Structural and optical properties of silver-doped zinc oxide sputtered films

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Abstract

Silver-doped ZnO (SZO) films were prepared by rf magnetron sputtering on glass substrates with specially designed ZnO target. For the doping source for target, we use AgNO3 powder with a various mixing ratio (0, 2, and 4 wt.%). We investigated a dependency of coating parameter, such as dopant content, in target and substrate temperature on structural and optical properties of the as-grown SZO films. The SZO films have a preferred orientation in the (002) direction. As amounts of the Ag dopant in the target were increased, the crystallinity as well as the transmittance and optical band gap were decreased while those properties were degenerated at 200 °C. And as the substrate temperature was increased, the crystallinity and the transmittance were increased. In details, changes of optical band gap for the SZO films were explained with the data obtained by XRD, XPS and using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

Keywords: Silver-doped ZnO (SZO) film; Structural properties; Optical properties; rf Magnetron sputtering; NEXAFS

1. Introduction

Recently, zinc oxide (ZnO) films have been broadly investigated for their use as transparent conductive oxide (TCO) electrode [1–4], film bulk acoustic resonator (FBAR) [5], surface acoustic wave (SAW) device [6], and gas sensor [7] because of their various electrical and optical properties in combination with large band gap, abundance in nature, and nontoxicity. In addition, the ZnO films could be deposited at relatively low deposition temperature [8] and good stability (in H2 plasma) [9]. The electrical property of ZnO was controlled by intrinsic defect, i.e., oxygen vacancies and/or zinc interstitials, which act as n-type donors. Many different methods, such as rf/dc sputtering [10], sol–gel method [11], metal organic chemical vapor deposition [12], and pursed laser deposition [13] have been used for the preparation of ZnO thin films. The structural, physical, and electrical properties of ZnO films were governed by deposition parameter [14], posttreatment [15], and doped material [16–18], such as Al, Ga, Sc, Y, Mn, Cu, Ag, etc. Among them, the Ag-doped ZnO (SZO) was taken in varied concentrations on the conductivity, photosensitiv-

ity, luminescent properties, nonlinearity, and electrical stability. Then, SZO film has been used for varistor [19], photocatalyst [20], low-emissivity (Low-E) coating, etc. However, there are not many reports on the systematic study of deposition parameter effect on film properties.

In this report, therefore, we investigate the effect of dopant and deposition temperature on the structural and optical properties of Ag-doped ZnO thin films.

2. Experimental

2.1. Target preparation

The targets in the experiment were specifically designed using high purity of zinc oxide (ZnO, 99.999%) and silver nitrate (AgNO3, 99.998%) powders. To dope with Ag, ethanol-based solutions of silver nitrate (AgNO3) were prepared and mixed with ZnO powder in a planetary milling for 24 h. The slurry was dried, and the obtained powder was calcinated at 500 °C for 5 h. Disk-shaped specimens of 1-in. diameter was obtained by high pressure. After being sintered for 1 h at 1200 °C, three different targets were
prepared with different weight percent (wt.%) of AgNO₃ in the targets: pure ZnO, 2 wt.% SZO, and 4 wt.% SZO.

2.2. Deposition conditions

The sputtering system was pumped down to $3 \times 10^{-6}$ Torr using turbo molecular pump. The working pressure which mainly consisted of a high-purity Ar (99.99%) gas was 32 mTorr. The glass substrates were cleaned in an ultrasonic cleaner for 10 min with acetone, alcohol, alkaline solution and then distilled water. All substrates were blown with dry nitrogen gas. ZnO films were deposited on the substrates at room temperature (RT) with rf power of 150 W after presputtering of the targets with Ar plasma for 5 min. Due to the practical applicability of SZO films, 150- to 200-nm-thick samples were typically prepared for optical measurements. The crystal structure, microstructure, and the thickness were observed using X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. X-ray photoelectron spectroscopy (XPS) was also utilized to analyze the chemical state of SZO films. The optical transmittance measurements were performed with a UV/visible spectrophotometer. The oxygen K-edge features of SZO films were also investigated using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

3. Results and discussion

3.1. Structural characterization

We investigated how the growth rate was related to deposition parameters, such as substrate temperature, target to substrate distance ($D_{ts}$), rf power, etc. Details of the ZnO growth have already been described in our previous papers [3,4].

