Research Article

Effects of Controlling the AZO Thin Film's Optical Band Gap on AZO/MEH-PPV Devices with Buffer Layer

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Organic/inorganic hybrid solar cells were fabricated incorporating aluminum-doped zinc oxide (AZO) thin films of varying optical band gap in AZO/poly(2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylene vinylene) structures. The band gaps were controlled by varying the flow rates of Ar and O₂ used to deposit the AZO. Devices with CdS buffer layer were also fabricated for improved efficiency. The effects of AZO optical band gap were assessed by testing the *I*-*V* characteristics of devices with structures of glass/ITO/AZO/MEH-PPV/Ag under AM1.5 illumination (100 mW/cm²). Efficiency was improved about 30 times by decreasing the AZO optical band gap, except in devices deposited without oxygen. A power conversion efficiency of 0.102% was obtained with the incorporation of a CdS buffer layer.

1. Introduction

Organic/inorganic hybrid solar cells are promising for their low manufacturing costs, facile processing, and applicability in flexible devices. They incorporate organic polymers such as MEH-PPV and poly(3-hexylthiophene) (P3HT) that act as light absorbers and electron donors. Efficient separation of charge carriers from their place of generation in the light absorption layers depends on the electron properties of the inorganic material and the morphology of its interface with the polymer [1, 2]. Therefore various inorganic semiconductors have been tested to improve efficiency; examples include cadmium selenide (CdSe) nanorods [3] and nanoparticles [4], cadmium sulfide (CdS) nanorods [5] and nanowires [6], ZnO thin film [7] and nanorods [8–10], and TiO₂ nanoparticles [11]. Controlling the optical band gap of inorganic materials through the use of Al-doped zinc oxide (AZO) is also promising as these stable thin films have high electron mobility and affinity. ZnO/P3HT devices' efficiencies have been doubled upon the incorporation of a

nanocrystalline CdS buffer layer that introduces a cascading energy band gap structure between the ZnO and P3HT [12].

This work reports improvement of PV performance by controlling the optical band gap of AZO in AZO/poly[2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylene vinylene] (MEH-PPV) devices. Furthermore, we introduced CdS thin-film buffer layer between AZO and MEH-PPV for improved efficiency.

2. Experimental Methods

Soda lime glass substrates were sequentially cleaned ultrasonically in acetone, isopropyl alcohol, and deionized water and dried in nitrogen gas. An indium tin oxide (ITO) transparent conductive oxide layer was deposited on each substrate by DC magnetron sputtering through a patterned shadow mask. The patterned ITO glass was annealed for 15 minutes by RTA under nitrogen and oxygen. The sheet resistance of the ITO conductive oxide was 30 Ω/□, measured by four-point probe. 3 wt.% AZO targets were formed from

FIGURE 1: (a) Transmittance spectra of AZO thin films with various optical band gaps. (b) Evaluation of the AZO thin films' $(\alpha h\nu)^2$ versus $h\nu$ curves.

high-purity ZnO (99.99%) and Al(OH)₃ (99.99%) powders. The AZO thin films' optical band gaps were controlled by varying the O₂ and Ar gas mixture used during the RF magnetron sputtering. Ratios of the flow rates of argon and oxygen of 15:0, 14.3:0.7, 14.1:0.9, and 13:2 were used. CdS layers were deposited on the AZO thin films by RF magnetron sputtering under an Ar gas flow of 25 sccm. 10 mg MEH-PPV polymer in 1 mL chloroform was then spin-coated as a thin film over the inorganic film. Ag anodes were deposited by electron beam evaporation under vacuum at below 4×10^{-8} Pa.

Scanning electron microscopy (SEM) was performed on a Hitachi S-4700 scanning electron microscope. Transmittance and absorption spectra were measured on a Cary 500 scan UV-Vis-NIR spectrophotometer. Photoluminescence spectra were recorded at room temperature under 325 nm He-Cd laser excitation. Energy conversion efficiencies were measured under 100 mW/cm² illumination from an AM1.5 solar simulator.

