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Electrical and Optical Properties of ZnO:MgF_2 with Ag Thin Film for Optoelectronic Sensor Application

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High-purity (99.99%) silver thin-film coatings were deposited on glass substrates using a DC magnetron sputtering system. Double-layer transparent conductive films were then prepared by depositing 97:3 at% zinc oxide-doped magnesium fluoride (ZnO:MgF_2) films on the silver coatings. The films were annealed at temperatures in the range of 200–500 °C under vacuum to promote structural rearrangement and reduce internal defects. The thickness, electrical properties, optical properties, surface characteristics, and figures of merit of the various films were examined and compared. The results showed that the double-layer film annealed at the highest temperature of 500 °C had the lowest resistivity of 1.68×10^{-5} Ω-cm. By contrast, the maximum optical transmittance (67.13%) and best quality factor (2.45×10^{-3} Ω^{-1}) were observed in the film annealed at the lowest temperature of 200 °C.

1. Introduction

In the face of dwindling fossil fuel reserves and the growing climate threat posed by carbon emissions, the development of sustainable and green energy sources has emerged as a critical concern. With its advantages of renewability, low environmental impact, and relatively low cost, solar energy is regarded as a leading candidate for meeting future global energy needs. Transparent conductive oxide (TCO) films play a key role in solar cells by facilitating light absorption and collecting and transporting the charge carriers generated by the absorbed light.(1) Besides solar cells, TCO films are widely used in many optoelectronic components, such as thin-film transistors and high-resolution displays.(2–6) TCO thin films were traditionally fabricated from indium tin oxide (ITO). However, in recent years, many alternatives to ITO films have been proposed, including ZnO, FTO, GaO, and SnO_2.(7–11) Among these materials, ZnO has many excellent physical and chemical properties, including a wide bandgap, high conductivity, and high carrier concentration. These favorable properties are largely due to its hexagonal wurtzite crystal structure. With an energy gap of 3.1 eV and a favorable work function, ZnO represents a highly promising alternative to ITO.

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In recent years, many groups have attempted to improve the optical transmittance and electrical properties of TCO films by combining the oxide film with a metal layer to form a double-layer structure that minimizes the light loss due to reflection and reduces the overall resistance of the structure.(11) Typically, these metal layers have the form of Al, Ag, Ti, Mo, and Mg thin films.(12–17) Among the various deposition methods used to prepare such double-layer films, RF magnetron sputtering is one of the most commonly used because of its ability to produce uniform films over a large area with strong adhesion to the substrate.(18–21)

In this study, a DC RF magnetron sputtering system is used to deposit thin Ag layers on glass substrates. The same system is then employed to deposit ZnO:MgF_2 thin films on the Ag layer to form double-layer structures. The double-layer films are annealed at various temperatures ranging from 200 to 500 ℃ to promote structural rearrangement and eliminate internal defects. The thicknesses, electrical properties, optical properties, structural properties, and surface characteristics of the various films are measured to determine the optimal double-layer structure for optical and electrical sensor applications.

2. Experiment Methods and Materials

The Ag films were deposited on glass substrates using a sputtering power of 20 W, a fixed bias of 10 mTorr, an argon gas flow rate of 15 sccm, and a sputtering time of 1 min. The sputtering process was performed using a commercially pure (99.99%) Ag target of 3 in. diameter and 0.25 in. thickness. The ZnO:MgF_2 oxide layer was prepared with a sputtering power of 80 W, a fixed bias of 6 mTorr, an argon gas flow rate of 15 sccm, and a sputtering time of 60 min. In the deposition process, a compound zinc oxide (ZnO) and magnesium fluoride (MgF_2) target of 3 in. diameter and 0.25 in. thickness were employed. The double-layer structures were annealed at temperatures between 200 and 500 ℃, in steps of 100 ℃. The thickness of the films was determined using a KLA Alpha-Step stylus profiler (Model AS-IQ). The electrical properties were assessed using an AHM-800B Hall Effect Measurement System. The optical properties were measured using a UV-VIS spectrometer (UV Solution 2900). Finally, the surface structure was observed by scanning electron microscopy (SEM, HITACHI SU-5000).

