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Study of OPD based on $PC_{60}BM$+P3HT bulk heterojunction

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Abstract. Junction organic photodetectors (OPD) based on the principle of photovoltaic generation have been widely studied. Firstly, this paper introduces the bulk heterojunction OPDs using ZnO for electron transport layer, $PC_{60}BM$+P3HT for active layer structure, and MoO_3 for hole transport layer to improve the photoelectric conversion efficiency. Secondly, the OPD device was prepared by specific experimental scheme, and the advantages of using the polymer-organic small molecular heterojunction were pointed out. Finally, the performance of the device was analyzed, including external quantum efficiency (E_{QE}), responsiveness, specific detectivity, dark current and so on in different bands. Finally, the shortcomings of the device are pointed out, and the improvement scheme and possible improvement direction are put forward to improve the photoelectric conversion efficiency and fabricate high performance organic photodetectors.

Keywords: Organic photodetector(OPD), Polymer-organic small molecular heterojunction (BHJ), Active layer,$PC_{60}BM$,P3HT

1. Introduction

The information society has an increasing demand for microelectronic devices, especially for compact, cost-effective, and powerful photodetectors (OPDs). Photodetectors are semiconductor devices used to convert light signals into electrical signals. They find extensive applications in monitoring different wavelengths and intensities of light, such as ultraviolet light for medical diagnostics and environmental monitoring, visible light for image sensing and industrial control, and infrared light for missile guidance and infrared thermal imaging, among others. Traditional photodetectors are mainly based on inorganic semiconductors, which are costly and complex to manufacture and lack mechanical flexibility [1]. In recent years, photodetectors based on organic semiconductors have gained widespread attention due to their immense potential applications in smartphones, personal computers, industrial monitoring systems, automotive, and military systems.

Organic semiconductors are divided into two main categories: small molecule organic semiconductors and polymer semiconductors. Small molecule organic semiconductors have a definite molecular weight and consist of single substances, with charge carrier transport mainly via intermolecular hopping. On the other hand, polymer semiconductors are formed by the repeated linking of one or more monomers, with carrier transport mechanisms primarily along the chain and between chains. Compared to this, carrier mobility in organic semiconductors is generally lower. However, organic semiconductors have several advantages [2]:

1) They exhibit good absorption characteristics within the visible light range, with absorption coefficients exceeding 105 cm^{-1} and large extinction coefficients, facilitating the fabrication of thin active layers with relatively low device fabrication requirements;
2) They have a low refractive index, overcoming the drawbacks of reabsorption and light refraction losses seen in inorganic light-emitting diode devices;
3) They have a low intrinsic defect concentration, with dark currents two orders of magnitude lower than those of inorganic photodetectors;
4) They offer unlimited variety, as the photoelectric properties of semiconductor materials can be tailored through molecular structure manipulation;
5) The materials are simple to prepare and purify, featuring cost-effective organic film fabrication processes, and are compatible with flexible substrates.

Therefore, this paper will focus on the principles and performance parameters of heterojunction-type organic photodetectors and point out some methods to improve the performance of OPDs.

2. Principle of Heterojunction OPDs

The structure of Organic Photodetectors (OPDs) originates from solar cell technology, influenced by the photovoltaic effect. Heterojunctions (HJs) are crucial in constructing OPDs, referring to the interface formed between two different semiconductor materials (n-type and p-type). In this contact region, due to the concentration gradient of carriers, most carriers will diffuse into the other semiconductor material, forming a non-neutral space charge region. The built-in electric potential generated causes the carriers to drift and limits the diffusion of electrons and holes until equilibrium is reached. Organic semiconductors have their respective Fermi levels, the lowest unoccupied molecular orbital (LUMO) levels, and the highest occupied molecular orbital (HOMO) levels. When two different organic semiconductors come into close contact, their Fermi levels align, creating a contact potential difference area. Common heterojunction structures include planar heterojunctions (PHJs), bulk heterojunctions (BHJs), and planar-bulk mixed heterojunctions (P-BMHJs) [3].

