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Low resistance and highly transparent ITO–Ag–ITO multilayer electrode using surface plasmon resonance of Ag layer for bulk-heterojunction organic solar cells

Jin-A Jeong, Han-Ki Kim *

Department of Display Materials Engineering, Kyung Hee University, 1 Seocheon-dong, Yongin-si, Gyeonggi-do 446-701, Republic of Korea

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ABSTRACT

We comprehensively investigated the electrical, optical, structural, mechanical, interfacial, and surface properties of ITO–Ag–ITO (IAI) multilayer electrodes grown on glass substrates by linear facing target sputtering (LFTS) for bulk-heterojunction organic solar cells (OSCs). Although the single ITO electrode with a thickness of 150 nm showed a fairly high sheet resistance of 34 Ω/square, the IAI multilayer electrode exhibited a very low sheet resistance of 4.4 Ω/square due to the low resistivity of the inserted Ag layer. Without using a substrate heating or post-annealing process, we were able to obtain an IAI multilayer electrode with a low sheet resistance, comparable to that of a crystalline ITO electrode, using the room-temperature LFTS process. In addition, the surface plasmon resonance (SPR) and antireflection of the optimized Ag layer significantly increased the optical transmittance of the IAI multilayer. It was found that the optimization of the thickness of the Ag layer is very important to obtain transparent IAI multilayer electrodes, because the SPR effect is critically affected by the Ag morphology. Moreover, the OSC fabricated on the optimized IAI electrode with an Ag thickness of 16 nm showed a higher power conversion efficiency (3.25%) compared to that prepared on the amorphous ITO electrode (2.35%), due to its low sheet resistance and high optical transmittance at 400–600 nm, which corresponds to the absorption wavelength of the organic active layer. This indicates that IAI multilayer electrodes grown by LFTS are promising transparent conducting electrodes for OSCs or flexible OSCs due to their very low resistivity and high optical transmittance.

1. Introduction

There is increasing interest in the use of organic solar cells (OSCs) as a possible low cost regenerative energy source and a cheap alternative to Si-based traditional photovoltaic cells [1–7]. Among the various types of OSCs, bulk-heterojunction OSCs using conjugated polymers and fullerene derivatives are the most widely investigated OSC system, due to their simple process and simple device structure as well as their ability to flex, roll and fold for portability. Until now OSCs consisting of poly-3-hexthiophene (P3HT) and [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) as the photo-active layer were mainly investigated and a power conversion efficiency (PCE) of nearly 5% was achieved [7,8]. To obtain high-performance OSCs with a high PCE, it is desirable that the anode electrode possess a high optical transmittance, low sheet resistance, and smooth surface, and that a low preparation temperature be used. In particular, a low-temperature process for preparing indium tin oxide (ITO) is critically required in low cost OSCs and flexible substrate-based OSCs, because the high temperature sputtering process is not suitable for these devices. Considering cost merit of the OSCs, the preparation of indium saving transparent conductive electrode is also an important issue in the OSCs or flexible OSCs [9–11]. Therefore, it is imperative to develop low-temperature grown ITO electrodes with a low sheet resistance and high transmittance for high-performance and low-cost OSCs. Recently, the ITO–metal–ITO multilayer system has attracted attention as an indium saving transparent conducting oxide (TCO) electrode for flexible organic light-emitting diodes (OLEDs) because low sheet resistance and high transmittance of the ITO–metal–ITO electrode can be obtained below total thickness of 90 nm [12,13]. It was reported that the dielectric–metal–dielectric structure can suppress the reflection from the metal layer in the visible region and achieve a selective transparent effect [14]. Lewis et al. [15] suggested that the electrical and mechanical properties of an ITO–Ag–ITO (IAI) anode could be remarkably improved by placing a continuous Ag layer between the ITO layers. In our previous works, we reported that InZnO–Ag–InZnO and InZnSnO–Ag–InZnSnO electrodes could provide a low sheet resistance and high transmittance, as well as superior flexibility in flexible OLEDs, due to the effect of the

* Corresponding author. Tel.: +82 31 201 2462; fax: +82 31 204 8114.
E-mail address: imdlhkkim@khu.ac.kr (H.-K. Kim).

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ductile Ag layer [16,17]. Although the application of ITO–metal–ITO multilayer electrodes in flexible OLEDs has been reported, the use of an IAI multilayer electrode in OSCs has not yet been reported in detail.

In this work, we investigated the electrical, optical, structural, interfacial and surface properties of IAI multilayer electrodes grown by a linear facing target sputtering (LFTS) at room temperature as functions of the Ag thickness. By making use of the surface plasmon resonance (SPR), antireflection, and metallic resistivity of the inserted Ag layer, we can obtain high-quality transparent electrodes with a high transmittance, low sheet resistance and figure of merit value at room temperature. Due to the improved electrical and optical properties of the IAI electrode, the OSCs fabricated LFTS-grown IAI multilayer electrode shows a PCE higher than the same OSCs fabricated on the LFTS-grown amorphous single ITO electrode. Using synchrotron X-ray scattering and scanning electron microscopy (SEM) examinations, we suggested a possible mechanism to explain the effect of the Ag morphology on the electrical and optical properties of the IAI multilayer electrode.

