[논문] 열처리공학회지, 제25권 제2호(2012)
J. of the Korean Society for Heat Treatment, *Vol. 25, No. 2, (2012) pp. 85~89*

Post Deposition Annealing Effect on the Structural, Electrical and Optical Properties of ZnO/Ag/ZnO Thin Films

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Abstract Transparent conductive ZnO/Ag/ZnO (ZAZ) multilayer films were deposited by Radio frequency (RF) magnetron sputtering and direct current (DC) magnetron sputtering. The effects of post deposition vacuum annealing temperature on the structural, electrical and optical properties of the ZAZ multilayer films were investigated. The thickness of ZAZ films is kept constant at ZnO 50 nm/Ag 5nm/ZnO 45 nm, while the vacuum annealing temperatures were varied from 200 and 400°C, respectively. As-deposited ZAZ films exhibit a sheet resistance of 6.1 Ω/ □ and optical transmittance of 72.7%. By increasing annealing temperature to 200°C, the resistivity decreased to as low as 5.3 Ω/ □ and optical transmittance also increased to as high as 82.1%. Post-deposition annealing of ZAZ multilayer films lead to considerably lower electrical resistivity and higher optical transparency, simultaneously by increased crystallization of the films.

(Received February 16, 2012; Revised March 8, 2012; Accepted March 21, 2012)

Key words: *ZnO, Ag, Multilayer, XRD, AFM, Figure of merit*

1. Introduction

The rapidly increasing use of transparent and conductive oxide (TCO) films for large-area displays has prompted the development and study of inexpensive TCO electrode materials that exhibit appropriate optical and electrical properties, simultaneously. Currently, metal-doped ZnO films have attracted much attention due to their high optical transmittance in the visible wavelength range, low electrical resistivity [1-3], and relatively low cost compared to other TCO materials such as tin-doped indium oxide (ITO) [4].

However, in AZO films, a high substrate temperature is required to obtain the necessary electrical resistivity [5]. Recently, sandwich structures of TCO/metal/TCO multilayer films were shown to provide better optical and electrical properties than conventional TCO films [6-8].

In this study, transparent and conducting ZnO/Ag/ZnO (ZAZ) multilayered films were prepared by RF reactive magnetron sputtering of ZnO, and DC magnetron sputtering of Ag, and then the influence of the Ag interlayer and post deposition annealing on the structural, electrical and optical properties of the films was investigated with X-ray photoelectron spectrometer (XPS), UV-Visible spectrophotometer, atomic force microscopy (AFM), X-ray diffractometer (XRD) and four point probes, respectively. ZnO films, which have the same thickness of 100 nm, were deposited under the same conditions as for the ZAZ films to compare the structural and optical and electrical properties. The figure of merit is applied to consider the optimal annealing temperature for application as transparent electrodes.

2. Experimental

Deposition of ZnO and ZAZ films was performed on glass substrate (size; 3 cm × 3 cm) in a reactive magnetron sputtering system equipped with two cathodes. RF (13.56 MHz) and DC power were applied to ZnO (3-in diameter, Purity; 99.99%) and Ag (3-in diameter, Purity; 99.9%) targets, respectively. The substrates were ultrasonically cleaned in acetone and methanol, rinsed in de-ionized water,

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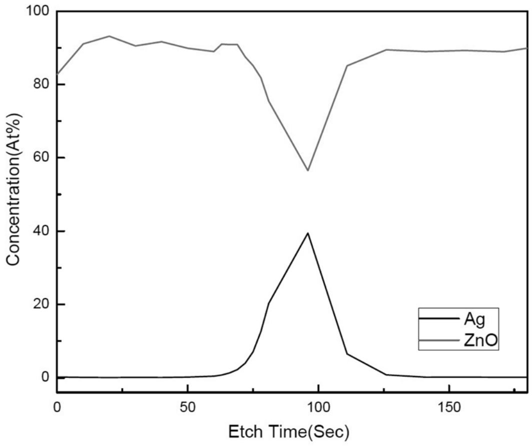

Fig. 1. A depth profile of the ZAZ films.

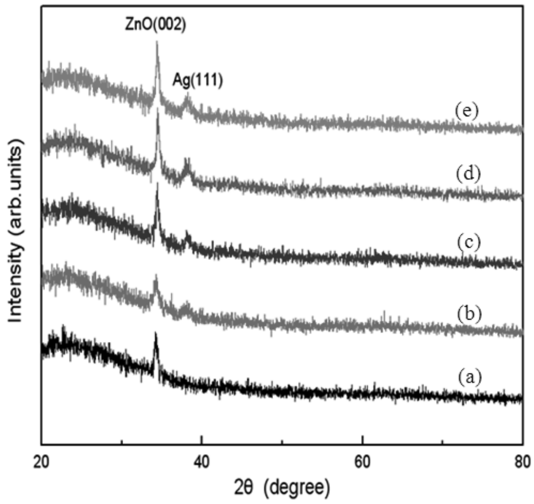

Fig. 2. XRD pattern of the ZAZ films. (a) As deposited ZnO film, (b) As deposited ZAZ film, (c) ZAZ films annealed at 200°C, (d) ZAZ films annealed at 300°C, (e) ZAZ films annealed at 400°C.

and then dried in flowing nitrogen gas before deposition. Prior to deposition, the chamber was evacuated to 1.3×10^{-4} Pa. ZnO films were deposited at 3×10^{-1} Pa in an argon (Ar) and the Ag interlayer were deposited in a pure Ar atmosphere of 1×10^{-1} Pa.