For PHJs, when the heterojunction is illuminated, if the energy of the incident photons exceeds the bandgap of the donor or acceptor semiconductor, absorption can occur, exciting electrons from the HOMO to the LUMO level in the semiconductor, as shown in Figure 1(a) and (b). For inorganic semiconductors, photons with energy exceeding the bandgap can easily generate free electrons, but for organic semiconductors, photon absorption produces a localized excited state on the molecule, known as an exciton, with a binding energy greater than thermal energy (ranging from 0.1 to 1eV). This is a key difference between organic and inorganic semiconductor materials. Excitons are difficult to spontaneously dissociate into free charges at room temperature; hence, charge collection requires their dissociation, which is highly effective near the interface of two materials with different electron affinities or ionization potentials, as shown in Figure 1(c). Excitons generated in the donor or acceptor semiconductor diffuse to the interface between the two, where under the influence of the contact potential difference, they overcome the binding energy of the exciton, separating the electron and hole into free carriers, known as efficient exciton dissociation. This process is over 1000 times faster than the radiative or non-radiative decay of photogenerated excitons, with nearly 100% charge separation efficiency. Free electrons pass through the donor-acceptor (D-A) interface to the acceptor, captured by the material with a high ionization potential, while holes are captured by the donor material with a low ionization potential, passing through their respective semiconductors to be collected by the electrodes, ultimately detecting the electric signal converted from the light signal, as shown in Figure 1(d) and (e) [1].

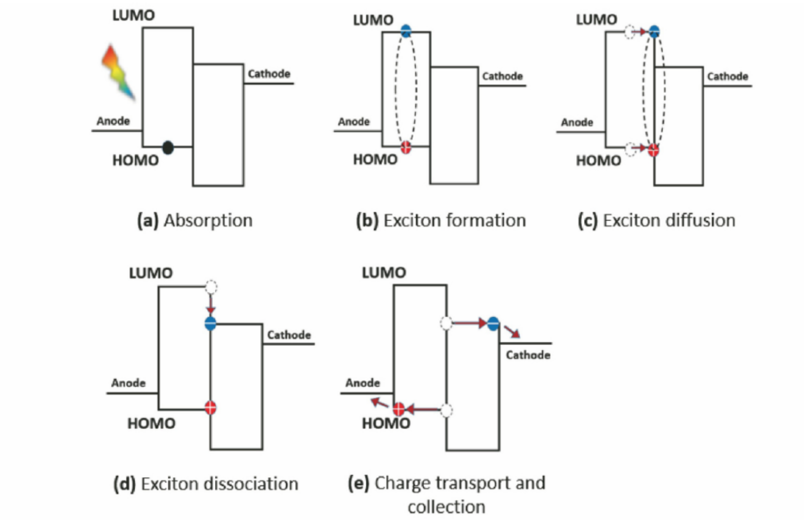

Figure 1. Schematic of photogenerated carrier generation in planar heterojunctions.

However, the diffusion length of excitons is typically only 1/10th of the depth of light absorption, greatly limiting the charge collection efficiency. To improve the quantum yield and effectively transmit photogenerated charges to the electrodes, a BHJ structure is formed by thoroughly mixing donor and acceptor materials. The BHJ structure greatly increases the contact area between the donor and acceptor materials, allowing more excitons to reach the D-A interface for effective dissociation and providing continuous paths for hole transport along donor molecules and electron transport along acceptor molecules [4]. The spatial distribution of donor and acceptor materials within the BHJ active layer greatly influences the photo and dark current characteristics. A well-formed BHJ structure creates an interpenetrating network beneficial for charge transport and reducing carrier recombination.

