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Citation: *Applied Physics Letters* **100**, 213302 (2012); doi: 10.1063/1.4707381

View online: <http://dx.doi.org/10.1063/1.4707381>

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Transparent conductive electrodes of mixed TiO_{2-x} -indium tin oxide for organic photovoltaics

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(Received 5 December 2011; accepted 27 March 2012; published online 22 May 2012)

A transparent conductive electrode of mixed titanium dioxide (TiO_{2-x})-indium tin oxide (ITO) with an overall reduction in the use of indium metal is demonstrated. When used in organic photovoltaic devices based on bulk heterojunction photoactive layer of poly (3-hexylthiophene) and [6,6]-phenyl C_{61} butyric acid methyl ester, a power conversion efficiency of 3.67% was obtained, a value comparable to devices having sputtered ITO electrode. Surface roughness and optical efficiency are improved when using the mixed TiO_{2-x} -ITO electrode. The consumption of less indium allows for lower fabrication cost of such mixed thin film electrode. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4707381>]

The importance of transparent conducting oxides (TCOs) has grown due to their rapidly increasing usage in applications such as touch panels, flat panel displays, and other optoelectronic devices including photovoltaic cells, photo-detectors, wave-guides, etc.^{1–5} Sputtered indium tin oxide (ITO) has been commonly used as TCO electrodes due to its excellent optical transparency, low resistivity, and high reliability.^{6–8} However, indium (In) resources are dwindling due to the fact that the element cannot be mined directly in significant amounts (in most industrial cases In is a byproduct of zinc mining). This, along with increasing demand for In by the rapidly expanding display industry, makes the search for alternative TCOs a critical area of research.

Zinc oxide (ZnO) based electrodes such as aluminum-doped zinc oxide (AZO), indium-doped zinc oxide (IZO), and gallium-doped zinc oxide (GZO) have been studied as substitutes for the usage of ITO electrode.^{5–7} Moreover, conductive polymers, carbon nanotubes (CNTs), and graphene have also been attempted as cost-effective candidates.^{8–10} In this article, we introduce a TCO that consists of mixed structure of co-sputtered titanium dioxide (TiO_{2-x}) and ITO. The proposed thin film leads to a significant reduction in the use of In, approaching nearly 40%, which translates into reduction in cost of In containing TCOs. Furthermore, the morphology of the mixed TiO_{2-x} -ITO layer reveals smoother grains than in the case of ITO. This results in better interfaces needed for some applications. For example, smoother electrode-polymer interfaces in organic electronics lead to reduction in leakage current^{11,12} and subsequently a better device performance. In our test bed based on organic photovoltaic (OPV) device, the use of TiO_{2-x} also improves the optical absorption of photoactive blend layers of poly (3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) when compared to ITO-based devices.

The conductive mixed electrode of TiO_{2-x} -ITO was deposited on glass by RF magnetron co-sputtering of TiO_{2-x} and ITO from targets of 7.6 cm diameter each. The co-deposition occurred at a working pressure of 3 mTorr using 20 sccm argon (Ar) flow at constant RF powers of 80 and 120 W on TiO_{2-x} and ITO target, respectively. In an attempt to compare device performance and thin film properties, pristine ITO electrodes were also deposited using the same RF power of 120 W. All electrodes were cleaned in acetone, methanol, and isopropanol using ultra-sonication. After ultraviolet ozone (UVO) surface treatment of both types of electrodes, poly (3,4-ethylenedioxythiophene):poly (styrene-sulfonate) (PEDOT:PSS, HC Starck Clevios P VP Al 4083) was spin-coated as a hole-transport layer. The PEDOT:PSS layer (40 nm) was dried in a nitrogen glove box at 150 °C for 30 min. A photoactive layer of P3HT:PCBM blend was prepared using a mixture of 30 mg P3HT and 24 mg PCBM in 1 ml of 1,2-dichlorobenzene (DCB), which was allowed to stir overnight at room temperature prior to the spin-coating step. The photoactive layer (150 nm) was spin-coated then dried at 150 °C for 30 min. The samples were then loaded into a vacuum chamber enclosed in a nitrogen atmosphere where bathocuproine (BCP, 15 nm) was thermally deposited at a rate of 0.5 Å/s. BCP served as an exciton blocking layer (EBL). This was followed by thermal deposition of silver (Ag, 100 nm) electrodes through metallic shadow masks to yield active device area of 20 mm². A base pressure of 1×10^{-7} Torr was used during the BCP and Ag deposition steps.

Surface morphology was acquired by using atomic force microscopy (AFM). Optical spectra of conductive oxides and photoactive layers were collected by UV-Vis-NIR spectrometer with diffuse reflectance accessory (DRA). Current density-applied voltage (J - V) characteristics were analyzed under air mass 1.5 global (AM 1.5 G) illumination at 100 mW/cm² by using a source measure unit (SMU) and a solar simulator. External (EQEs) and internal quantum

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FIG. 1. Schematic diagram of device structure of an organic photovoltaic device used in this work, and AFM surface image of (a) ITO and (b) mixed TiO_{2-x} -ITO (scan size: $2\text{ }\mu\text{m} \times 2\text{ }\mu\text{m}$).

efficiencies (IQEs) were also evaluated in air using 350–700 nm excitation wavelength range at 10 nm intervals.

