



Original Article

Characteristics of Ag-Doped ZnO Thin Films Prepared by Sputtering Method

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Abstract: This paper presents the preparation of Ag-doped ZnO bulk sample by solid state reaction and Ag-doped ZnO thin films by sputtering method. The effects of doping concentration (1, 2 and 4%) on the properties of the thin films were investigated. Various methods were utilized to investigate characteristics of the samples: X-ray diffraction, Raman scattering spectroscopy, photoluminescence, energy dispersive X-Ray spectroscopy, scanning electron microscopy, atomic force microscope, absorption spectroscopy and Hall measurement. The study results show that Ag diffused into ZnO crystal lattice after heat treatment at 1,200°C. As-prepared thin film samples exhibited low resistivity in the order of $10^{-3}\Omega\cdot\text{cm}$. The film doped with 2% Ag shows the lowest resistivity of $1.8\times 10^{-3}\Omega\cdot\text{cm}$, which is potential for making transparent electrodes in optoelectronics.

Keywords: Transparent conductive oxide, ZnO:Ag, sputtering, Hall measurement.

1. Introduction

For decades, transparent conductive oxide (TCO) has been studied and widely used in electronic devices. For processing the electrodes, TCO needs to have low resistivity ($\rho\sim 10^{-3}\Omega\cdot\text{cm}$) and high transmittance ($>70\%$). Many studies reported fabrication of doped ZnO thin film with low resistivity

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in the order of $10^{-4} \div 10^{-2} \Omega \cdot \text{cm}$. Among commonly used dopants for ZnO, the most promising candidates are Al, In, Ga, Co, P... [1-5]. Ag is also considered as suitable for doping into ZnO thanks to properties such as antibacterial ability, high conductivity, low absorption coefficient in visible region [6-8]. However, the number of studies on Ag doped ZnO is less than those on others metal dopants.

Ag doped ZnO (ZnO:Ag) shows both n and p type conduction, depending on Ag location in ZnO crystal lattice [9]. A substitution of Ag^+ at Zn^{2+} site will create shallow acceptor, making ZnO a p-type semiconductor. On the other hand, if Ag locates at interstitial sites or O sites, donor levels will be formed in bandgap, then ZnO will become n-type semiconductor. Since these defects altogether coexist in ZnO lattice, the conduction type of ZnO depends on the competition between Ag_{Zn} and Ag_i .

Some techniques have been used to fabricate Ag-doped ZnO thin film such as pulsed laser deposition (PLD), molecular beam epitaxy (MBE), radio frequency sputtering. Using PLD method, Guptan [10] prepared n-type ZnO:Ag thin film with resistivity of $3 \times 10^{-3} \Omega \cdot \text{cm}$. Myers [9] produced 2 types of ZnO:Ag thin film: n-type with resistivity of $2 \Omega \cdot \text{cm}$ and p-type with resistivity of $200 \Omega \cdot \text{cm}$. Kim [11] reported the success of fabricating p-type ZnO:Ag thin film with resistivity of $7.25 \times 10^{-2} \Omega \cdot \text{cm}$ by MBE technique. N-type and p-type ZnO thin films were also deposited by Deng [12] in 2010 by sputtering with resistivity of $0.85 \Omega \cdot \text{cm}$ and $18.2 \Omega \cdot \text{cm}$, respectively. The resistivity of Ag-doped ZnO in literature is still relatively high for making electrodes.

In this paper, we present the results of manufacturing and studying properties of Ag doped ZnO bulk samples by solid state reaction and ZnO:Ag thin films by sputtering method. The fabricated ZnO:Ag thin films have low resistivity in the order of $10^{-3} \Omega \cdot \text{cm}$, which are potential candidates for transparent electrodes in optoelectronics.

2. Experiment

All materials were purchased from Merk Germany. Bulk samples were prepared by solid state reaction at high temperature. ZnO powder (99.99%) was milled thoroughly with AgNO_3 powder (99.8%) in 8 hours. Polyvinyl alcohol was used as cohesion compound. The mixture powder was pressed under pressure of 7 tons/cm^2 , then annealed at different temperatures (600°C , 800°C and 1200°C) in 4 hours. The products are Ag-doped ZnO bulk samples with different Ag concentrations (0%, 1%, 2% and 4%).

