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Synthesis and characterization of hysteresis-free zirconium oligosiloxane hybrid materials for organic thin film transistors

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ABSTRACT

Zirconium oligosiloxane resin was synthesized by a sol-gel reaction and UV-curing for organic thin film transistors (OTFTs) application. The synthesized resin has long-term stability and durability, which could be easily processed to produce a smooth coating on Si substrate. The dielectric constant of the film increased from 2.46 to 4.67 according to the variation of zirconium content. In addition, a low leakage current density of 10^{-6}–10^{-7} A/cm^2 at 2 MV/cm was obtained. Pentacene-based OTFTs were fabricated using the synthesized hybrimer as the gate dielectric layer, and their performances were optimized by tuning the ratio of zirconium and siloxane. Organic thin film transistors with zirconium oligosiloxane gate insulator were found to exhibit excellent performances with enhanced mobility at low applied voltage, a high on/off ratio, and nearly-hysteresis-free transfer characteristics.

1. Introduction

Organic thin film transistors (OTFTs) have attracted increasing attention for electronics applications [1–5] owning to their light weight, flexibility, and ease of manufacture compared to general Si technology. Gate insulator plays an important part in the performance of OTFTs. Especially, polymer gate dielectrics are drawing great interests due to its flexibility and solution process techniques and thus fuelled the current surge in research interest [6–9]. Typical examples including poly(4-vinyl phenol) (PVP), polyimide (PI), poly(vinyl alcohol) (PVA), and so on. However, polymer gate insulators have limits to their practical application, which can result from their restricted dielectric properties, high driving voltage and severe hysteresis behavior. Some groups reported the OH groups present in PVP have been attributed to cause hysteresis behavior [10,11]. Another approach utilized metal oxides for the gate dielectrics, which depended on their high dielectric constant providing large gate capacitance [12,13]. However, surface of a high-k metal oxide dielectric usually lead to high hysteresis, which originally from numerous hydroxyl polar groups as defects and trap sites [14–16]. Many papers developed a bilayer insulator consisting of metal oxide and polymer to reduce the hysteresis behavior [17], but the fabrication process becomes a little complicated. So the developments of low-temperature processable, OH group-free polymer gate insulator are indispensable for fabricating electrically stable and superior OTFTs on flexible substrates. Sol-gel derived inorganic and organic hybrid materials (Hybrimers) have been extensively developed for their particular advantages, including individual and combined characteristics of organic and inorganic [18,19]. Our groups reported that organoalkoxysilane-based hybrids as gate insulator, the field-effect mobility of the OTFT reached to 4.9 cm^2/Vs was obtained [20]. But it causes very large hysteresis, which hinders further application. Recently, Choi et al. [21] studied methacrylate hybrimers could be promising candidates for gate dielectrics in low process temperature and solution-processable. However, they have low dielectric constant due to the existence of symmetrical phenyl groups, inducing high voltage operation. Thus it is indispensable to increase the dielectric constant while enhancing devices performances as well as low or free hysteresis, so that they can be effectively utilized in wide range of application.

In this study, a robust method to increase devices performance and control the current hysteresis of OTFT has been presented. The zirconium-oligosiloxane resin was synthesized by sol-gel method without the addition of water for hydrolysis, which can minimize the amount of residual OH groups, as shown in Scheme 1. Then, zirconium oligosiloxane hybrid coating films have been fabricated by spin coating and UV irradiation. The electrical property and surface morphology of hybrimer thin films were investigated. Moreover, the performance of OTFTs based on hybrimer gate

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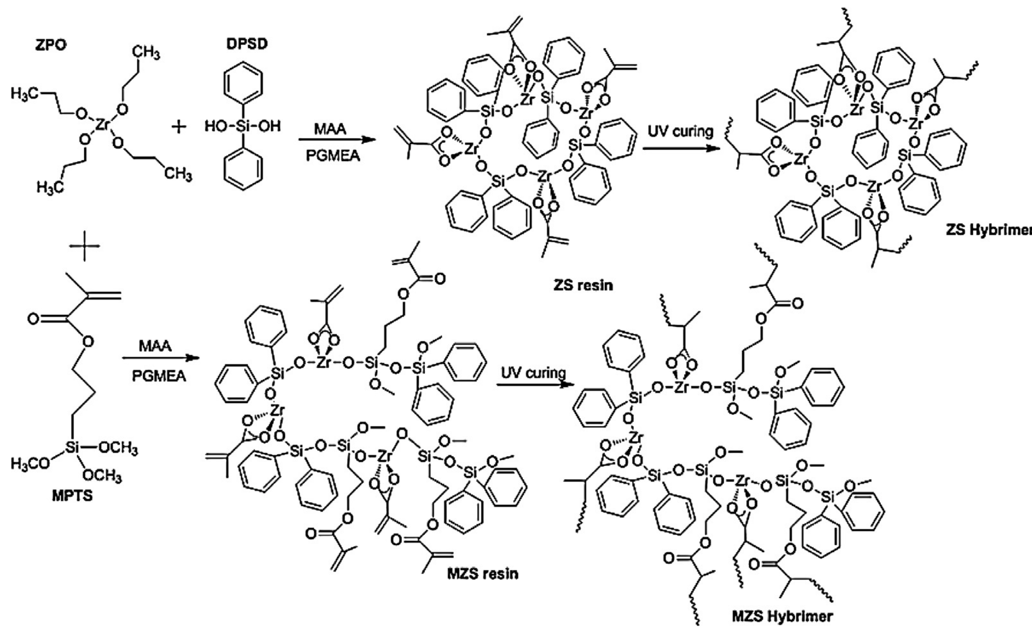

