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Transparent and conductive titanium indium zinc oxide/Ag/titanium indium zinc oxide multilayer films deposited by radio frequency magnetron co-sputtering

Yu-Ri Lee [a,b], Eun-Mi Kim [a], Jeong-Pyo Oh [a], Byeong-Yun Oh [c], Dong-Chan Shin [b,1], Gi-Seok Heo [a,*]

[a] National Center for Nanoprocess and Equipment, Korea Institute of Industrial Technology, 1110-9 Oryong-dong, Buk-gu, Gwangju 500-480, Republic of Korea
[b] Department of Advanced Materials Engineering, Chosun University, 375 Seosuk-dong, Dong-gu, Gwangju 501-759, Republic of Korea
[c] Renewable Energy Team, Research and Development Division, LINKLINE I&C, 959-25 Daechon-dong, Buk-gu, Gwang-ju 500-470, Republic of Korea

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ABSTRACT

Multilayer transparent films with lower electrical resistance than the widely used transparent conductive electrodes, were prepared at room temperature on flexible PES [poly(ether sulfone)] substrates using an RF-magnetron co-sputtering system. The multilayered films consisted of three layers, titanium indium zinc oxide (TIZO)/Ag/TIZO. The optical and electrical properties of the multilayered TIZO/Ag/TIZO structure were investigated in relation to the thickness of each layer. A transparent and conductive film with a sheet resistance of 7.7 Ω/□ and an average transmittance of 92% (normalized to the flexible PES substrate) at 550 nm, was obtained at thicknesses of PES/TIZO(100 nm)/Ag(10 nm)/TIZO(40 nm). The surface roughness (root mean square, RMS) values of the obtained multilayer films were below 1 nm. Overall, the properties of the film were comparable or superior to those of other multilayer films such as indium tin oxide (ITO)/Ag//ITO, indium zinc oxide (IZO)/Ag/IZO, and indium zinc tin oxide (IZTO)/Ag/IZTO. For this reason, the new TIZO/Ag/TIZO multilayer film may serve as a viable, high-efficiency alternative for electrode applications in flexible photovoltaic cells.

1. Introduction

Transparent, conductive electrode films, showing the particular characteristics of good conductivity and high transparency, are of considerable research interest because of their potential for use in optoelectronic applications, such as photovoltaic cells and flat panel displays [1–4]. The most common transparent conductive electrode materials are indium tin oxide (ITO) and fluorine tin oxide (FTO). Indium oxide (In_2O_3)-based material has been doped with tin (Sn) to improve its electrical conductivity. On the other hand, FTO is well known to be thermally stable up to 650 °C, and thereby suitable for the thermal processes used in preparing amorphous silicon solar cells, or dye-sensitized solar cells (DSSCs) [5–7]. These kinds of materials currently play an important role as transparent electrodes for photovoltaic cells and flat panel displays. However, increasing technological demand for next-generation optoelectronic devices makes it necessary to investigate more advanced materials and structures with lower resistivity and higher transparency.

Recently, ITO/metal/ITO multilayers have gained much attention as promising anode materials for organic light-emitting diodes (OLEDs) because the dielectric/metal/dielectric multilayer system can suppress the reflection from the metal layer and obtain a selective transparency effect [8–10]. Lewis et al. [11] suggested that the electrical and mechanical properties of an ITO/Ag/ITO anode could be remarkably improved by placing a continuous silver (Ag) layer between the ITO layers. Kim et al. [12,13] also reported that InZnO/Ag/InZnO and InZnSnO/Ag/InZnSnO electrodes could provide low sheet resistance and high transmittance, as well as superior flexibility in flexible OLEDs, due to the effect of the ductile Ag layer.

In our previous work [14], we reported a combinatorial investigation of titanium indium zinc oxide (TIZO) as a transparent conductive electrode film, specifically, for flexible solar cells and displays. Although it was deposited at room temperature, a high-quality amorphous TIZO film with a resistivity of 3.8×10^{-4} Ω cm and transmittance of 92% (normalized to the flexible PES substrate) at 550 nm, were obtained after reducing the amount of indium content used in conventional ITO and IZO films.

