

The study of defect state of 2,7-dipyrenyl-9-phenyl-9-pyrenyl fluorene through admittance spectroscopy



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ABSTRACT

Up to now, the defect state in organic semiconductors has still not been thoroughly studied, especially for the synthesized materials. 2,7-Dipyrenyl-9-phenyl-9-pyrenyl fluorene (DPPPF) was a wonderful synthesized luminescent material in organic electronics. Research has found that the capacitance could reflect the defect state density of the special positions in the depletion region. So in this report, the admittance spectroscopy method was used to study the defect state of DPPPF, during which the Walter and Mott–Schottky models were applied to extract the defect distribution of the material. And in addition, the Gaussian model was used to describe the width of defect state distribution. The result showed that in the DPPPF, the total defect density was about $6 \times 10^{16} \text{ cm}^{-3}$, with the distribution range of 0.32–0.70 eV.

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1. Introduction

The organic semiconductor materials could be easily synthesized or modified by chemistry method. So the number of the organic semiconductors has been soaring over the past years, which is much larger than that of inorganic semiconductors. However, as for organic materials, after simple electronic device characterization, most of the synthesized materials were discarded without careful research of their physical properties such as that in inorganic semiconductors. In spite of the large amount of the newly synthesized materials, up to now, most of the physical research literatures still center on commonly organic electronic materials such as NPD, Alq₃, MEH-PPV, etc.

Except for doping technology in inorganic semiconductors, the defect state in organic semiconductors always leads to some detrimental influences on the device performance because such defects could change the electric field of the device, decrease the carrier mobility and even suppress the activity of the device [1].

Several measuring methods have been reported on the study of defect state, such as modulated photocurrent [2], photoconductivity [3], time of flight (TOF) [4], deep-level transient spectroscopy [5]. Recently, admittance spectroscopy method has been used to study the carrier dynamics of organic semiconductors [6–11]. Walter et al. introduced this method into the study of the defect state in Cu(In,Ga)Se₂ [12]. And then Reis et al. began to apply it to the defect state research of organic semiconductor CuPc and ZnPc [13]. However, although scientists understood the importance of defect state in organic semiconductors [14–17], the reported literature on research of defect state through admittance spectrum was still limited [13], which was not corresponding to the large amount of the organic materials. So in this report, the admittance spectroscopy method was used to study the defect state of 2,7-dipyrenyl-9-phenyl-9-pyrenyl fluorene (DPPPF, chemical structure is inset in Fig. 1), which was a wonderful newly synthesized luminescent organic semiconductor and also showed the hole transporting characteristic [18,19].

Currently, TOF is a common method for research of defect state. However, the amount of materials needed in TOF method is greatly more than that in admittance spectroscopy method. TOF method always requires a film thickness of at least 1 μm (or several μm) in order to get a well-defined flight distance. Sometimes it is very expensive to obtain the smooth film with

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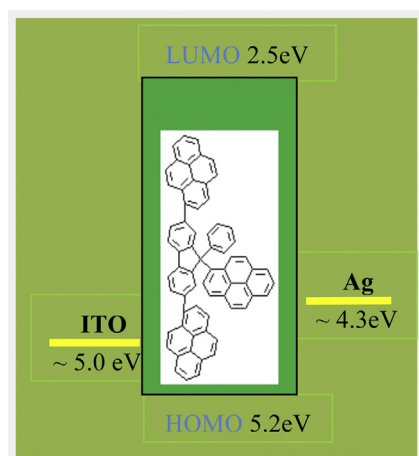


Fig. 1. The device energy level diagram and the inset is the chemical structure of DPPPF.

such thickness through vacuum deposition method because it always needs to consume the materials with amount of one or several gram weight. As to some synthesized organic semiconductors, it is difficult to obtain such amount since the synthesis method sometimes is very complex. Moreover, the operation of the TOF instrument is very complicated and the instrument is also expensive. To the best of our knowledge, the above two reasons could explain why most of the newly synthesized organic materials have not been carefully investigated through the powerful TOF technology. In contrast, for admittance spectroscopy method, the thickness of organic materials could greatly decreased to 100–300 nm. For example, in this report, the thickness of DPPPF was only 150 nm. Then the amount of the needed organic materials could be greatly decreased, which is a predominant characteristic for the admittance spectroscopy method. In addition, the instrument is greatly cheaper and much easier to be operated than that of TOF method. So this paper also showed the admittance spectroscopy method for research of defect state could be easily and widely

applied to other organic materials, especially to the newly synthesized materials.