Figures 1(a) and 1(b) show device structure and AFM surface image of ITO and mixed TiO_{2-x} -ITO electrodes, respectively. The AFM scan depicts a relatively smoother surface of the mixed TiO_{2-x} -ITO electrode than pristine ITO. It has been documented in published literature that ITO films grown by conventional sputtering process possess mostly a columnar structure which results in rougher surface.¹² In our case, ITO films with a nominal thickness of 150 nm show roughness of higher root-mean-square (RMS) and peak-to-valley (PTV) values than those of mixed TiO_{2-x} -ITO layers. The typical RMS roughness of ITO and TiO_{2-x} -ITO over a $5\text{ }\mu\text{m} \times 5\text{ }\mu\text{m}$ scan is 3.89 and 2.40 nm, respectively. This represents a 38% improvement in the RMS value of mixed electrode over ITO. The PTV values are 26.6 and 22.8 nm for ITO and TiO_{2-x} -ITO electrode,

FIG. 2. Normalized optical transmission (left) spectra of ITO, mixed TiO_{2-x} -ITO, and normalized absorption (right) spectrum of P3HT:PCBM photoactive layer. (ITO, red dashed line; mixed TiO_{2-x} -ITO, black solid line; and P3HT:PCBM, blue dotted line).

respectively. High peaks over the electrode surface can contribute to leakage and, in many cases, present a short circuit path, thus lowering device performance.

Figure 2 shows a comparison of normalized optical transmission spectra of conductive oxide layers and absorption spectra of P3HT:PCBM photoactive layer. As can be seen, the maximum transmission of the mixed TiO_{2-x} -ITO layer corresponds nearly to the peak optical absorption spectra of organic photoactive blend film at 510 nm. However, the sputtered ITO layer shows a shift in its transmission peak with respect to the 510 nm maximum absorption peak of the photoactive layer. This contributes to some reduction in number of absorbed photons passing through the ITO anode, which in turn may result in lower photocurrent generation.

Measured J - V characteristics are shown in Fig. 3. The calculated power conversion efficiency (PCE) of organic solar cells using ITO and mixed TiO_{2-x} -ITO is 3.60% and 3.67%, respectively. Devices using conventional ITO exhibit slightly greater short circuit current density (J_{sc}) as shown in Table I, while devices having mixed electrode of TiO_{2-x} -ITO show better fill factor (FF), due to improved electrode-polymer interface. Smoother surface morphology of OPVs has been studied and shown to decrease the series resistance (R_s) and provide better charge conduction.¹³ The sheet resistance (R_{sh}) of mixed TiO_{2-x} -ITO electrode ($18.1 \pm 0.8\text{ }\Omega/\square$) is three-fold higher than that of ITO ($6.2 \pm 0.2\text{ }\Omega/\square$). Nevertheless, the series resistance of the OPV device based on mixed electrode is comparable to that of ITO, as shown in Table I. The smooth surface of TiO_{2-x} -ITO may also assist in enhancing the charge extraction and collection efficiency at the oxide-polymer interface.

TABLE I. Device parameters of organic photovoltaic devices having ITO and mixed TiO_{2-x} -ITO electrodes.

Device electrode	PCE (%)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	R_s (Ωcm^2)
ITO	3.60	11.2	0.58	55	4.33
TiO_{2-x} -ITO	3.67	11.1	0.59	56	6.51

FIG. 3. J - V characteristics of P3HT:PCBM organic photovoltaic device using conductive electrodes of ITO and mixed TiO_{2-x} -ITO (ITO, red dashed line with circles; mixed TiO_{2-x} -ITO, black solid line with squares).

FIG. 4. (a) External and (b) internal quantum efficiency of P3HT:PCBM solar cells using sputtered ITO and mixed TiO_{2-x} -ITO electrodes (ITO, red dashed line with circles; mixed TiO_{2-x} -ITO, black solid line with squares).

The data for EQE (Fig. 4(a)) supports the improved device performance of TiO_{2-x} -ITO mixed electrode. In this case, the EQE is higher at 450 to 550 nm, which also corresponds to the wavelength range of higher intensity in the absorption spectra for P3HT:PCBM blends. In this regard, the maximum EQE value for devices using the mixed TiO_{2-x} -ITO electrode is 62.2% at 510 nm. On the other hand, the EQE for ITO-based device shows maximum value of 63.3% at 600 nm, which is less effective than device based on mixed TiO_{2-x} -ITO electrode. The IQEs of the two devices are almost identical in the overall spectrum range as shown in Fig. 4(b) regardless of electrodes. Similar IQEs of

both devices indicates less significant electronic effects except the enhanced optical absorption.¹⁴

In summary, we demonstrated that a TiO_{2-x} -ITO mixed thin film is a viable alternative to ITO as an electrode in devices such as solar cells. In this case, some performance enhancement can be seen in OPV devices using the mixed electrode when compared to pristine ITO thin film. The mixed electrode allows for better optical spectrum overlap with the photoactive layer, thus enhancing the photon absorption. In addition, the surface morphology of the mixed electrode is smoother than ITO, which results in improved electrode-polymer interfaces leading to better FF. The PCE of devices based on active layer of P3HT:PCBM and TiO_{2-x} -ITO mixed electrode is comparable to devices using pure ITO sputtered electrodes. These results are encouraging as they allow the use of electrodes that require less of the rare indium and, in turn, lower cost of production.

G.E.J. would like to acknowledge KAUST for support. KS. L. and G.E.J. acknowledge Dr. Inho Kim (KIST) for useful discussions. In addition, this work is partially supported by the New and Renewable Energy of Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant (2011T100200034) funded by the Korea Ministry of Knowledge Economy (HK. K.).

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