Journal of the Korean Physical Society, Vol. 55, No. 1, July 2009, pp. 197~201

Enhanced Properties of Transparent Conductive Oxide Films Prepared on PEN Substrates with a $(SiO_2)_{40}(ZnO)_{60}$ Gas Barrier Layer

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(Received 26 August 2008, in final form 17 January 2009)

A $(SiO_2)_{40}(ZnO)_{60}$ (SZO) film with a very low water vapor transmission rate (WVTR) below 10^{-3}g/m^2/day was coated as a gas barrier layer on a poly-ethylene naphthalate (PEN) substrate by rf-magnetron sputtering. This PEN with a SZO gas barrier layer was used as a flexible substrate for various transparent conductive oxide (TCO) films, such as In_2O_3-SnO_2 (ITO), Al-doped ITO (AITO) and In_2O_3-ZnO (IZO). Their electrical and optical properties were compared to the TCO films deposited on a bare PEN substrate without a gas barrier layer. We found that compared with the TCO films without gas barrier layer, the TCO films with a SZO gas barrier layer showed an enhanced electrical conductivity and electrical stability after bending around a 10-mm-radius cylinder. The enhanced electrical properties were considered to be the result of the SZO film acting as a blocking barrier layer against water vapor permeation or organic-solvent diffusion from the PEN substrate during deposition of the TCO films and as a buffer layer easing damage due to bending. Thus, we suggest that the PEN with a SZO barrier layer is sufficiently transparent and has a superior ability to protect against the permeation of water vapor so that it can be applied to TCO films for flexible displays.

PACS numbers: 73.61.-r, 78.66.Jg, 81.15.Cd
Keywords: Gas barrier, Flexible substrate, TCO, WVTR, Bending test, RF-magnetron sputtering

I. INTRODUCTION

In the packaging industry, the deposition of a diffusion barrier on a polymer film is of increasing interest to prevent gases like oxygen, carbon dioxide, or water vapor from permeating through the material. The thin barrier films, which are approximately 10-100 nm in thickness, are produced by sputtering, electron beam evaporation, or plasma-enhanced chemical vapor deposition (PECVD) [1–3]. Recently, inorganic thin films, such as AlO_x, SiO_x and SiON, have been studied as gas barrier films on polymer substrates for oxygen and water vapor [4–7]. However, since these barrier films show a water vapor transmission rate (WVTR) and an oxygen transmission rate (OTR) that are too high to be applied to displays, a new barrier materials is required. We reported in a prior work that thin composite films consisting of SiO_2 and ZnO (SZO) as a thin passivation layer of organic light-emitting diodes (OLEDs) showed superior protection ability against the permeation of water vapor. It was also reported that a thin composite SZO film has a very low WVTR below 10^{-3}g/m^2/day [8].

In this work, inorganic thin composite $(SiO_2)_{40}$ $(ZnO)_{60}$ films were deposited on poly-ethylene naphthalate (PEN) substrates as a gas barrier layer by using an rf-magnetron sputtering method. These PENs with a thin composite barrier layer were used as flexible substrates for various transparent and conducting oxide (TCO) films, such as In_2O_3-SnO_2 (ITO), Al-doped ITO (AITO), In_2O_3-ZnO (IZO) [9,10]. TCO films were deposited on PEN substrates with or without a gas barrier by using an rf-magnetron sputtering method and their electrical and optical properties were compared with each other. The surface morphologies of the TCO films were also analyzed from their scanning electron microscope (SEM) or atomic force microscope (AFM) images. In addition, the electrical stabilities of the TCO films were evaluated based on changed in the sheet resistance due to bending damage.

II. EXPERIMENTAL WORK

A composite powder of $(SiO_2)_{40}(ZnO)_{60}$ was mixed by using a ball mill for 24 hours with additional hand milling and was calcined at 600 °C for 3 hours to remove the moisture. A 2-inch target was made under a pressure of 12 tons by using a Caver press and was solidified at 1000 °C for 2 hours in air. It was used as the sputter target for a gas barrier layer on the PEN substrates. PEN substrates with a size of 50 × 50 mm^2 were cleaned sequentially by using distilled water and alcohol, which

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were placed parallel to the target surface at a distance of 80 mm after achieving a base pressure of 10^{-5} Torr by using a diffusion pump. The SZO films, 350-nm thick, were deposited on as a gas barrier layer PEN substrates at room temperature under a pure Ar gas pressure of 1.2 × 10^{-3} Torr. These PEN substrates with a SZO barrier layer were used as substrates for various TCO films. Well-mixed powders of In_2O_3 and SnO_2 with a composition rate of 90 : 10 wt.% (ITO), Al(2 wt.%)-doped ITO (AITO) and In_2O_3 and ZnO with a composition rate of 78 : 22 wt.% (IZO) were calcined at 1000 °C in air and were used as sputter targets for various TCO films. The sputter targets were made by using the same processes as was used for the SZO target.

