Sensors and Materials, Vol. 30, No. 11 (2018) 2541–2547
MYU Tokyo

S & M 1697

Effect of Annealing Temperature on Optical and Electrical Properties of ZnO/Ag/ZnO Multilayer Films for Photosensor

Tao-Hsing Chen* and Hao-De Su

Department of Mechanical Engineering, National Kaohsiung University of Science and Technology,
Kaohsiung 807, Taiwan

(Received March 28, 2018; accepted August 22, 2018)

Keywords: ZnO/Mo/ZnO multilayer film, sputtering, annealing temperature, optical and electrical properties

In this study, transparent thin films of ZnO/Ag/ZnO were deposited on Corning glass substrates by radio-frequency (RF) magnetron sputtering, and the effect of different annealing temperatures on the transmittance, electrical, and crystalline properties of the grown films was investigated. The results showed that the multilayered films exhibited a transmittance of approximately 80% at an annealing temperature of 300 °C. The resistivity (3.95×10^{-5} Ω-cm) was also the lowest at 450 °C, the mobility was 14.7 cm^2/V-s, and the carrier concentration was 5.75×10^{21} cm^{-3}. The experiments showed that as the annealing temperature was raised, the transmittance increased up to 450 °C. After this, the transmittance decreased. However, resistivity continued to drop with further increase in temperature, accompanied by an increase in crystal grain size.

1. Introduction

Transparent conducting oxides (TCO) now play a vital role as an electrode material and are applied most in solar cells, flat panel displays, and organic light-emitting diodes (OLEDs).(1–8) ZnO is one of the most important materials used in many electrical applications for transparent conductive contacts in solar cells,(9–12) organic light-emitting components, flat monitors, gas sensors,(13) photosensors,(14–16) and touchscreens, for example.

The conductivity of ZnO thin films can be greatly improved by doping ZnO with another element, and multilayered films using metals such as Ag, Cu, Ti, and Al have received much attention. It has been found that Mo-doped zinc oxide is very useful for the fabrication of a diversified range of devices. This is because the high electrovalence of the Mo atom successfully substitutes for a Zn atom and donates electrons.(17–19) The element Ag is another choice since it offers the highest electrical conductivity. At the same time, the inclusion of a Ag layer within ZnO layers may lead to the enhancement of optical characteristics.(20,21)

Radio-frequency (RF) magnetron sputtering has many advantages for the deposition of thin films, including low substrate temperature, good surface roughness, and low cost. However,

*Corresponding author: e-mail: thchen@nkust.edu.tw
https://doi.org/10.18494/SAM.2018.2056

ISSN 0914-4935

the properties of the deposited films are largely dependent on the sputtering parameters. In this study, a Ag metal layer was deposited between two ZnO thin-film layers. Sputtering was done at room temperature and resulted in a transparent ZnO/Ag/ZnO conductive multilayer film. The effect of annealing temperature on the microstructural, electrical, and optical characteristics of ZnO/Ag/ZnO multilayer films deposited on the glass substrates were investigated.

2. Materials and Methods

An RF magnetron sputtering system (I-Shien) was used with ceramic ZnO targets and a pure Ag (99.99%) target at room temperature at a base pressure of less than 6 mTorr. The Corning glass substrate used was cut into suitable sizes and chemically cleaned using acetone before use. The RF sputtering was carried out without heating the substrate; there was no oxygen present and the parameters were carefully controlled. The ZnO/Ag/ZnO multilayer films on the glass substrate were then annealed for 40 min at temperatures of 200, 300, and 450 °C. The specimens were examined using an X-ray diffractometer (XRD), and the XRD patterns were recorded. The photoelectric properties such as light transmittance, resistivity, and carrier concentration were measured using a spectrophotometer (UV Solution 2900) and a Hall measuring instrument. Finally, the surface morphology of the films was examined by scanning electron microscopy (SEM; JEOL 7001) and the grain size was measured using the SEM measuring tool.

