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Letter

Organic field-effect transistors based on low-temperature processable transparent polymer dielectrics with low leakage current

Jing Zhang [a,b], Hongfei Zhu [a,b], Lei Zhang [a,b], Chong-an Di [a,*], Wei Xu [a,*], Wenping Hu [a], Yunqi Liu [a], Daoben Zhu [a,*]

[a] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100039, PR China

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ABSTRACT

A solution-based transparent polymer was investigated as the gate dielectric for organic field-effect transistors (OFETs). Organic thin films (400 nm) are readily fabricated by spin-coating a polyhydrazide solution under ambient conditions on the ITO substrates, followed by annealing at a low temperature (120 °C). The smooth transparent dielectrics exhibited excellent insulating properties with very low leakage current densities of $\sim 10^{-8}$ A/cm^2. High performance OFETs with evaporated pentacene as organic semiconductor function at a low operate voltage (-15 V). The mobility could reach as high as 0.7 cm^2/Vs and on/off current ratio up to 10^4. Solution-processed TIPS-pentacene OFETs also work well with this polymer dielectric.

1. Introduction

Organic field-effect transistors (OFETs) have received extensive attentions in the past decades due to their potential applications in low-cost and flexible electronics. As most of the charge carriers transport at the first several organic molecules layers on the surface of dielectrics, gate dielectric and semiconductor/dielectric interface play important roles in OFETs which greatly influenced the device performances. Comparing to the traditional inorganic SiO$_2$ insulator, polymer dielectrics are considered ideal replacements because of their diverse properties, favorable film-forming characteristics, and tunable surface chemistry for the control of device critical interfacial trap state densities [1,2]. Various flexible dielectric thin films have found applications in OFETs replacing SiO$_2$ gate dielectric recently [3]. In previous reports, polymer dielectric materials, such as poly(4-vinyl phenol) (PVP) [4], poly(methylmethacrylate) (PMMA) [5], poly(styrene) (PS) [6], poly(perfluorobutenylvinylether) (CYTOP) [7], and poly(acrylic acid) (PAA) [8] have been widely studied by many research groups. Organic–inorganic hybrid dielectrics, [9] polymer blending materials [10] have also been applied into organic electronics. However, most of those materials suffered the problems of poor solvent resistance, high curing temperatures or high leakage current.

In OFETs, high mobilities mainly depended on the few semiconductor layers that near the dielectrics. The semiconductor/dielectric interface influenced greatly on the ordering of semiconductor molecules. For example, while the octyltrichlorosilane (OTS-8) self-assembled monolayer (SAM) on a thermal SiO$_2$ surface could efficiently enhance the device performance [11]. Hence the dielectric surface properties were of great importance to the interfacial interactions of organic semiconductor with gate dielectric. The tunable surface chemistry of polymers meets the need greatly and solution process abilities for OFETs are crucial to the fabrication of printed, integrated, transistor circuits [12]. So for the fabrication of OFETs through solution process, the polymer gate dielectrics which could not be dissolved by liquid deposition of soluble organic semiconductors are essential. We have been searching for ideal

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[*] Corresponding authors.
E-mail addresses: wxu@iccas.ac.cn (W. Xu), zhudb@iccas.ac.cn (D. Zhu).

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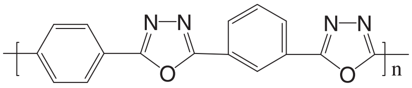

Scheme 1. The chemical structures of polyisophthalic hydrazide.

OFET gate dielectrics that could be compatible with flexible substrate, be processable or printable from solution, and also be insoluble in the common solvents used for the deposition of organic semiconductor. Here we reported a transparent organic dielectric fabricated by spin-coating and then a low-temperature annealing of a soluble polymer material:polyisophthalic hydrazide (chemical structure see Scheme 1). In a previous work, we have successfully used the pyrolyzed Ink-jet printed thin film of such polymer as organic electrodes in high performance OFETs [13]. The utilization of polyhydrazide as both electrode and dielectric materials in OFETs implied its unique bifunctional use in organic electronics.

Polyisophthalic hydrazide has very high polymer melt temperature. The polymer is just soluble in dimethyl sulfoxide, *N*,*N*-dimethylacetamide, or *N*-methylpyrrolidone and unsoluble in the common solvents as reported [14]. Tough excellent films could be obtained from the solution, especially using *N*,*N*-dimethylacetamide.

