Effects of the sputtering power on the crystalline structure and optical properties of the silver oxide films deposited using direct-current reactive magnetron sputtering*

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This paper reports that a series of silver oxide (Ag_xO) films are deposited on glass substrates by direct-current reactive magnetron sputtering at a substrate temperature of 250 °C and an oxygen flux ratio of 15:18 by modifying the sputtering power (SP). The Ag_xO films deposited apparently show a structural evolution from cubic biphased (AgO + Ag_2O) to cubic single-phased (Ag_2O), and to biphased (Ag_2O + AgO) structure. Notably, the cubic single-phased Ag_2O film is deposited at the SP = 105 W and an AgO phase with ⟨220⟩ orientation discerned in the Ag_xO films deposited using the SP > 105 W. The transmissivity and reflectivity of the Ag_xO films in transparent region decrease with the increase the SP, whereas the absorptivity inversely increases with the increase of the SP. These results may be due to the structural evolution and the increasing film thickness. A redshift of the films' absorption edges determined in terms of Tauc formula clearly occurs from 3.1 eV to 2.73 eV with the increase of the SP.

Keywords: Ag_xO film, direct-current reactive magnetron sputtering, x-ray diffraction, optical properties

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1. Introduction

As reported,[1−4] silver oxide (Ag_xO) film has a tuned energy band gap ranging from 1.2 eV–3.4 eV, which is due to different stoichiometries, crystalline phases and properties arising from different deposition techniques. The tuned energy band gap makes the Ag_xO film have a tuned transparent region from near infrared to visible, and to near ultraviolet. The Ag_xO film with these super optical properties has received much attention due to its potential applications for the short-wavelength optical and magneto-optical storage since the 1990s. Fuji *et al.*[5] and Kim *et al.*[6] independently argued that Ag_xO film can be used as a readout layer for the optical disks and as a mask layer for the magneto-optical disks. The thermal decomposition of the Ag_xO film heated by a focused laser to Ag particles is involved in data read-in and read-out process. Gao *et al.*[7,8] previously reported that the deposited Ag_xO film is biphased (AgO + Ag_2O) via direct-current reactive magnetron (RM) sputtering (DC-RM sputtering). The AgO phase is thermodynamically unstable and decomposes to Ag_2O at about 200 °C, whereas the Ag_2O phase is the most thermodynamically stable one among the possible phases of the Ag_xO and decomposes to Ag particles at about 300 °C. Chiu *et al.*[9] also reported that the critical thermal decomposition temperatures (CTDT) of the AgO and Ag_2O phases are approximately 160 °C and 380 °C, respectively.

Ag_xO films can be prepared by chemical-bath deposition,[4] thermal-evapouration combined with glow discharge[1,10] and RM sputtering.[3,7,8,11−15] Of these, DC-RM sputtering is widely used due to the advantage of easy control of the atomic ratio of oxygen. However, as previously reported by Gao *et al.*,[7,8] the Ag_xO film deposited by DC-RM sputtering is usually biphased (AgO + Ag_2O) and single-phased Ag_2O film is difficult to prepare only by increasing the oxygen flux ratio (OFR) (OFR = $[O_2]/[Ar]$). Recently, Gao *et*

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al.[14−18] reported that the cubic single-phased Ag_2O film can be deposited on glass substrate by DC-RM sputtering using the sufficient oxygen technique combined with the substrate heating. The optical properties and the thermal stability of the Ag_2O film were investigated by using ellipsometry and rapidly thermal processing, which indicates that the Ag_2O film has a CTDT of approximately 200 °C. The result shows that the substitute of the Ag_2O film into Ag_xO film may deal with the bottleneck of the application for the optical and magneto-optical disks.

Although the effects of substrate temperature (T_s) and OFR have been intensively studied on the crystalline structure and optical properties of the Ag_xO films, effect of the sputtering power is not reported yet. In this work, a series of Ag_xO films were deposited on glass substrates by DC-RM sputtering using $T_s = 250$ °C and OFR = 15/18 at different sputtering power (SP). The effect of the SP on the film's crystalline structure and optical properties was intensively studied using x-ray diffractometry, energy dispersive spectroscopy (EDS) and spectrophotometry, in order to obtain the optimal SP value for the single-phased Ag_2O film.

