Photoinitiator-free Photosensitive Polyimide Gate Insulator for Organic Thin Film Transistor

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Abstract

We have prepared and investigated the properties of photoinitiator-free photosensitive polyimide gate insulatos for organic thin-film transistors (OTFTs). The precursor was prepared from a dianhydride, 3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA) and novel aromatic diamine, 7-(3,5-diaminobenzoyloxy) coumarine (DA-CM). Photo-patternability of the polyimide precursor film and surface morphology of the films before and after photo-patterning process were investigated and negative pattern with a resolution of 50 μm was obtained nicely. In addition, we have fabricated OTFTs with pentacene and photosensitive polyimide as a semiconductor and a gate insulator, respectively. According to the device geometry, the μ, current modulation ratio and subthreshold swing of the devices were around 0.2~0.4 cm^2/Vs, more than 10^5 and around 3~5 V/dec, respectively.

1. Objectives and Background

Since the first demonstration of field effect of small organic molecules polymeric material [1,2], OTFTs have attracted lots of attention. Recently tremendous amount of researches have been focused on the OTFTs, one of the most important components to fabricate low cost large area flexible displays and low-end electronics [3]. The performance of OTFTs has been improved significantly in the past decade and is almost comparable to hydrogenated amorphous silicon transistors (*a*-Si:H TFT). However, those OTFTs comparable to *a*-Si:H TFT in performance were mainly fabricated with organic semiconductors and inorganic gate insulators, which are not really OTFTs [4-7]. Although there have been much research on organic and polymeric semiconductors for channel materials, there have been lack of research on organic gate insulators, which are extremely vital for the commercialization of reliable high performance OTFTs. The requirements for such gate insulators for OTFT are that they should have relatively high dielectric constant, heat and chemical resistance and photosensitivity. In addition to those requirements, they should have pinhole free thin film formability with high breakdown voltage and long-term stability, and be comparable with organic semiconductors. Previously, a few of polymeric gate insulators such as poly(vinylphenol) (PVP) [8,9,10], poly(methlymethacrylate) (PMMA) [11], polyvinylalcohol (PVA) [12] and benzocyclobutene (BCB) [13] have been reported. But, they did not meet all the requirements. Therefore, most of the researches on polymeric gate insulators were oriented to meet those basic requirements to improve the performance of OTFTs such as reducing leakage current and threshold voltage, and increasing current modulation ratio and mobility, etc by modifying surface properties and changing dielectric constant of gate insulators.

One more requirement for gate insulators to be applicable to organic active matrix display and integrated circuit is their photo-patternability for the creation of access to gate electrode. It is believed that this photo-patternability give us great potential to minimize the manufacturing cost for large-area organic electronics and to simplify the complicated fabrication processes dramatically. The most popular and reliable pattering process is photolithography followed by etching and removing photoresist. The harsh patterning process is not the best way for the soft and weak polymeric gate insulators. Therefore, it is necessary to design and pattern photosensitive polymeric gate dielectrics (PSPD). With PSPD, the photo patterning process can be simplified dramatically.

Recently we have designed and prepared an initiator-free photo-patternable polyimide, which can be extensively used in the microelectonics industry owing to their excellent chemical and physical properties, from 3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA) and novel aromatic diamine, 7-(3,5-diaminobenzoyloxy) coumarine (DA-CM). An initiator-free soluble photosensitive polyamic(acid) precursor was synthesized by conventional polycondensation of BTDA and DA-CM under N_2 atmosphere. The photosensitive polyamic(acid) was thermally converted to its corresponding polyimide. Photo-patternability of the polyimide precursor films and electrical characteristics of polyimide films were investigated. In addition, we have fabricated OTFTs with pentacene, which is one of the best well known organic semiconductors, and photosensitive polyimide as a semiconductor and a gate insulator, respectively. The OTFT characteristics are going to be discussed in more detail with the electrical properties of the photosensitive polyimide films.

