Performance Improvement by Inserting an Electrodeposited ZnO into ITO/Organic Solid Interface in Organic Solid-state Solar Cells

Kohshin Takahashi,* Taiki Nishi, Syouko Suzaka, Yasunori Sigeyama, Takahiro Yamaguchi,
Jun-ichi Nakamura,† and Kazuhiko Murata†
Division of Material Engineering, Graduate School of Natural Science and Technology, Kanazawa University,
Kakumamachi, Kanazawa 920-1192
†*E&I Materials Research Laboratory, Nippon Shokubai Co., Ltd., 5-8, Nishi Otabi-cho, Suita, Osaka 564-8512*

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When an electrodeposited ZnO was inserted into the ITO/PV (PV: bisbenzimidazo[2,1-a:2′,1′-a′]antra[2,1,9-def:6,5,10-d′e′f′]diisoquinoline-6,11-dione) interface in ITO/PV/MEH-PPV/Au sandwich-type solar cells (MEH-PPV: poly[2-methoxy-5-(2′-ethylenehexyloxy)-1,4-phenylenvinylene], the cell performance was remarkably improved, resulting in 1.24% of energy conversion yield under the irradiation of AM 1.5–100 mW/cm^2.

Since Tang reported energy conversion efficiency up to 1% by using a phthalocyanine/perylene pigment *p–n* heterojunction cell,[1] much effort has been done to provide organic solar cells with low-cost and practical energy conversion. However, the efficiency is still small because of low light utility originating from the cell structure and small carrier mobility of the organic materials. Further detailed investigation on the photovoltaic effect is necessary to fabricate practical organic solar cells. Recently, we reported air-stable and efficient organic solar cells by penetrating conjugated polymers into a vacuum-deposited thin solid film of PV pigment.[2] In the cells, larger photocharge separation area having effective electron and hole migration networks arose from penetrating soluble conjugated polymers into a small opening formed by insoluble microcrystalline PV particles of less than 20 nm, therefore the photocurrent being enhanced. However, the small opening was not always prepared, because the surface morphorogy of the deposted PV was influenced by that of the substrate plate and also the vacuum-deposition condition to make the PV particles of less than 20 nm was very severe.

In this work, we tried to prepare larger photocharge separation area by controlling the surface unevenness of zinc oxide ZnO inserted into the indium–tin oxide (ITO)/PV interface. The surface unevenness of ZnO may be easily controlled by an electrodepositing method compared to by a spray pyrolysis or spin-coating method.

A transparent ITO substrate with the sheet resistance of less than 10 Ω/cm^2 was purchased from Furuuchi Chemicals. The organic compounds and their abbreviations used in this study are shown in Figure 1. A conjugated polymer MEH-PPV, a PV pigment, and a poly(styrenesulfonate)/poly(2,3-dihydrothieno[3,4-b]-1,4-dioxin) PEDOT 1.3 wt % dispersion in water were purchased from the American Dye Source Inc., SYNTEC, and Aldrich Chemicals, respectively, and used without further purification. An ITO/In/PV/MEH-PPV/PEDOT/Au sandwich-type solar cell was fabricated as our previous papers.[2,3] The active area of solar cells was 4 mm^2. The film thickness was about 5 nm for In, about 35 nm for PV, and about 40 nm for MEH-PPV. The thickness was monitored by an Ulvac CRTM-7000 oscillating quartz thickness controller or a Hitachi U-3310 spectrophotometer, being confirmed by an atomic force microscopy SII SPI3800N. When thin ZnO layer was used instead of 5 nm-In layer, the ZnO with hexagonal crystal lattice was electrodeposited on a precleaned ITO substrate by the literature method.[4] The average film thickness was estimated by the consumed electric charge and the density of 5.6 g/cm^3 on the assumption of Faradic efficiency of 100%. Before spin-coating the PEDOT interlayer of about 50 nm thickness, ultra thin gold layer of about 0.2 nm thickness was deposited onto the organic solid film by vacuum evaporation to improve the adhesion of PEDOT. The simulated solar light AM 1.5–100 mW/cm^2 employed in this work was obtained by a Kansai Kagakukikai XES-502S. The wavelength dependence of incident photon to current conversion efficiency *IPCE* was taken on a JASCO SM-250. The surface morphorogy and the absorption spectra were measured by the atomic force microscopy and the UV-spectrophotometer, respectively. The ionization potential was estimated from photoelectron spectroscopy in air (PESA) by a Riken Keiki model AC-2.[5] The surface potential was measured by Kelvin's method employing a TREC Model 320C.