TCO films with a thickness of about 180 nm were deposited on PEN substrates with or without a SZO barrier layer at room temperature under an Ar gas atmosphere of 0.4 – 1.2 mTorr at an rf power of 40 W by using the rf-magnetron sputtering method and their electrical and optical properties were compared with each other. The electrical stabilities of the TCO films with and without a gas barrier layer after bending test were also evaluated. The film thicknesses of the SZO and the TCO films were measured by using an α-step profiler (VEECO Co.). The surface and the cross-sectional morphologies of the TCO films were observed by using SEM (Hitachi Co.). We confirmed with an electron probe micro-analyzer (EPMA, Shimadzu Co.) that the composition ratios of the deposited films were almost consistent with those of the targets. The optical transmission spectra of the films were measured in the wavelength range from 300 nm to 900 nm by means of an ultraviolet-visible-near-infrared spectrophotometer (UV-VIS, Shimadzu Co.). The electrical stabilities of the TCO films were evaluated based on changes in the sheet resistance after bending around a cylinder with a radius of 10 mm.

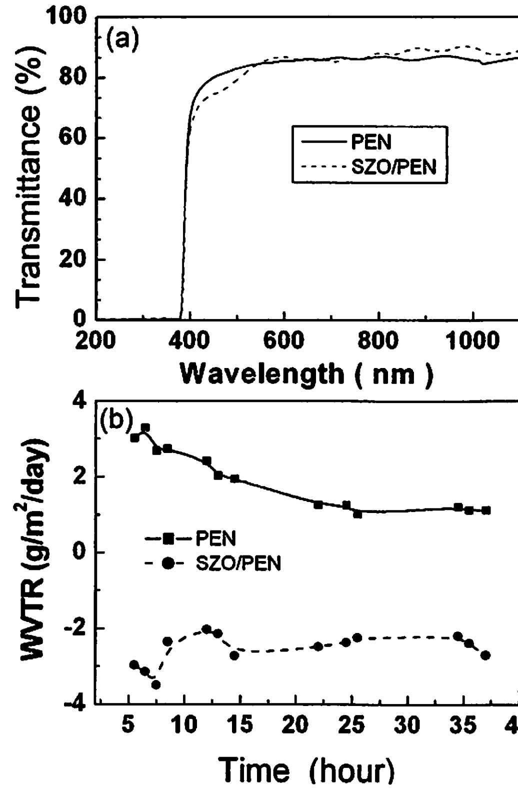

Fig. 1. (a) Optical transmission spectra and (b) water vapor transmission rate (WVTR) for bare PEN and PEN with a SZO barrier layer of 350 nm.

III. RESULTS AND DISCUSSION

Figure 1(a) shows optical transmission spectra for bare PEN and for PEN with a SZO barrier layer of 350 nm. The bare PEN shows a high transmittance of over an average 85% in the visible range. This high transmittance is maintained even after deposition of the SZO barrier layer on the PEN substrate. Thus, the SZO film shows very excellent transmittance, over an average 85%, in the visible range, what is high enough for use as a barrier layer on a polymer substrate for a flexible display. In Fig. 1(b), we show the WVTR graph of the SZO/PEN, what were measured by using the Mocon test. For comparison, that of bare PEN substrate is also shown. The bare PEN substrate show a relatively low WVTR of 1 – 3 g/m^2/day as compared to other polymer substrates, such as polyether sulfone (PES: 40 g/m^2/day) and polyethylene terephthalate (PET: 70 g/m^2/day) [8]. However, the SZO/PEN shows that negative values are measured for the WVTR. The negative values means that the SZO film has a WVTR less than $10^{-3}$$g/m^2$/day because $10^{-3}$$g/m^2$/day is the limit that can be measured by using the Mocon test [8]. Fig. 1 shows that the SZO film has a very excellent transmittance and provides superior protection ability against the permeation of water vapor. These are sufficient for it to be used as a barrier layer on a polymer substrates for flexible displays.

