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Transparent Conducting Multilayer Electrode (GTO/Ag/GTO) Prepared by Radio-Frequency Sputtering for Organic Photovoltaic's Cells

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Abstract

Indium free consisting of three alternating layers GTO/Ag/GTO has been fabricated by radio-frequency (RF) sputtering for the applications as transparent conducting electrodes and the structural, electrical and optical properties of the gallium tin oxide (GTO) films were carefully studied. The gallium tin oxide thin films deposited at room temperature are found to have an amorphous structure. Hall Effect measurements show a strong influence on the conductivity type where it changed from n-type to p-type at 700°C. GTO/Ag/GTO multilayer structured electrode with a few nm of Ag layer embedded is fabricated and show the optical transmittance of 86.48% in the visible range (λ = 380~770 nm) and quite low electrical resistivity of ~10^{-5} Ω cm. The resultant power conversion efficiency of 2.60% of the multilayer based OPV (GAG) is lower than that of the reference commercial ITO. GTO/Ag/GTO multilayer is a promising transparent conducting electrode material due to its low resistivity, high transmittance, low temperature deposition and low cost components.

Keywords: Transparent conductive oxide, Gallium Tin Oxide (GTO), RF Sputtering, Structural and optical Properties, Bulk hetero-junction Organic Photovoltaic's Cells (BHJ-OPVs), and power conversion efficiency

1. INTRODUCTION

Transparent conducting oxides (TCO) are the unique materials which possess low resistivity characteristics while maintaining high optical transparency. The inherent properties, transmittance and electrical conductivity of the TCOs are important factors which make them potential candidates for TCE applications such as plasma display panels, flat panel displays, touch panels, solar cells, organic light emitting diode, gas sensors and other optoelectronic devices [1]. The increased utilization of many transparent electrodes has accelerated the development of inexpensive TCO materials [2]. Indium tin oxide (ITO) is well known for TCO materials because of its excellent electrical and optical properties. However, due to the high cost and scarcity of indium in TCO, there is urgent need of an alternative material with low cost and similar properties [3]. Zinc oxide film is cheaper than ITO but it shows the poor thermal stability. In contrast, Tin Oxide (SnO_2) film shows the best thermal and chemical stability which is inexpensive to manufacture and has good mechanical durability, but a high resistivity. SnO_2 is an n-type semiconductor with a wide band gap of approximately 3.7 eV [4-6]. Poor electrical conductivity can be improved by controlling stoichiometry or doping with impurities [7-12]. Researchers are dedicated to find new transparent conductive electrodes such as nanotubes, graphene, metal nanowires, dielectric-metal-dielectric (D/M/D) and related structures. D/M/D materials have been suggested as a candidate to overcome the limits of both the electrical and optical properties of single layer TCOs. It allows both the overall carrier concentration and the mobility to be increased, prevailing to some extent the limitation imposed by ionized impurity scattering in metal oxide single layers. In DMD structure, an insertion of metal layer as Ag [13], Ni [14], Cu [15] and Au [16] shows good conductivity. Sandwiching a thin metal layer between two dielectric layers D/M/D has been presented as an alternative approach to obtain the combined benefits of high transmission as well as the excellent conductivity of metals. Studies on a variety of multilayer electrodes [17-24] have been investigated for indium free transparent conducting oxides for organic photovoltaic's cells. Ellmer et al. recently published: either Ag nanostructures or D/M/

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D multilayer structure electrode has been suggested to attain lower resistivity than 1×10^{-4} Ω cm of ITO. In this study, gallium tin oxide (GTO) and silver (Ag) were chosen as a dielectric and metal material in the D/M/D structure. Multilayer thin films consisting of three alternating layers GTO/Ag/GTO (GAG) have been fabricated by radio-frequency (RF) sputtering for the applications as transparent conducting oxides. The structural, electrical and optical properties of single layer gallium tin oxide (GTO) thin films are characterized. Bulk hetero-junction organic photovoltaic's (BHJ-OPVs) devices with a normal structure were fabricated on GTO/Ag/GTO (GAG) multilayer electrodes at room temperature in which the PEDOT: PSS was used as a hole transparent layer (HTL). PEDOT: PSS is a p-type semiconductor, a good hole transport material and assures better hole collection from the polymer into the electrode. These devices were then characterized in terms of the open circuit voltage (V_{oc}), current density (J_{sc}), fill factor (FF) and power conversion efficiency (PCE) which were compared to OPV devices with an ITO electrode as a reference.