2. Experiment

A series of Ag_xO films were deposited on glass substrates by DC-RM sputtering for 30 min at T_s = 250 °C and a working pressure of 2.0 Pa using SP of 55, 65, 85, 105, 120, and 135 W with OFR = 15/18. A high-purity (99.995%) rectangular Ag plate of size 220 mm×80 mm×5 mm was used as the sputtering target. In order to avoid the unfavorable effect on film quality, the glass substrates were rinsed sequentially with acetone and alcohol in an ultrasonic bath for 10 min, and then heated to 300 °C in an ultrahigh vacuum chamber previously evacuated to a base pressure below 4×10^{-4} Pa. The film's structure was measured via x-ray diffractometry (XRD, Philips PANA-lytical X'pert) and cold-field scanning electron microscopy (SEM, JEOL-JSM-6700F). CuKa ($\lambda = 1.540598$ nm) was used as the x-ray source and the XRD spectra measured with grazing angle of 5°. The film's optical reflectivity, transmissivity and absorptivity were measured by ultraviolet-visible-near infrared spectrophotometry (Shimadzu UV-3150).

3. Results and discussion

3.1. Crystalline structure

Figure 1 represents the XRD patterns of the Ag_xO films deposited by using different SP values. Clearly, the Ag_xO films deposited using the SP < 105 W show two diffraction peaks at $2\theta = 32.6°$ and 37.5°, the diffraction peak at 32.6^o arises from the diffraction of the cubic Ag_2O (111) planes, whereas the diffraction peak at 37.5° is apparently asymmetric and is regarded as the superposition of the cubic AgO (200) and Ag_2O (200) diffraction peaks. This indicates that the Ag_xO film deposited using SP < 105 W is biphased (AgO+Ag_2O) and is Ag_2O ⟨111⟩ preferentially oriented. The intensities of the Ag_2O (111) diffraction peak and the diffraction peak at 37.5° increase and decrease, respectively, with the increase of the SP. Note that the intensity of the Ag_2O (111) diffraction peak reaches the maximum value, whereas the diffraction peak at 37.5° completely disappears at SP = 105 W. This indicates that the cubic single-phased Ag_2O film is deposited at the SP = 105 W, which is in good agreement with the EDS of the Ag_xO film deposited using the SP = 105 W as given in Fig. 2.

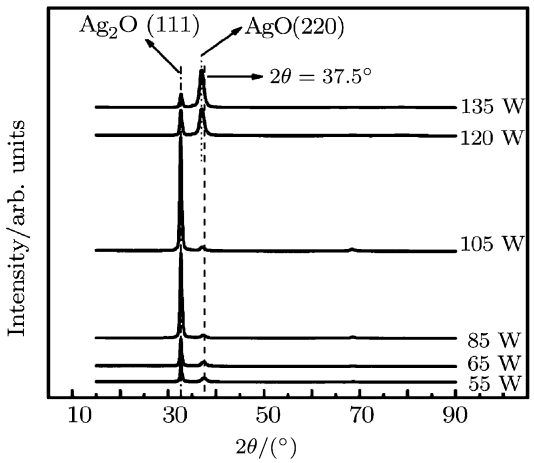


Fig. 1. The XRD patterns of the Ag_xO films deposited using different SP values.

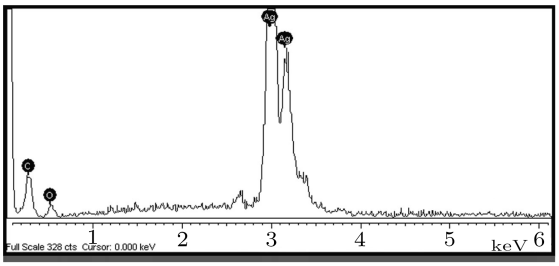


Fig. 2. Energy dispersive spectroscopy of the Ag_xO film deposited using sputtering power of 105 W.

The EDS was obtained using the function attached with the scanning electron microscope (SEM). In SEM measurement, carbon was firstly sprayed on the film surface in order to improve the film's conductive ability and to obtain a clear surface morphology.

