RSC Advances

Title:

Polyimide (PI): High-Quality Polymer Dielectric film with the Features of Anti-Solvents, Large-Area Consistency for Field-Effect Transistors

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Abstract

In this work, the properties of polyimide (PI) as the dielectric film are systematically investigated. PI films are processed by spin-coating method at various conditions. Subsequently, the leakage current, unit-area capacitance and morphologies of these films are characterized. Then anti-solvent property is certified by comparing the films before and after the solvent treatments. Organic filed-effect transistors based on PI dielectric films and pentacene active films show uniform performance distribution in large area. Furthermore, a single crystal of 2,7-dihexyl-dibenzo[d, d′]thieno[3,2-b;4,5-b′]dithiophene (C6-DBTDT) is obtained on the PI film by solution-processed method and exhibits good electrical properties with the highest mobility of 3 $cm^2 V^{-1}s^{-1}$ and $I_{on}/I_{off} > 10^5$. It is believed that this kind of PI polymer dielectric film has potential application in solution-processed, flexible and large-area organic electronics.

Introduction

Organic thin-film transistors as the indispensable components of integrated circuits have attracted extensive attention due to their irreplaceable superiorities, such as low-cost, large-area processing and good compatibility with flexible substrates [1-4]. Over the past two decades, remarkable progresses have been made to improve the performance of organic field-effect transistors (OFETs), which have exceeded polycrystalline silicon and are promising for flexible, lightweight electronic applications, such as radio frequency identification devices, complementary circuits, displays and plastic electronics [5-7]. Thereinto, the charge mobility of p-type [8] organic thin-film FETs has reached up to 23.2 $cm^2 V^{-1} s^{-1}$ and n-type OFETs [9] exhibit the mobility as high as 6 $cm^2 V^{-1} s^{-1}$. It has been acknowledged that the dielectric film plays a crucial role for the achievement of these high-performance organic devices[10]. The roughness, surface energy and trap density of the dielectric film have directly influenced the morphology of the active layer and then further determined the transport of the charge carrier [11-13]. In addition, uneven dielectric location in the large area results in wide distribution of the device performances, which is a handicap for fabricating the qualified organic circuits[14].

At present, there are three kinds of dielectrics in organic electronics: inorganic insulator, self-assembled monolayer (SAM) dielectric and polymer dielectric. The first one has good chemical resistance and unique heat endurance. However, the process to manufacture such inorganic dielectric film is always extremely complicated, expensive and incompatible with flexible substrates [15]; the second one is often applied to prepare low-operating voltage, low-power dissipation devices. But the instability limits its practical application in large area organic electronics [16]; the last one is polymer insulator, which can be easily prepared by solution-processed method and compatible with flexible substrates [17-19]. Numbers of polymer dielectrics, such as polymethyl methacrylate (PMMA), polystyrene (PS), polyvinyl alcohol (PVA) and so on, have been proposed to achieve high performance OFETs [20-21]. Nevertheless, these polymer insulator films can be easily etched by conventional solvents and have poor heat endurance, which becomes limitations for their applications in integrated circuits

[22-23]. Therefore, it is necessary to introduce a new polymer dielectric that can endure this oppressive preparation process.

Polyimide (PI) is a good candidate of polymer dielectric film [24-26] and in our work, we do systematical research on this polymeric insulator. The leakage current, unit-area capacitance and the morphologies of these films are characterized. Then anti-solvent property is certified by comparing these films before and after organic solvent treatment. Large-area thin film OFET arrays show uniform mobility and threshold voltage distribution. Furthermore, solution-processed single crystal OFETs based on 2,7-dihexyl-dibenzo[d,d′]thieno[3,2-b;4,5-b′]dithiophene (C6-DBTDT) [27] are built on the PI films. Bottom-gate top-contact OFETs are constructed by manually gluing Au-films, which exhibit excellent electrical properties with the highest mobility up to 3 $cm^2 V^{-1} s^{-1}$ and $I_{on}/I_{off} > 10^5$. It is believed that this kind of polymer insulator has potential application in solution-processed organic electronics.