3. Results and Discussion

3.1 Film thickness and optical transmittance

The thickness of both as-sputtered and annealed double-layer films was approximately 41.8 nm. Table 1 shows the optical transmittance values of the various films. The average optical transmittance varies between approximately 60 and 67% and reaches a maximum value in the sample annealed at 200 ℃.

For each double-layer structure, the energy gap was calculated as(22)

$$(\alpha h\upsilon)^2 = A(h\upsilon - Eg), \tag{1}$$

Table 1
Optical properties of $ZnO:MgF_2/Ag$ structures annealed at different temperatures.

Average optical transmittance (%)	
Annealing temperature (℃)	80 W/60 min
As-deposited	66.36
200	67.13
300	63.27
400	60.49
500	60.38

where A is a constant, and α and $h\upsilon$ are the absorption coefficient and incident photon energy, respectively. It is seen that $(\alpha h\upsilon)^2$ varies linearly with hυ, which allows the maximum energy gap (Eg) of the double-layer structure before annealing to be estimated as 3.76 eV (see Fig. 1). The energy gap was essentially insensitive to changes in the average transmittance of the film, which suggests that the double-layer $Ag/ZnO:MgF_2$ structure acts as a wide-bandgap (WBG) semiconductor. As shown in Table 1, the average transmittance, and thus the energy gap value, decreases as the annealing temperature increases beyond 300 ℃. This reduction may be attributed to various factors, including grain growth effects, compositional changes, oxidation, and decomposition processes.

3.2 Effects of annealing temperature on electrical properties

Table 2 shows the electrical properties of the as-deposited and annealed $ZnO:MgF_2/Ag$ films. For the annealed samples, the resistance decreases progressively with increasing annealing temperature. The lowest resistance (1.68×10^{-5} Ω-cm) thus occurs in the film annealed at the highest temperature of 500 ℃. This finding suggests that the diffusion of the Ag atoms into the $ZnO:MgF_2$ layer increases at higher temperatures. The diffused atoms substitute some of the atoms in the $ZnO:MgF_2$ matrix, thereby increasing the conductivity and lowering the resistance.

3.3 Surface characteristics

The surface characteristics of the as-deposited and annealed samples were observed by SEM. As shown in Fig. 2(a), the as-deposited film contains no obvious holes or cracks. Moreover, as the annealing temperature increases, the surface becomes smoother and denser [Figs. 2(a)–2(e)]. In addition, crystallites are formed on the surface at temperatures exceeding 300 ℃, as discussed in Sect. 3.5.

3.4 Figure of merit

For transparent conductive films, the figure of merit (FOM) is usually determined on the basis of the resistance value (lower is better) and optical transmittance (higher is better) as follows:(23,24)

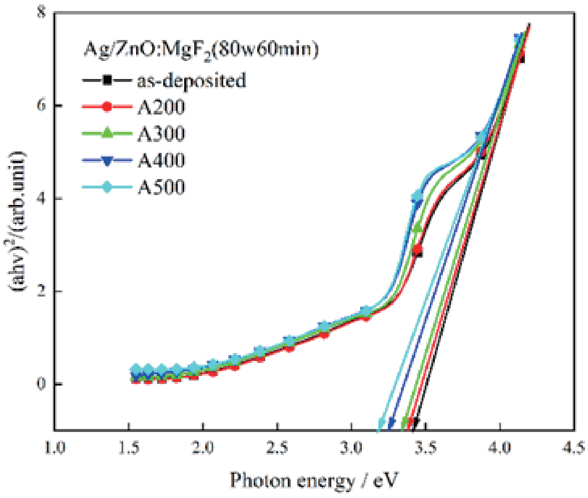

Fig. 1. (Color online) Energy gaps of $ZnO:MgF_2/Ag$ structures annealed at different temperatures.

Table 2
Electrical properties of $ZnO:MgF_2/Ag$ films annealed at different temperatures.

