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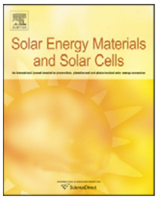

# Inverted organic solar cells with $TiO_x$ cathode and graphene oxide anode buffer layers

Abd. Rashid bin Mohd Yusoff, Hyeong Pil Kim, Jin Jang*

*Department of Information Display and Advanced Display Research Center, Kyung Hee University, Dongdaemun-ku, Seoul 130–171, Republic of Korea*

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ABSTRACT

Titanium oxide ($TiO_x$) was introduced as an electron selective layer between the active layer and bottom electrode in inverted organic solar cells with graphene oxide (GO) an anode interfacial layer. The device with $TiO_x$ exhibited a significant enhancement in power conversion efficiency compared to that without $TiO_x$, which indicates that $TiO_x$ efficiently blocked holes at the active/bottom layer. This device exhibits good stability over 2160 h of storage with only 3.67% reduction in efficiency. The dependence of the device performances on $TiO_x$ film thickness was also investigated.

## 1. Introduction

Since a successful increment in power conversion efficiency up to 10.7% [1], organic solar cells have been the center of attention. Organic solar cells based on the building block of polymer:fullerene can be considered as one of the most promising architectures due to its low-cost, and scalability. In the last few years, organic solar cells have gained a remarkable progress in which the highest power conversion efficiency to date is 10.7% [1]. Although the efficiency has gone upto 10.7%, this value is still inadequate compared to its counterpart inorganic solar cells which makes it unsuitable and further improvement is needed before it can be widely marketable.

Recently, solution processed metal oxide semiconductor has been employed in organic solar cells as hole and electron buffer layers [2–19]. Titanium oxide ($TiO_x$) is one of the most studied metal oxide semiconductors which have high electron mobility, and high transparency in visible wavelength region. In addition, it also has excellent chemical and thermal stability, environmentally stable, non-toxicity, inexpensive, and easy in processing. $TiO_x$ can be deposited from various methods namely sputtering [20], sol–gel [21], pulsed laser deposition [22], metal organic chemical vapor deposition [23] and electrochemical deposition [24]. Among these methods, the sol–gel process is compatible with roll-to-roll processing at room temperature; it can be used at a low temperature, it is cost effective, simple in composition control, and able to provide good and smooth thin films. Recent works have focused on annealing, and preparation procedure. Nevertheless, works on thickness variation of $TiO_x$ have rarely been carried out.

In the present article, we have integrated poly(N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole) (PCDTBT) and (6,6)-phenyl $C_{61}$-butyric acid methyl ester ($PC_{61}BM$) as an electron donor and acceptor, respectively, given that PCDTBT:PCBM has set a historic record of *PCE* 7.1% in BHJ solar cells [25]. PCDTBT:PCBM is sandwiched between $TiO_x$ and GO as cathode and anode buffer layer, respectively. Our fabricated inverted cell offers a few advantages namely (i) no ITO/PEDOT:PSS interface involved, (ii) used air stable materials, and (iii) long lifetime and stability.

As the efficiency of organic solar cells increases, stability becomes more important. Therefore, we also performed lifetime and stability test of our fabricated inverted solar cells over a period of 2160 h of storage, and it is found that after 2160 h the efficiency deteriorated by only 3.67%. This incredible long life-time and high stability are attributed to the use of $TiO_x$ and GO; avoiding the use of PEDOT:PSS.

## 2. Experimental

### 2.1. Preparation of sol–gel derived $TiO_x$

The preparation steps of sol–gel-derived $TiO_x$ have been reported elsewhere [2].

### 2.2. Device fabrication

The inverted solar cells were fabricated on pre-cleaned indium tin oxide (ITO) coated glass substrates, with a sheet resistance of 10–15 $\Omega/cm^1$. For thickness variation study, the thickness of $TiO_x$ was varied from 0 to 40 nm by changing spin speed, and then annealed at 250 °C for 10 min. The $PCDTBT:PC_{70}BM$ at a 1:4 weight ratio in 1.25 wt% 1,2 dichlorobenzene solution was then

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* Corresponding author. Tel.: +82 2 961 0270; fax: +82 2 961 9154.
*E-mail address:* jjang@khu.ac.kr (J. Jang).