A deposition distance of 6 cm between the target and substrate was maintained throughout deposition, and the substrate rotation speed was set to 10 rpm. The substrate temperature was monitored using a k-type thermocouple in contact with the substrate surface. Although the substrate was not heated intentionally, the substrate temperature was observed to be near 60°C due to the plasma heating. By controlling the deposition time, a thickness of 100 nm was achieved in both ZnO and in ZnO 50 nm/Ag 5 nm/ZnO 45 nm multilayer films.

After deposition, ZAZ films were annealed in a vacuum of 1×10^{-2} Pa for 30 minutes at 200 300, and 400°C, respectively. The film thickness was confirmed with a surface profilometer. Over a wavelength interval from 300 to 800 nm, optical transmittance was measured by a UV-Vis Spectrophotometer (Carry100 Cone, Varian).

The optical transmittance of glass substrate was also measured for comparison and it has an optical transmission of nearly 91% in the visible wavelength range. High resolution XRD (X'pert PRO MRD, Philips) at the Korea Basic Science Institute (Daegu center) was used to observe thin film crystalline and grain size is calculated using the full width at half maximum (FWHM) of XRD pattern [9]. The depth profile of ZAZ films is observed by XPS (Theta probe, Thermo Electron) at the Korea Basic Science Institute (Busan center) and surface root mean square (RMS) roughness was evaluated by using AFM (XE-100, Park systems). The electrical properties were measured by Hall Effect measurements (HMS 3000, Ecopia).

3. Results and discussion

Structural characterization was necessary to evaluate the performance of the ZAZ films, because structure affects both optical and electrical properties of films. Fig. 1 shows the depth profile in XPS spectrum for ZAZ films with 5 nm-thick Ag interlayer and Fig. 2 shows the XRD patterns of the as-deposited and post deposition annealed ZAZ films, respectively.

XRD pattern obtained from as deposited ZnO and

ZAZ films show the diffraction peaks of ZnO (002) and when the annealing temperature reached 200-400°C, the intensities of the ZnO (002) and Ag (111) peaks in films is increased. The FWHM of the ZnO (002) and Ag (111) peak is decreased due to crystallization [9].

The transmittance of ZAZ films is also important in display applications. The optical transmittance spectra in the UV-Vis. regions of ZnO and ZAZ films prepared with and without the annealing process are shown in Fig. 3 As deposited ZnO and ZAZ films show the optical transmittance of 85% and 72.7%, respectively, while the annealed ZAZ films at 200°C showing a better performance of 82% in the visible wavelength range.

It is well known that the optical transmittance of transparent conducting oxide (TCO) films depends upon their crystalline because the grain boundary in the films absorbs the visible light and results in low transmittance. As shown by the XRD pattern, the

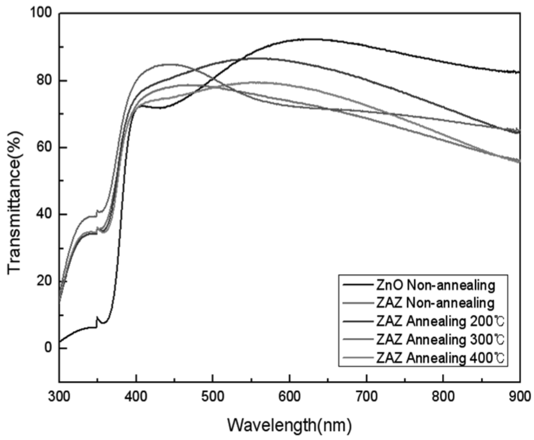

Fig. 3. Optical transmittance of the ZnO and ZAZ films post deposition annealed at different temperatures.