2. EXPERIMENTAL

GTO/Ag/GTO thin films were prepared on glass substrates (Corning Eagle XG 0.7mm, Alkaline Earth Boro-Aluminosilicate) for the fabrication of the OPVs device by radio frequency sputtering (rf, 13.56 MHz). The substrate was ultrasonically precleaned in acetone, methanol and deionized water for 10 min each respectively in order to remove impurities on the substrate surface. The bottom GTO layer was sputtered using 2 inch GTO (composited with 20 at. % gallium and 80 at. % tin (SnO_2) ceramic target at an RF power of 100 W and working pressure of 0.27 Pa. Silver (Ag) (RND, Korea, Ag 99.99%) intermediate metal layer was deposited by RF sputtering at 50 W under an Ar plasma gas pressure of 0.27 Pa. Finally the top GTO layer was sputtered via the same method used to sputter the GTO bottom layer composited with 20 at. % gallium and 80 at. % tin (SnO_2). For the uniformity of the thin films, the substrate was constantly rotated at a rate of 7 rpm during sputtering process. The target to substrate was fixed at 70 mm during the sputtering process. The optimized GAG multilayer and commercial ITO electrodes were specially designed laser patterned for the fabrication of the conventional bulk hetero-junction OPVs. The experimental procedure for device fabrication of conventional organic photovoltaics is already explained [3]. Schematic diagrams depicting the overall device structure of the OPVs are illustrated in Fig. 3 (a). X-ray diffraction (XRD) analysis (Rigaku Dmax 2500/server) with CuKα radiation (wavelength=1.5418 Å) was performed to investigate the crystallographic structure of the GTO films. Electrical resistivity, carrier concentration, and hall mobility were characterized using Hall Effect measurement. Optical transmittance of the films was measured using a UV-Visible spectrometer (Perkin Elmer UV/Vis spectrometer Lambda 18) in the wavelength range from 200~900 nm. The active area of the fabricated device was 0.09 cm^2. The electrical properties of the OPV devices were recorded using a Keithely 2400 source-measure unit under ambient conditions. The photocurrent was obtained under illumination from a Thermal Oriel solar simulator (Am 1.5 G, 100 mA/cm^2). The light intensity was calibrated using Si photovoltaic's (PV) solar cells.

3. RESULTS AND DISCUSSIONS

3.1 Structural, Optical and Electrical Properties of GTO thin films

The transmittance and sheet resistance of the tin oxide (SnO_2) based transparent conducting films doped with Zinc (Zn), Gallium (Ga), Antimony (Sb), Manganese (Mn), and Fluorine (F) at room temperature deposited and compared as shown in our previously published papers [25]. In general, the transmittance of all the films goes on increasing with the increase of the oxygen content. Gallium tin oxide shows the transmittance higher than 80% compared with other p- type doped SnO_2 (Ga, Sb, and Mn). The optical transmittance of the GTO thin films deposited at room temperature as a function of oxygen contents (0~5.0 at. %) is shown in Fig. 1(a). With increasing the oxygen contents, $T_{ave(380\sim770\ nm)}$ of GTO films gradually increased from 71.3 % to 82.2%. The sputtered GTO thin films have a high packing density due to their high kinetic energy of particles and the thickness of the GTO films was ~120 nm deposited at different oxygen contents measured using scanning electron microscopy (not shown here). The XRD patterns of GTO thin films with different oxygen contents are plotted in 2Q ranges 20^o~80^o as shown in Fig. 1 (b). All the as grown GTO thin film deposited at room temperature are found to be amorphous. The dependence of the refractive index (*n*) and extinction coefficient (*k*) of GTO films on the O_2/Ar+O_2 ratio. The '*n*' and '*k*' value decreases on increasing the oxygen ratio as can be shown in Fig. 1 (c).

The electrical properties of GTO thin films as deposited and annealed at various temperatures were studied. Annealing