Experimental section

In this work, PI films were prepared by spin-coating onto indium tin oxide (ITO) substrates and all substrates were cleaned with deionized water, acetone, and isopropyl alcohol in ultrasound for 10 minutes respectively, and then dried with quickly purged N_2. The substrates were further cleaned in oxygen plasma for 5 minutes. PI precursor (polyimide acid, PAA) films were firstly spin-coated on ITO substrates at different speed (2000 rpm, 4000 rpm, 6000 rpm and 8000rpm) for 30 seconds. Then, these films were cross-linked to form solid PI films with annealing temperature of 300 ^oC. After that, the morphologies and thicknesses of these films were investigated by atomic force microscope (AFM) with tapping mode.

In order to measure the leakage current and unit-area capacitance of PI films, the devices with ITO/PI/Au (100 nm) sandwich structure were fabricated. The specific capacitance as a function of frequency based on PI film was tested by electrochemical method. The leakage current of PI was characterized by Keithley 4200-SCS semiconductor analyzer. Bottom-gate top-contact OFETs were fabricated employing PI as dielectric film, pentacene film as the active layer. Firstly, approximately 50 nm thickness pentacene film was thermally evaporated at a base pressure 2×10^{-3} Pa with a rate of 0.1–0.3 Å/s, then the devices were completed after 20 nm Au electrode deposited through a shadow mask, and tested by Keithley 4200-SCS semiconductor analyzer at ambient atmosphere.

Alternatively, the PI films were immersed in acetone, isopropyl alcohol for 5 min, dealt by ultrasound for 5 min respectively, dried by quickly purged N_2, and then the properties of these films were tested to check the anti-solvent property directly. Furthermore, C6-DBTDT was dissolved in chlorobenzene solvent with concentration about 0.3 mg/ml.[27] Therefore, C6-DBTDT single crystals were obtained on the solvent treated PI films by drop-casting method, then OFETs based on single crystals were constructed by manually gluing Au-films and characterized by Keithley 4200-SCS semiconductor analyzer at ambient atmosphere.

Results and discussion

The chemical structures of PAA and PI were shown in **Fig. 1a**. The morphologies of these PI films with different speeds were characterized by AFM (**Fig. 1S)**. Smooth and compact PI films were observed and these films exhibited a root-mean-square roughness value of 0.21 ± 0.04 nm without major defects, such as pinholes or cracks, which was beneficial for the growth of the qualified semiconductors and enhancing the charge-transport at the interface. On the other hand, the thickness of the PI films varied from 1200 nm to 500 nm **(Fig. 1b)** along with the coating speed increased from 2000 rpm to 8000 rpm, producing the capacitance of per unit from 2.3 nF/cm^2 elevated up to 6.1 nF/cm^2 (**Fig. 1c)**. At the same time, all of PI films had a low leakage current density **(Fig. 1d)**, which demonstrated excellent insulating property.

In order to confirm the applicability of PI films as dielectric layer in organic electrics, bottom-gate top-contact OFETs (inset of **Fig. 2a)** were constructed with pentacene as active layer and tested in ambient air. Here we discussed experiment with 4000 rpm prepared PI film as an example. The typical transfer characteristic of the device is shown in **Fig. 2a**, with the mobility extracting from the saturation region of 0.31 $cm^2 V^{-1}s^{-1}$ and on/off ratio up to 9.9×10^6, which was comparable with results of the previous reports [28-29]. The output characteristic is shown in **Fig. 2b**. The device also showed the expected gate modulation of the drain current (I_D) in both the linear and saturation regimes. Also, the devices fabricated on different thickness of PI films had perfect electronic properties (**Fig. S2)**. As is well known, organic circuit is required to integrate identical transistors in quantity for realizing a special function. Therefore, it is necessary to guarantee the properties of the devices keeping high stability and unification in macroscopic area. In this work, the threshold voltages and mobilities of thirty randomly selected transistor devices have been recorded over large area. As shown in **Fig. 2c**, the threshold voltage of 73.3% devices is between -15 V and -19 V, with average voltage of -16.6 V, standard deviation 2.4 and the mobility **(Fig. 2d)** varies between 0.21~0.24 $cm^2 V^{-1} s^{-1}$. All of these data have directly proved the large-area uniformity of PI films and that could be applied to process large-area organic circuits in the future. Simultaneously, the morphologies of the pentacene films with different spinning speed are characterized by AFM mapping **(Fig. S3)**. The pentacene films had compact structure and showed good crystallinity. The average grain size was about 200 nm and arranged densely, which helps obtain high performance devices. Subsequently, the n-type organic transistors based on N, N` -1H, 1H-perfluorobutyl dicyanoperylenecarboxydiimide (PDIF-CN_2) also had good electrical properties with the mobility of 2.45 x $10^{-6}cm^2 V^{-1}s^{-1}$, on/off ratio of 8.4 x 10^2 and threshold voltage -6 V in ambient atmosphere, where the output and transfer characteristics of PDIF-CN_2 OFETs are shown in **Fig. S4**. All of these data have confirmed the applicability of PI dielectric film in organic electronics.