ZnO:Ag thin films were deposited by RF sputtering method in Ar atmosphere under operating pressure of 1 Pa with target made of the as-prepared bulk samples. Sputtering time was 20 minutes while sputtering power was fixed at 175W. ULVAC's mini Sputter device (Japan) were used to fabricate thin films in this research. The samples were characterized with various techniques including X-ray diffraction (D5005, Druker), Raman scattering spectroscopy LabRam HR800 (Horiba Jobin Yvon), photoluminescence Fluorolog FL3-22 (JobinYvon Spex), Energy dispersive X-Ray spectroscopy, scanning electron microscopy, atomic force microscope AFM XE-100 (Park Systems), absorption spectroscopy Jasco V-750 and Hall measurement HMS-3000 (Ecopia).

3. Results and discussion

Fig. 1 presents XRD patterns of Zn:Ag bulk samples (4% at. of Ag) annealed at 600°C , 800°C and 1200°C in 4 hours. All the samples exhibit polycrystal hexagonal wurtzite $C6v$ structure with

characteristic diffraction peaks corresponding to reflections from (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes. In addition, peaks at 38.01° , 44.30° and 64.34° in the XRD patterns also suggested the existence of Ag in the samples annealed at 600 and 800 °C. The disappearance of these peaks at annealing temperature of 1200 °C suggested that Ag had diffused into the lattice of ZnO and the sample is single phase. The results show that annealing temperature of 1200 °C is required to obtain pure and single phase sample. Hence, samples doped with 1, and 2% of Ag were also prepared at 1200 °C. The bulk samples were then used as target for fabrication of Ag doped ZnO thin films by sputtering method.

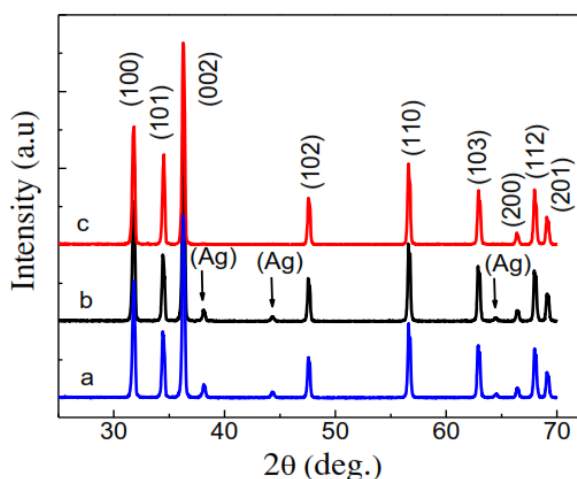


Figure 1. XRD patterns of ZnO:Ag (4%) bulk samples annealed at 600°C (a), 800 °C (b) and 1200 °C (c).

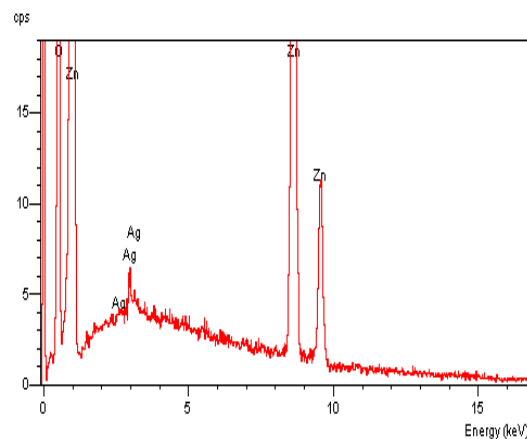


Figure 2. EDS spectrum of thin film ZnO doped with 4% Ag, sputtered at 175W.

Typical EDS spectrum of 4% Ag-doped thin film (Fig.2) shows that the sample only contains Zn, O and Ag and reconfirm the purity of the film. No new peak was observed in Raman spectra (Fig. 3) of samples with various concentration of Ag. The results suggest that Ag did not change the crystal lattice of ZnO. Two prominent peaks at $\sim 100 \text{ cm}^{-1}$ (E_2^{low}) and 438 cm^{-1} (E_2^{high}) correspond to vibration of zinc and oxygen lattice, respectively. $A_1(\text{LO})$ mode, which was absent in Raman spectra of ZnO thin films, was observed clearly at 570 cm^{-1} for doped samples. It should be note that the relative intensity of $A_1(\text{LO})$ mode (normalized to Si peak at 302 cm^{-1}) which is commonly considered as a sign of defect or defect complexes of oxygen vacancies, zinc interstitial, increase with doping concentration.

Fig. 4 shows transmission spectra of Ag doped ZnO thin films. The undoped sample shows a relatively high transmittance of more than 90 %. The doped samples show moderate transmission of above 50% in the visible region. With increasing concentration of Ag, the transmittance decreases, accompanied with a red shift of the absorption edge. The bandgap energy E_g of ZnO and ZnO:Ag can be extrapolated by the intersection between the linear part of $(\alpha h\nu)^2$ vs. $h\nu$ plot and x axis. The data is given in Table 1. The bandgap of ZnO show only slight variation at different doping concentration.