In this work, TIZO/Ag/TIZO multilayer films were prepared at room temperature on PES substrates using an RF-magnetron co-sputtering system. The optical and electrical properties of the multilayered structures were investigated according to the thickness of each layer. High-quality TIZO/Ag/TIZO multilayer films, with sheet resistance lower than conventional ITO or IZO films, were obtained. The characteristics of these TIZO/Ag/TIZO multilayers have not yet been reported.

* Corresponding author. Tel.: +82 62 6006 171; fax: +82 62 600 6509.
E-mail addresses: dcshin@chosun.ac.kr (D.-C. Shin), gsheo@kitech.re.kr (G.-S. Heo).
[1] Tel.: +82 62 230 7191; fax: +82 62 236 3775.

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2. Experimental details

The TIZO/Ag/TIZO multilayer films were prepared on PES [poly(ether sulfone)] substrates (i-Components Co.) using an RF-magnetron co-sputtering system. Fig. 1 shows a schematic diagram of the system, which consists of a vacuum chamber reactor (ULVAC MB07-4501) equipped with four 4-in. sputtering guns. A TiO_2 [99.99%, 4-in.] and a 10 wt.% Zn-doped In_2O_3 (IZO) [99.99%, 4-in.] target was used to deposit the TIZO film. Co-sputtering of the TIZO film was conducted at the RF power of 200 W (IZO) and 50 W (TiO_2). The sputter chamber was initially evacuated to a base pressure of $\leq 2 \times 10^{-6}$ Pa, and the working pressure for film deposition was maintained at 0.17 Pa using Ar (24.8 sccm) and O_2 (0.2 sccm) ambient gases. The Dst (substrate-target) distance was 150 mm, perpendicularly. The substrate holder was rotated during sputtering. The deposition rate of the TIZO film was 5 nm/min. An Ag [99.99%, 4-in.] target was used to deposit Ag film between two TIZO layers. Ag films were deposited by the RF-magnetron sputtering system with the conditions of Ag RF power of 100 W and the working pressure of 0.17 Pa using Ar gas only (25 sccm). During deposition of the multilayer films, the substrate was maintained at room temperature. The total thickness of the deposited TIZO/Ag/TIZO multilayer films was maintained at 150 nm. The fixed thickness of the bottom TIZO film deposited on the PES substrate was 100 nm. The thickness of the inserted Ag layer varied from 4 to 14 nm, and the thickness of the upper TIZO layer deposited on the Ag layer, also varied from 36 to 46 nm in response to the thickness of the Ag layer.

The sheet resistance was analyzed using a four-point probe system (NAPSON, RT-3000/RG-100). The optical properties of the films were investigated using a UV–VIS–NIR spectrophotometer (Varian, Cary 5000). The composition of the films was examined by energy dispersive X-ray spectroscopy (EDS, JSM 7000 F) at 15 kV. The microstructure and interface structure of the deposited TIZO/Ag/TIZO multilayers were characterized by atomic force microscopy (PSIA, XE-200) in non-contact mode, the field emission-scanning electron microscopy (FEI, Quanta 200) operated at 20 kV, and the transmission electron microscopy (FEI, Tecnai G2 F30) operated at 300 kV. The cyclic-bending test was carried out using a bending tester (Z-tec, ZB-100) at a frequency of 0.5 Hz for 150 cycles, in which constant linear movement was maintained with a 35 mm stroke.