In this paper, the adopted device uses ITO as the anode and Ag as the cathode, with ZnO as the electron transport layer and MoO_3 as the hole transport layer, and the active layer composed of $PC_{60}BM$+P3HT bulk heterojunction, as shown in Figure 2(a). ITO (indium tin oxide) is chosen for its excellent conductivity and transparency, serving as an excellent anode material that allows light to reach the active layer. One advantage of MoO_3 as a hole transport layer is its lower work function, which aids the transfer of holes from the organic semiconductor to the anode, reducing electron-hole recombination, and improving device efficiency and stability. ZnO is a common electron transport layer material, offering good electron transport properties and appropriate energy level alignment to facilitate electron transport from the active layer to the cathode and reduce contact resistance with the anode. $PC_{60}BM$ and P3HT form a widely studied system. Compared to other organic mixtures, this polymer-fullerene mixture exhibits faster mobility, stronger absorption capabilities, and higher quantum efficiency. As an organic photoelectric material, the formation of a bulk heterojunction exhibits excellent photoelectric performance, effectively absorbing light energy and converting it into charge carriers, thus achieving photodetection functionality. The formation of the bulk heterojunction interface also aids in the effective separation of photogenerated carriers, transporting electrons and holes across different materials, thus enhancing the response speed and sensitivity of the photodetector. The device energy levels are shown in Figure 2(b), where the staggered energy level distribution facilitates electron and hole transport and also suppresses the dark current to some extent. Overall, this device has significant advantages and rationality [5].

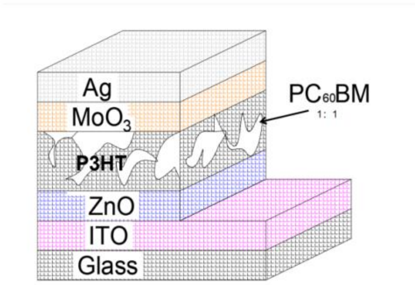

Figure 2(a) depicts the device structure (with uneven thickness).

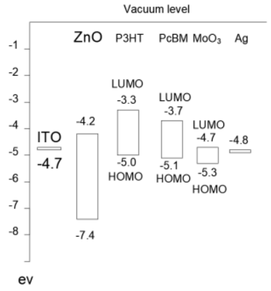

Figure 2(b) shows the device energy levels.

3. Experimental Scheme

The process mainly consists of four parts: ITO cleaning, solution preparation (ZnO precursor and active layer), spin-coating of ZnO and active layer, and deposition of MoO_3 and Ag.

Specific operations: ITO Cleaning: Mark the number (on the back of ITO), peel off the protective film; scrub with detergent, rinse thoroughly with deionized water, place on a substrate holder for ultrasonic cleaning in deionized water for 30 minutes, followed by acetone ultrasonication for 1 hour, repeat twice, isopropanol ultrasonication for 30 minutes, repeat twice; after blowing dry with nitrogen, treat in UVO for 10-15 minutes. When not in use, keep the cleaned substrates on a cleaning rack, soaked in isopropanol with cling film sealed, and when needed, blow dry with a gun and immediately place in UVO; UVO for 20 minutes. Solution Preparation: [ZnO Precursor] Scheme 1: Weigh x mg (usually 30 µL) of ethanolamine, then weigh 3.5938x mg of zinc acetate dihydrate, add 36.38216x µL of 2-methoxyethanol, stir at room temperature for over 3 hours. Scheme 2: 110 mg of zinc acetate dihydrate + 1 mL of 2-methoxyethanol + 31 µL ethanolamine, stir at 400-600 rpm at room temperature for over 3 hours. [Active Layer]: 5 mg donor P3HT + 5 mg acceptor $PC_{60}BM$ (1:1; w/w) dissolved in 0.5 ml of chlorobenzene (CB), total concentration of 20 mg/ml, add DIO (0.5% vol.), stir at 50°C for over 12 hours. Spin-Coating ZnO Layer: Take 10-20 µL of the mixed solution, spin-coat at 4000 rpm for 40 seconds in an ambient air environment, followed by annealing at 200°C for 30 minutes in ambient air. Spin-Coating Active Layer: Take 20-30 µL of the active layer mixture, spin-coat at 2000 rpm for 40 seconds inside a glove box, followed by annealing at 110°C for 10 minutes. Deposition of MoO_3 and Ag: Performed by thermal evaporation at 206°C.The process flow is illustrated in Figure 3.