2. Results

Synthesis: The aromatic diamine (DACM) with photo-crosslinkable moiety and polar carboxylic group as a side chain was successfully synthesized. The photosensitive polyimide precursor (BTDA-DACM) from BTDA and DACM was synthesized by conventional polycondensation under N_2 atmosphere.

Photo-patterning: The image of scanning electron microscopy (SEM) and the surface profile of the negatively patterned polyimide thin film were shown in Figure 1, where bright area represents the UV-exposed and developed area after UV-irradiation. The photo-patterning resolution was as small as 50 µm as indicated in Figure 1. It is believed that photo-patterning characteristic of BTDA-DACM polyimide precursor is due to the photo crosslinkable double bond of cumarine moiety of DACM. Upon exposed to UV-light, the UV-exposed part of the film was crosslinked rendering it insoluble in organic solvent. It was already reported that a smooth gate dielectric surface improves molecular ordering in organic semiconductor active layer leading to improved field effect carrier mobility. So it is important to check the change of surface properties before and after photo-patterning processes. We have obtained atomic force microscopy (AFM) images before and after photo-patterning. The morphology was almost identical each other and the root mean square (rms) surface roughness was almost same, 5 Å and 5.7 Å for the films before and after photo-patterning, respectively indicating that the BTDA-DACM PSPI was chemically stable during the developing processes.

