

The Role of Oxide Thin Layer in Inverted Structure Polymer Solar Cells

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ABSTRACT

The role of wide band gap oxide thin layer in inverted structure polymer solar cells was investigated by employing oxide films of TiO₂ and Nb₂O₅ approximately 10 nm in thickness deposited onto FTO substrates. The experimental results demonstrated that the thin oxide layer serving to separate the electron collecting electrode and the photoactive film of a blend of poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) was necessary to promote the formation of continuous uniform PCBM film to block holes in P3HT from being recombined with electrons in collecting electrode. A use of TiO₂ buffer layer leads to power conversion efficiency as high as 2.8%. As for Nb₂O₅, in spite the fact that its conduction band is higher than the LUMO level of PCBM polymer acting as electron transport material, a power conversion of 2.7%, which was only slightly different from the 2.8% achieved for the cell employing TiO₂. These experimental results suggest a tunneling mechanism for the electrons to transport from the PCBM to collecting electrode over the oxide film, instead of a diffusion through the oxide film arising from either energy or concentration difference of the photogenerated electrons.

Keywords: Polymer Solar Cell, Oxide Thin Film, TiO₂ Thin Film, Nb₂O₅ Thin Film

1. Introduction

Photovoltaic cells based on conjugated polymer and fullere bulk heterojunction composites have attracted much attention for renewable energy due to their promising properties such as low production cost, their lightness, light weight, mechanical flexibility and the possibility of fabricating them on large area [1-5]. Recent the power conversion efficiency (PCE) of the bulk heterojunction polymer solar cells has reached as high as 7.4% in conventional device structures [6]. Conventional organic photovoltaics, OPVs generally consist of an active layers sandwiched by a high work function and transparent metal oxide as the anode such as PEDOT:PSS and a low function metal as the cathode such as Al [7]. In spite of high PCE, the conventional OPVs can suffer from degradation of the cathode due to their sensitivity to oxygen and moisture in air. Therefore, the devices in this structure exhibit short lifetime [8-10]. In order to overcome these problems, the inverted device structures is an alternative solution to improve the durability, because it uses a more air-stable high work function electrode such (Ag, Au) as back contact to collect holes while using an inorganic semiconductor for buffer layer to collect electrons.

The usage of inorganic semiconductor embedded into the conjugated polymer have several attributes as electron acceptors, including relatively high electron mobility, high electron affinities, hole-blocking ability and good physical and chemical stability [11-16].

In this work we report the fabrication of inverted polymer solar cells and investigate the role of thin dense metal oxide films in the inverted polymer solar cells using dense film of TiO₂ and Nb₂O₅. These two oxides were purposely selected in view of the bottom of conduction band of TiO₂ lower than the LUMO level of PCBM and that of Nb₂O₅ higher than the LUMO level of PCBM. It was found that such a very thin metal oxide films between the electron collecting electrode and active layers was necessary to promote the formation of continuous uniform PCBM film and thus block the holes in P3HT from being recombined with the electrons in collecting electrode.

2. Experiment Details

2.1. Preparation of TiO₂ Sol and Nb₂O₅ Sol

TiO₂ sol was prepared by hydrolyzing titanium alkoxide in an acidic aqueous. Typically, 1 mL of titanium iso-

propoxide was added to 20 mL of distilled water containing 0.5 mL of hydrochloric acid. A white precipitate appeared in the beginning. After stirring for about 30 min, the precipitate completely dissolved, resulting in the formation of a TiO_2 sol in light yellow color. The fabrication of Nb_2O_5 sol was adopted a similar process and recipe, except the replacement of titanium isopropoxide with niobium ethoxide.

2.2. Fabrication of Solar Cell Devices

The FTO glass substrate was cleaned with DI water, acetone and isopropanol. The sol of TiO_2 or Nb_2O_5 was employed to form a thin film on the FTO glass substrate through a spin-coating method. The substrates with TiO_2 or Nb_2O_5 thin film then suffered a thermal treatment at 450°C for 1 h to convert the TiO_2 or Nb_2O_5 to crystalline phase. A chlorobenzene solution of P3HT:PCBM (1:0.8 by weight) containing 20 mg/ml P3HT and 16 mg/ml PCBM was prepared by stirring in glovebox at 60°C for overnight. The solutions were allowed to cool down to room temperature and then filtered with a $0.2\ \mu\text{m}$ polytetrafluoroethylene (PTFE) filter. For the device fabrication, the as-prepared P3HT/PCBM blend solution was spin-coated onto the FTO glass substrate coated with TiO_2 or Nb_2O_5 thin film (note: at 1000 rpm for 30 s) pretreated with oxygen plasma for 10 min. The samples were then baked at 225°C for 1 min to allow self-organization of P3HT, as well as to remove residual solvent and to some extent improve the contact between the polymer and oxide film. On the P3HT:PCBM blend layer, a diluted poly (3,4-ethylene-dioxythiophene)—poly (styrene sulfonic acid) (PEDOT:PSS, Clevis P VP AL 4083) solution was spin-coated to form hole-transport layer. The films were consequently baked at 120°C for 10 min. Finally, a 100 nm thick silver film was deposited on the PEDOT:PSS to work as top electrode.