Fig. 1(a) shows the XRD patterns obtained from 150-nm-thick SZO films prepared with different sputtering targets at room temperature and 150 W. As shown in Fig. 1(a), only the (002) diffraction peak is observed at $2\theta = 33.6–34.3^\circ$, indicating that all of the obtained films had a preferred orientation with the $c$-axis perpendicular to the substrate. In addition, the peaks position of the (002) plane was also shifted to lower $2\theta$ values with increasing amounts of Ag content. The reason is that the lattice parameter of SZO was increased in the $c$-axis with increasing Ag dopant. In previous works, Park et al. [1] reported that the small Al ions (53 pm) was substituted into the Zn⁺ (72 pm) site in the Al-doped ZnO crystal. Therefore, the $2\theta$ values of the (002) plane increased because crystal size decreased. Conclusively we can conclude that the big Ag ions (122 pm) were substituted into the Zn⁺ (72 pm) in the SZO crystal. Moreover, the intensity of (002) peaks gradually decreased and broadened according to increasing Ag dopant. Not only the full width half maximums (FWHMs) but also the intensity of the peaks were carried out to evaluate the crystalline quality of the films. As a result, the FWHMs of the (002) peaks decreased with increasing Ag dopant (0.28°, 0.40°, and 0.61°, respectively). The reason is that the crystallinity decreased with increasing Ag dopant in SZO films because of the Ag⁺ substituted into Zn⁺ site.

Fig. 1(b) shows that the XRD spectra for SZO films were prepared on glass with 4 wt.% SZO target from room temperature to 200 °C. In these results, the intensity of the (002) peaks increased with increasing substrate temperature at 100 °C. However, the intensity of the (002) peak decreased at 200 °C. At this time, the FWHMs of the (002) peaks were not changed (about 0.43°). This is caused by the crystallinity of the deposited films which improved with increasing substrate temperature at <100 °C. But the crystallinity of SZO film was retrograde at 250 °C.

SEM micrograph analysis (Fig. 2) indicated the granular character of the deposited films. The average grain size measured from these micrographs was in the range of 25–40 nm. This result did not relate to the amount of Ag dopant.
3.2. Optical properties

We measured that the average transmittance in the visible range was from 90% to 85% with the increase of the Ag content. With Ag content increasing, the absorption edge slightly shifted to a longer wavelength region [Fig. 3(a)]. However, the result of Fig. 3(c) shows the average transmittance was decreased with increasing the $T_{sub}$ (from 80 to 50%). The reason is that the metallic property grown (to illustrate following XPS analysis) in SZO film with $T_{sub}=200$ °C.

The optical gap (Eg) of the SZO film can be obtained by plotting $x^2$ vs. $h\nu$ ($x$ is the absorption coefficient and $h\nu$ is the photon energy) and extrapolating the straight-line portion of this plot to the photon energy axis [1]. Fig. 3(b) shows the variation of optical band gap as a function of Ag contents. It showed that a band gap narrowing down with increasing Ag contents. The reason is that the Ag$^+$ was substituted into the Zn$^+$. However, Eg change by varying temperatures could not be observed in Fig. 3(d).

3.3. Chemical state on the surface

Fig. 3(b) shows that XP survey spectra obtained after Ar sputtering for an SZO film was prepared at RT with 4 wt.% AgNO$_3$-doped ZnO target. Zinc, oxygen and Ag peaks are observed, and there was no contamination except for carbon [Fig. 4(a)].

With high-resolution XPS spectra of Zn 2p$_{3/2}$, O 1s, and Ag 3d considering their atomic sensitivity, one could get the formation in the SZO film (see Table 1). Table 1 shows the percentages of silver became 0, 1.04, and 1.94 in the SZO films as dopant increased from 0 to 4 wt.%. It was certified that it is due to dopant increase that ZnO ratio to stoichiometry in the SZO films. We can observe that ZnO films became stoichiometry as substrate temperature increased in Table 1. However, deposition at 200 °C dropped crystallinity and transmittance. These were caused by metallic character grown in the SZO film. We can observe that the quantity of zinc greatly increased in the SZO film in Table 1(5).

