Electrical and optical characteristics of transparent conducting Si-doped ZnO/hole-patterned Ag/Si-doped ZnO multilayer films

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A R T I C L E  I N F O
Keywords:
Si-doped ZnO
Hole-patterned Ag layer
Transparent conducting electrode
Finite-difference time-domain simulation

A B S T R A C T
Hole-patterned Ag layers were first used to form Si-doped ZnO (SZO)/hole-patterned Ag/SZO multilayers and their optical and electrical properties were characterized. Unlike conventional oxide/metal/oxide multilayers, all samples exhibited two characteristic features: (i) a sinusoidal wavelength dependence of the transmittance with double maxima, and (ii) undulation in the visible transmittance, but not in the infrared transmittance. With increasing SZO thickness, the transmittance maxima were red-shifted, and the visible transmittance window widened. The carrier concentration decreased from 7.42×10²² to 2.4×10²² cm⁻³, and the sheet resistances varied from 7 to 10 Ω/sq with increasing SZO thickness. Haacke's figure of merit (FOM) was calculated for the SZO-based multilayer films. The 40 nm-thick SZO multilayers had the highest FOM of 15.9×10⁻³ Ω⁻¹. Finite-difference time-domain (FDTD) simulations were undertaken to interpret the measured transmittance. Based on the FDTD simulations, the undulating transmittance was attributed to surface plasmon-polaritons.

1. Introduction
Transparent conductive electrodes (TCEs) play an important role in the fabrication of efficient photovoltaic devices such as organic photovoltaic cells (OPVs) and organic light-emitting diodes (OLEDs) [1–3]. A wide variety of TCEs have been investigated for use in the fabrication of high efficiency OPVs and OLEDs. Sn-doped indium oxide (ITO) is the most widely used TCE in organic optoelectronic devices because it has high transmittance in the visible spectrum (over 85%) and has low resistivity (~10⁻² Ω cm) [4]; it also exhibits good energy-level alignment, resulting in efficient hole injection into the organic layers [5–7]. However, there is a great demand for developing new TCEs that are more cost-effective and have better opto-electrical properties than ITO. In this regard, a thin Ag film sandwiched between two oxide layers, namely an oxide/Ag/oxide multilayer, has been extensively investigated [8–10]. The thicknesses of the Ag and oxide layers, respectively, have been in the range of 7–20 nm and 20–70 nm. These oxide/Ag/oxide (O/Ag/O) samples were shown to yield low sheet resistances and a visible transmittance of >85% because of the different refractive indices of Ag and oxides [11–16]. In particular, ZnO/Ag/ZnO multilayers have been widely studied by many researchers [17–21] because ZnO is non-toxic [22] and abundant in nature [23]. For instance, Sahu et al. [18] investigated the dependence of the opto-electrical properties of ZnO/Ag/ZnO on Ag thickness, and showed that the use of a 6 nm-thick Ag film resulted in a sheet resistance of ~3 Ω/sq and a transmittance of ~90% at 580 nm. In addition, multilayers with Al- and Ga-doped ZnO have been also studied [24–27]. For example, Miao et al. [24] investigated the electrical and optical properties of AZO/Ag/AZO multilayer films prepared with radio-frequency (RF) magnetron sputtering as functions of Ag and AZO layer thicknesses and reported that the AZO/Ag/AZO (30 nm/10 nm/30 nm) samples had the highest transmittance of 80.5% in the visible spectrum. Crupi et al. [25] also studied the opto-electrical properties of AZO/Ag/AZO multilayers with various Ag thicknesses and showed the highest value for Haacke’s figure of merit (FOM) of approximately 9×10⁻³ Ω⁻¹ for an Ag layer thickness of 9.5 nm. Park et al. [27] investigated the physical properties of Ga-doped ZnO/GZO/Ag/GZO multilayer electrodes for use in bulk heterojunction organic solar cells and reported that the GZO/Ag/GZO electrodes had a sheet resistance of 6 Ω/sq and an optical transmittance of 87% at 550 nm.
Consequently, organic solar cells fabricated with GZO/Ag/GZO electrodes showed higher power conversion efficiency (2.84%) than those with GZO electrodes (1.57%). To our knowledge, however, multilayer films with Si-doped ZnO (SZO) [28] have not been studied hitherto.

Thus, in this study, we investigated the optical and electrical properties of SZO-based multilayer films as a function of SZO layer thickness. It should be stressed that unlike the previous studies [8–21,24–27], the middle Ag layer was hole-patterned (Fig. 1), i.e., SZO/hole-patterned Ag/SZO multilayer films. Haacke’s FOM was calculated to characterize the performance of the multilayers. Finite-difference time-domain (FDTD) simulations were carried out to interpret the characteristic transmittance spectra.

