This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Title:
Polyimide (PI): High-Quality Polymer Dielectric film with the Features of Anti-Solvents, Large-Area Consistency for Field-Effect Transistors

Authors:
Yunze Li¹*, Deyang Ji²*, Huanli Dong², Jingze Li¹, Wenping Hu²

Affiliations:
¹State Key Laboratory of Electronic Thin Films and Integrated Devices, School of Microelectronics and Solid-State Electronics, University of Electronic Science and Technology of China, Chengdu 610054, China
²Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Correspondence and requests for materials should be addressed to J.L. (lijingze@uestc.edu.cn) and W.H. (huwp@iccas.ac.cn).

* These authors contributed equally to this work.

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 (C62DBTDT) is obtained on the PI film by solution-processed method and exhibits good electrical properties with the highest mobility of 3 cm² V⁻¹ s⁻¹ and I_on/I_off > 10⁵. 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.\(^1\) 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.\(^5\) Thereinto, the charge mobility of p-type organic thin-film FETs has reached up to 23.2 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and n-type OFETs 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.
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 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) 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
\begin{equation*} \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \end{equation*} 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 \( \text{N}_2 \). 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 °C. 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 $2 \times 10^{-5}$ 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. 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 electronics, 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 cm² V⁻¹ s⁻¹ and on/off ratio up to 9.9×10⁶, which was comparable with results of the previous reports²⁸-²⁹. 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 cm² 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-CN₂) also had good electrical properties with the mobility of 2.45 x 10⁻⁶ cm² V⁻¹ s⁻¹, on/off ratio of 8.4 x 10² and threshold voltage -6 V in ambient atmosphere, where the output and transfer characteristics of PDIF-CN₂ 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. 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
\( \text{cm}^2\text{V}^{-1}\text{s}^{-1} \), \( I_{\text{on}}/I_{\text{off}} \) 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
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 \( \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) 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 \( \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) and \( I_{\text{on}}/I_{\text{off}} > 10^7 \). It is believed that
this kind of polymer insulator has great potential application for large-scale
fabrication of solution-processed organic electronics.

Acknowledgements
This work was partly supported by funding from the Science and Technology Bureau of Sichuan Province of China (No. 2015HH0033); The National Natural Science Foundation of China (Nos. 21473022, 51303185, 51222306, 61201105, 91222203, and 91233205); the Ministry of Science and Technology of China (2014CB643600); the Fundamental Research Funds for the Central Universities (No. ZYGX2012Z003); the China-Denmark Co-project, TRR61 (NSFC-DFG Transregio Project); and the Chinese Academy of Sciences.

Notes and references:


27 P. He, Z. Y. Tu, G. Y. Zhao, Y. G. Zhen, H. Geng, Y. P. Yi, Z. R. Wang, H. T. Zhang,
**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
Figure 2
Figure 3
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.