3. Results and discussion

Fig. 2 shows the sheet resistance values of the TIZO single-layer and the TIZO/Ag/TIZO multilayered films deposited on PES substrate, as a function of thickness of each layer. The 150 nm-thick TIZO single-layer film (without an inserted Ag interlayer) had a sheet resistance of 32.2 Ω/□. However, insertion of an Ag interlayer remarkably lead to reduced sheet resistance as shown in Fig. 2. It was shown that the sheet resistance of the TIZO/Ag/TIZO multilayers significantly decreased with an increasing Ag thickness. In particular, the TIZO/Ag/TIZO multilayers with an Ag thickness >8 nm showed a sheet resistance that is low enough (≤10 Ω/□) to be applicable for metal film. These resistance values could stand comparison with the values previously reported for ITO/Ag/ITO, IZO/Ag/IZO, and IZTO/Ag/IZTO multilayers [11–13,15]. It was reported that the decrease in sheet resistance with the increase in Ag thickness in a dielectric/metal/dielectric multilayer system could be attributed to a transition of Ag atoms from islands to a continuous film [12,15,16]. The conductivity enhancement of the TIZO/Ag/TIZO multilayer, compared to IZO, was effected not only by the low sheet resistance of the TIZO single layer film, but also by the remarkably improved conductivity resulting from placing an Ag layer between the TIZO layers. The elemental composition ratio of the TIZO single layer-film used for this study was 3/68/29 [Ti/In/Zn, at.%] by energy dispersive X-ray spectroscopy. This means that we could actually reduce expensive indium content when we use TIZO/Ag/TIZO multilayers compared to ITO/Ag/ITO multilayers based on commercial ITO film [In content: 83 at.% (In/(In + Sn), at.%)].

Fig. 3 shows the transmittance and reflectance curves (normalized to the flexible PES substrate) of the TIZO single-layer and TIZO/Ag/TIZO multilayer films deposited on PES substrate as a function of thickness of each layer. It was observed that TIZO single-layer and TIZO/Ag/TIZO multilayer films showed comparatively high transmittance values (above 80%) at 550 nm accept the PES/TIZO(100 nm)/Ag(14 nm)/TIZO(36 nm) multilayer as shown in Fig. 3b. However, in the near-infrared region, the TIZO single-layer showed higher transmittance compared to multilayer films as shown in Fig. 3a. The transmittance curves of the TIZO/Ag/TIZO multilayers depended on the thickness of the inserted Ag layer. In the near-infrared region, the transmittance of the TIZO/Ag/TIZO multilayers decreased, and their transmittance

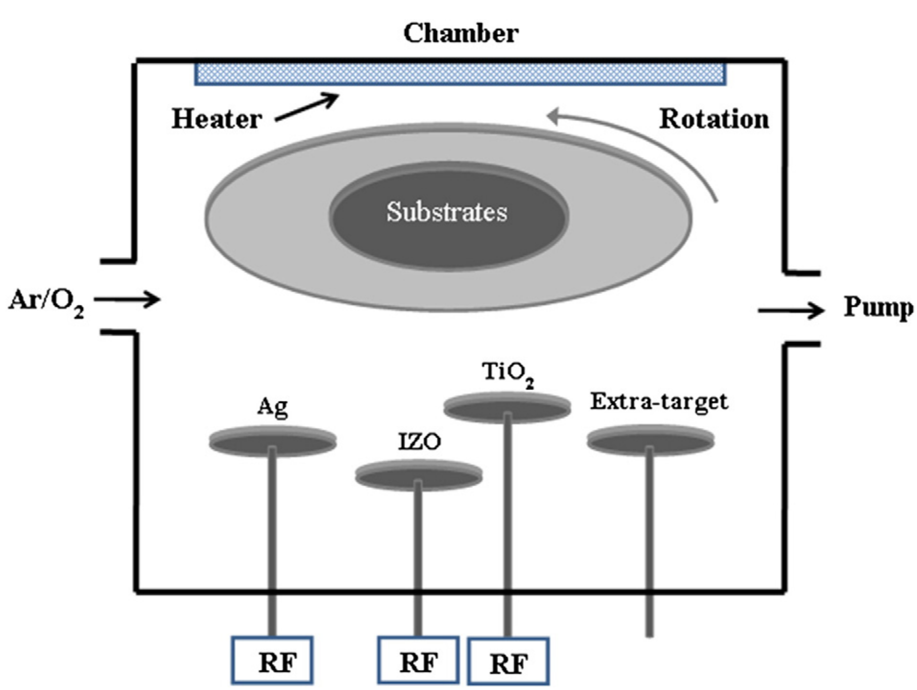

Fig. 1. Schematic diagram of the RF-magnetron co-sputtering system.