2. Results and discussion

Transparent dielectric thin films were fabricated via spin-coating from the polyhydrazide solution. The polyisophthalic hydrazide was prepared as our previous report [13]. The film thickness was tunable by adjusting the solution concentration. After a large amount of experimentions, the optimal condition was found to be that: dissolve 100 mg polyhydrazide in 1 mL *N*,*N*-dimethylacetamide (DMA), then such homogeneous solutions were stirred for 60 min at room temperature and spin-coated onto warm ITO substrates (FET gate contact) after filtration. Next, the spin-coated films were annealed at 120 °C for 30 min in vacuum or N_2 atmosphere to eliminate the solvent completely. This temperature was found to be optimum to get a low leakage current. After annealing, the films were cooled to room temperature to form the designed homogeneous dielectric films.

The surface properties of dielectrics were evaluated with atom force microscopy (AFM) and transmittance measurement as shown in Fig. 1. The stable polymer film showed ultrasmooth surfaces and its root-mean-square (RMS) roughness was 3–4 Å. The surface morphology of the uniform, pinhole-free film was shown in Fig. 1(a). Fig. 1(b) showed the transmittance of this film (red), in comparison with that of ITO (black). Above the wavelength of 450 nm, a ca. 1400 nm thick film had a transmittance of >93%, which was higher than that of ITO (with an ITO thickness of about 80 nm and sheet resistance <9 Ω cm^{-2}). The surface energy of the polyhydrazide film calculated by Owens–Wendt–Rabel–Kaelble method (OWRK) model was about 49.2 mN/m, which is suitable for the deposition of organic semiconductors with high compatibility [15]. The principal electrical characteristics for gate dielectric films are the capacitance and leakage current. Hence, gold arrays were thermally evaporated on polymer dielectric films with ITO glass substrates. The electrical properties of the polymer dielectrics were investigated by capacitance–voltage (*C*–*V*) measurements and current–voltage (*I*–*V*) measurements using the Au/dielectric/ITO structure. Capacitance measurements were carried out using the sandwich electrode configuration ranging between 1 and 100 kHz. The capacitance (C_i) of such polyhydrazides film showed slight frequency dependence from 100 to 100 M Hz, as shown in Fig. 2(a). The relative dielectric constant was calculated to about 4.4. A capacitance of about 1.1×10^{-8} F/cm^2 was observed for the used 400 nm thick polymer films. Fig. 2b showed the current density–voltage characteristics of the polyhydrazide dielectric with a thickness of 400 nm, the polymer film exhibited an extremely low leakage current. With the bias of 20 V, the current density was observed below 10^{-8} A/cm^2. The current of polyhydrazide gate dielectric was robust and extremely resistant to common organic solvents used for spin-coating, including alcohol, toluene, and chlorinated solvents such as chloroform, chlorobenzene, dichlorobenzene, etc. Such good stability implied that subsequent liquid

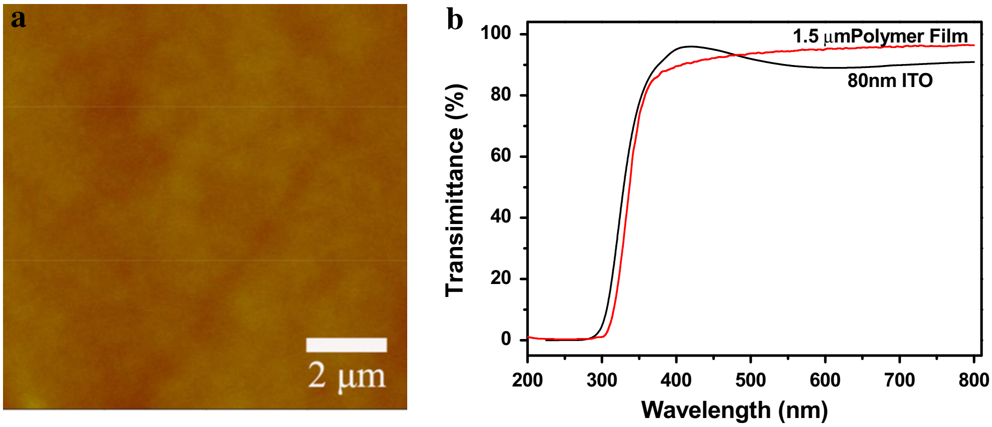

Fig. 1. (a) AFM micrograph of the polymer dielectric (height scale 30 nm) and (b) transmittance of the polymer film (red) and ITO (black). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