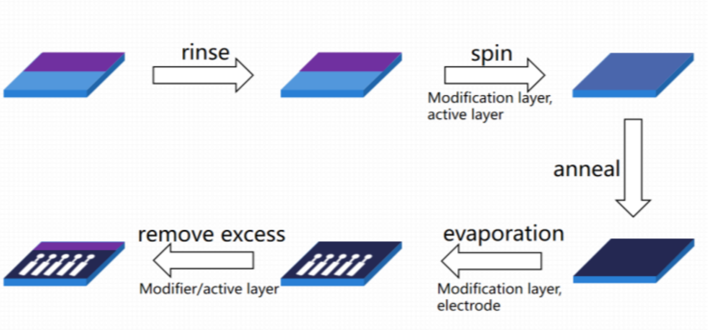

Figure 3. Device Fabrication Process

4. Performance Parameters of Junction-type OPD

Key performance parameters of junction-type photodetectors include external quantum efficiency (E_{QE}), responsivity (R), detectivity (D*), and response time.

External quantum efficiency (E_{QE}) is an important performance parameter, defined as the ratio of the number of electrons flowing in the external circuit per unit time to the number of incident photons at a single wavelength, reflecting the photoelectric conversion capability of the photodetector. The E_{QE} of the junction-type photodetector can be expressed as follows:

$$E_{QE} = \frac{I_{\text{ph}}/\text{e}}{P_{\text{in}}/hv} = A(\lambda)\eta G(\lambda)Q(\mu\tau)$$

Where: I_{ph} is the photocurrent, its value in practical applications is the measured light current (I_L) minus the dark current (I_D); e is the elementary charge; P_{in} is the incident optical power; hν is the photon energy; A(λ) is the optical absorption; ηG(λ) is the quantum efficiency; Q(μτ) is the charge collection efficiency.

2. The responsivity is the ratio of the photocurrent to the incident optical power.:

$$R_O = \frac{I_{\text{ph}}}{P_{\text{in}}}$$

3. The detectivity reflects the ability of the detector to detect weak light, with a higher value indicating a stronger ability of the device to detect weak light. That is:

$$D^* = \frac{R}{(2\text{qJ}_d)^{1/2}}$$

5. Device Performance Evaluation

Before testing the samples, a standard silicon device is needed as a control group. The standard silicon test is shown in Figure 4.1.

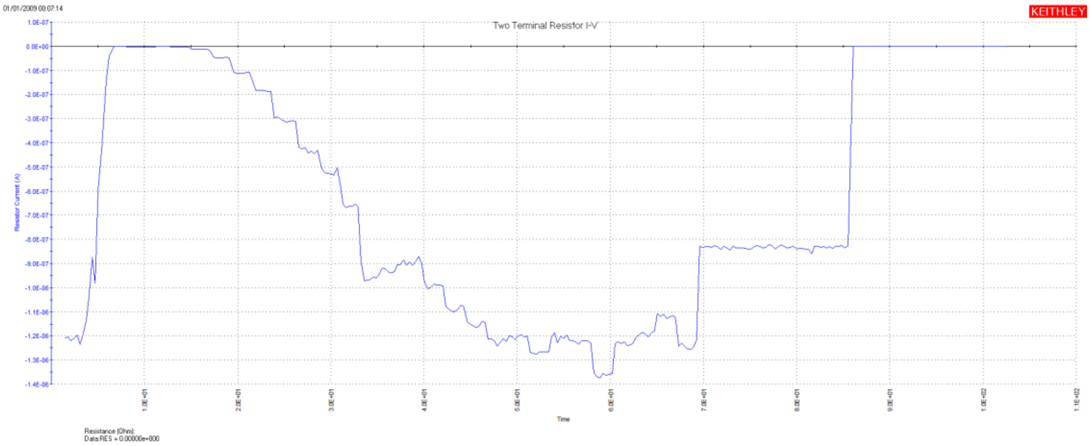

Figure 4.1. Standard Si Control

1. Different wavelength segments of external quantum efficiency, dark current, responsivity, etc., are analyzed and processed for the device. We found that the device performs well across the entire visible light spectrum. In Figure 4.2, the EQE reaches up to around 70%; in Figure 4.3, the responsivity is also around 0.4 A/W. In Figure 4.4, the detectivity is also in the order of 10^{13} in this wavelength band. The highest external quantum efficiency can reach between 20% and 30%, still showing some gap compared to today's junction-type organic photodetectors. According to relevant literature, the highest external quantum efficiency for this device has exceeded 80%. Therefore, further improvements are needed in our device structure to enhance the external quantum efficiency.