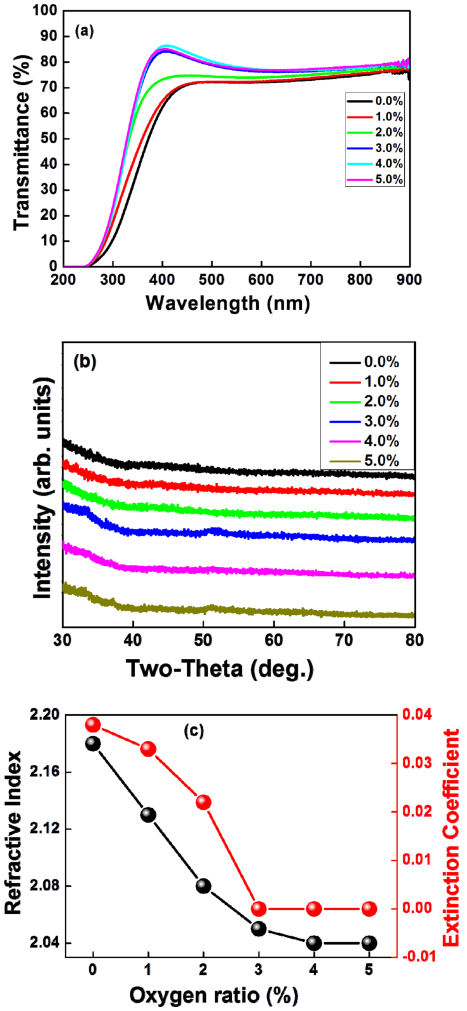

Fig. 1. (a) Optical transmittance of the GTO thin films with various oxygen contents (0~5.0 at. %), (b) XRD plots of GTO thin films on glass substrates and (c) Refractive index (*n*) and extinction coefficient (*k*) of GTO thin films at various O_2+Ar/O_2 ratio @ 510 nm wavelength.

temperature seems to have a significant effect in controlling the conductivity type of the film [26]. According to the hall measurements, the annealing temperature could activate gallium as effective acceptor and mainly fill Sn lattice sites. However higher annealing temperature also produces more intrinsic point defects which act as a donor in the films resulting in higher resistivity at > 600°C. Thus there exists an optimum temperature for p-type GTO thin films which is around 700°C. But, GTO films annealed at 700°C data is not reproducible. The electrical resistivity, carrier concentration and mobility of GTO thin films as grown and annealed at different temperatures are summarized in Table 1.

The surface morphology of Ag thin film deposited on the different oxide materials (i.e. ZTO, FZTO, WO_3 and so on)

Table 1. Electrical properties of GTO thin films as deposited and annealed at various temperatures

	ρ (Ω cm)	n_e (cm^{-3})	μ (cm^2/Vs)	Type
As grown, RT	9.80×10^{-2}	1.35×10^{19}	4.71	n
400°C	1.97×10^{-2}	4.40×10^{19}	7.21	n
500°C	1.89×10^{-2}	3.94×10^{19}	8.37	n
600°C	2.37×10^{1}	5.36×10^{17}	0.52	n/p
700°C	5.10×10^{0}	4.55×10^{17}	6.38	p

bottom layer as a function of thickness is already studied in our previous published papers [3,25,27,28]. With increasing the Ag thickness (7~8 nm), surface morphology of the film shows the island structure. Smooth surface was observed at the Ag thickness of (9~10 nm) as reported in previous papers.

3.2 GTO/Ag/GTO multilayer electrode

Essential MACLEOD OPTICAL COATING DESIGN SOFTWARE was used to simulate the symmetric GTO/Ag/GTO multilayer electrodes. Using the estimated refractive index (*n*) and extinction coefficient (*k*) values, we simulated the normal transmittances of various GTO/Ag/GTO/glass multilayer thin films as plotted in Fig. 2 (a). Dielectric layer stacks around a mid layer of a metal thin film (Ag) can produce very high transmittance in the visible spectral range. A multilayer thin film structure with maximum transmittance can be designed using the Macleod simulation software. 3.0 at. % GTO films as a top and bottom layer shows the highest transmittance value 87.20 % and after 3.0 at. % transmittance gets saturated from the simulation data as shown in Fig. 2(a). The thickness of the Ag was fixed 9 nm based on the previous published papers [3,25]. The transmittance of the GAG multilayer electrode (3.0 at. %) as a function of thickness of the GTO films and commercial ITO are shown in Fig. 2 (b). The sheet resistance and average transmittance $T_{ave.(380\sim770\,nm)}$ of the multilayer electrode GTO (35 nm)/ Ag (9 nm)/ GTO (35 nm) is 86.48% and 9.51 Ohm/sq. The commercial ITO shows the average transmittance of 86.60 % and sheet resistance 12.20 Ohm/sq. It is well known, resistivity is proportional to the reciprocal of the product of carrier concentration (n_e) and mobility (μ). The resistivity of the multilayer GAG electrode was nearly saturated at ~10^{-5} Ω cm.