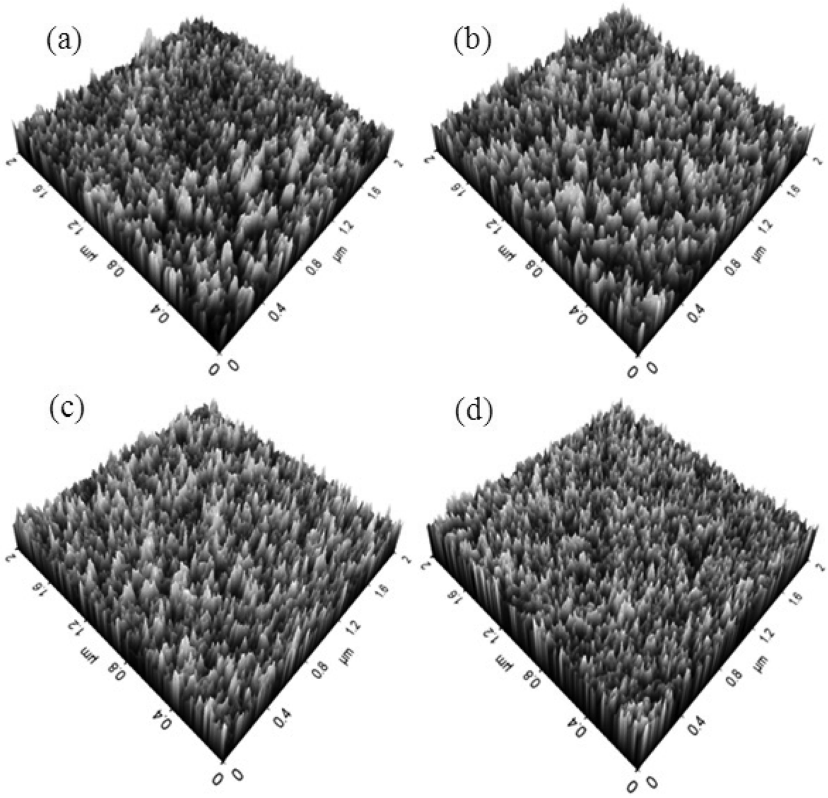

Fig. 4. AFM images of the ZAZ films. (a) As deposited ZAZ film, (b) ZAZ films annealed at 200°C, (c) ZAZ films annealed at 300°C, (d) ZAZ films annealed at 400°C.

Table 1. Figure of merit of the ZAZ films post-deposition annealed at different temperatures

ZAZ Films	Optical Transmittance (%)	sheet Resistance (Ω/□)	Figure of Merit (Ω^{-1})
As deposited film	72.7	6.1	6.6×10^{-3}
Annealing at 200°C	82.0	5.3	2.4×10^{-2}
Annealing at 300°C	75.0	5.6	1.0×10^{-2}
Annealing at 400°C	74.6	10.6	8.0×10^{-3}

improved optical transmittance of the post deposition annealed films is attributed to the poly-crystallization of the films. Consistent with this finding, Yang et al. reported that ITO films prepared on a polycarbonate substrate by RF magnetron sputtering have an optical transmittance of 75% [10]. Thus, the optical transmittance values of as deposited ZAZ films in this study were reasonable.

Fig. 4 shows the AFM image of the ZnO and ZAZ films prepared with and without the annealing process. Surface roughness of TCO films is an important factor in determining the quality of the OLED device. In OLED devices, the distance between anode and cathode is only several hundred nanometers. Therefore, it is critical to prepare anode TCO films that have smooth surfaces to eliminate the current leakage pathways caused by rough surfaces. The annealed films at 200°C show the lower RMS roughness of 1.7 nm than that of the conventional magnetron sputtered TCO films [11].

The optical and electrical performance of the ZAZ films was evaluated using a figure of merit (FOM) [12]. The FOM is defined as FOM = T^{10}/Rs where T is the optical transmittance in a visible wave length and Rs is the sheet resistance. The FOM for as-deposited films and annealed films are compared in Table 1. The FOM reaches a maximum of value of $2.48 \times 10^{-2}\Omega^{-1}$ for ZAZ films annealed at 200°C and then the FOM decreased with annealing temperatures. The reason of the deteriorated optical and electrical properties of the films annealed above 200°C is attributed to the diffusion of Ag inter layer into ZnO films. Recently, H. Lee reported the similar results in ZnO/Au/ZnO films prepared by RF magnetron sputtering method [13].

Since higher FOM means better quality of TCO films, it can be concluded that the post-deposition annealing process for ZAZ film is very effective method to improve the optical, structural, and electrical properties of the films.

4. Conclusion

ZnO 50 nm/Ag 5 nm/ZnO 45nm multilayer films were deposited onto glass substrate to investigate the effect of the post-deposition annealing temperature on the structural, electrical and optical properties of the films. Although as-deposited ZAZ films showed the diffraction peaks of ZnO (002) and Ag (111) planes, the FWHM of the ZnO (002) peak is decreased with annealing temperature due to crystallization.

ZAZ films annealed at 200°C show the higher optical transmittance of 82% in a visible wavelength region and lower sheet resistance of 5.3 Ω/□. From the observed results in this study, it can be concluded that the annealing process is very effective method to improve the optical and electrical properties of ZAZ films.

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