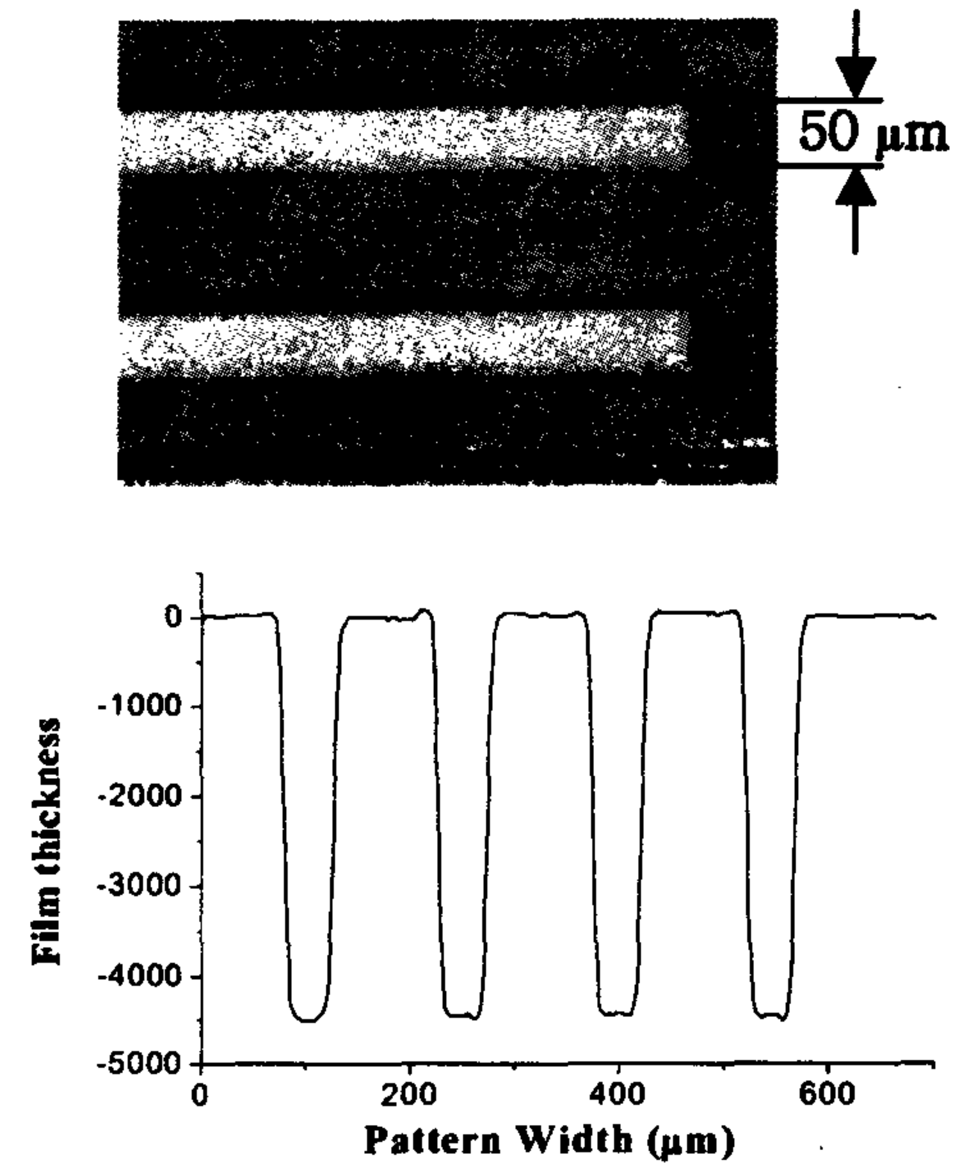

Figure 1. Image (top) nning electron microscophy (SEM) and the surface profile (bottom) of the negatively patterned polyimide thin films.

Device Characterization: Field effect measurements of OTFTs were carried out using top contact geometry. The typical p-type output (I_{ds} vs V_{ds}) characteristic curves of the device at various gate voltages were shown in Figure 2. At a given negative V_g, I_{ds} initially increase linearly with negative V_d for $|V_d| < |V_g|$ (linear regime), and saturates for $|V_d| \geq |V_g|$ (saturation regime) due to pinch off of the accumulation layer. Also the transfer characteristic curves were shown in Figure 2. The field effect carrier mobility (μ) was calculated in the saturation regime using the relationship between the drain current (I_{ds}) and gate voltage (V_{gs}).

$$\mathrm{I}_{ds} = \frac{WC_i}{2L}\mu\left(V_{gs} - V_T\right)^2$$

where I_{ds} is the drain current at the saturated regime, W and L are, respectively, the channel width and length, C_i is the capacitance per unit area of the gate insulator layer, and V_{gs} and V_T are the gate voltage and threshold voltage. V_T of the device was determined from the plot of square root of drain current ($\sqrt{I_{ds}}$) and gate voltage (V_g) by extrapolating the measured data to I_{ds}=0. The field effect mobility (μ) calculated from the plot of $\sqrt{I_{ds}}$ and V_{gs}. V_{gs} is swept from +20 to -50V while the drain voltage V_{ds} is set at -40 V. μ was found to be 0.2 cm^2/V·s, while the subthreshold voltage was about -13 V for a device with the channel length (L) of 50 μm, width (W) of 2 mm, the pentacene thickness of 600nm and the photosensitive polyimide gate insulator thickness of 300 nm (C_i=92.4 pF/cm^2). The current modulation ratio (I_{ON}/I_{OFF}) was around 2x10^5 when V_g was scanned from 20 to -50 V. The subthreshold swing (ss), which is the measure of how sharply the device transits from off to on, was 5 V per decade. The ss is relatively large in comparison to that of a-Si TFT or even that of pentacene TFT with inorganic gate insulators. It is possibly related to a large density of interface states between semiconductors and gate insultors. [14]

3. Conclusions

An initiator-free photo-patternable gate insulator was synthesized for the application to the organic thin film transistors (OTFTs). The initiator-free photosensitive polyimide gate insulator pentacene-based organic thin-film transistors (OTFTs) with good performance were demonstrated. According to the device geometry, the μ, current modulation ratio and subthreshold swing of the devices were around 0.2~0.4 cm^2/Vs, more than 10^5 and around 3~5 V/dec, respectively.