When the thin In layer was inserted into the ITO/PV interface in the ITO/PV/MEH-PPV/PEDOT/Au sandwich-type solar cell, the performance was remarkably enhanced, see Table 1, where the PEDOT layer prevented a short-circuit of the sandwich-type cell and improved the photovoltaic properties. This is because the in-

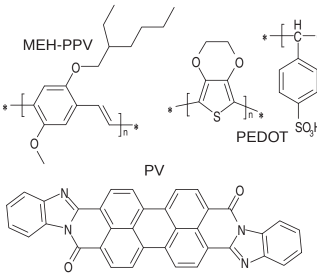

Figure 1. Structures and abbrebiations of employed chemical compounds.

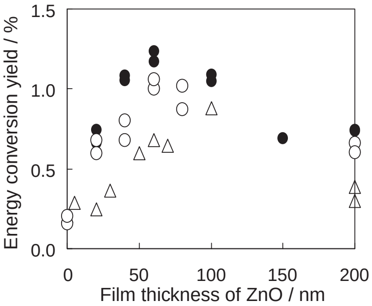

Figure 2. Dependence of energy conversion yield on the film thickness of ZnO in the ITO/ZnO/PV/MEH-PPV/PEDOT/Au solar cells. The electrode potential to deposit the ZnO was −1.0 V vs Ag/AgCl (△), −1.3 V (●), and −1.6 V (○).

Table 1. Performance of organic solar cells under illumination of AM 1.5–100 mW/cm^2

Type	J_{sc}^{a} /mA cm^{-2}	V_{oc}^{b} /V	FF^{c}	η^{d} /%
ITO/PV/MEH-PPV/PEDOT/Au	1.37	0.61	0.25	0.21
ITO/In/PV/MEH-PPV/PEDOT/Au	3.77	0.54	0.51	1.04
ITO/ZnO/PV/MEH-PPV/PEDOT/Au	4.04	0.62	0.50	1.24

^{a}Short-circuit photocurrent. ^{b}Open-circuit photovoltage. ^{c}Fill factor. ^{d}Energy conversion yield.

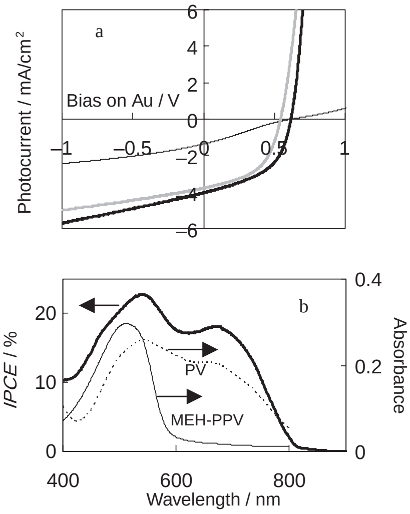

Figure 3. (a) Current-voltage curves for ITO/PV/MEH-PPV/PEDOT/Au (—), ITO/In/PV/MEH-PPV/PEDOT/Au (▬), and ITO/ZnO/PV/MEH-PPV/PEDOT/Au (▬) solar cells under illumination of AM 1.5–100 mW/cm^2. (b) The photocurrent action spectrum for the ITO/ZnO/PV/MEH-PPV/PEDOT/Au cell and the absorption spectra of the MEH-PPV and PV solid films. The film thickness was 40 nm for MEH-PPV and 35 nm for PV.

terface resistance was reduced by the In insertion as demonstrated by the increase of the short-circuit photocurrent J_{sc} and the fill factor FF.