3. Results and Discussions

Transmittances were measured between 300 nm and 2000 nm to assess the AZO samples' optical band gaps (Figure 1). In direct band gap semiconductors, intrinsic absorbance occurs near the band edge. Absorption coefficients were calculated using Lambert's law. The AZO thin films' optical band gaps were estimated by extrapolating the linear portions of plots $(\alpha h\nu)^2$ versus $h\nu$ using the relation $\alpha h\nu = A(h\nu - E_g)^{1/2}$, where T is the transmittance, t is the film's thickness, α is the absorption coefficient, $h\nu$ is the photon energy, A is a constant, and E_g is the direct optical band gap [13]. Optical band gaps of the AZO films deposited at argon and oxygen ratios of 15:0, 14.3:0.7, 14.1:0.9, and 13:2 were calculated to be

3.29, 3.35, 3.54, and 3.61 eV, respectively. The optical band gap increased as the O₂ partial pressure during deposition decreased due to Al ions being substituted into the ZnO lattice [14]. The AZO thin film showed an optical band gap of 3.29 eV, similar to that of intrinsic ZnO. PV performances of the AZO thin films in devices with MEH-PPV generally increased as the AZO's optical band gap decreased, except in devices deposited without oxygen (Table 1). Sheet resistance, from Hall measurements, decreased from $1.08 \times 10^6 \Omega/\square$ to $69.18 \Omega/\square$ as the optical band gap of the AZO increased. Concurrently, bulk carrier concentration increased from $-1.45 \times 10^{19}/\text{cm}^3$ to $-6.73 \times 10^{20}/\text{cm}^3$. Devices deposited without oxygen showed good charge collection because of low sheet resistance and high carrier concentration. As the AZO's optical band gap decreased, the electron barrier between the lowest unoccupied molecular orbital (LUMO) levels of MEH-PPV and AZO decreased [15].

Absorbances of the devices' layers were calculated from transmittance spectra; the PL spectrum of MEH-PPV was also measured (Figure 2). The optical absorption of MEH-PPV film peaked at 500 nm, showing an edge at 590 nm in the visible region. CdS thin film began to absorb slowly from around 550 nm to 490 nm. The optical absorptions of AZO and intrinsic ZnO thin film were in the UV region. The PL spectrum of MEH-PPV thin film shows that photoinduced charge transfer occurred in the MEH-PPV thin film [16].

Previous insignificant PV performances have been attributed to the great electron barrier between the LUMO levels of MEH-PPV and AZO [15], and the movement of electrons to the cathode from charge carrier separation may have been limited. CdS thin films were used as buffer layers between the MEH-PPV and AZO. CdS thin film started to absorb slowly from around 550 nm to 490 nm (Figure 2). The optical band gap of CdS thin film was 2.2 eV. The CdS layer, with an optical band gap of 2.2 eV, created a cascading

TABLE 1: Average PV performances of various AZO thin films in devices with MEH-PPV.

Sample	O ₂ flow rate (sccm)	Ar flow rate (sccm)	optical band gap (eV)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
1	0	15	3.61	0.371	0.16	25.54	0.019
2	0.7	14.3	3.54	0.147	0.012	23.12	0.001
3	0.9	14.1	3.35	0.234	0.116	24.36	0.008
4	2	13	3.29	0.321	0.264	28.19	0.03

TABLE 2: Average PV performances of AZO/CdS/MEH-PPV and AZO/MEH-PPV devices.

Sample	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
AZO/MEH-PPV	0.321	0.264	28.19	0.03
Device with buffer layer	0.497	0.478	31.96	0.102

FIGURE 2: Absorption spectra of intrinsic ZnO, AZO, CdS, and MEH-PPV thin film (left). PL spectrum of MEH-PPV thin film (right).

energy band gap structure between the AZO and MEH-PPV (Figure 3(a)) in the device structure that was characterized by SEM (Figure 3(b)).

The I - V behaviors of AZO/MEH-PPV bilayers were compared with AZO/CdS/MEH-PPV devices (Figure 4 and Table 2). AZO layers of 3.29 eV optical band gap were used as they resulted in the highest energy conversion efficiency (Table 1). V_{oc} and J_{sc} were doubled in the device with a CdS buffer layer under simulated AM1.5 illumination (Figure 4). These results were attributed to the cascading energy band gap structure of the CdS between AZO and MEH-PPV. This CdS layer could be photoexcited to produce additional photocurrent to improve energy efficiency, similar to in the AZO and MEH-PPV layers [9].

4. Conclusions

The PV efficiency of MEH-PPV/AZO hybrids could be increased by controlling the optical band gap of the AZO

FIGURE 3: (a) An energy band diagram. (b) The AZO/CdS/MEH-PPV device and its cross-section SEM image.

FIGURE 4: I - V characteristics of AZO/CdS/MEH-PPV and AZO/MEH-PPV devices.

thin film. Addition of a CdS buffer layer also significantly improved PV efficiency. These results demonstrate that controlling the optical band gap of ZnO and hybrid organic/inorganic solar cells with buffer layers can provide promising improvements to hybrid PV technologies.

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