2. Experimental

The DPPPF (inset in Fig. 1) was synthesized in our laboratory [18,19], which was used as the research target in this report. The device was fabricated on the ITO glass. Before device fabrication, ITO substrate was cleaned with ethanol, acetone and plasma water, respectively, and then washed by ultrasonic bath. After drying, it was treated for 3 min by UV–ozone in order to increase its work function. DPPPF (150 nm) and then Ag (200 nm) were coated onto ITO respectively through vacuum sublimation under 10^{-4} Pa. The thickness of each layer was measured by a quartz oscillator. The active area of the device was 18 mm^2 . The admittance, as a function of frequency, was measured by the ac impedance model of electrochemical workstation CHI 660C. An ac small signal with an amplitude of 20 mV ($f=10^0\text{--}10^5 \text{ Hz}$) was sent into the device as the perturbation signal. To avoid the interference of environment, the admittance spectrum measurement was performed in the shielding box at room temperature.

The fabricated device was ITO/DPPPF (150 nm)/Ag (200 nm). The work function of the UV–ozone treated ITO [20] was close to the highest occupied molecular orbital (HOMO) of DPPPF [18,21]. So the ITO/DPPPF interface was approximately Ohm's contact. On the other hand, few electrons could be injected from cathode because the lowest unoccupied molecular orbital (LUMO) of DPPPF is greatly lower than the work function of Ag (Fig. 1). So hole current was the dominant current.

3. Results and discussions

The defect states in the band gap depend on their energies and positions, which also contribute to the junction capacitance. If the angular frequency of the alternating signal is low enough, all the defect states could follow the alternating signal. So the capacitance would reflect the defect state density $N(E_t)$ of the special position in the depletion region. The position is determined by the intersection point between the Fermi level and the energy level

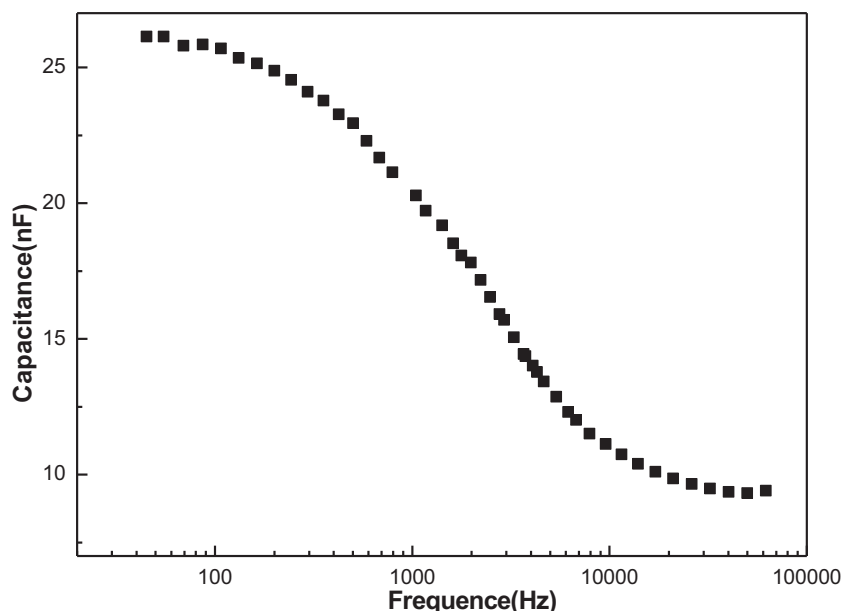


Fig. 2. The capacitance spectra of DPPPF under 0 V.

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