Figure 2 shows optical transmission spectra of various TCO films prepared on two different substrates: (a) a bare PEN substrate and (b) a PEN substrate with a SZO barrier layer. TCO films prepared on the bare PEN (TCOs/PEN) also show a high transmittance over an average of 85%, in the visible light range. However, TCO films prepared on a PEN substrate with a SZO barrier (TCO/SZO/PEN) substrate show a somewhat lower transmittance in the visible range as compared to that of TCOs/PEN. In particular, the transmittance decreases more in wavelength region below 450 nm. However, this decrease is not a serious problem for display applications. In spite of the transmittance decrease, it is worth noticing that TCOs/SZO/PEN shows a high transmittance of over an average 80% in the visible range, where is high enough to use it as a transparent electrode for flexible displays.

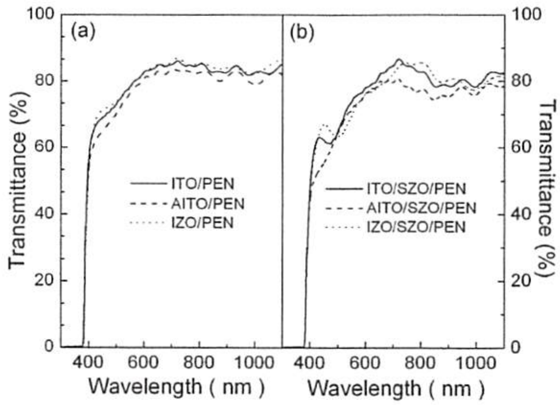

Fig. 2. Optical transmission spectra of various TCO films.

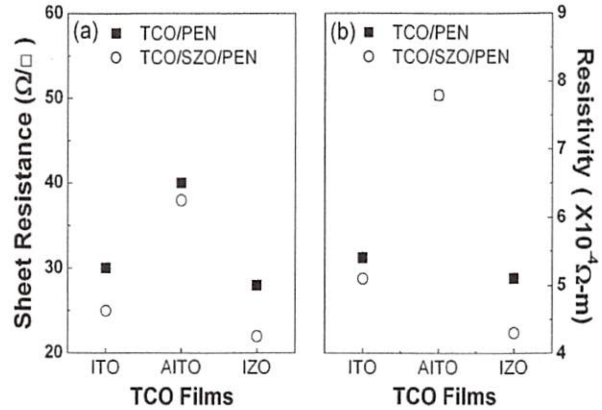

Fig. 3. Sheet resistances and resistivities of TCO films with and without a SZO gas barrier layer on a PEN substrate.

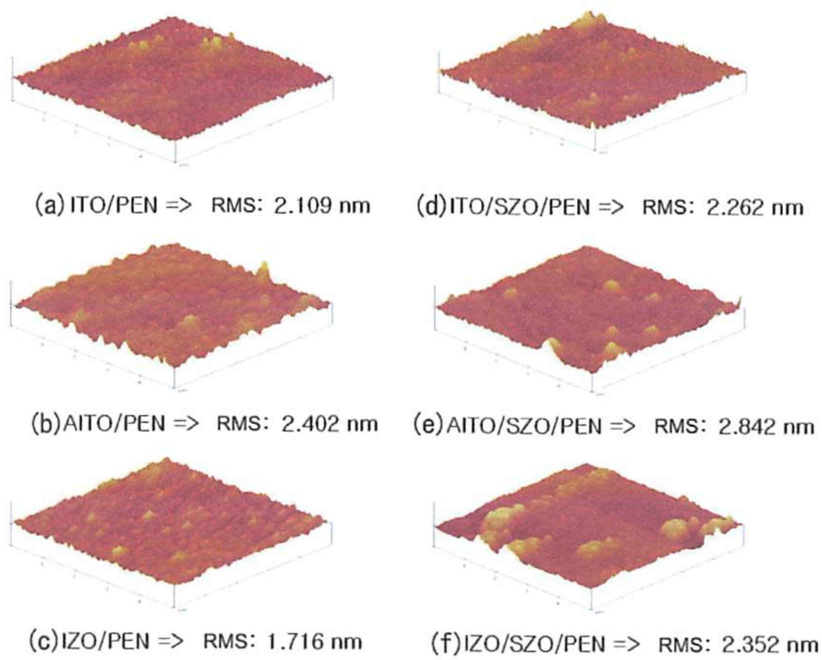

Fig. 4. AFM images of TCO films.