In order to increase the J_{sc} value by increasing the photocharge separation area at the PV/MEH-PPV interface, we examined to employ an electrodeposited ZnO instead of the In layer. Figure 2 shows the dependence of the energy conversion yield η of the ITO/ZnO/PV/MEH-PPV/PEDOT/Au solar cell on the average film thickness of ZnO and on the electrodeposited potential. The maximum η value was obtained for the thickness of 60 nm and at -1.3 V vs Ag/AgCl of the electrodeposited potential. We obtained better performance of $J_{sc} = 4.04$ mA/cm^2, Voc $= 0.62$ V, $FF = 0.50$ and energy conversion yield of 1.24% under illumination of AM 1.5–100 mW/cm^2 for the air-stable ITO/ZnO/PV/MEH-PPV/PEDOT/Au solar cell. The cell performance was summarized in Table 1 and Figure 3a. Since the photocurrent action spectrum of the ITO/ZnO/PV/MEH-PPV/ PEDOT/Au solar cell was approximately consistent with the summation of the absorption spectra of MEH-PPV and PV as shown in Figure 3b, the photocurrent generation was responsible for the photo-induced excited-state of the MEH-PPV and PV molecules.

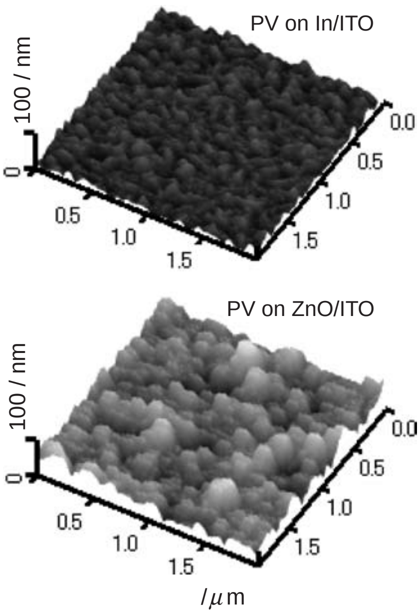

Figure 4. AFM images of the vapor-deposited PV (35 nm) solid surfaces on In (5 nm)/ITO and ZnO (60 nm)/ITO substrates. The number of the parenthesis are the aerage film thickness. The ZnO was electrodeposited at -1.3 V vs Ag/AgCl.

Figure 4 showed AFM images of the vapor-deposited PV (average thickness, 35 nm) surfaces on In (average thickness, 5 nm)/ITO and on ZnO (average thickness, 60 nm)/ITO substrates. These morphorogy of the PV surfaces followed that of the under-layer surfaces of In/ITO and ZnO/ITO. The peak to valley length of 60 nm of the PV surface on the ZnO/ITO was approximately twice compared to that on the In/ITO. However the diameter of the mountain on the ZnO/ITO was approximately 200 nm, being twice compared to that on the In/ITO. After all, the real interface area was approximately the same at the both PV/MEH-PPV interfaces. Thus the photocharge separation area at their PV/MEH-PPV interfaces hardly changed. It was estimated from both of PESA and Kelvin's method that Fermi level of In on ITO was about -4.4 eV vs vacuum level. Though it is well known that ZnO is an n-type semiconductor, Fermi level of the electrodeposited ZnO was not obtained by Kelvin's method, perhaps because the ZnO had considerably large electric resistance. Fermi level of ZnO may lie deeper than that of In, the ZnO electrode being unfavorable for withdrawing photo-produced electrons in the PV layer compared to the In electrode. Nevertheless, the energy conversion yield of the ITO/ZnO/PV/MEH-PPV/PEDOT/Au solar cell was improved compared to the ITO/In/PV/MEH-PPV/PEDOT/Au solar cell. This improvement may be attributed to the smooth electron transfer in the energetically well-arranged n-type semiconductors, ZnO and PV.

Since the performance improvement was observed even by such a primitive examination for inserting the electrodeposited ZnO into the ITO/PV interface, it will be possible to make further more efficient and air-stable solar cell by controlling the surface morphorogy and the electric resistance of the ZnO.

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