Table 1 gives the detailed elemental analysis result of the EDS in Fig. 2. The C element in Table 1 is from the carbon sprayed on the film surface and the O element from both the Ag_xO and the absorptive carbon oxide. Although the atomic ratio of Ag to O is about 1.72 and has a slight deviation from 2, the Ag_xO film deposited at the SP = 105 W is almost single-phased Ag_2O film if the O element from the absorptive carbon oxide is canceled.

Table 1. Detailed elemental analysis result of the energy dispersive spectroscopy for the Ag_xO film deposited using SP of 105 W.

element	weight %	atomic %
C K	8.73	37.14
O K	7.23	23.07
Ag L	84.04	39.79
totals	100.00	100.00

With further increasing the SP, noticeably, an apparent diffraction peak appears at about 37°, which originates from the diffraction of the tetrahedral AgO (220) planes. In addition, the intensity of the Ag_2O (111) diffraction peak begins to clearly decrease, indicating that the Ag_xO film deposited at the SP > 105 W is biphased (Ag_2O + AgO) and has no longer the Ag_2O ⟨111⟩ preferential orientation. Notably, with the SP reaching 135 W, the intensity of the tetrahedral AgO (220) diffraction peak is apparently over that of the Ag_2O (111) diffraction peak, indicating that the Ag_xO film is AgO ⟨220⟩ oriented. The tetrahedral AgO phase is not reported and its formation mechanism is not well understood. The formation of the tetrahedral AgO phases may be attributed to the enhanced surface bombardment and to the increase of film deposition rate.

Figure 3 shows the full width at half maximum (FWHM) of the Ag_2O (111) diffraction peak for the Ag_xO films deposited using different SP values. The film's FWHM apparently decreases firstly and then increases with increasing the SP. The FWHM has a minimum value at SP = 105 W. This indicates that the Ag_xO film is best crystallized at this SP, which coincides with the fact that the single-phased Ag_2O film is deposited at the SP = 105 W. Figure 4 shows the plot of the deposition rate versus SP for the Ag_xO films deposited by using different SP. The film's deposition rate is equal to the ratio of the film thickness to the deposition time of 30 min. The film thickness d was determined in terms of the interference oscillation in the reflectivity spectra using the relation

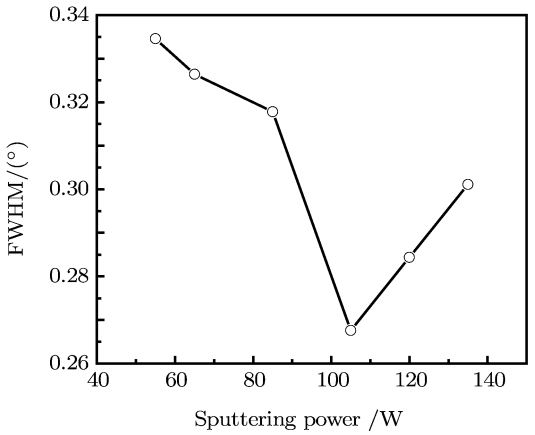


Fig. 3. Full width at half maximum (FWHM) of the Ag_2O (111) diffraction peak for the Ag_xO films deposited by using different SP values.

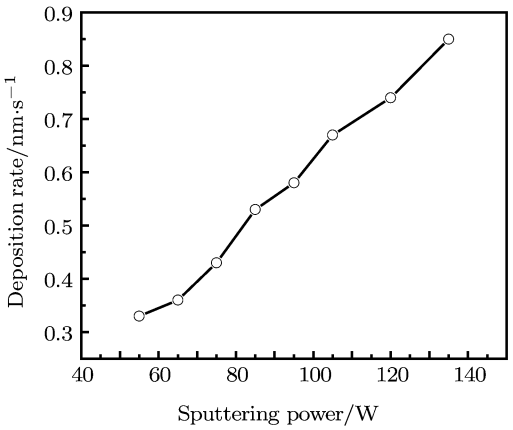


Fig. 4. Plot of the deposition rate versus SP for the Ag_xO films deposited by using different SP values.