Figure 3 shows (a) the sheet resistances and (b) the resistivities of various TCO films deposited on PEN substrates with and without a SZO barrier layer. The thicknesses of the TCO films and the barrier layer were about 180 nm and 350 nm, respectively. TCOs/SZO/PEN shows reduced sheet resistances and resistivities as compared to TCOs/PEN. Because most plastic substrates, including PEN, contain water vapor and other adsorbed particles, such as organic solvents, vaporization of these particles deteriorates the adhesion of the TCO films to the plastic substrate. Mixing of these vaporized gases in the sputtering process will also affect the properties of the deposited TCO films [11]. However, if a proper barrier layer, like a SZO layer, is coated on the PEN substrate, it would be reasonably expected to suppress the diffusion of vapors from the substrate so that TCO films with an improved quality might be obtained. Therefore, the enhanced electrical conductivity of TCOs/SZO/PEN in Figs. 3(a) and (b) is considered to be a result of the SZO layer acting as a layer protecting against water vapor or organic solvents diffusion from the PEN substrate during deposition of the TCO films.

Figure 4 shows AFM images of TCO films with a thickness of 180 nm deposited on PEN substrates with and without a SZO barrier layer of 350 nm. Although TCOs/SZO/PEN show a somewhat rough surface as

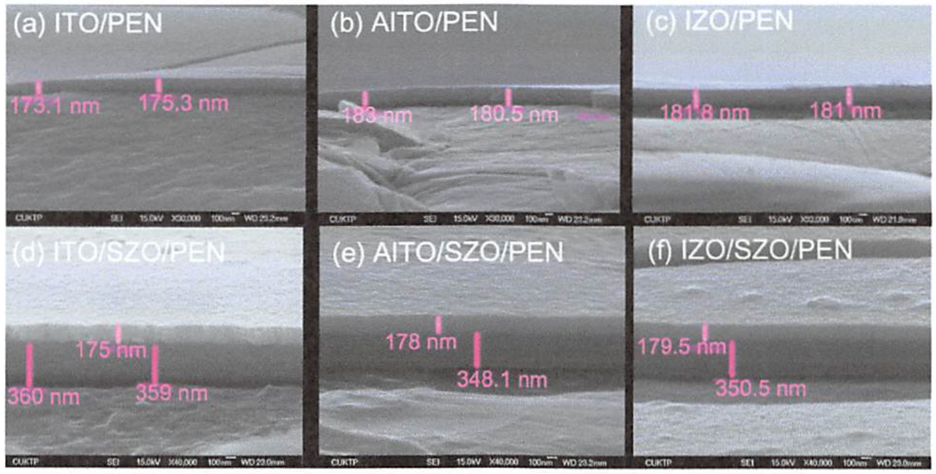

Fig. 5. SEM images for TCOs/PEN and TCOs/SZO/PEN.

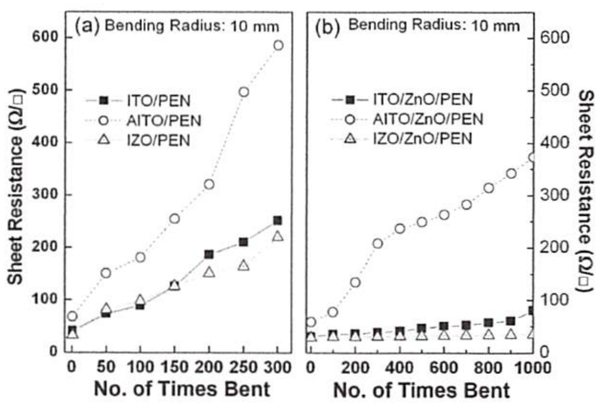

Fig. 6. Sheet resistance as a functions of the number of bending times.