ZnO: MgF_2 (80 W/60 min) / / Ag (20 W/1 min)			
Annealing temperature (°C)	Resistivity (Ω-cm)	Mobility (cm^2/Vs)	Carrier concentration (cm^{-3})
As-deposited	2.65×10^{-4}	1.63	1.45×10^{19}
200	3.17×10^{-5}	3.04	9.49×10^{19}
300	2.24×10^{-5}	3.77	1.01×10^{20}
400	2.09×10^{-5}	4.17	5.31×10^{20}
500	1.68×10^{-5}	5.57	3.05×10^{21}

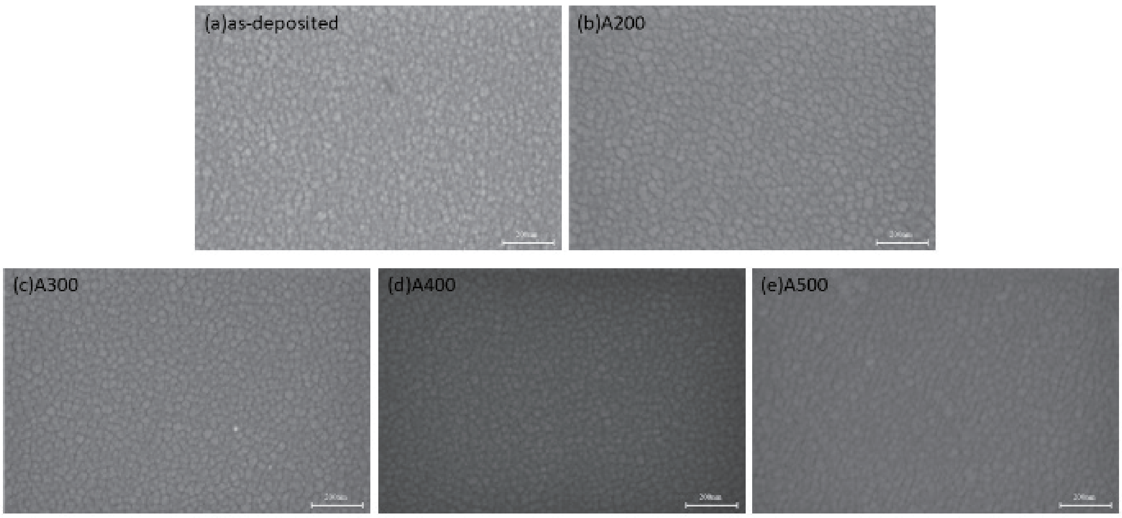

Fig. 2. SEM surface images of various samples: (a) as-deposited and annealed at (b) 200, (c) 300, (d) 400, and (e) 500 °C.

$$\varnothing_{TC} = \frac{T_{av}^{\ 10}}{R_{sh}}, \tag{2}$$

where T_{av} is the average visible transmittance, R_{sh} is the sheet resistance, and the unit is Ω^{-1}. As shown, the FOM is proportional to the 10th power of the optical penetration rate. Thus, the quality of the double-layer film is determined mainly by its transmittance.

Table 3 shows the FOM values of the as-sputtered and annealed double-layer films. The results indicate that the optimal FOM ($2.45 \times 10^{-3}\ \Omega^{-1}$) is obtained at an annealing temperature of 200 °C.(25–27)

3.5 XRD properties and crystal grain size

The XRD patterns in Fig. 3 show that the as-deposited double-layer film has an amorphous structure. The amorphous structure is maintained under the lowest annealing temperature of 200 °C. However, when the annealing temperature increases to 300 °C, the film begins to crystallize, with the main growth direction along the (002) plane and an Ag peak corresponding to (111). The (002) peak intensity is stronger than that of the Ag peak, indicating that the main growth direction of the film occurs along the C axis. As the annealing temperature increases, the (002) peak shifts toward a higher angle. This observation is consistent with the findings of previous studies that, as the energy of atomic activity increases, structural defects are reduced, causing a reordering of the lattice structure and a shift of the diffraction peak to the right.

The crystallite size can be calculated by substituting the peak XRD value into Scherrer's formula:(28)

$$D = \frac{0.9\lambda}{\beta \cos\cos\theta}, \tag{3}$$

where D is the grain size, λ is the incident angle of the X-rays at 0.15418 nm, θ is the Bragg angle, and β is the full width at half-maximum (FWHM). Since λ and θ are constants, D and β are inversely related. In other words, the grain size increases as the FWHM decreases.

Figure 4 shows the FWHM values and crystallite sizes of the ZnO:MgF_2/Ag films annealed at temperatures higher than 300 °C. The maximum FWHM and minimum grain size occur in

Table 3
FOM of ZnO:MgF_2/Ag films annealed at different temperatures.

