Evolution of the structural and optical properties of silver oxide films with different stoichiometries deposited by direct-current magnetron reactive sputtering*

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Nitrogen doping of silver oxide (Ag_xO) film is necessary for its application in transparent conductive film and diodes because intrinsic Ag_xO film is a p-type semiconductor with poor conductivity. In this work, a series of Ag_xO films is deposited on glass substrates by direct-current magnetron reactive sputtering at different flow ratios (FRs) of nitrogen to O_2. Evolutions of the structure, the reflectivity, and the transmissivity of the film are studied by X-ray diffractometry and sphectrophotometry, respectively. The specular transmissivity and the specular reflectivity of the film decreasing with FR increasing can be attributed to the evolution of the phase structure of the film. The nitrogen does not play the role of an acceptor dopant in the film deposition.

Keywords: silver oxide film, nitrogen doping, optical properties, magnetron reactive sputtering

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1. Introduction

The use of a silver oxide (Ag_xO) film as an optical film has a promising future due to its unique optical properties. Büchel *et al.*[1] suggested that an Ag_xO film deposited by magnetron reactive sputtering can be used as a surface-plasmon and surface-enhanced Raman spectroscopy source. Particularly, Ag_xO film has been found to have a promising application in optical and magneto–optical storage since 1992. Previous investigations indicated that Ag_xO contains several phases, namely, AgO, Ag_2O, Ag_3O_4,[2] Ag_4O_3,[3] and Ag_2O_3 phases, of which Ag_2O is the most stable thermodynamically.[4] Owing to different stoichiometries, crystalline phases, and properties arising from different deposition techniques, Ag_xO film has a tunable band gap range between 1.2 eV and 3.4 eV.[4–7] Tominaga[8] first reported that Ag_xO film can act as a CD-R storage material for replacing the traditional organic material. It was suggested that Ag_xO film could also be used as a readout layer in an optical disk or as a mask layer.[9–11] However, lowering the critical thermal decomposition temperature (CTD) of Ag_xO film has been urgently needed for the mass production of the high-density optical and magneto–optical disks. Gao *et al.*[12] recently reported that the single-phased Ag_2O film deposited by direct-current magnetron reactive sputtering (DC sputtering) can lower the CTD to approximately 200 °C.

The optical properties of Ag_xO film have been intensively studied by using different research methods such as reflectance and transmittance spectra,[13–16] spectroscopic ellipsometry, and the single-oscillator model.[17,18] However, only a small amount of information has been reported about the electrical properties of the film. A few reports indicate that Ag_xO film has poor conductivity (10^{-7} S) and is a p-type semiconductor. To facilitate the application of the film to transparent conductive film and diodes, an improvement of its conductivity is urgently needed. The-

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oretically, doping nitrogen to substitute oxygen may improve the conductivity of the film. However, the influence of nitrogen on Ag_xO film is not yet clear. In this work, the effect of nitrogen on the evolution of the microstructural and optical properties of Ag_xO film deposited by DC sputtering using X-ray diffractometry and spectrophotometry is intensively studied. Nitrogen doping is expected to improve the conductivity of Ag_xO film and provide a deep insight into the mechanism.

2. Experimental procedure

A series of Ag_xO films was deposited on glass substrates by DC sputtering at a working pressure of 2.0 Pa and a substrate temperature of 250 °C using different flow ratios (FRs) of nitrogen to O_2. During the film deposition, the sputtering power was maintained at 105 W. The O_2 and Ar flow rates were maintained at 15 sccm and 18 sccm, respectively. Prior to the film preparation, the glass substrate was rinsed sequentially with acetone and alcohol in an ultrasonic bath for 15 min, and then put into an ultrahigh vacuum chamber with a base pressure of below 4×10^{-4} Pa and heated to 300 °C. The film structure was measured by using an X-ray diffractometer (Philips PANA-lytical X'pert) with a CuKα ($\lambda = 1.540598$ nm) as the radiation source. The optical reflectivity and transmissivity of the filns were measured by using an ultraviolet-visible-near infrared spectrophotometer (Shimadzu UV-3150). Atom ratios of N to O, and to Ag in the films were determined by energy dispersive spectrometry (EDS). All the measurements were conducted at room temperature.

