitive functional groups such as methacrylate groups to the siloxane. In this article, we synthesized photo-patternable methacryl-grafted hybrimers (MD) and fabricated thin MD gate dielectric layer under 100 nm for low-voltage OTFTs by solution process. We also investigated the properties of MD gate dielectrics and the performance of OTFTs depending on the thickness of MD gate dielectrics.

2. Experimental

Methacryl-grafted hybrimer resin containing oligosiloxanes grafted by methacryl radicals was synthesized using a simple non-hydrolytic sol–gel reaction. 3-(Trimethoxysilyl)propyl methacrylate (MPTMS, Aldrich) and diphenylsilanediol (DPSD, TCI) were used as precursors without further purification. Barium hydroxide monohydrate ($Ba(OH)_2{\bullet}H_2O$, Aldrich) was used as a catalyst to promote a condensation reaction between the two precursors. The total proportion of MPTMS and DPSD together was 1:

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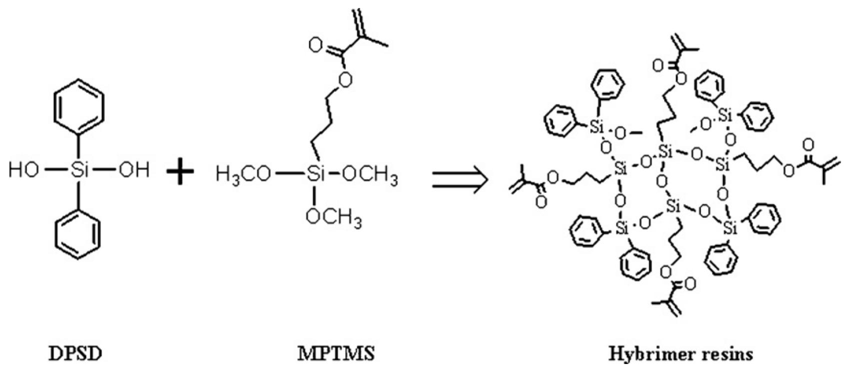

Fig. 1. Schematic synthesis diagram of hybrimers by a non-hydrolytic sol–gel reaction of diphenylsilanediol and methcryloxypropyltrimethoxysilane.

1 molar ratio. Synthesis of the MD resin was briefly illustrated in Fig. 1. The hybrimer thin films were deposited on highly doped silicon wafer with resistivity of 0.01 Ω cm. The solutions of MD hybrimer diluted in propylene glycol monomethyl ether acetate (PGMEA) were spin coated at 5000 rpm for 30 s on the substrate. Thickness of the dielectrics was controlled by varying the concentration of the MD hybrimer solution. The deposited films were exposed to UV light (λ = 365 nm, Hg lamp) for 90 s and thermally cured at 150 °C for 2 h in air condition. Aluminum dots were then thermally evaporated on the gate dielectrics to prepare the metal-insulator-semiconductor (MIS) capacitors. The electrical properties of the MD thin films including capacitance and leakage current density were measured using Al/MD thin film/Si structures with an HP4194A impedance analyzer and a Keithley 236 source-measure unit. We measured the surface roughness and the water contact angle of the MD thin films using an atomic force microscopy (AFM) (XE/100, PSIA) and a contact angle analyzer (Phoenix 150, SEO), respectively.

OTFTs were fabricated by using a top contact geometry. A 50-nm-thick pentacene active layer (Polysis, without purification) was thermally evaporated on MD dielectrics at a rate of 0.6–0.8 Å/s at substrate temperature of 80 °C. Gold was thermally evaporated on the pentacene films through a shadow mask to form source and drain electrodes. The OTFTs had a channel length of 50 μm and channel width of 3000 μm. Electrical characteristics of the OTFTs were measured using an HP 4155A semiconductor parameter analyzer. The crystallographic ordering and the morphology of pentacene on the hybrimer thin films were measured using a X-ray diffraction (XRD, D/MAX-RC diffractometer, Rigaku) and an AFM, respectively.

3. Results and discussion

Fig. 2 shows the current density-electric field (J-E) characteristics of the MD dielectrics as a function of the MD thin film thickness. In the thickness range between 40 and 100 nm, the dielectric strength, which is measured at leakage current density of 10^{-6} A/cm^2 [10], were higher than 2.5 MV/cm. The leakage current densities at 1 MV/cm increase from 4 to 15 nA/cm^2 as the film thickness decrease. Although the leakage current density of 40 nm MD dielectric layer is higher than that of the 300 nm MD dielectric layer, it is low enough to be used as gate dielectric in OTFTs. The dielectric constant of the MD dielectric film was 3.1, which was calculated from the film thickness and capacitance. The leakage current density and the dielectric strength of the hybrimer thin films are much better than those of the commonly used solution-processable polymer gate insulators in OTFTs [11–13].

Hybrimer thin films were fabricated by the condensation reaction between two precursors and by the polymerization of the methacryl groups. The condensation reaction between the methoxy groups of MPTMS and hydroxyl groups of DPSD forms the oligosiloxane networks. Oligosiloxane networks are cross-linked via polymerization under UV irradiation due to the photosensitivity of methacryl groups in MPTMS, which allows the hybrimer thin film to be more dense and robust. In addition, there are few hydroxyl groups in the hybrimer gate insulator [6] because the non-hydrolytic sol–gel reaction to fabricate the hybrimer does not use the water which is necessary to hydrolyze the precursor. The formation of totally cross-linked 3-dimensional networks and few hydroxyl groups in hybrimer gate insulator give the low leakage current density and high dielectric strength of hybrimer thin film.

It is known that surface properties such as surface energy and roughness of gate dielectrics are one of the most important factors affecting the performance of the OTFTs. The water contact angles of the MD thin films were as high as ~80° regardless of the film thickness. This result indicates that they have the hydrophobic surface and their surface energies are independent of the thickness since MPTMS and DPSD has a hydrophobic functional groups grafted on silicon such as phenyl or methyl groups. The surface morphologies of the MD thin films with different thicknesses were examined by AFM. Fig. 3 shows the AFM surface images of the MD thin films with various film thicknesses. The MD thin films have pin-hole free surface and their RMS roughness is as low as ~5 Å irrespective of the film thickness, which shows that the MD thin films have the very smooth surface.

Since MD thin films have the good electrical properties such as low leakage current densities and high dielectric strength, and the smooth and hydrophobic surface down to around a 40-nm-thick film, MD hybrimer can be used as the gate dielectrics in OTFTs. It

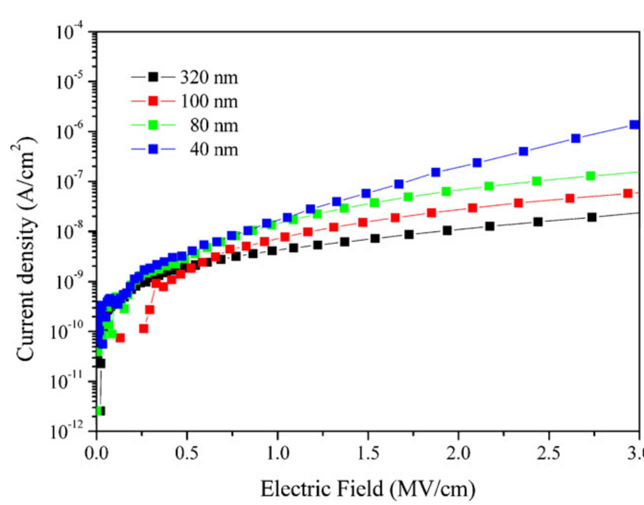

Fig. 2. Leakage current densities of MD hybrimer thin films with different thickness.