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Microelectronic Engineering 65 (2003) 279–284

MICROELECTRONIC ENGINEERING

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Electrical characteristics of diodes fabricated with organic semiconductors

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Received 20 June 2002; received in revised form 17 August 2002; accepted 19 August 2002

Abstract

Organic diodes have been fabricated using 1,4,5,8-naphthalene-tetracarboxylic-dianhydride (NTCDA), poly(3,4-ethylenedioxythiophene) (PEDT), doped with poly(styrenesulfonate) (PSS) and polypyrrole (PPy) by simple and low-cost spin coating and thermal evaporation techniques. The current–voltage (I–V) characteristics have been investigated at room temperature, showing the breakdown voltages of about 9 V and the rectification ratios in excess of 4.1×10^3 for both NTCDA/PPy and NTCDA/(PEDT/PSS) diodes. The significant influence of acetone treatment on I–V characteristics is observed for NTCDA/PPy diodes.

Keywords: Organic diode; Organic semiconductor; Poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate); 1,4,5,8-Naphthalene-tetracarboxylic-dianhydride; Polypyrrole

1. Introduction

Since the 1990s, conducting polymers have been the focus of enormous technological and scientific effort for large area device application due to their low cost and easy processing. Poly(3,4-ethylenedioxythiophene) (PEDT) doped with poly(styrenesulfonate) (PSS) 1,4,5,8-naphthalene-tetracarboxylic-dianhydride (NTCDA) and polypyrrole (PPy) have attracted much attention as new organic electronic materials applicable to microelectronic devices. PEDT/PSS is optically transparent p-type semiconducting polymer [1]. PPy is an air-stable, solution processable p-type semiconducting polymer and has very good mechanical strength for commercial use in batteries [2]. These two types of polymers can be deposited cost-efficiently by the spin-coating technique. NTCDA is a widely used n-type organic semiconductor.

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0167-9317/02/$ – see front matter
PII: S0167-9317(02)00901-2

Up to now, much effort has been devoted to the preparation and characterization of metal–organic Schottky junctions and photodiodes [3–6]. Some researchers have attempted to fabricate the organic p–n junction by electrochemical or photochemical processes [7]. However, there are few reports on the fabrication and properties of junctions based on two different types of organic semiconductors with the lithographic technique.

Here, two organic diodes, NTCDA/PPy and NTCDA/(PEDT/PSS), are presented, showing both rectifying and breakdown behavior. Undoped NTCDA is used as an n-type organic semiconductor for both diodes. The p-type semiconducting polymers of the diodes are PPy and PEDT doped with PSS. A particularly simple and low-cost way to fabricate the organic diodes, spin-coating, is demonstrated. Their current–voltage characteristics were investigated in the atmosphere at room temperature. The effect of acetone attack in the fabrication process on current–voltage characteristics was observed for the NTCDA/PPy diodes.

2. Experimental

Fig. 1 shows the schematic cross-section view of the fabricated organic diodes with aluminum as the RIE mask. For the fabrication of organic diodes, an n-type heavily doped silicon wafer with a low resistivity of about 0.001 $\Omega \times$ cm was used as an electrode and substrate. Due to the moisture sensitivity of NTCDA, after cleaning the silicon substrate, a layer of undoped NTCDA 600 nm thick was thermally evaporated at a low deposition rate on the silicon substrate at room temperature to improve the film crystalline quality. During the deposition, the pressure in the vacuum chamber was kept at about 1×10^{-7} Torr. After that, for the NTCDA/(PEDT/PSS) diode and NTCDA/PPy diode, PEDT/PSS or PPy about 1 μm thick was then deposited on the NTCDA layer by spin-coating. Then the films were cured at 120 °C for 5 min and slowly cooled to room temperature. Following that, both kinds of organic diodes were formed by the RIE (reactive ion etching) technique. As shown in Fig. 1, a layer of aluminum 150 nm thick was thermally evaporated as the metal pattern mask for the RIE etching. Upon patterning the aluminum with the photolithography technique, the RIE process was utilized to strip the photoresist and to etch the PEDT/PSS (or PPy) and NTCDA layers. Finally, the organic diodes were formed after the wet etching of aluminum layer. During this whole fabrication process, acetone was avoided due to its significant adverse influence on the diode performances.

To characterize the organic diodes, current–voltage measurements were performed on a Keithley SMU236 unit in atmosphere at room temperature.

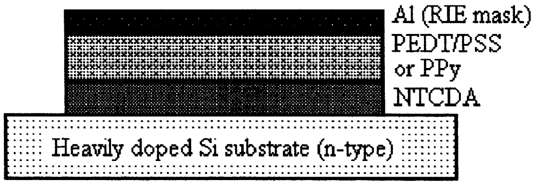

Fig. 1. Schematic structure of organic diodes with Al as the pattern mask for RIE etching.