2. Experimental procedure

SZO/hole-patterned Ag/SZO multilayer thin films were consecutively deposited onto Corning EAGLE XG glass substrates at room temperature using radio frequency (RF) magnetron sputtering (for SZO) and electron beam evaporation (for Ag). Ceramic SZO targets (ZnO:SiO2=99.9:0.1 wt%, 99.99% purity) were used. Before being loaded into the sputtering chamber, the glass substrates (1.5x1.5 cm2) were cleaned with acetone, methanol, and deionized water for 15 min per cleaning agent in an ultrasonic bath, and finally dried in a N2 stream. Prior to deposition, the SZO targets were presputtered for 30 min to remove contaminants. SZO was deposited using a RF power of 90 W. During sputtering, the glass substrate was constantly rotated at a speed of 12 rpm for SZO. The nanoimprint lithography technique was used to deposit a hole-patterned Ag layer on the bottom SZO layer, and a SZO layer was deposited on top of the hole-patterned Ag layer. The thickness of the top and bottom SZO films varied from 8 to 56 nm, while the patterned Ag layer was fixed at 13 nm. A scanning electron microscope (SEM) image of a hole-patterned Ag layer is shown in Fig. 1(a). There is a well-defined array of holes (150 nm in diameter and a pitch of 300 nm), as shown in the insets (right top and left bottom) in Fig. 1(a). Fig. 1(b) shows an atomic force microscope (AFM) image of a SZO/hole-patterned Ag/SZO (40 nm/13 nm/40 nm) multilayer film; the Ag holes appear as white dots. The thicknesses of the multilayer films were determined with high-resolution transmission electron microscopy (HRTEM JEM-2100F, JEOL, Jeol). Fig. 1(c) shows a bright field TEM image obtained from a SZO/hole-patterned Ag/SZO film. It is noted that the thickness of the Ag layer is somewhat irregular. The inset that was taken from a ~100 nm-thick TEM region exhibits holes as marked by the arrows. Hall measurements by the van der Pauw technique were performed with a magnetic field of 0.55 T (HMS 3000, Ecopia). The four-point-probe technique was used for sheet resistance measurements. Transmittance of the multilayers was measured with a UV/visible spectrometer (UV-1800, Shimadzu). The crystal structure of the multilayers was determined with X-ray diffraction (XRD, ATX-G, Rigaku). In addition, the surface morphologies of hole-patterned Ag and multilayer films were characterized using an SEM (S-4200, Hitachi) and an AFM (XE-100, Park systems), respectively.

3. Results and discussion

Fig. 2 exhibits the XRD patterns obtained from the SZO/hole-patterned Ag/SZO multilayer films as a function of SZO layer thickness. Regardless of the SZO layer thickness, all samples show a broad peak at ~22.5° that is caused by the glass substrate. Except for the Ag-only sample, all of the multilayer samples have peaks at 2θ=34.2° and 62.6° that correspond to the (002) and (103) planes of ZnO, respectively (JCPDS No. 65-3411). It is noted that the intensity of the peaks increases with increasing SZO thickness. This indicates that the crystallinity improves as the SZO thickness increases. Regardless of the SZO thickness, all of the multilayer samples also have peaks at 2θ=38.2°, 44.2°, and 64.6°, corresponding to the (111), (200), and (220) planes of Ag (JCPDS No. 87-0720), respectively.

Fig. 3 shows the transmittance spectra from the SZO/hole-patterned Ag/SZO multilayer films as a function of SZO layer thickness. The transmittance illustrates characteristic features. First, all samples show the sinusoidal wavelength dependence of the transmittance, namely, two overall maxima in the visible and infrared spectra. This is very different from those of conventional O/Ag/O samples, showing
a kind of parabolic dependence of the transmittance on wavelengths [8–21, 24–27]. Second, for all samples (including a hole-patterned Ag-only layer), there are several dips in the visible transmittance, leading to undulated transmittance, but no dips in the infrared transmittance. In addition, the transmittance maxima shifted toward longer wavelengths as the thickness of the SZO layer increased from 0 to 56 nm and the carrier concentration decreased (as shown later in Fig. 4). This is in agreement with the general behavior of TCOs [29]. The visible transmittance window widens with increasing SZO layer thickness. The feature is related to plasmon-absorption-dependent reflections due to the increasing carrier concentration with decreasing SZO thickness [11]. The 40 nm-thick SZO sample gives the highest overall visible transmittance among all of the samples. For example, the transmittance at 575 nm is measured to be ~39%, ~57%, ~81%, ~86%, and ~72% for the 0, 8, 24, 40, and 56 nm-thick samples, respectively.
function of the SZO thickness. All the samples exhibited two characteristic transmittance features: sinusoidal wavelength dependence of the transmittance and undulating visible transmittance. Furthermore, the transmittance maxima were red-shifted, and the visible transmittance window widened with increasing SZO thickness. The carrier concentration gradually decreased, while the sheet resistances slightly increased with increasing SZO thickness. The 40 nm-thick SZO multilayers had the highest FOM. Based on the FDTD simulations, the undulated visible transmittance was explained by surface plasmon-polaritons. These results show that SZO/hole-patterned Ag/SZO (40 nm/13 nm/40 nm) samples could be potentially important in applications of TCE in photovoltaic and photonic devices.

Acknowledgements

This work was supported by the Korea Evaluation Institute of Industrial Technology (Grant no. 10049601) and WC300 R&D (Grant no. S2317456) through the Korea Institute for Advancement of Technology (KIAT), which is funded by the Small and Medium Business Administration. S.-K.K. was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), which is funded by the Ministry of Science, ICT, and Future Planning (NRF-2013R1A1A1059423).

References