3. Results and Discussion

3.1 XRD structural analysis

The XRD patterns of ZnO/Ag/ZnO thin films deposited on glass substrates at different annealing temperatures are shown in Fig. 1. It can be clearly observed from the figure that all the multilayer samples have diffraction peaks at (002) that correspond to a ZnO plane. As the

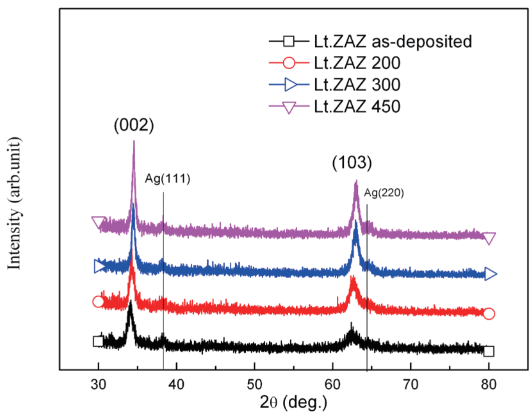

Fig. 1. (Color online) XRD results for ZnO/Ag/ZnO multilayer films at different annealing temperatures.

annealing temperature increases to 450 °C, another peak (103) appears also corresponding to a ZnO crystalline structure. Furthermore, we can also see the (111) peak of the Ag element. The increased annealing temperature provides energy that affects the sputtered particles and enhances surface mobility, which, in turn, improves the crystalline structure.

3.2 Electrical analysis

Figure 2 shows the resistivity, mobility, and carrier concentration of the ZnO/Ag/ZnO multilayer films annealed at different temperatures. It can be seen that the resistivity of the films decreases with an increase in annealing temperature, and the films have the lowest resistivity at an annealing temperature of 450 °C. This may be due to a decrease in the oxygen vacancy concentration. The resistivity is 3.95×10^{-5} Ω-cm for an annealing temperature of 450 °C. This high annealing temperature also improves the carrier concentration and mobility.

3.3 Transmittance analysis

Figure 3 shows the optical properties of ZnO/Ag/ZnO multilayer films annealed at different annealing temperatures. The transmittance over a range of wavelengths from 200 to 800 nm gradually increased with an increase in annealing temperature, and the average was slightly higher than that of the unannealed film. When these thin films are annealed, a phenomenon in which the grains are reformed occurs, which changes the energy gap slightly. With more energy being applied because of the higher temperature, the rate and extent of reforming change. 450 °C seems to be the ideal temperature for the optimization of the material properties. The optical band gap (E_g) of the multilayer films can be calculated by considering the electron transitions from the valance band to the conduction band caused by the absorption of one photon of energy hv by the thin film. For semiconductors with a direct band gap, the absorption coefficient is given by Shan *et al.* as[22]

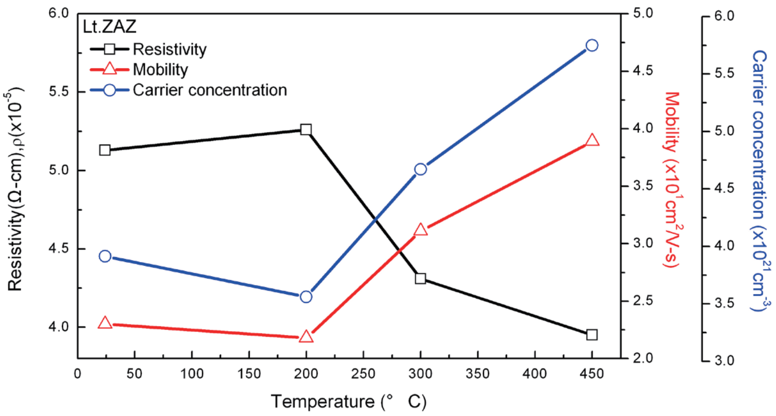

Fig. 2. (Color online) Electrical properties of ZnO/Ag/ZnO multilayer films annealed at different temperatures.

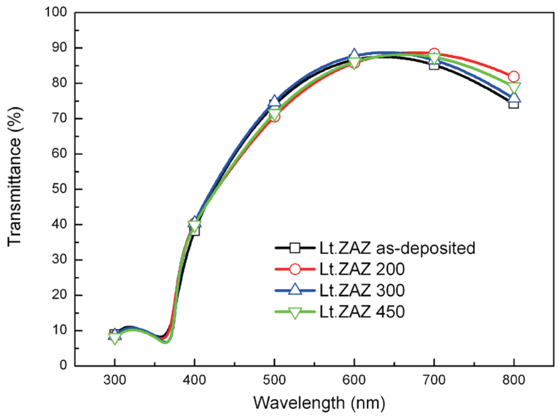

Fig. 3. (Color online) Optical properties of ZnO/Mo/ZnO multilayer films annealed at different temperatures.