It is noted that the majority of polymer insulators are easily damaged by solvents, which prevent their applications from the solution-processed technique, such as photolithography and ink-jet printing [30-32]. Here, anti-solvent measurements were done on the PI film. The capacitance **(Fig. 3a)** and leakage current density **(Fig. 3b)** of the PI films have no noticeable variation before and after the solvent treatment. Moreover, there was no obvious change of the surface morphology before **(Fig. 3c)** and after **(Fig. 3d)** solvent treating, illustrating that the solvents had not seriously damaged the surface structure as well as the bulk structure of the PI films. Subsequently, OFETs were constructed on the solvent treated PI films and showed good electrical properties **(Fig. S5)**, following with the average mobility of 0.4 $cm^2V^{-1}s^{-1}$, I_{on}/I_{off} up to 10^7, which are the same level as those on untreated PI films.

In order to demonstrate the wide applicability of PI dielectric film, solution-processed C6-DBTDT (chemical structure shown in **Fig. 4a**) single crystals were prepared on the solvent treated PI films through drop-casting method. As shown in optical microscope image (**Fig. 4b**), the microribbon-like single crystal had a regular configuration and uniform color with its length over than 100 μm. Then, bottom-gate top-contact OFET (**Fig. 4c**) was constructed by manually gluing Au-films [33-35] with PI as dielectric and tested in ambient air. The typical transfer characteristic of the device is shown in the **Fig. 4d**, with the mobility extracting from the saturation region of 3 $cm^2 V^{-1}s^{-1}$ and on/off ratio up to 10^5.

Conclusions

In conclusion, PI as dielectric film was processed by spin-coating method at various conditions. The as-fabricated PI film had very smooth surface and pin-hole free structure, leading to negligible leakage current. Then anti-solvent property was excellent since the solvent treated PI films did not show noticeable change concerning the surface morphology and the film structure. The thin film OFETs were constructed on both the solvent treated and untreated PI films with the pentacene films as the active layers, illustrating uniform electric performance distribution even in a large area. Furthermore, the single crystal OFET of C6-DBTDT was achieved on the solvent treated PI film by solution-processed method and exhibited good electrical properties with the highest mobility of 3 $cm^2 V^{-1}s^{-1}$ and $I_{on}/I_{off} > 10^5$. It is believed that this kind of polymer insulator has great potential application for large-scale fabrication of solution-processed organic electronics.

Acknowledgements

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Figure captions:

Figure-1: (a) The chemical structure of polyimide acid (PAA) and polyimide (PI). (b) The thickness of the film versus the spin speed. (c) The capacitance per unit of the PI films. (d) The leakage current per unit of the films.

Figure-2: (a) Typical transfer and (b) output characteristics of the pentacene thin film transistor on the PI dielectric film; (c) The distribution of threshold voltages and (d) mobility on the large-area PI dielectric film.

Figure-3: (a) The capacitance and (b) Leakage current before and after the solvent treatments, (c) AFM images of the PI film before and after the solvent treatments.

Figure-4: (a) The chemical structure of C6-DBTDT. (b) Optical micrograph of C6-DBTDT single crystal fabricated on the PI film. (3) Optical microscope of the OFET transistor fabricated by manually gluing Au-films. (d) Typical transfer characteristics of the single crystal transistor.