The schematic diagrams depicting the overall device structure of the OPVs are illustrated in Fig. 3 (a). The thickness of the hole transport (PEDOT: PSS) and photo active layer (P3HT: $PC_{60}BM$) layer were ~100 nm. Bulk hetero-junction organic photovoltaic's

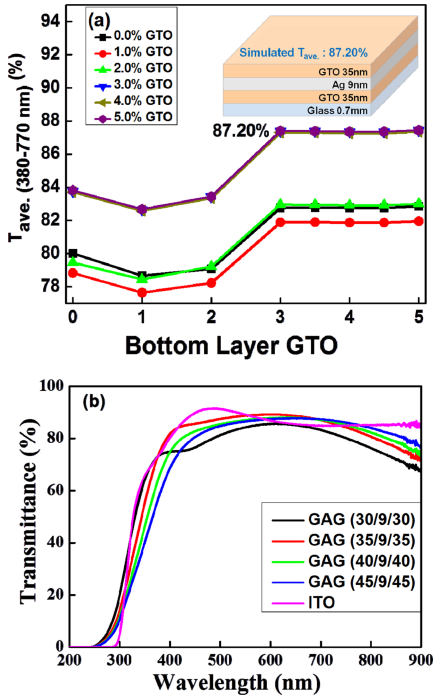

Fig. 2. (a) Simulated average transmittance and (b) Optical transmittance of GTO/Ag/GTO multilayer electrodes as a function of GTO thickness and commercial ITO.

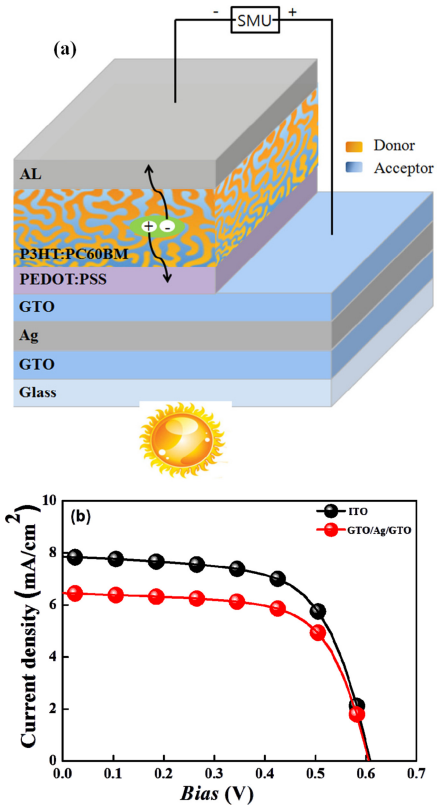

Fig. 3. (a) Schematic diagram of the fabricated BHJ-OPVs and (b) Current density versus voltage characteristics of the fabricated multilayer GTO (35 nm)/Ag (9 nm)/GTO (35 nm) and commercial ITO electrode.

(BHJ-OPV's) was fabricated on the optimized GTO/Ag/GTO and commercial ITO electrode. Current density-voltage (*J-V*) curve of BHJ-OPV's from the GTO/Ag/GTO multilayer electrode and the commercial ITO as a transparent electrode is shown in Fig. 3 (b). The commercial ITO shows open circuit (V_{oc}) of 0.61 V, short circuit current (J_{sc}) of 7.86 mA/cm^2, fill factor (FF) of 0.64, and power conversion efficiency (PCE) of 3.05 %. Whereas, GTO (35 nm)/Ag (9 nm)/GTO (35 nm) multilayer electrode shows a V_{oc} of 0.61 V, J_{sc} of 6.46 mA/cm^2, FF of 0.66, and PCE of 2.60%. These values were lower than that of commercial ITO as the absorption of the P3HT: $PC_{60}BM$ active layer mainly appeared at the wavelength of 400~600 nm. Low PCE can be attributed to the factors of photon flux and difference in energy barrier between transparent electrode and hole transparent layer.

4. CONCLUSION

In this paper, we study about the structural, electrical, optical properties and the influence of *n*, *k* value of GTO film in the average transmittance of the multilayer electrode (GAG). Indium free GTO (35 nm)/Ag (9 nm)/GTO (35 nm) multilayer transparent conducting electrodes show sheet resistance as 9.51 W cm and average transmittance as 86.48% which is very close to simulation data. The resultant power conversion efficiency of 2.60% of the multilayer based OPV is lower than that of the reference commercial ITO which can be explained with the factors of photon flux and lower transmittance at wavelengths of 400~600 nm compared to that of commercial ITO electrode

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