Figure 1 shows a schematic configuration of the as-fabricated inverted polymer solar cell. The semiconducting metal oxide TiO_2 and Nb_2O_5 thin films are approximately 10 nm in thickness characterized by observing the cross-section SEM image of the films. The thicknesses of the polymer layer are about 300 nm and 30 nm for P3HT:PCBM and PEDOT:PSS, respectively.

3. Results and Discussion

Prior to investigation of the as-prepared inverted structure polymer solar cells, a device with structure of FTO/P3HT:PCBM/PEDOT/Ag, *i.e.*, not including an oxide thin film to separate the FTO glass substrate and polymer layers, was studied as a reference. The result is shown in **Figure 2**. One can see that there is no photovoltaic response at all. This is in agreement with what is pointed out in literature that an inverted structure poly-

mer solar cell includes a buffer layer to prevent direct contact between the FTO and polymer layers.

Shown in **Figure 3** are the current density (J)—voltage (V) curves of the inverted structure polymer solar cells, in which a layer of TiO_2 or Nb_2O_5 thin film was deposited on FTO glass substrate to separate the blend of P3HT and PCBM polymers and the collecting electrode. It can be seen that for the substrates using TiO_2 and Nb_2O_5 dense films the values of short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}) show very small difference. Power conversion efficiencies (η) for the cells with TiO_2 and Nb_2O_5 are 2.8% and 2.7%, respectively. Taking into account the above result shown in **Figure 2**, it strongly suggests that a thin metal oxide film as buffer layer between the electron collecting electrode and the blend of P3HT and PCBM polymers is necessary to form inverted structure hybrid solar cells.

A dependence of the solar cell efficiency on the thickness of the buffer layer was also studied. **Table 1** summarizes the values of short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and power conversion efficiency (η) of inverted TiO_2 /P3HT:PCBM/PEDOT/Ag and Nb_2O_5 /P3HT:PCBM/PEDOT/Ag solar cell. For TiO_2 and Nb_2O_5 with one-cycle spin-coating, the devices present similar efficiencies around 2.7% - 2.8%. However, as increasing the spin-coating cycle, which leads to an increase in the film thickness, the

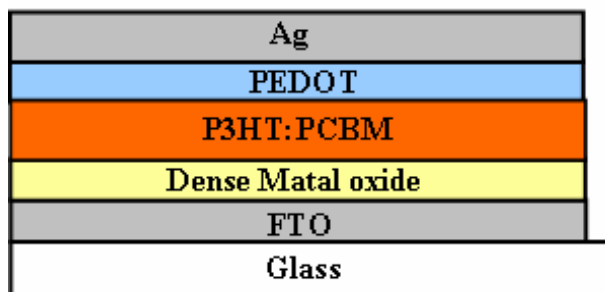


Figure 1. Schematic configuration of inverted structure polymer solar cell.

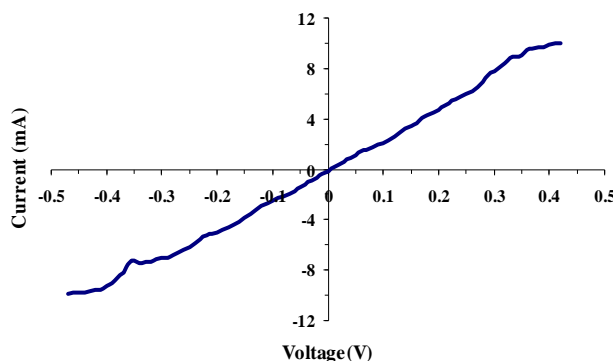


Figure 2. I-V curve for FTO/P3HT:PCBM/PEDOT/Ag.

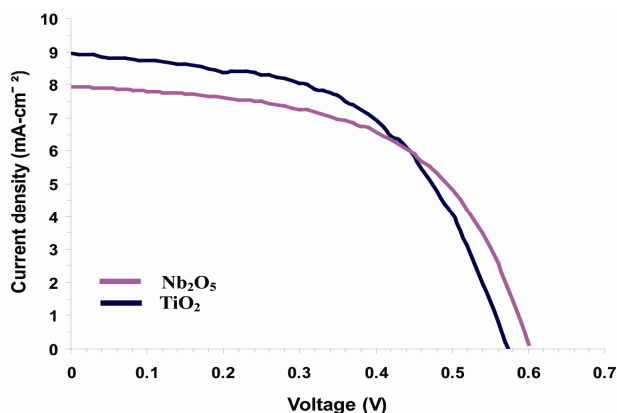


Figure 3. *J-V* curves of the hybrid solar cells based on TiO_2 and Nb_2O_5 thin film.

power conversion efficiency decreased from 2.8% to 2.3% in the case of TiO_2 and decreased from 2.7% to even zero in the case of Nb_2O_5 . Meanwhile, the short-circuit current density and fill factor can be also seen a significant decrease.