Figures:

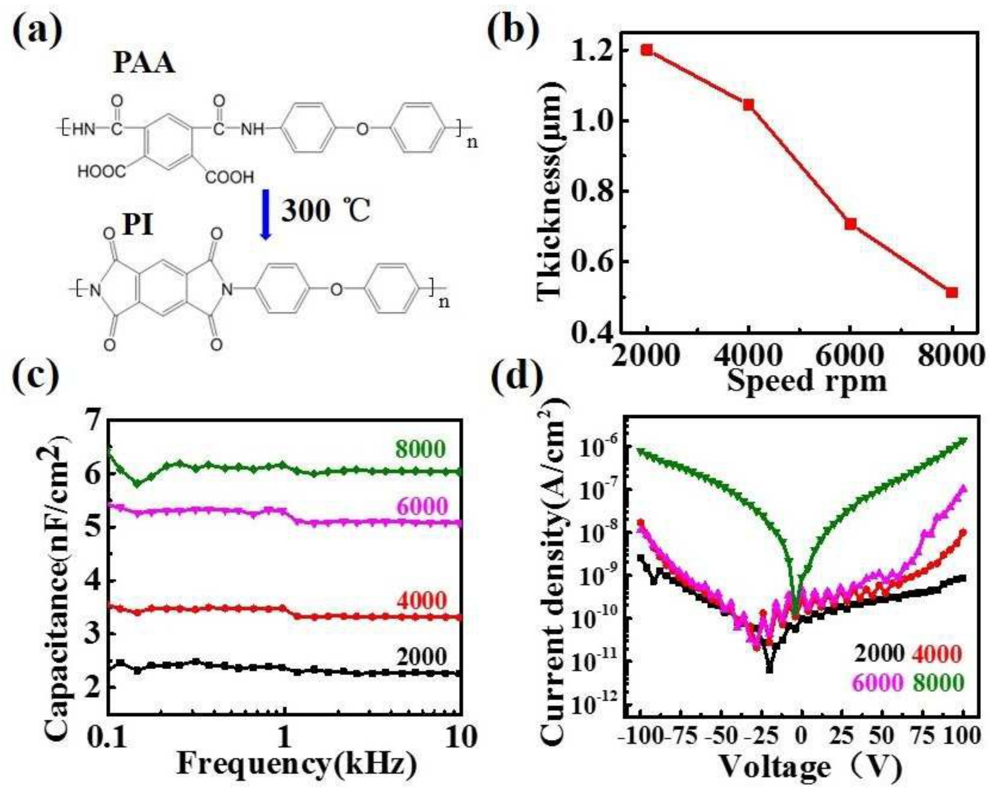

Figure-1

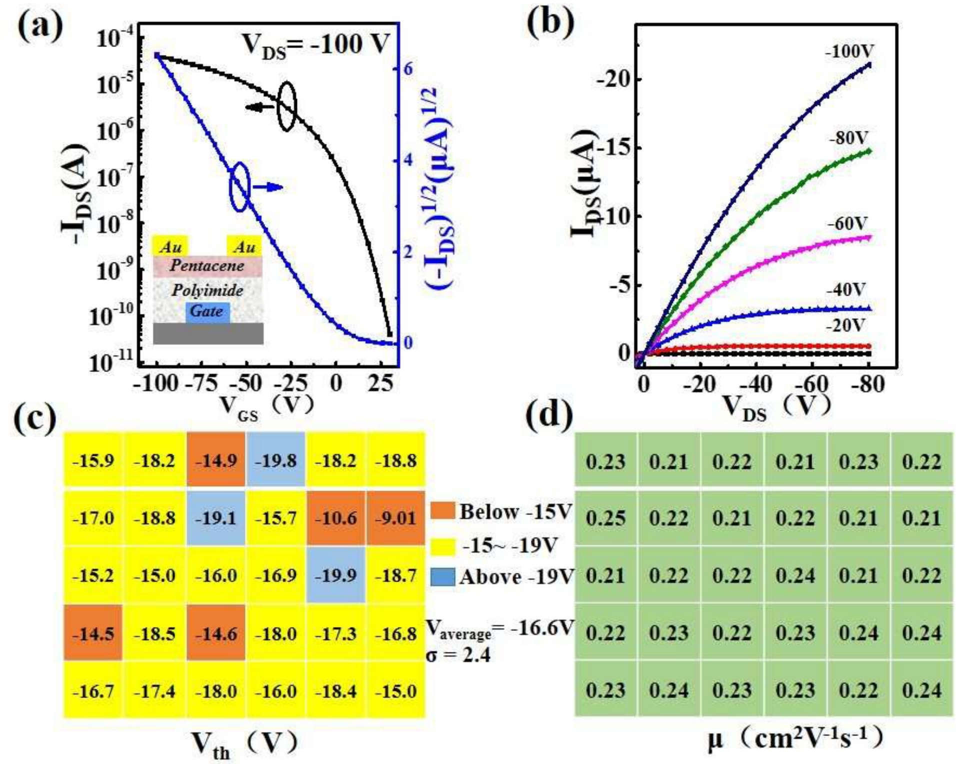
(a)
V_{DS}= -100 V
$-I_{DS}$(A)
$(-I_{DS})^{1/2}(\mu A)^{1/2}$
V_{GS} (V)
Au
Au
Pentacene
Polyimide
Gate
(b)
I_{DS}(μA)
V_{DS} (V)
-100V
-80V
-60V
-40V
-20V
(c)
-15.9 -18.2 -14.9 -19.8 -18.2 -18.8
-17.0 -18.8 -19.1 -15.7 -10.6 -9.01
-15.2 -15.0 -16.0 -16.9 -19.9 -18.7
-14.5 -18.5 -14.6 -18.0 -17.3 -16.8
-16.7 -17.4 -18.0 -16.0 -18.4 -15.0
Below -15V
-15~ -19V
Above -19V
$V_{average}$= -16.6V
σ = 2.4
V_{th} (V)