2. Experimental

The IAI multilayer electrodes were prepared by means of a specially designed LFTS system and thermal evaporation at room temperature. To realize low temperature and plasma-damage-free sputtering, we designed the LTFS system with linear facing guns to confine the high-density plasma between the ITO (10 wt% SnO_2 doped In_2O_3 Samsung corning precision glass) targets during the sputtering process [18–21]. Fig. 1 shows the schematics of the LFTS system and principle of plasma confining the plasma between the ITO targets. The identical rectangular ITO targets ($250 \times 100\,mm^2$) are placed parallel to and at a distance of 70 mm from each other (target-to-target distance) [19]. During the ITO sputtering process, most electrons and charged ions spiral with the helix pitch along the direction of the high-density magnetic field, which is generated perpendicular to both of the ITO target planes and oscillate between the two ITO targets, due to their negative voltage, of ITO targets as shown in Fig. 1(a). Thus, the oscillating electrons and charged ions can be effectively confined by the high-density magnetic field applied perpendicular to both ITO target planes. Fig. 1(b) shows a picture of the plasma efficiently confined between the ITO targets during the room temperature sputtering process. The substrate is located 100 mm away from the common axis of the ITO target. Both the top and bottom ITO films with a thickness of 40 nm were deposited using the LFTS system under identical conditions on glass substrates. Under the optimized sputtering conditions (constant Ar and O_2 flow rates of 10 and 0.5 sccm, respectively, DC power of 600 W and working pressure of 1 mTorr), a 40-nm-thick bottom ITO film was deposited on a glass substrate with dimension $15 \times 15\,mm^2$. After the deposition of the bottom ITO film, Ag films were deposited on the bottom ITO film by a thermal evaporator at a deposition rate of 0.02 nm/s. The Ag film thickness was monitored with a quartz crystal microbalance during Ag thermal evaporation. Subsequently, a 40-nm-thick top ITO film was deposited on the evaporated Ag film by LFTS under deposition conditions identical to those used for the bottom ITO film. For comparison, a reference ITO (150 nm) film was prepared using LFTS at room temperature. The sheet resistance and resistivity of the IAI multilayer electrode were measured by means of a portable four-point probe and Hall measurement. To calculate the resistivity of the inserted Ag layer, the sheet resistance of a single ITO layer with a thickness of 40 nm was also measured by the portable four-point probe. The optical transmittances of the IAI multilayer electrode and single ITO electrode were also measured in the wavelength range 220–800 nm by an ultraviolet (UV)/visible spectrometer (Lambda 35). For comparison, the simulation of the optical transmittance in the IAI layer was carried out using an emissive thin film optics (ETFO) simulator as a function of the Ag thickness. To investigate the microstructure of the IAI electrode with different Ag thicknesses, X-ray scattering examination was employed. In addition, the change in morphology of the inserted Ag layer was examined by the X-ray reflectivity method as a function of the Ag thickness. The synchrotron X-ray scattering measurements were carried out at the 5C2 GIST beam line at the Pohang Light Source (PLS). The wavelength of the incident X-rays was set to 1.243 Å by a double bounce Si(111) monochromator. AES depth profiling with an energy of 10 keV and current of the electron beam of 0.0236 μA was carried out to investigate the interfacial reaction between Ag and the ITO layer prepared under the optimized growth conditions. Furthermore, the surface-related excitation in the Ag layer was analyzed using X-ray photoelectron spectroscopy. The surface morphology of the Ag layer grown on the bottom ITO film was examined as a function of the Ag thickness by field emission scanning electron microscopy (FESEM JSM-6500F) at an operating voltage of 15 keV.

To compare the performances of the OSCs fabricated on the LFTS grown IAI and single ITO electrode grown under the optimized conditions, we prepared standard bulk-heterojunction OSCs on the IAI multilayer electrode and single ITO electrode, respectively. To remove the contaminants on the IAI and single ITO electrodes, the samples were mechanically cleaned with a specially prepared detergent and then ultrasonically cleaned with organic solvents, i.e. acetone, methanol and isopropyl alcohol successively for 10 min each at room temperature.

After the cleaning process, a ~20 nm thick layer of poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron PVPAI 4083) was spin coated on the IAI and single electrodes, followed by drying at 100 °C for 10 min in air using a hot plate. The photo-active layer composed of interconnected networks of electron donors and acceptors, a blend of poly (3-hexylthiophere) (P3HT, Rieke Metals) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6) C61(PCBM, Nano-C) in di-chlorobenzene with a weight ratio of 1:1, was spin coated on top of the PEDOT:PSS layer in an N_2 atmosphere, and then annealed at room temperature for 2 h to enhance the degree of P3HT ordering. Device fabrication with an island-type cathode design was completed by thermal evaporation of a Ca/Al (20 nm/100 nm) metal top electrode by using a metal mask with an area of $4.66\,mm^2$ under vacuum at a pressure of 10^{-6} Torr. The photocurrent density–voltage (J–V) curves were measured with a Keithley 4200 source measurement unit an in N_2 filled glove box. The cell performance was measured under an illumination intensity of $100\,mA/cm^2$ from a 1 kW Oriel solar simulator with an AM 1.5 G filter. For accurate measurement, the light intensity was calibrated using a radiant power meter and a reference silicon solar cell certified by NREL (PVM188 with a KG5 color-filtered window).

3. Results and discussion

Fig. 2 shows the sheet resistance and resistivity of the IAI multilayer electrode grown on a glass substrate as a function of the average Ag thickness at a constant 40 nm thickness of the bottom and top ITO films. Both the bottom and the top ITO was grown at a constant DC power of 600 W, working pressure of 1 mTorr, Ar/O_2 flow ratio of 10/0.5 sccm and target-to-glass substrate distance of 80 mm. In the case of the IAI sample with 6-nm-thick Ag layer, it shows a fairly high sheet resistance