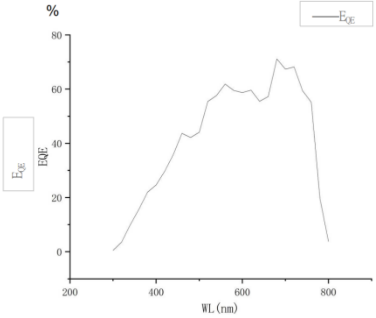

Figure 4.2. Device External Quantum Efficiency

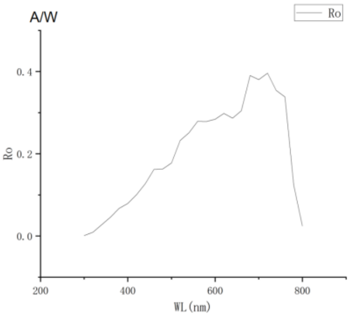

Figure 4.3. Device Responsivity

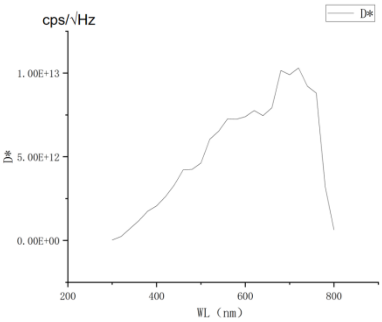

Figure 4.4. Device Detectivity(R)

2. Experimentally, at -5V voltage, the dark current density of the device is 4.6057E-9 mA/cm2, which is also in the order of 10^{-9}. The influence of dark current is negligible.

3. Figure 4.3 shows the J-V characteristics of the OPD based on P3HT:PC_{60}BM. From the figure, it can be seen that the dark current at 0V is significantly lower, about six orders of magnitude less than the current generated under normal illumination; when stabilized, the dark current is three orders of magnitude smaller than the photocurrent. When analyzing the external quantum efficiency, the impact of the dark current is almost negligible, which is a major achievement of our experiment. This figure is only from one of our samples, and a total of four device samples were screened, along with a standard Si control group.

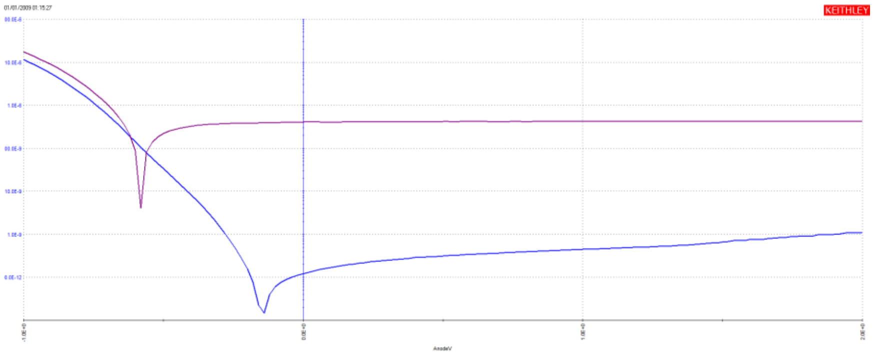

Figure 4.5. J-V characteristic curve of the OPD (top: current during illumination, bottom: dark current)

6. Progress and Outlook

6.1. Improvement in the Design of the Active Layer Structure

At the current stage, we have essentially realized a bulk heterojunction organic photodetector and analyzed its performance. In comparison with planar heterojunction types, we found that the size of the leakage current is mainly influenced by the interface energy levels between the metal and the semiconductor, as shown in Figure 5 (left). To avoid charge injection from the metal electrode into the device under reverse bias voltage, it is necessary to increase the work function of the metal as much as possible and increase the potential barrier between the metal and the organic semiconductor for carrier transport. Although it is possible to accelerate charge collection by applying an external electric field to achieve faster response and higher efficiency, doing so may lead to leakage current injection from the electrode, increasing the device's dark current and thus adversely affecting its performance. In bulk heterojunctions (BHJs), both donor and acceptor molecules are distributed throughout the entire active layer and are very close to the electrodes, resulting in a small effective barrier for charge injection and high leakage current, as shown in Figure 5 (middle).