(d)
0.23 0.21 0.22 0.21 0.23 0.22
0.25 0.22 0.21 0.22 0.21 0.21
0.21 0.22 0.22 0.24 0.21 0.22
0.22 0.23 0.22 0.23 0.24 0.24
0.23 0.24 0.23 0.23 0.22 0.24
μ ($cm^2V^{-1}s^{-1}$)

Figure-2

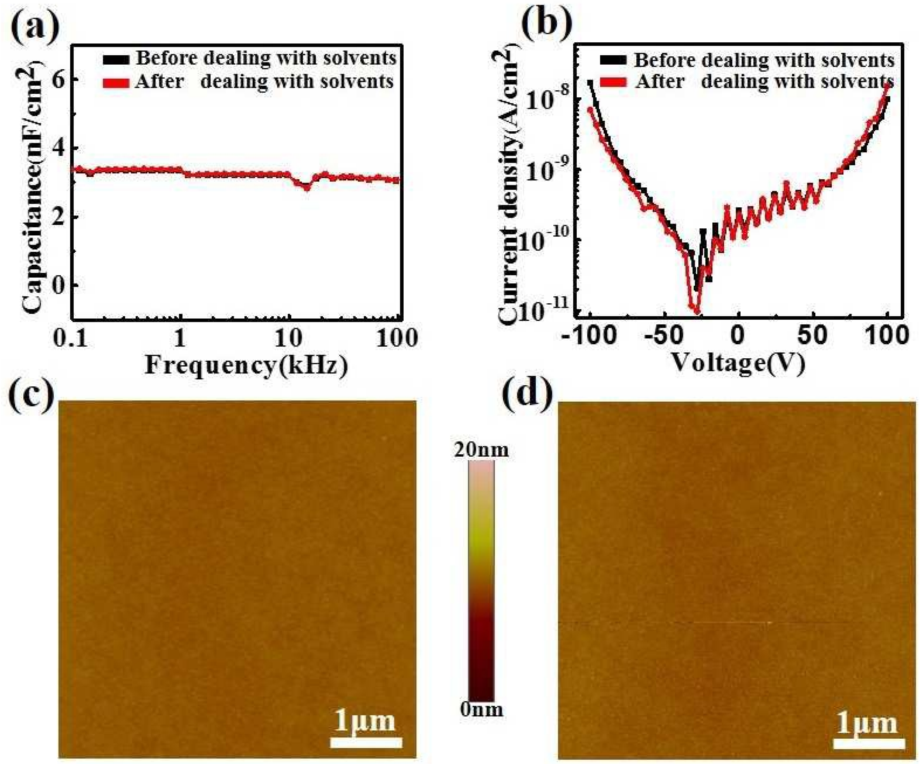
(a)
Before dealing with solvents
After dealing with solvents
Capacitance(nF/cm2)
0
2
4
6
0.1
1
10
100
Frequency(kHz)
(b)
Before dealing with solvents
After dealing with solvents
Current density(A/cm2)
10-8
10-9
10-10
10-11
-100
-50
0
50
100
Voltage(V)
(c)
1µm
20nm
0nm
(d)
1µm