3. Results and discussion

Figure 1 shows the X-ray diffraction patterns of the Ag_xO films deposited by DC sputtering at different FR values. Figure 1(a) indicates that the relatively integrated intensity of the Ag_2O (111) diffraction peak first decreases and then increases with the FR increasing from 0.00 to 1.33. The Ag_xO film deposited at the FR = 0.00 is single-phased and the Ag_2O film is polycrystalline. The Ag_2O (111) diffraction peak, however, almost disappears at the FR = 0.67, and the diffraction peak at about 37.80° can be decomposed into an AgO (200) diffraction peak at 37.40° and an Ag_2O (200) diffraction peak at 38.02°, as shown in Fig. 2. Characteristic Ag diffraction peaks begin to appear at the FR =1.33 and become more obvious at the FR = 2.00, indicating that the silver particles from the Ag target are not completely oxidized under a sufficient FR condition. The Ag_xO film deposited at the FR =2.00 is a biphase (Ag_2O + Ag) compound.

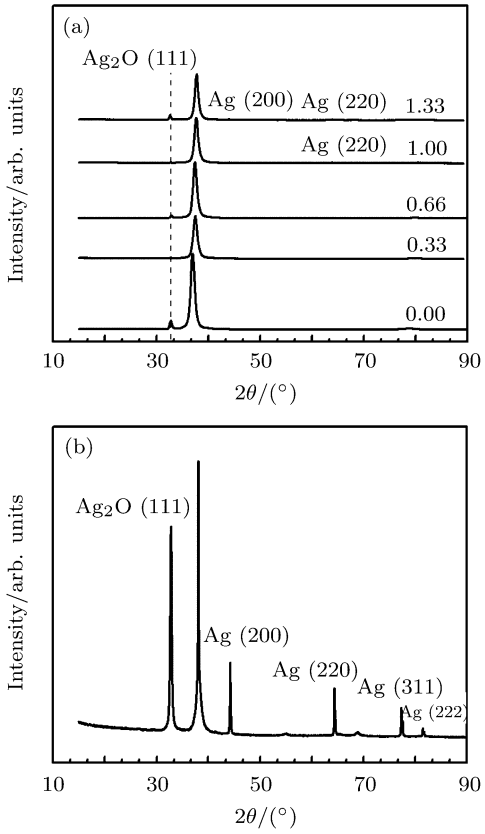


Fig. 1. X-ray diffraction patterns of the Ag_xO films deposited at flow ratios of nitrogen to O_2 of (a) 0.00–1.33 and (b) 2.00, respectively.

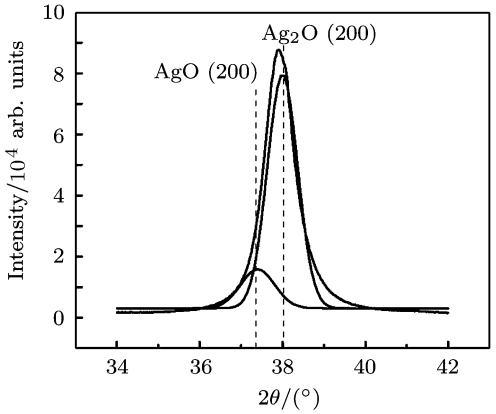


Fig. 2. Gaussian fittings of the observed diffraction peak at 37.80°.