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coated on the pre-cleaned ITO-coated glass substrates at 700 rpm for 25 s on top of $TiO_x$ layer and baked at 70 °C for 1 h. The GO aqueous solution was supplied by Graphene Supermarket and used as received without further purification. A thin layer of GO (7.5 nm) was coated from aqueous solution at 1000 rpm for 25 s. Later, the films were annealed at 200 °C for 20 min. Next, the thermal evaporation of 100 nm of Al as the top electrode was carried out in high vacuum (base pressure of $\sim 1 \times 10^{-8}$ Torr). The active areas of our constructed inverted solar cells were 0.2 cm × 0.2 cm. After being transferred into the glove-box, the completed inverted solar cells were encapsulated with a transparent encapsulation glass, glued with UV-curable resin, followed by 1 min exposure to ultraviolet light. The performances of the inverted solar cells were obtained from *J–V* characteristics which were measured using a Keithley 2400 LV source meter. Solar cell performance was achieved by using a solar simulator with Air Mass 1.5 Global (AM 1.5 G) with an irradiation intensity of 100 mW/cm$^2$. All measurements were carried out at room temperature, under relative humidity of ~60%. The stability measurements were carried out according to the ISOS-L-1 procedures except that all our devices were kept in vacuum instead of ambient air in order to check the stability of the materials [26]. The EQE measurements were performed using EQE system (Model 74000) obtained from Newport Oriel Instruments USA and HAMAMATSU calibrated silicon cell photodiode was used as a reference diode. The wavelength was controlled with a monochromator 200–1600 nm. All measurements were carried out without any photo-masking.

### 2.3. Thin film characterization

The transmittance measurements of ZnO, ZnO/PCDTBT:PC$_{70}$BM, and ZnO/PCDTBT:PC$_{70}$BM/GO films coated on ITO-glass substrates were recorded at room temperature with SCINCO S4100 spectrophotometer. AFM imaging was carried out in air using Digital Instrument Multimode equipped with a nanoscope IIIa controller. XRD measurements were carried out in air on a X'PERT PRO of PANalytical Diffractometer with a Cu K$\alpha$ source (wavelength of 1.5405 Å).

## 3. Results and discussion

Fig. 1(a) shows the energy levels of studied device. A deep HOMO level of $TiO_x$ (8.1 eV) makes it suitable as a hole blocking material while a matching work function of GO (4.9 eV) and Al (4.3 eV) makes it easy for holes to be transferred to Al top electrode. As can be seen from this energy alignment, a barrier-less for electrons dissociated from the generated excitons to be transferred from the LUMO level of the photoactive layer to the conduction band of $TiO_x$ is one of the advantages of the studied device. When the device is illuminated, the excitons will be generated at the polymer, and an ultrafast dissociation of these excitons at donor–acceptor interface will take place. The electrons transport and collecting from 3.6 eV (PCDTBT) to 4.4 eV ($TiO_x$) can be visualized at the cathode side. On the other hand, the holes transport and collecting processes can be realized as the holes from 6.1 eV of PCBM will be moved to the 4.9 eV of GO, and later collected at the top electrode.