$$d = \lambda_1\lambda_2/2(\lambda_1 n_2 - \lambda_2 n_1), \tag{1}$$

where λ_1 and λ_2 denote the wavelengths of the two adjacent interference peaks, n_1 and n_2 denote the refractive indexes, taking the value of 2.51. The film's deposition rate almost linearly increases with the increase of the SP value. Meanwhile, the surface bombardment caused by the ions is enhanced with the increase of the SP, which will deeply affect the film's microstructure and optical properties. Figure 5 shows the average grain size of the Ag_2O phase along ⟨111⟩ orientation as calculated in terms of Scherrer's formula

$$D = 0.9\lambda/(\beta\cos\theta), \tag{2}$$

where λ, β and θ are the x-ray wavelength (λ = 1.540598 nm), FWHM and Bragg diffraction angle,

respectively. Apparently, the D firstly increases and then decreases with the increase the SP. Especially, the D reaches the maximum of approximate 30.6 nm at the SP = 105 W. The D only changes between 24.5 nm and 30.6 nm with the increase of the SP. The change in the D with increase of the SP may be attributed to the enhanced surface bombardment and to the increasing film stress. On the one hand, the increasing film deposition rate can make a larger film stress due to the poor mobility on the film surface, which may restrain the film crystallization and result in the formation of the large-sized grain. On the other hand, the enhanced surface bombardment can favourably help the formation of small-sized grains. The double effects can reasonably explain the change mechanism of the D with the increase of the SP. Notably, the effect of the latter is dominated at the SP $>$ 105 W.

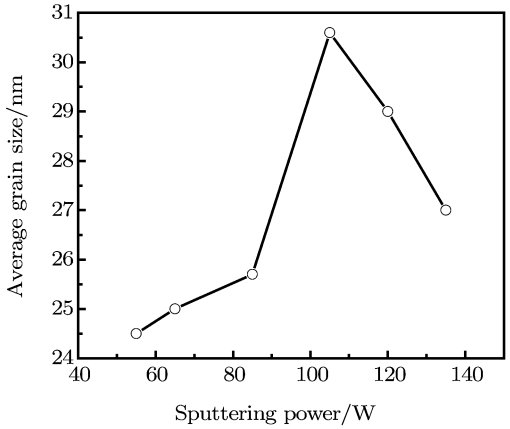


Fig. 5. Average grain size of the Ag_2O phase along ⟨111⟩ orientation as calculated in terms of Scherrer's formula.

3.2. Optical properties

Figure 6 represents the transmissivity spectra of the Ag_xO films deposited by using different SP values. The interference-induced oscillation appears in near infrared region, indicating a good transparency in near infrared region. The transmissivity in transparent region decreases with the increase of the SP, which is attributed to the structural evolution and to the increasing film thickness. Figure 7 represents the reflectivity spectra of the Ag_xO films deposited by using different SP values. The interference-induced oscillation apparently appears in near infrared and visible regions. The oscillation period is much smaller than that in transmissivity spectra, indicating the existence of a rough surface. Figure 8 gives the absorptivity spectra of the Ag_xO films deposited by using different SP values. As shown in Fig. 8, the film's absorptivity obviously increases with the increase of the SP. A redshift of the film's absorption edge clearly occurs from 3.2 eV to 2.75 eV. The transmissivity and reflectivity of the Ag_xO films in transparent region decrease with the increase of the SP value, whereas the absorptivity inversely increases with the increase of the SP.

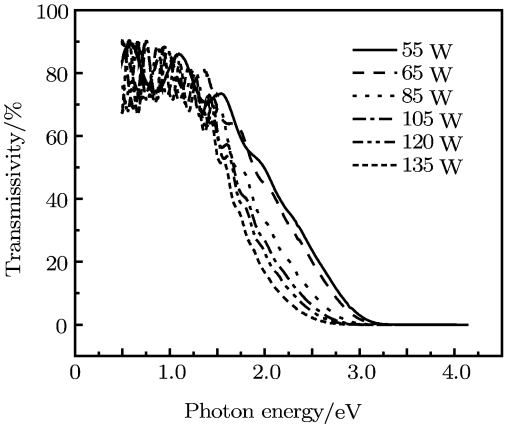


Fig. 6. Transmissivity spectra of the Ag_xO films deposited by using different SP values.