Scheme 1. Synthesis and fabrication of zirconium oligosiloxane hybrid materials by a sol-gel reaction and UV curing.

insulator was also characterized. Optimal conditions were explored that produce hysteresis-free OTFTs through low-temperature curing, which opens the possibility of operating hysteresis-free devices with outstanding performances.

2. Experimental

2.1. Materials

All reagents were analytical reagent. 3-(trimethoxysilyl)propyl methacrylate (MPTS), diphenylsilanediol (DPSD), barium hydroxide monohydrate ($Ba(OH)_2{\cdot}H_2O$), zirconium n-propoxide (ZPO) and methacrylic acid were purchased from Sigma-Aldrich (U.S.A.). Polyethylene glycol methyl ether acetate (PGMEA) was supplied from J.T. Baker. Irgacure 184 of photoinitiators was obtained by Miwon (Korea). All materials were used as received without further purification.

2.2. Preparation and fabrication of films

Zirconium oligosiloxane resin was synthesized by a published sol-gel condensation reaction [22]. To achieve the optimum electrical characteristics, we investigated how different mole proportions of the components influenced the performance of OTFTs. Here we used an adapted fabrication process that prepared the hybrid dielectric films as follows: The total proportion of MPTS, DPSD, and ZPO was listed in Table 1. Firstly, ZPO was modified by MAA with a mole ratio of 2:1 or 1:1 to reduce the reaction rate between MPTS, DPSD and ZPO. After 1–2 h stirring, MPTS was added to the chelated ZPO and continued stirring together for 20 min at ambient temperature. Meanwhile, DPSD was dissolved in PGMEA at 80 °C with a 3:1 wt. ratio to form a clear solution. Next, the DPSD solution was slowly added to the mixture of MPTS and ZPO. With the addition of $Ba(OH)_2{\cdot}H_2O$ (0.2 mol%) to the mixed solution, the condensation reaction was performed at 80 °C for 10 h. The synthesized resin was subsequently filtered to remove the impurity. To fabricate the MZS hybrimer coating film, Irgacure 184 was added to the synthesized resin as a photo-initiator for photo-polymerization of the acrylate groups. In the case of preparing ZS resin, the procedure remains the same except adding MPTS. Different resin with varied ZPO, DPSD, MPTS content was prepared. The resin was diluted by PGMEA solvent to prepare the uniform and smooth films. The coating solution was spin-coated on the clean Si or SiO_2 substrate. The deposited film was pre-dried at 80 °C for 60 s on a hot plate, followed by exposure to UV light at 2 mJ/cm^2, and finally dried at 180 °C for 2 h in a vacuum oven to remove solvents and organic residuals.

Table 1
Composition ratio of chemicals for synthesis of zirconium oligosiloxane resin.

Sample	MPTS	DPSD	ZPO	MAA
(Mole ratio)				
MZSA	1	6	2	2
ZSB	–	6	2	2
ZSC	–	6	1	2
MZSa	1	6	3	3
MZSb	1	6	3	6
ZSe	–	6	3	3
ZSf	–	6	3	6
ZSg	–	6	6	6

2.3. Device fabrication and characterization

For the fabrication of bottom-gate, top contact OTFTs, metal Au was deposited on the SiO_2 substrate as a bottom gate electrode, Al electrode was subsequently coated as a buffer layer through a shadow mask. The hybrid gate dielectrics (100–300 nm) were prepared by spin coating. An organic active layer and source-drain electrode materials were then deposited sequentially through a shadow mask via thermal evaporation, deposition was finished with a 75 nm thick pentacene layer as an organic active layer, then a 50 nm thick Au layer as the source and drain electrodes under a pressure of 1×10^{-3} Torr and a rate of 1–2 Å/s, respectively. The channel length and width are 40 and 50–250 um. FT-IR measurement was performed using a FT/IR-4200 (JASCO, Japan), and Kosaka ET-3000 surface profilometer was used to measure film thickness. The surface characterizations of dielectric films were investigated using X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific). Phoenix 300 equipment and atomic force microscopy (N8 ARGOS, Bruker-Nano, Germany) were used to