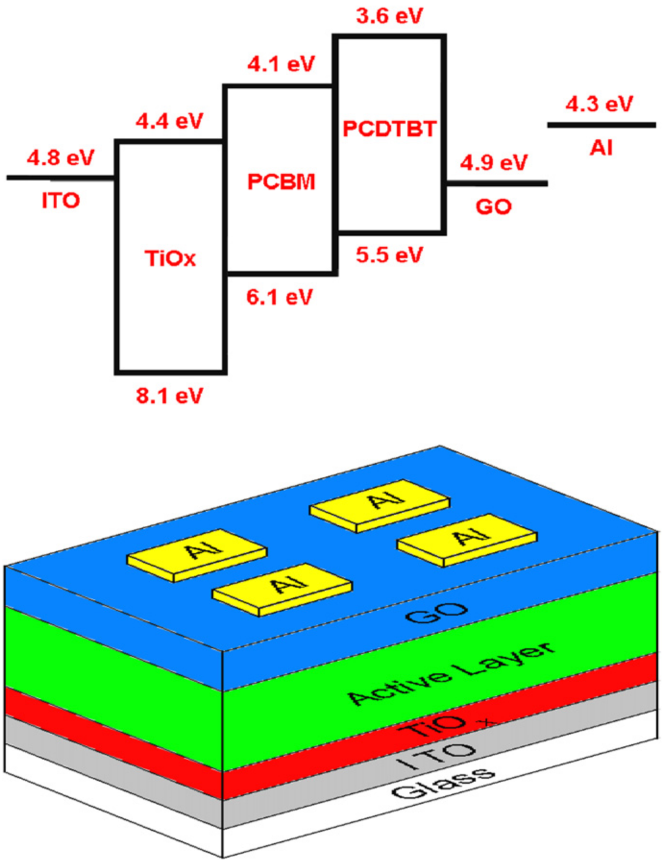

**Fig. 1.** (Top) Proposed energy level alignment of studied device. The HOMO and LUMO level of $TiO_x$ (8.1 and 4.4 eV), PCDTBT (5.45 and 3.6 eV), PCBM (6.1 and 4.1 eV), GO (4.9 eV), respectively. (Bottom) Cross-section view of the inverted organic solar cells (glass/ITO/$TiO_x$/PCDTBT:PCBM/GO/Al).

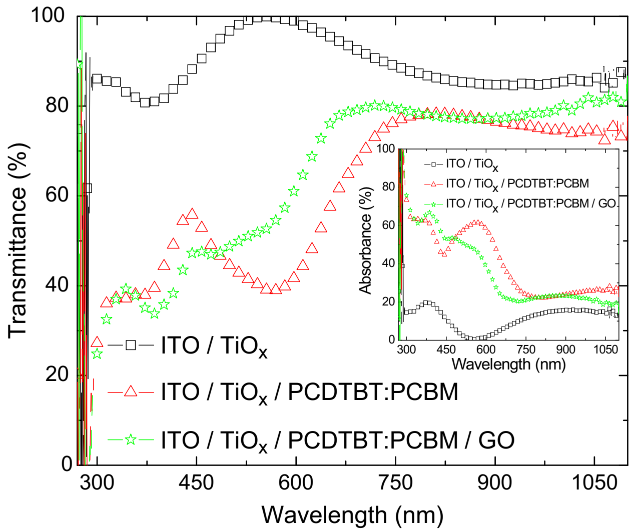

**Fig. 2.** Transmission spectra of glass/ITO/$TiO_x$, glass/ITO/$TiO_x$/PCDTBT:PCBM, and glass/ITO/$TiO_x$/PCDTBT:PCBM/GO. Inset: absorbance spectra of glass/ITO/$TiO_x$, glass/ITO/$TiO_x$/PCDTBT:PCBM, and glass/ITO/$TiO_x$/PCDTBT:PCBM/GO.

Fig. 2 displays the transmittance spectra of $TiO_x$, $TiO_x$/PCDTBT:PCBM, and $TiO_x$/PCDTBT:PCBM/GO recorded at room temperature. As we can see from this figure, the recorded $TiO_x$ spectrum shows a high transparency with an average transparency (from 400–650 nm) of 94.27%. As we coated 80 nm of PCDTBT:PCBM on to the $TiO_x$ thin film, the transparency decreases to 46.23%, and this value increased to 53.26% as we added a GO layer on to them. The increment of the transparency as we coated a thin layer of GO thin film from 400–750 nm appears to be due to the reflectance at the interface of ITO/$TiO_x$/PCDTBT:PCBM/GO, and GO/Air. The high $J_{sc}$ can be attributed to the back reflection at the Al top electrode. Note that GO refractive