Figure-3

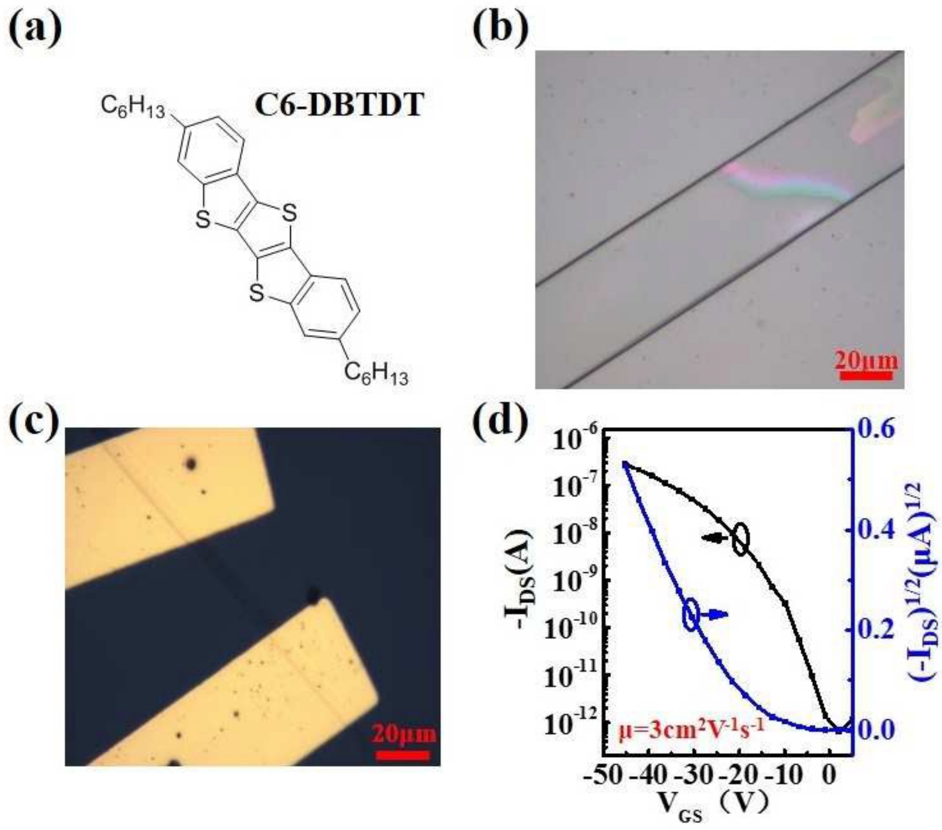
(a)
C6-DBTDT
C_6H_{13}
S
(b)
20μm
(c)
20μm
(d)
$-I_{DS}$(A)
$(-I_{DS})^{1/2}(\mu A)^{1/2}$
μ=3cm^{2}V^{-1}s^{-1}
V_{GS} (V)

Figure-4

Graphic abstract

Solvent treated and untreated polyimide dielectric films show the same smooth surface, and the electrical performances of organic field-effect transistors on the large area are identical.