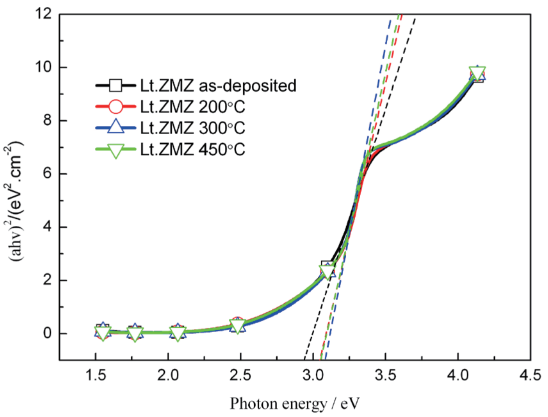

Fig. 4. (Color online) Plots of $(ahv)^2$ vs hv for ZnO/Ag/ZnO multilayer films annealed at different temperatures.

$$ahv = (hv - E_g)^{1/2}, \quad (1)$$

where a is the absorption coefficient, E_g is the optical band gap energy, h is the Planck constant, and m is the photon frequency. Figure 4 shows the calculated optical band gaps for annealed ZnO/Ag/ZnO multilayer films. The band gap increased from 3.21 to 3.31 eV as annealing temperature increased. The increase in the band gap of ZnO/Ag/ZnO thin films may be due to the defects introduced after Ag^+ is substituted for Zn^{2+} and to the differences in the electronegativity and annealing temperature.[14,23]

3.4 Surface morphology analysis

Figures 5(a)–5(d) show SEM images of the surfaces of four different ZnO/Ag/ZnO thin films. Figure 5(a) is the image of an unannealed film surface, and Figs. 5(b)–5(d) are images of the surfaces of films annealed at 200, 300, and 450 °C, respectively. It can be seen that the grain size increases with rising annealing temperature. We also investigated the growth of sputtered particles using the XRD patterns. Equation (2) below enables us to determine the grain size of the material. D is the grain size, β is the XRD peak full width at half-maximum (FWHM), λ is the wavelength of the incident X-ray, cosθ is the diffraction angle of incident light, and λ and cosθ are constant values. Equation (2) implies that the decrease in FWHM indicates the increase in grain size, so β becomes the main cause of grain size. As shown in Fig. 6, it can be seen that the grain size increases with annealing temperature, in agreement with the SEM analysis.