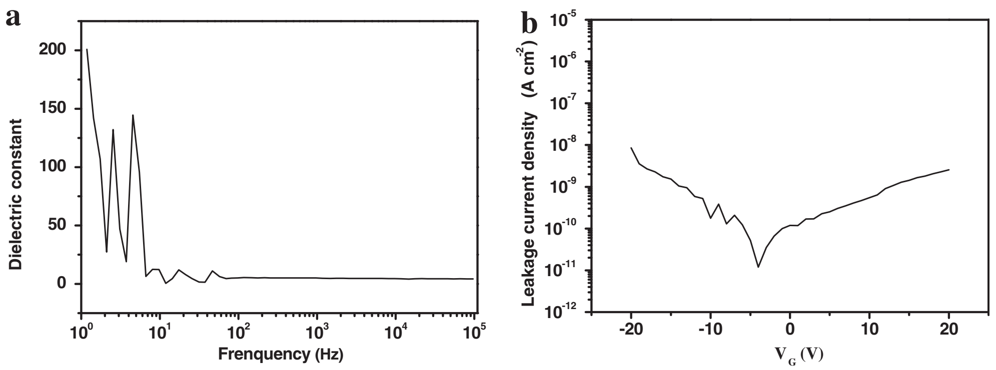

Fig. 2. (a) Frequency dependence of dielectric constant of polymer film cured at 120 °C for 1 h. Thickness of polyisophthalic hydrazide film was 400 nm and (b) leakage current density versus voltage plots.

deposition of the semiconductor layer followed by annealing may did not lead to any dimensional and structural damages or adverse electrical performance consequences to this polymer dielectric.

Semiconductor layers were deposited both by evaporation (pentacene) and drop-casting (TIPS-pentacene) to demonstrate the compatibility of the polymer dielectrics with the semiconductor materials. The OFET device was completely by thermal evaporation of Au electrodes through a shadow mask to define the source/drain contacts. The FET measurements were carried out with a Micromanipulator 6150 probe station in a clean and metallically shielded box at room temperature in air, and recorded using a Keithley 4200 SCS. For our study, top-contact OFET devices were fabricated using both SiO_2 and polyhydrazides as the gate dielectrics.

OFETs fabricated with pentacene (40 nm) on polyhydrazide dielectrics showed excellent performance with a field-effect mobility of 0.7 cm^2/Vs and an on/off ratio of 3×10^4 at a low gate bias of -15 V. Contrastively, the pentacene thin film OFETs based on commonly used inorganic SiO_2 dielectrics showed mobility about 0.1 cm^2/Vs