ZnO:MgF_2/Ag	
Annealing temperature (°C)	FOM (Ω^{-1})
As-deposited	2.62×10^{-4}
200	2.45×10^{-3}
300	1.92×10^{-3}
400	4.83×10^{-4}
500	5.22×10^{-4}

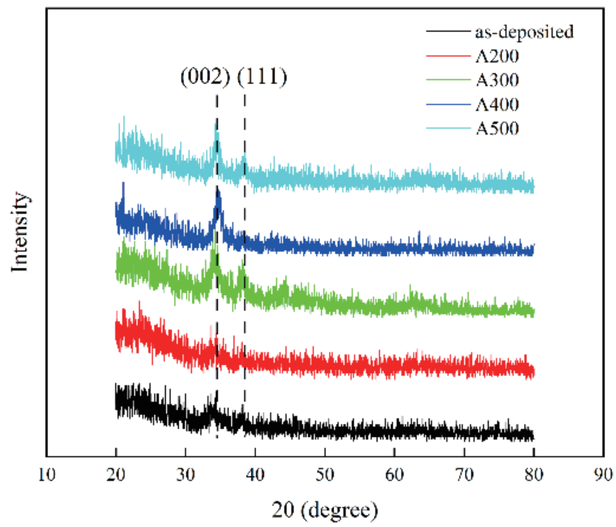

Fig. 3. (Color online) XRD patterns of ZnO:MgF_2/Ag films annealed at different temperatures.

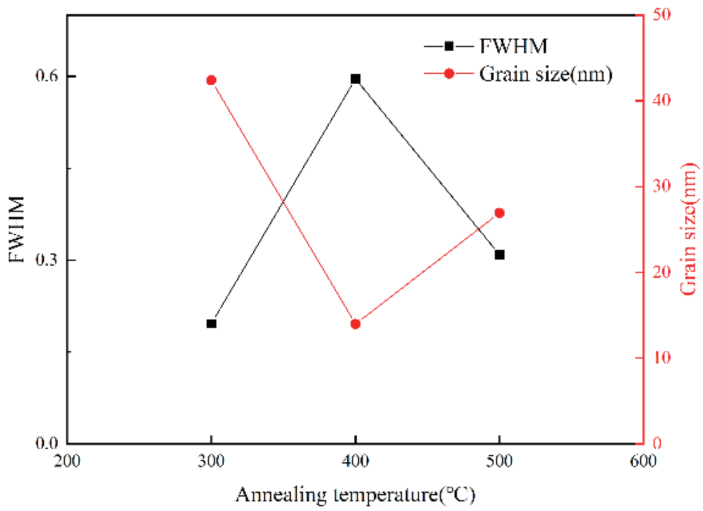

Fig. 4. (Color online) FWHM and grain size of ZnO:MgF_2/Ag films annealed at different temperatures.

the film annealed at 400 °C. As the temperature increases, the FWHM and grain size decrease and increase, respectively, as the result of a further reorganization of the crystal structure under higher temperatures.

4. Conclusions

Double-layer ZnO:MgF_2/Ag films were deposited on glass substrates and then annealed at temperatures ranging from 200 to 500 °C. The film annealed at 200 °C exhibited the highest average transmittance of 67.13% and the best quality factor of 2.45×10^{-3} Ω^{-1}. In contrast, the film annealed at the highest temperature of 500 °C demonstrated the lowest resistance of 1.68×10^{-5} Ω-cm. The maximum energy gap value of 3.76 eV was observed in the as-sputtered film. The SEM images showed that the film surface remained flat and dense at all annealing temperatures. The ZnO:MgF_2/Ag films showed an amorphous structure under the as-deposited condition and following annealing at the lowest temperature of 200 ℃. However, a crystalline structure with a dominant ZnO peak emerged at annealing temperatures of 300 ℃ or higher. Crystalline growth occurred mainly in the (002) direction. The intensity of the ZnO peak increased with increasing temperature, indicating a more prominent crystalline structure. The FWHM increased with increasing annealing temperature and was accompanied by a decrease in the crystallite size. Overall, the results suggest that the ZnO:MgF_2/Ag thin film is a promising candidate for optical sensors.

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