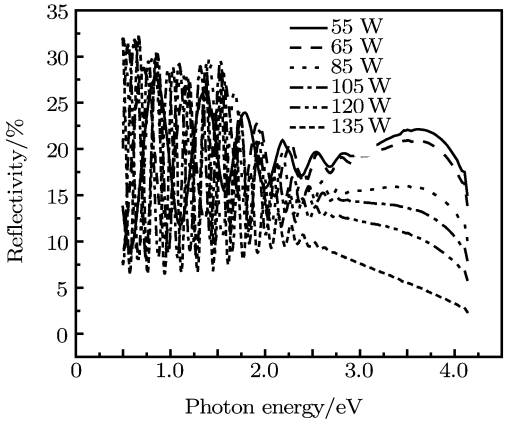


Fig. 7. Reflectivity spectra of the Ag_xO films deposited by using different SP values.

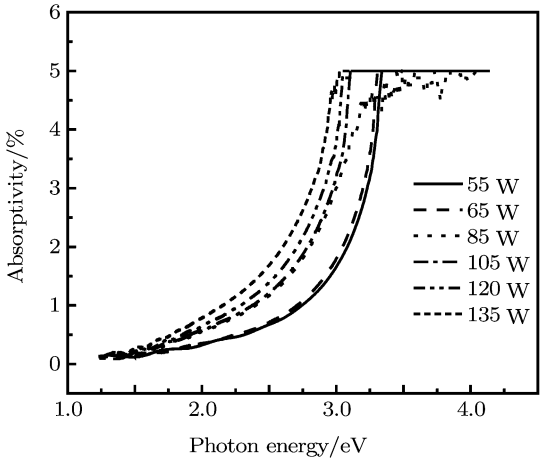


Fig. 8. Absorptivity spectra of the Ag_xO films deposited by using different SP values.

Figure 9 shows the calculated optical band gap ($E_{g,dir}$) of the Ag_xO films deposited by using different SP in terms of Tauc formula

$$(ah\nu)^2 = B(h\nu - E_{g,dir}), \quad (3)$$

where a is the film's absorptive coefficient near absorption edge, B is a structure-related constant, h is Planck's constant, and ν is the frequency of the incident photon. The $E_{g,dir}$ value can be obtained by extrapolating the linear segments of the curves towards the x axis. The a can be extrapolated by using the relation

$$\alpha = (1/d)\ln((1-R)^2/T), \quad (4)$$

where d is the film thickness, T and R are the film's transmissivity and reflectivity, respectively. The film's $E_{g,dir}$ decreases from 3.1 eV to 2.73 eV with the increase of the SP, which is almost in agreement with the absorptive edge determined by using absorptivity spectra. This indicates that the Ag_xO film is a direct-transition optical semiconductor material. In addition, the cubic single-phased Ag_2O film deposited at SP = 105 W has an $E_{g,dir}$ of approximate 2.86 eV,

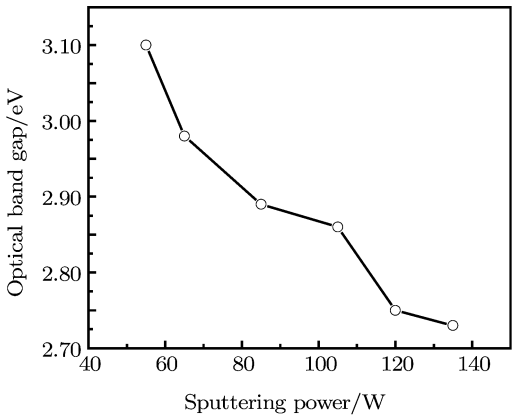


Fig. 9. Calculated optical band gap of the Ag_xO films deposited using different sputtering power in terms of Tauc formula.

slightly larger than that reported by Gao *et al.*,[14] which may be due to the difference in the microstructure of the Ag_2O film deposited by using different process parameters.