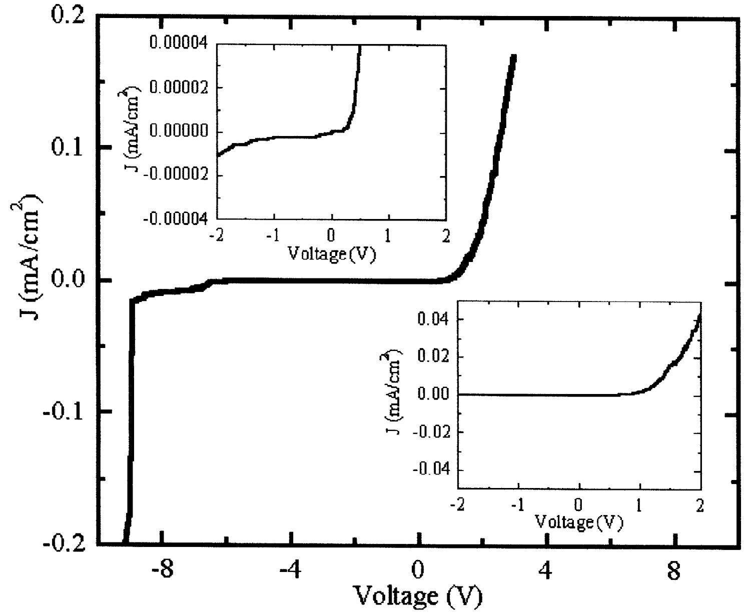

Fig. 2. Current–voltage characteristics of NTCDA/PPy diode with an active area of 0.25 mm^2.

3. Results and discussion

The measured current density versus voltage characteristics of NTCDA/PPy and NTCDA/(PEDT/PSS) diodes at room temperature are illustrated in Figs. 2 and 3, respectively. Forward bias is defined here as positive voltage applied to the PPy or PEDT/PSS contact. From the experimental data, the rectification ratios can be found to be $\sim 4.5 \times 10^3$ for NTCDA/PPy at 2 V and $\sim 4.1 \times 10^3$ for NTCDA/(PEDOT/PSS) at 3 V. The turn-on voltage of the NTCDA/(PEDT/PSS) diode is about 1.7 V, which is higher than that of the NTCDA/PPy diode, about 1.2 V. The NTCDA/(PEDT/PSS) diode has a lower current density at the forward bias compared to the NTCDA/PPy diode. The reason for the difference is attributed to the different material properties like bandgap and Fermi energy level.

The interface properties between the n-type organic material and the p-type organic material depend on the relative energies of the Fermi energy levels, the highest occupied molecular orbit (HOMO) levels and the lowest unoccupied molecular orbit (LUMO) levels. Usually the Fermi levels of the two materials align at the interface. However, due to weak van der Waals intermolecular bonding between organic semiconductors, the Fermi level would move freely at the organic interface and thus allowing the vacuum level to align [8]. The contact barrier would be determined by the ionization energy difference between two organic semiconductors. Here, the ionization energy is defined as the energy separation of the low binding energy edge of the HOMO from the vacuum level.

The bandgap (E_g) of NTCDA is determined to be 3.3 eV from the absorption spectrum and its energetic distance between conduction band and Fermi level ($E_C - E_F$) is less than 0.37 eV at 30 °C [9]. The work function and the bandgap of PEDT is 5.16 eV [10] and about 1.6 eV [11], respectively.

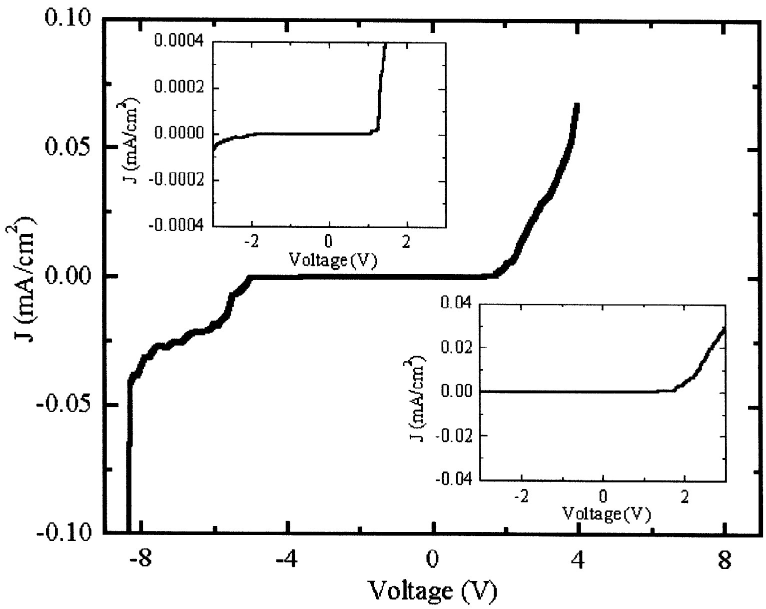

Fig. 3. Current–voltage characteristics of NTCDA/(PEDT/PSS) diode with an active area of 1 mm^2.