Figure 4 shows schematic picture of the energetic levels of Nb_2O_5 , TiO_2 , PCBM and P3HT. The conduction band (CB) of TiO_2 is lower than the lowest occupied molecular orbital (LOMO) energy level of P3HT and PCBM which allows electrons to transport from LOMO energy level of PCBM into the CB of TiO_2 . Note that the conduction band of Nb_2O_5 is higher than the LUMO of PCBM. That means the electron transport from the LOMO energy level of PCBM into the CB of Nb_2O_5 is not possible. However, in our study as the results shown in **Table 1**, a power conversion of 2.7% was indeed achieved while Nb_2O_5 serves as the buffer layer. More importantly, the achieved efficiency 2.7% is approximately equal to that (2.8%) obtained for TiO_2 (**Table 1**). Such a scenario strongly suggests that the electrons seem to transfer from the PCBM to collecting electrode through a tunneling process, as shown in **Figure 5**. Along with an increase in the thickness of Nb_2O_5 , it presents decreased short-circuit current density, open-circuit voltage, fill factor and power conversion efficiency. The efficiency even drops to zero in the case of thicker Nb_2O_5 film.

The above experimental observation that shows poor performance based on thick film indicates that excessively increased thickness of the dense metal oxide film beyond tunneling distance plays a negative role in the photovoltaic process. In other words, the transport of electrons unlikely occurs in a diffusion way in view of the receipt of efficiency in the case of Nb_2O_5 and a quick decrease in the efficiency as slightly increased thickness of the buffer layer. Considering the fact that no photovoltaic response can be obtained in the absence of oxide buffer layer, the role of the oxide layer is believed to promote

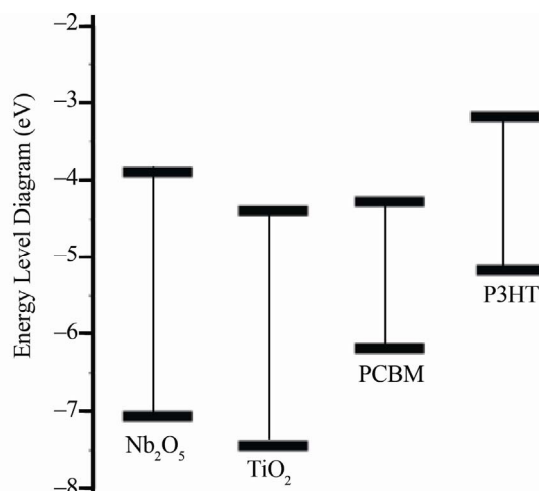


Figure 4. Schematic drawing of the energetic levels of Nb_2O_5 , TiO_2 , PCBM and P3HT.

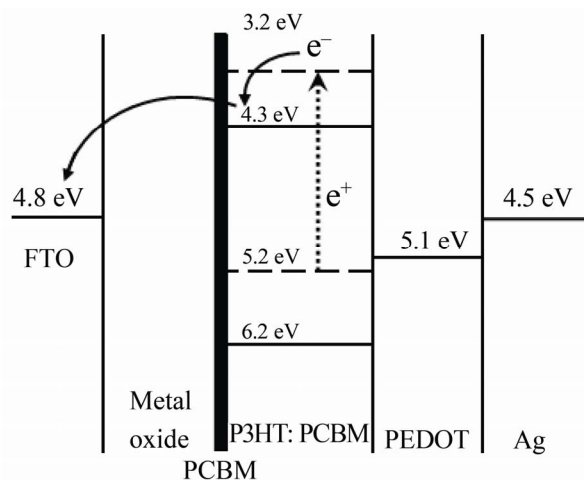


Figure 5. Energy diagram and charge transfer process of the as-discussed photovoltaic device with FTO/dense metal oxide /P3HT:PCBM/PEDOT/Ag structure.

Table 1. Summary of the performance of inverted structure polymer solar cells with buffer layer of TiO_2 and Nb_2O_5 .

Metal Oxide	Time of Cycle	V_{oc}	J_{sc}	FF (%)	η (%)
		(V)	($\text{mA}\cdot\text{cm}^{-2}$)		
TiO_2	1	0.574	8.95	53.9	2.8
	2	0.602	8.87	43.1	2.3
Nb_2O_5	1	0.602	7.94	55.8	2.7
	2	0.32	1.08	24.7	0

the formation of continuous uniform PCBM film so as to prevent the P3HT from touching with the FTO substrates and as such avoid the holes in P3HT from being recombined with the electrons in the collecting electrode. Therefore, charge separation in our hybrid solar cell occurs at the interface between P3HT and PCBM.

4. Conclusions

Our study demonstrates that a thin oxide film coating on FTO glass substrate is necessary in inverted structure polymer solar cells to protect P3HT from touching the FTO substrates and promote the formation of continuous uniform PCBM film to block holes from being recombined. The electrons transport from the PCBM to the collecting electrode on FTO glass substrate through a tunneling process. A thick buffer layer would not allow the occurrence of electron tunneling and therefore leads to low efficiency or even no photovoltaic response in the inverted structure solar cells.

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