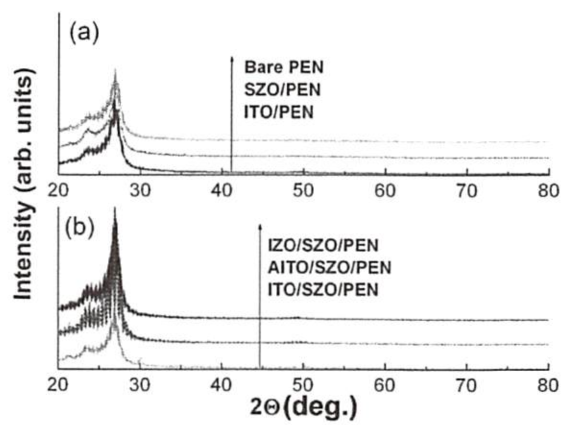

Fig. 7. X-ray diffraction (XRD) patterns of (a) TCOs/PEN and (b) TCOs/SZO/PEN.

compared to TCOs/PEN, TCOs/SZO/PEN has relatively uniform surfaces, with root mean square (RMS) roughness of less than 3 nm. The surface roughness of TCO films can be estimated from the RMS values.

In Figure 5, we show cross-sectional SEM images for TCOs/PEN and TCOs/SZO/PEN. We cut TCOs/PEN and TCOs/SZO/PEN by bending them into a right angle in liquid nitrogen to obtain their cross sections. In this process, TCO films were exfoliated from the PEN substrate for TCOs/PEN, as shown in Figs. 5(a), (b) and (c). However, no exfoliations are observed for TCOs/SZO/PEN, as shown in Figs. 5(d), (e) and (f). Therefore, the SZO layer inserted between the TCO film and the PEN substrate plays a roll not only as a barrier layer blocking permeation of water vapor but also as a buffer layer improving the adhesion of the TCO film to the substrate. The SZO films is also expected to improve the electrical stability against external stress, like bending damage. In this work, the electrical stabilities of various TCO films were evaluated based on sheet resistance changes during bending around a cylinder with a radius of 10 mm. The results are presented in Fig. 6.

Figure 6 shows the change in the sheet resistance for TCO films with and without a SZO gas barrier layer on the PEN substrate as a function of the number of bending times. The sheet resistances of TCOs/PEN increase remarkably with increasing number of bending times while for TCO/SZO/PEN films, the sheet resistance increase due to bending is significantly eased. In particular, ITO/SZO/PEN and IZO/SZO/PEN show strikingly enhanced electrical stabilities against the bending. The enhanced electrical stabilities are also expected to be a result of the SZO layer improving the adhesion of the TCO film to the substrate.

Figure 7(a) shows X-ray diffraction (XRD) patterns of TCOs/SZO/PEN. For comparison, those of bare PEN, SZO/PEN and ITO/PEN are also shown in Fig. 7(b). All XRD patterns show a similar pattern. No crystalline peaks except two peaks below $2\theta = 30°$, are observed. However, the two peaks below $2\theta = 30°$ are caused by the PEN substrate. Thus, the XRD patterns of Fig. 7 indicate that the SZO barrier layer and all the TCO layers are amorphous. Thus, we report that SZO is a very suitable material, with a dense amorphous structure, for use as a gas barrier or a passivation layer for polymer substrates or OLEDs.

IV. SUMMARY

In this work, $(SiO_2)_{40}(ZnO)_{60}$ (SZO) films were coated on PEN substrates as a gas barrier layer. The PEN substrate with a SZO gas barrier shows a very low water vapor transmission rate of less than $10^{-3}g/m^2/day$. These PEN substrates were used as flexible substrates for various TCO films, such as In_2O_3-SnO_2 (ITO), Al-doped ITO (AITO) and In_2O_3-ZnO (IZO). The electrical conductivity and the electrical stability of the TCO films deposited on PEN substrates with a SZO gas barrier (TCOs/SZO/PEN) were significantly improved as compared to those of TCO films deposited on bare PEN substrates (TCOs/PEN). The improved electrical conductivity was considered to be a result of the SZO layer acting as a blocking barrier to water vapor or organic solvent diffusion from PEN during deposition of the TCO films. In addition, the improved electrical stability was also considered to be a result of SZO layer acting as a buffer layer, improving adhesion of the TCO film to the substrate. Thus, we suggest that the PEN substrate with a SZO barrier layer is sufficiently transparent and has a superior protection ability against the permeation of water vapo. Thus, it can be applied as a flexible substrate for TCO films.

ACKNOWLEDGMENTS

This work was supported by the research fund of Catholic University of Daegu.

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