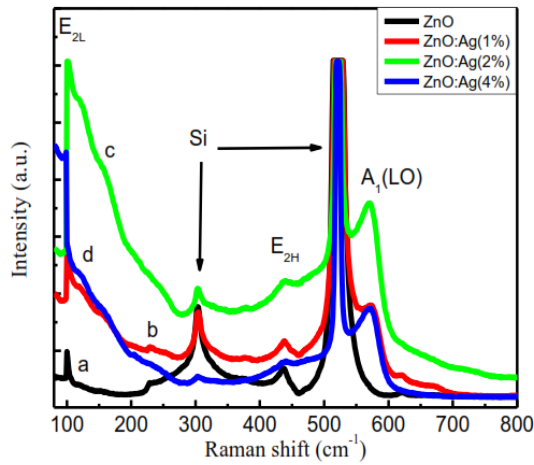


Figure 3. Raman spectra of ZnO thin film (a) ZnO doped with Ag of 1% (b); 2% (c) and 4% (d).

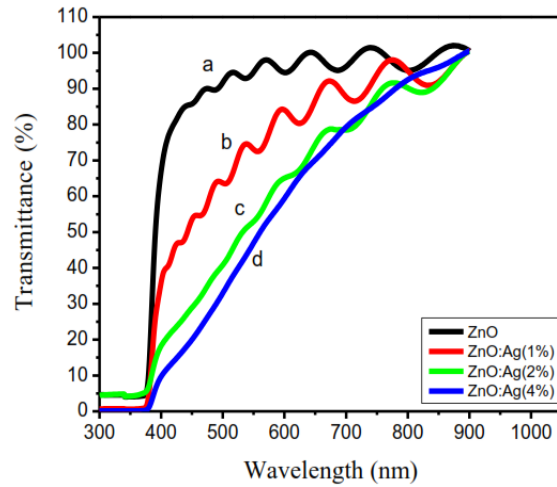


Figure 4. Transmission spectra of ZnO thin film (a) and ZnO doped with Ag of 1% (b); 2% (c) and 4% (d).

Table 1. Band gap of ZnO:Ag thin films with different doping concentrations (0%, 1%, 2%, 4%) sputtered at 175W.

Sample	ZnO	ZnO:1% Ag	ZnO:2% Ag	ZnO:4% Ag
E_g (eV)	3.23	3.23	3.12	3.20

Hall measurement shows that the grown thin films are n-type, of good conductance with resistivity in the order of $10^{-3} \Omega \cdot \text{cm}$. It should be noted that mobility of 4% sample is smaller than the sample of lower doping. It can be understood that higher doping likely results in formation of defects due to the difference in radii of Zn and Ag ions. These defects will reduce the mobility of carrier in the films. These results agree with the increasing intensity of $A_1(\text{LO})$ in Raman spectrum as discussed above. Some Ag atoms might locate at interstitial sites which are also not favorable for creating free carrier. Reduction in carrier concentration and decrement in mobility lead to notable elevation of resistivity of 4% samples as shown in Table 2. The lowest resistivity of $1.8 \times 10^{-3} \Omega \cdot \text{cm}$ is achieved for sample doped with 2% of Ag. The low resistivity of Ag doped ZnO thin films in this research is very promising when compared with other reports [9-14] an open the possibility for using as transparent electrode in optoelectronic field.

Table 2. Electrical properties of ZnO thin films (1%, 2% and 4% of Ag) at different sputtering powers.

Sputtering power	Thin film	Carrier concentration ($\times 10^{20} \text{cm}^{-3}$)	Mobility ($\text{cm}^2/\text{V} \cdot \text{s}$)	Restivity ($\times 10^{-3} \Omega \cdot \text{cm}$)
175W	ZnO :Ag (1%)	1.9	18.9	3.1
	ZnO :Ag (2%)	4.9	13.7	1.8
	ZnO:Ag (4%)	0.2	5.5	59.7

4. Conclusion

Ag doped ZnO bulk samples with different Ag concentrations were prepared by the solid state reaction. XRD patterns show that annealing at 1200 °C is required for Ag to diffuse into ZnO crystal lattice. Ag doped ZnO thin film samples were fabricated by RF magnetron sputtering method with target made of the asprepared bulk samples. All thin films are conductive with resistivity in the order of $10^{-3}\Omega\cdot\text{cm}$. Further optimization of synthetic parameter is expected to lower the resistivity and improve the transparency of the films and is currently underway. The good conductivity and transmission of the samples open the possibility to be applied in optoelectronic devices.

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