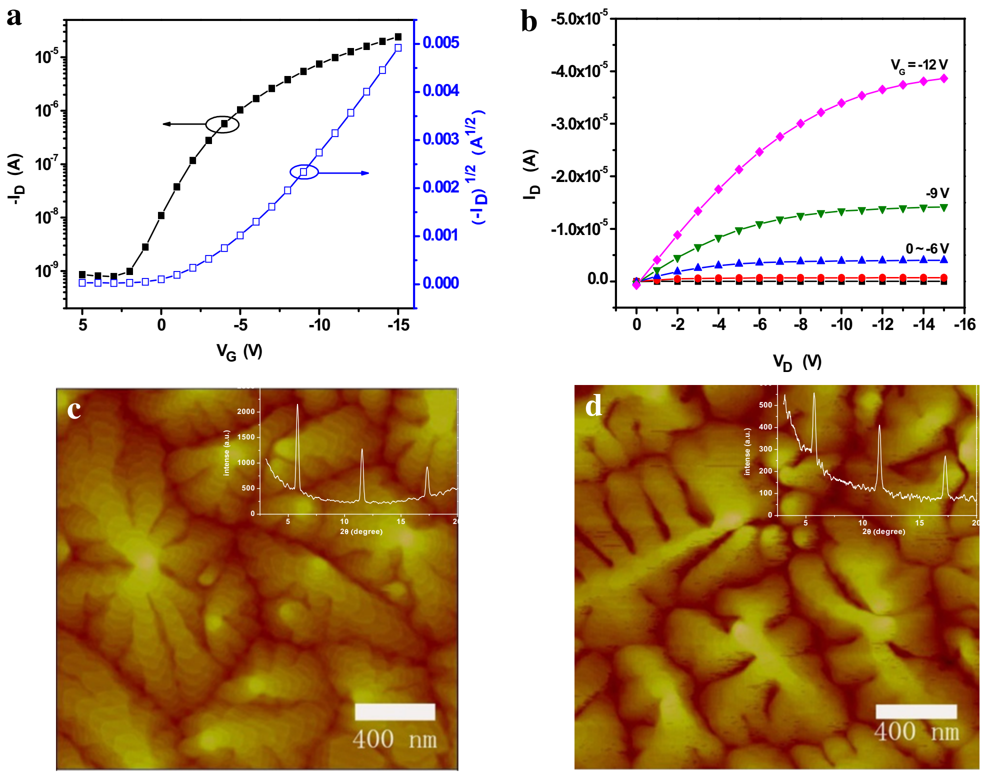

Fig. 3. (a) Transfer characteristic ($V_D = -10$ V) and (b) output characteristic of a typical pentacene OFET with polymer dielectric (T_s = 20 °C, W = 5300 μm, L = 110 μm). AFM images and XRD patterns of pentacene OFETs: layers with (c) polymer and (d) SiO_2 dielectrics.

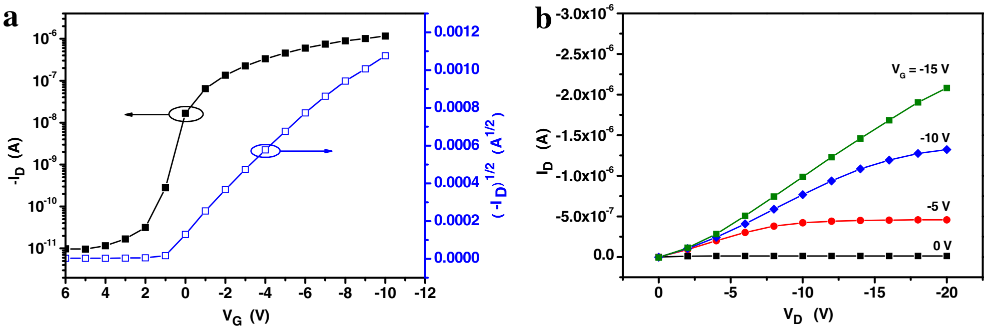

Fig. 4. (a) Transfer characteristic ($V_D = -10$ V) and (b) output characteristic of a TIPS-pentacene OFET with polymer dielectric.

with all the other conditions the same ($V_D = -100$ V). The output and transfer curves of pentacene based OFETs on ITO substrates were showed in Fig. 3(a) and (b). The higher electronic performance for the polymer dielectrics may attributed to the larger grain size and less grain boundaries. Fig. 3(c) and (d) shows the AFM images and XRD patterns of the pentacene films grown on the polymer and SiO_2 surfaces, respectively. The pentacene film on polymer showed highly crystallinity since the first reflection located at $2\theta = 5.7°$ was very sharp and intense. In contrast, pentacene film grown on SiO_2 substrate was far more textured and showed lower crystallinity. AFM images of pentacene films on the two different dielectric surfaces revealed similar trend in grain size. Obviously decrease of grain boundaries on polymer surface were observed compared to film grown on SiO_2 surface.

Fig. 4(a) and (b) shows the output and transfer curves of a typical TIPS-pentacene based OFET on ITO substrates, respectively. All curves displayed good linear and saturation behaviors with very low leakage current at $V_D = 0$ V. The field-effect mobility of such polymer dielectrics device could range from 0.10 to 0.22 cm^2/Vs and an on/off ratio as high as 1×10^5. The TIPS-pentacene OFETs based on commonly used inorganic SiO_2 dielectrics showed mobility about 0.05 cm^2/Vs with all the other conditions the same ($V_D = -100$ V), comparatively. The improvement of the device performance based on polyhydrazide could be attributed to the suitable surface energy which induced more continuous films [16].

3. Conclusions

In summary, polyisophthalic hydrazide has been identified as dielectric layer in low-cost OFETs. This polymer was only soluble in DMA or DMSO and can be applied by simple spin-coating method. The curing temperature of the polymer is sufficiently low to permit using of numerous durable, plastic materials as substrates in OFETs. The cured films are uniform, transparent, pinhole free, and low leakage current. In addition, common organic solvents do not readily attack these resins. Good transistor performances were observed with pentacene and TIPS-pentacene as organic semiconductors. All of these devices were operated at a comparatively low voltage. With our previous results, polyhydrazide showed unique bifunctional use in organic electronics as both electrode and dielectric materials.

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