It is observed that the phase structure of the film evolves from single-phase Ag_2O to a biphase complex

of Ag_2O and AgO, and then to a biphase complex of Ag_2O and Ag with FR increasing. However, no diffraction peaks related to nitrogen compounds are discerned. Table 1 presents the EDS results of the Ag_xO films deposited at different FR values. Clearly, no nitrogen atoms are observed in the deposited Ag_xO films. Both the XRD and the EDS results indicate that the nitrogen doping as an acceptor dopant is not realized. In order to further confirm the conclusion, the dark conductivities of the Ag_xO films deposited separately at FR values of 0.33, 0.67, 1.00, and 1.33 were measured using the four-probe method. Their dark conductivities are 6.25×10^{-7} S, 4.17×10^{-7} S, 5.00×10^{-7} S, and 4.00×10^{-7} S, respectively. The low conductivity directly confirms that nitrogen is not doped in the Ag_xO film as an acceptor dopant.

Table 1. EDS analysis results of the Ag_xO films deposited at different flow ratios of nitrogen to O_2.

FR	N/%	O/%	Ag%
0.33	0.00	26.13	73.87
O.67	0.00	34.07	65.93
1.00	0.00	29.08	70.92
1.33	0.00	28.32	71.68
2.00	0.00	24.47	75.53

Figure 3 demonstrates the specular transmissivities of the Ag_xO films deposited at different FR values. The film transmissivity gradually decreases with FR increasing. Especially, the transmissivity is lowered to approximately zero at the FR = 2.00, where no clear interference oscillation is observed. The change in the film transmissivity is inherently attributed to the structural evolution of the film. In addition, a redshift on the film absorption edge occurs with FR increasing. Figure 4 shows the specular reflectivities of the Ag_xO films deposited at different FR values. Similar interference oscillations are also clearly observed in the reflectivity spectra at FR values of below 2.00. The film reflectivity gradually decreases with FR increasing. Especially, the reflectivity is lowered to about zero in the short wavelength region at FR = 2.00. According to Fig. 1, the Ag_xO film deposited at FR = 2.00 is a biphase compound of Ag_2O and Ag. The specular reflectivity of the film at the FR seemingly increases. However, it is different from the measured result in Fig. 4. The difference may be attributed to the specular measurement of the rough film surface rather than the scattered reflection measurement by using the integral sphere.

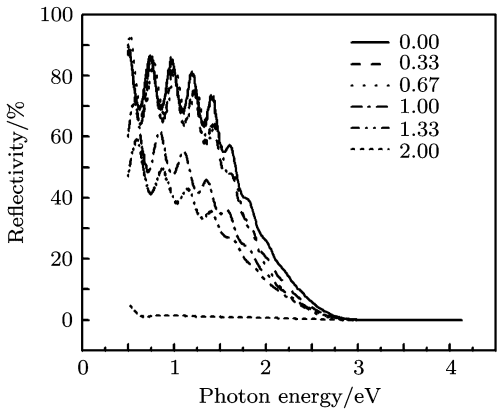


Fig. 3. Specular transmissivities of the Ag_xO films deposited at different flow ratios of nitrogen to O_2.

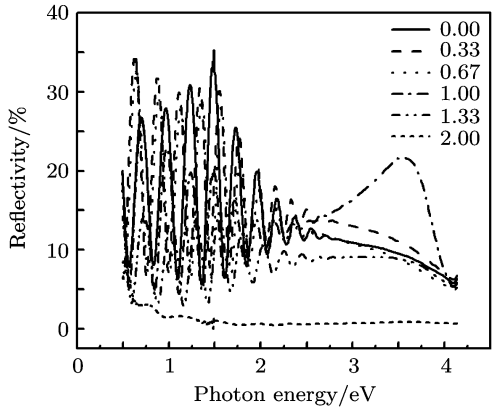


Fig. 4. Specular reflectivities of the Ag_xO films deposited at different flow ratios of nitrogen to O_2.

4. Conclusion

An evolution of the film phase structure, from single-phase Ag_2O to a biphase complex of Ag_2O and AgO, and then to a biphase complex of Ag_2O and Ag, is clearly observed when FR increases. When the FR value is increased, both the specular transmissivity and the specular reflectivity of the deposited Ag_xO films deposited gradually decrease, which can be attributed to the evolution of the film phase structure. The nitrogen does not play the role of an acceptor dopant in the film deposition.

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