4. Conclusion

A series of the Ag_xO films were deposited on glass substrates by DC-sputtering at $T_s = 250$ °C using different SP. The Ag_xO films apparently show a structural evolution from cubic biphased (AgO + Ag_2O) to cubic single-phased (Ag_2O), and to biphased (Ag_2O + AgO) with the increase of the SP from 55 W to 135 W. With the SP < 105 W, the Ag_xO film is cubic biphased (AgO + Ag_2O) and is Ag_2O ⟨111⟩ preferentially oriented. Especially, the cubic single-phased Ag_2O film with ⟨111⟩ preferential orientation is deposited at SP = 105 W. With the SP > 120 W, the Ag_xO film is biphased (Ag_2O + AgO) and is the tetrahedral AgO ⟨220⟩ preferentially oriented. The formation of the tetrahedral AgO phase with ⟨220⟩ orientation is not well understood, which may be attributed to the enhanced surface bombardment and to the increase of film deposition rate. The transmissivity and reflectivity of the Ag_xO films in transparent region decrease with the increase the SP value, whereas the absorptivity inversely increases with the increase the SP. These results may be due to the structural evolution and to the increasing film thickness. A redshift of the film's absorption edge determined in terms of the absorptivity spectra occurs from 3.2 eV to 2.75 eV, which is nearly in agreement with the $E_{g,dir}$ calculated in terms of Tauc formula, indicating that the Ag_xO film deposited is a direct-transition optical semiconductor material. The cubic single-phased Ag_2O film deposited at SP = 105 W has an $E_{g,dir}$ of approximate 2.86 eV, slightly larger than that reported by Gao *et al.*,[14] which may be due to the difference in the microstructure of the Ag_2O film using different process parameters.

References

[1] Rivers S B, Bernhardt G, Wright M W, Frankel D J, Steeves M M and Lad R J 2007 *Thin Solid Films* **515** 8684

[2] Fortin E and Weichman F L 1964 *Phys. Status Solidi* **5** 515

[3] Pierson J F, Wiederkehr D and Billard A 2005 *Thin Solid Films* **478** 196

[4] Varkey A J and Fort A F 1993 *Sol. Energy Matt. Sol. Cells* **29** 253

[5] Fuji H, Tominaga J, Men L, Nakano T, Katayama H and Atoda N 2000 *Jpn. J. Appl. Phys.* **39** 980

[6] Kim J, Fuji H, Yamakama Y, Nakano T, Büchel D, Tominaga J and Atoda N 2001 *Jpn. J. Appl. Phys.* **40** 1634
[7] Gao X Y, Wang S Y, Li J, Zheng Y X, Zhang R J, Zhou P, Yang Y M and Chen L Y 2004 *Thin Solid Films* **455–456** 438
[8] Gao X Y, Liu X W, Wang S Y, Liu Y F, Lin Q G and Lu J X 2008 *Chin. Phys. Lett.* **25** 1449
[9] Chiu Y, Rambabu U, Hsu M H, Shieh H P D, Chen C Y and Lin H H 2003 *J. Appl. Phys.* **94** 1996
[10] Bock F X, Christensen T M, Rivers S B, Doucette L D and Lad R J 2004 *Thin Solid Films* **468** 57
[11] Pierson J F and Rousselot C 2005 *Surf. Coat. Technol.* **200** 276
[12] Barik U K, Srinivasan S, Nagendra C L and Subrahmanyam A 2003 *Thin Solid Films* **429** 129
[13] Qiu J H, Zhou P, Gao X Y, Yu J N, Wang S Y, Li J, Zheng Y X, Yang Y M, Song Q H and Chen L Y 2005 *J. Korean Phys. Soc.* **46** S269
[14] Gao X Y, Feng H L, Ma J M, Zhang Z Y, Lu J X, Chen Y S, Yang S E and Gu J H 2010 *Physica* B **405** 1922
[15] Gao X Y, Feng H L, Zhang Z Y, Ma J M and Lu J X 2010 *Chin. Phys. Lett.* **27** 026804
[16] Gao X Y, Feng H L, Ma J M and Zhang Z Y 2010 *Chin. Phys.* B **19** 090701
[17] Zhang Z Y, Gao X Y, Feng H L, Ma J M and Lu J X 2011 *Acta Phys. Sin.* **60** 016110 (in Chinese)
[18] Zhang Z Y, Gao X Y, Feng H L, Ma J M and Lu J X 2011 *Acta Phys. Sin.* **60** in press (in Chinese)