$$D = \frac{0.9\lambda}{\beta\cos\theta} \quad (2)$$

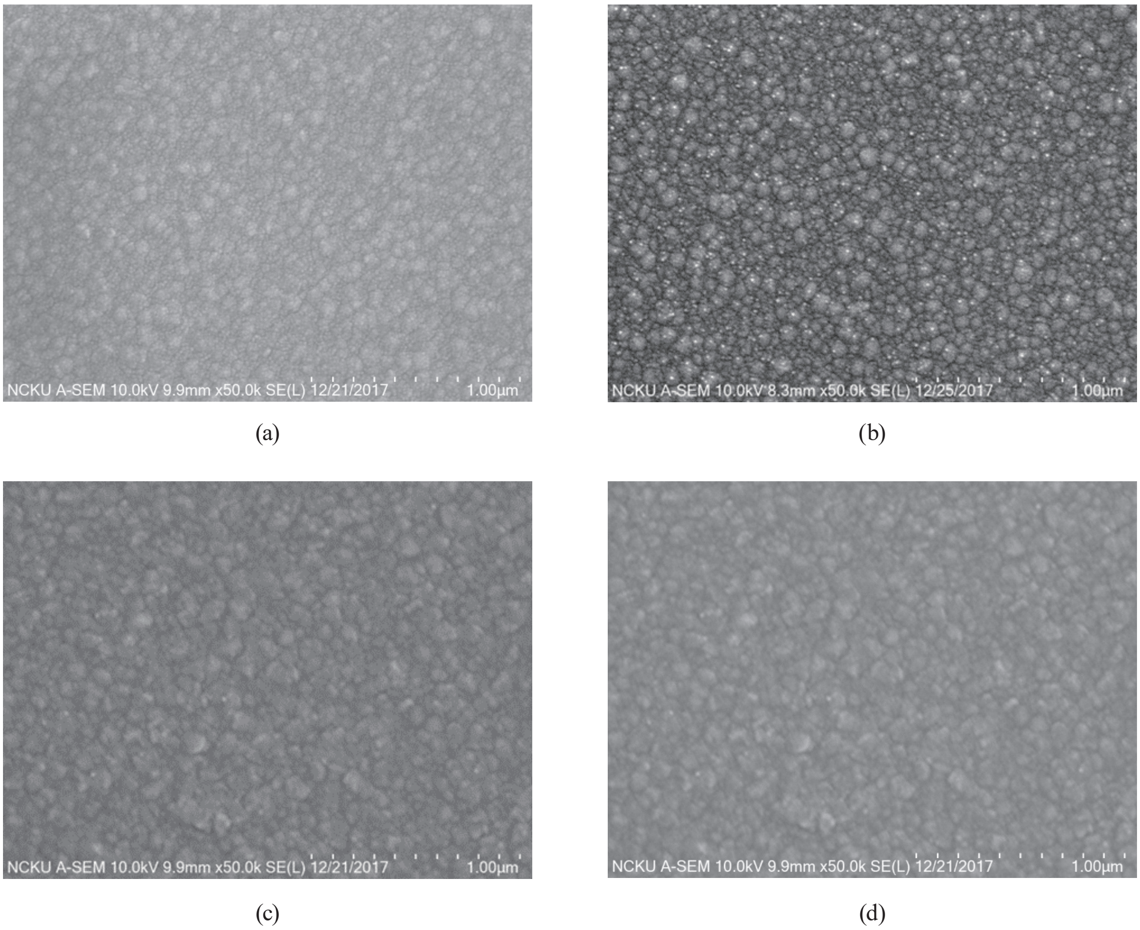

Fig. 5. SEM images of surface features for different annealing temperatures. (a) As-deposited, (b) 200 °C, (c) 300 °C, and (d) 400 °C.

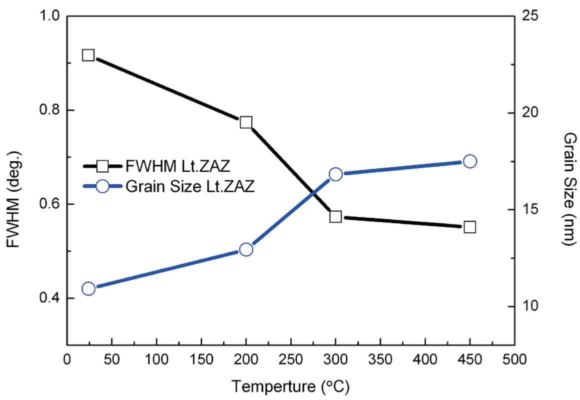

Fig. 6. (Color online) Results of FWHM analysis of ZnO/Ag/ZnO multilayer thin films annealed at different temperatures.

4. Conclusions

ZnO/Ag/ZnO multilayered thin films can be easily deposited as transparent conducting coatings by RF magnetron sputtering. Transmittance is relatively high in the visible range and increases slightly with annealing temperature. These multilayer films can be optimized to have a low resistance (3.95×10^{-5} Ω-cm) by annealing at a temperature of 450 °C. The results indicated that ZnO/Ag/ZnO multilayer films have good transmittance and the highest responsivity with a narrow band gap and low resistivity. The multilayer film may be used as an optical sensor in optoelectronic applications.

Acknowledgments

The authors would like to express their sincere gratitude to the Ministry of Science and Technology for financial support of this project under Contract No. MOST 106-2628-E-992-302-MY3.

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About the Authors

Tao-Hsing Chen received his B.S. degree from National Cheng Kung University, Taiwan, in 1999 and his M.S. and Ph.D. degrees from the Department of Mechanical Engineering, National Cheng Kung University, Taiwan, in 2001 and 2008, respectively. From August 2008 to July 2010, he was a postdoctoral researcher at the Center for Micro/Nano Science and Technology, National Cheng Kung University, Taiwan. In August 2010, he became an assistant professor at National Kaohsiung University of Applied Sciences (renamed National Kaohsiung University of Science and Technology), Taiwan. Since 2016, he has been a professor at National Kaohsiung University of Science and Technology. His research interests are in metal materials, TCO thin films, thermal sensors, and photosensors. (thchen@nkust.edu.tw)

Hao-De Su received his B.S. degree from National Kaohsiung University of Applied Sciences (renamed National Kaohsiung University of Science and Technology), Taiwan, and his M.S. degree from National Kaohsiung University of Science and Technology in 2018. He is now serving in the military. (s952313@gmail.com)