The difference between the conduction band edge and vacuum level for PPy is 2.5 eV and the E_g is 3.16 eV. Its polaron level is about 5.19 eV relative to the vacuum level [12]. Thus, from our experiment barriers for NTCDA/(PEDT/PSS) and NTCDA/PPy diodes, the HOMO of NTCDA can be deduced to be about 6.9 eV from the vacuum level. Then, the LUMO of NTCDA will be 3.6 eV from the vacuum level.

From the reverse part of the curves in Figs. 2 and 3, the breakdown voltages for the NTCDA/PPy and NTCDA/(PEDT/PSS) are about 9 and 8.3 V, respectively. Both of these kinds of organic diodes show an abrupt breakdown behavior.

Acetone is a very common solution for photoresist removal in photolithographic process. However, acetone was found to significantly affect the electrical characteristics of diodes in our experiment. From the measured data of NTCDA/PPy diodes immersed in an acetone solution for about 3 min, a significant change of the *I–V* characteristics as shown in Fig. 4 was observed due to the acetone attack. Unlike that of diodes without acetone treatment, the current–voltage characteristics are found to be symmetric without abrupt breakdown behavior (Fig. 4). The rectification ratio is dramatically decreased by three orders compared to that of diodes without acetone treatment and the breakdown voltage is reduced to about one-third. Furthermore, the current density is about 1000 times lower under the same forward bias condition after this treatment. This effect should be attributed to the strong influence of acetone on the conducting properties of PPy by changing the doping level. Thus, acetone should be avoided in the fabrication process of an NTCDA/PPy diode. As an alternative approach to patterning polymers, the RIE process as described in Experimental can be used because of its advantages such as clean and dry etching.

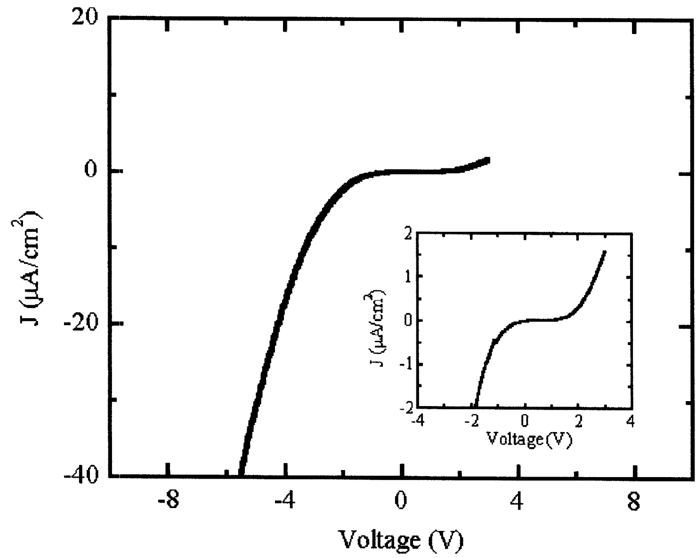

Fig. 4. Current–voltage characteristics of NTCDA/PPy with an active area of 0.25 mm^2 after the acetone treatment.

4. Conclusions

By thermal evaporation and low-cost spin coating techniques, two kinds of organic diodes consisting of NTCDA as an n-type semiconductor and PEDT/PSS or PPy as a p-type semiconducting polymer were successfully fabricated. The *I–V* characteristics were analyzed at room temperature. The nonlinear *I–V* curves show the rectifying behavior with a rectification ratio of above 4.1×10^3. The turn-on voltage of the NTCDA/(PEDT/PSS) diode is about 1.7 V and that of the NTCDA/PPy diode is about 1.2 V. The diodes have the abrupt breakdown characteristics under the reverse-bias of around 9 V. Acetone treatment will significantly affect the current–voltage characteristics of a NTCDA/PPy organic diode, resulting in a three times lower breakdown voltage and about three-order lower current density and rectification ratio. To avoid the acetone attack, RIE process with the aluminum as the mask was developed to pattern the organic diodes.

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