3.4. Oxygen K-edge features of SZO films

Chen et al. [21] reported a comparison of oxygen K-edge NEXAFS spectra of several 3d transition metal oxides with the different number of d-electron (TiO$_2$-$d^0$, CrO$_3$-$d^3$, FeO-$d^6$, NiO-$d^8$, and ZnO-$d^{10}$, etc.). Here, the O K-edges had four features. The four O K-edge features could be assigned to the one-electron transition from the O 1s orbital to the $2t_{2g}$, $3e_g$, $3a_{1g}$, and $4t_{1u}$ orbitals of TiO$_2$, respectively. Grunes et al. [22] reported that this assignment was in essential agreement with a tight-binding extended Huckel band structure calculation. The simple one-electron excitation scheme could be used to explain the qualitative differences in the transitions to the two molecular orbitals ($2t_g$ and $3e_g$). Then, the number of O K-edge features and...
their peak positions were very different from one metal oxide to another. Greatly, the 10 electrons in ZnO completely occupied both the 2t_{2g}, and 3e_{g} orbitals, giving rise to the disappearance of any sharp features in the energy range <535 eV. The lowest unoccupied molecular orbital for ZnO was the 3a_{1g} orbital, which was most likely the origin for the broad O K-edge feature at 538 eV [21]. Fig. 5 shows the O K-edge features by the amount of the Ag dopant. Here, the O K-edge features of pure ZnO appeared broadly at 540 eV but disappeared under 535 eV. According to the amount of the Ag dopant, whole change was not observed greatly. When the MO theory is applied to several molecular orbitals, we say it is band. In addition, occupied MO represents valence band, and unoccupied MO represent

<table>
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<th>Composition</th>
<th>Zn (wt%)</th>
<th>O (wt%)</th>
<th>Ag (wt%)</th>
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<td>51.48</td>
<td>48.52</td>
<td></td>
</tr>
<tr>
<td>2 wt.% SZO film (RT)</td>
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<tr>
<td>4 wt.% SZO film (RT)</td>
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<tr>
<td>4 wt.% SZO film (200 °C)</td>
<td>60.75</td>
<td>37.14</td>
<td>2.11</td>
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</table>

Table 1: The compositions of the SZO films prepared by rf magnetron sputtering.

![Fig. 3](image-url) Optical transmittance of SZO films prepared (a) at RT with different AgNO₃ contents in the target and (c) at different substrate temperatures with 4 wt.% SZO target. The optical band gap of the SZO films (b) at RT with different AgNO₃ contents in the target; (d) at different substrate temperatures with 4 wt.% SZO target.

![Fig. 4](image-url) XP survey spectra of 4 wt.% SZO film after Ar sputtering.
conduction band. Because the NEXAFS feature appears when the electron excites to unoccupied MO, we can say that it express many of information of conduction band. In detail, the peak increased gradually about 543 eV caused by the increase of density of conduction band by Ag doping. This was expected to peak which was caused by Ag–O created by the Ag dopant. NEXAFS was measured after Ar ion sputtering for 10 min to remove adsorbed species on the surface of the SZO film.

4. Conclusions

Silver-doped ZnO (SZO) films with various Ag contents (0, 2, and 4 wt.%) were prepared by rf magnetron sputtering on glass substrates with extraordinarily designed ZnO target. The structural and optical properties of SZO films depended on coating parameter, such as dopant content, in target and substrate temperature. The sputtered SZO films have a preferred crystalline orientation of (002) direction. As amounts of the Ag dopant in the target were increased, the angles of (002) peaks were shifted to lower, indicating that the lattice parameter of SZO film was increased in the c-axis with increasing the amounts of the Ag dopant. Therefore, we can conclude that the big Ag ions (122 pm) were substituted into the Zn+ (72 pm) site in the SZO crystal. As the amounts of the Ag dopant in the target were increased, the crystallinity and the transmittance were decreased, while the substrate temperature decreased. But the crystallinity and the transmittance of SZO films were decreased at 200 °C due to various of composition by Ag ion diffusion. When the SZO films were stoichiometric, the crystallinity and the transmittance increased. The optical band gap was narrowed with increasing Ag contents. This was expected because the change of valence band produced by Ag–O due to the Ag+ was substituted into the Zn+ site.

Acknowledgments

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References


Fig. 5. Oxygen K-edge near-edge X-ray absorption fine structure (NEXAFS) spectra measured from the SZO films with different AgNO3 contents in the target at RT.