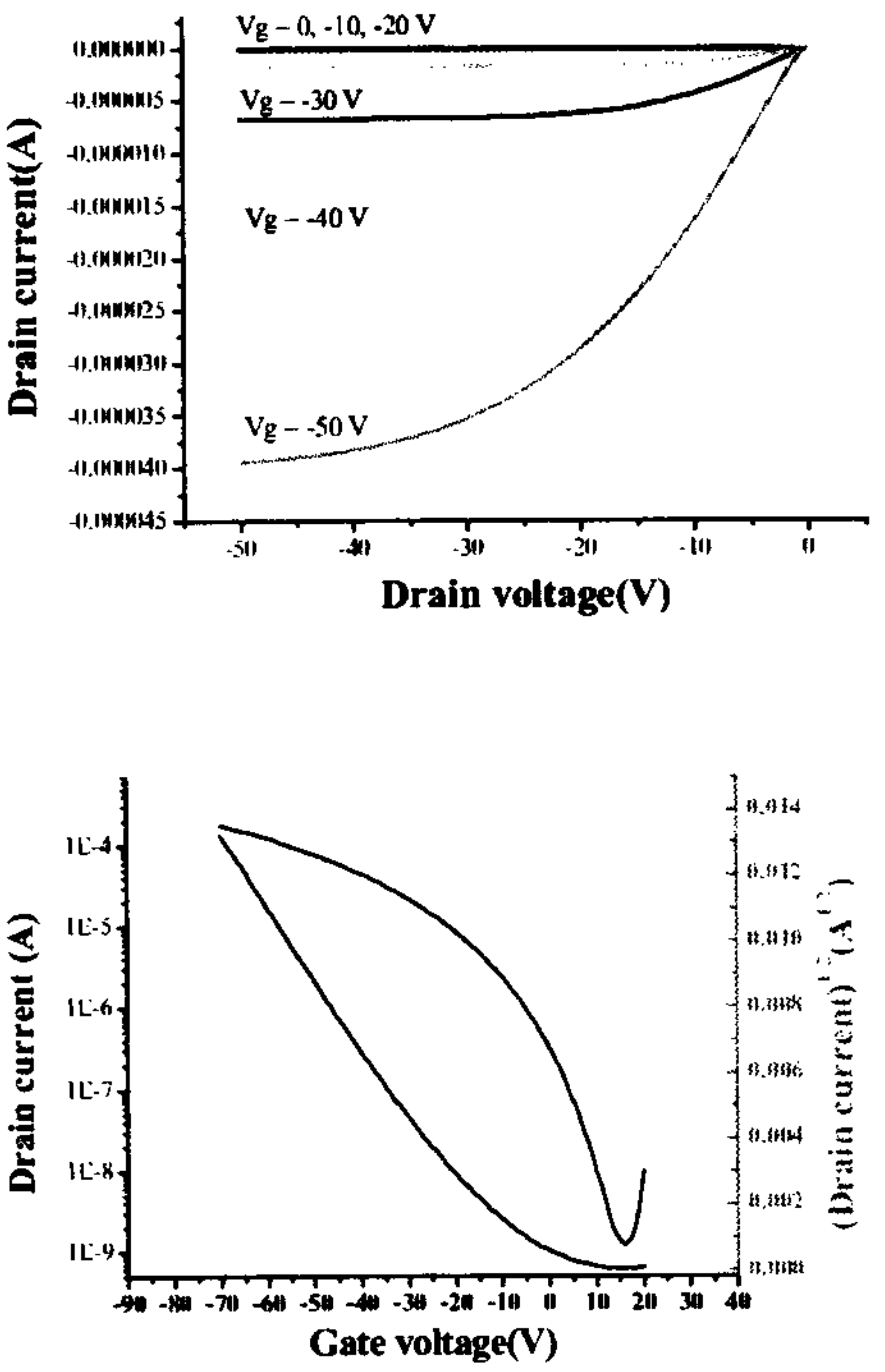

Figure 2. Output (top) and transfer (bottom) charateristic curves of OTFT.

4. References

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