Considering the drawbacks of both approaches, since our BHJs have a short exciton diffusion length, limiting efficient exciton dissociation, we can maintain a bulk heterojunction distribution within the device and induce donor (acceptor) enrichment near the anode (cathode) to form a P-BMHJ structure, as shown in Figure 5 (right). This is also the main direction of our upcoming experiments.

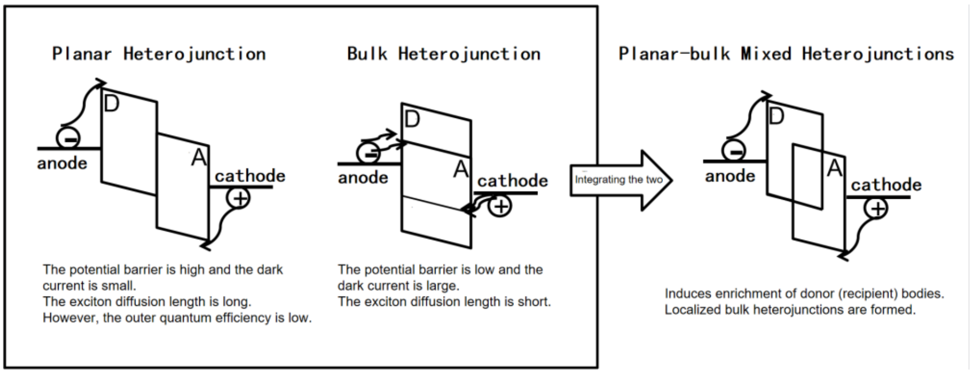

Figure 5. Design of P-BMHJ

Induction method: Currently pending.

To further reduce the dark current, we can use electron blocking layers (EBL) and hole blocking layers (HBL) to prevent charge injection under reverse bias voltage and prevent generated excitons from diffusing to the electrodes, effectively improving the device's performance, as shown in Figure 6. In contrast, in planar heterojunctions as shown in Figure 5 (left), each electrode only contacts one organic material, resulting in low leakage current.

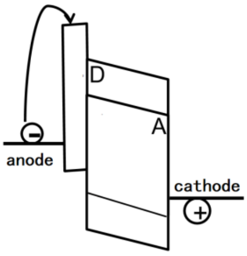

Figure 6. Addition of EBL to Bulk Heterojunction

6.2. Design of the Electron Transport Layer

First, optimize the ZnO thin film deposition quality to increase the film resistivity, thereby improving the sensor's response speed. Secondly, reduce the thickness of the ZnO film to avoid cracking caused by lattice mismatch.

6.3. Minimizing the Impact of Exciton Recombination on Device Performance

The recombination of photogenerated excitons is detrimental to the improvement of the device's responsivity and efficiency. To address this issue, a exciton blocking layer can be inserted to effectively prevent excitons from diffusing to the electrodes, thereby reducing exciton quenching at the organic/metal interface and improving device performance.

6.4. Spectral Response Range

Expanding the spectral response range of OPDs is another hot research direction, and using wide-bandgap materials for broad absorption is an effective means. We will further review literature to understand this.

7. Conclusion

By using ITO as the anode, Ag as the cathode, and ZnO and MoO_3 as the electron transport layer and hole transport layer respectively, we successfully constructed an organic photodetector. In terms of the active layer, we chose a bulk heterojunction formed by $PC_{60}BM$ and P3HT. The results of this study demonstrate that the photodetector has good photoelectric performance and stability, with a normal operating wavelength range of 520nm to 750nm, indicating potential application prospects.

First, through material selection and device structure optimization, we achieved high photoconversion efficiency and response speed. Secondly, we conducted detailed performance testing of the device and verified its excellent performance in photodetection through analysis of photocurrent-illumination curves, spectral response, and dark current. Finally, we evaluated the stability of the device and demonstrated its reliability in long-term stable operation and repeated testing.

In future work, we will conduct extensive literature research and experiments to address the issues mentioned above and implement solutions to prepare high performance organic photodetectors.

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