Effect of substrate temperature on microstructure and optical properties of single-phased Ag_2O film deposited by using radio-frequency reactive magnetron sputtering method*

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Using a radio-frequency reactive magnetron sputtering technique, a series of the single-phased Ag_2O films are deposited in a mixture of oxygen and argon gas with a flow ratio of 2:3 by changing substrate temperature (T_s). Effects of the T_s on the microstructure and optical properties of the films are investigated by using X-ray diffractometry, scanning electron microscopy and spectrophotometry. The single-phased Ag_2O films deposited at values of T_s below 200 °C are (111) preferentially oriented, which may be due to the smallest free energy of the (111) crystalline face. The film crystallization becomes poor as the value of T_s increases from 100 °C to 225 °C. In particular, the Ag_2O film deposited at T_s = 225 °C loses the ⟨111⟩ preferential orientation. Correspondingly, the film surface morphology obviously evolves from a uniform and compact surface structure to a loose and gullied surface structure. With the increase of T_s value, the transmissivity and the reflectivity of the films in the transparent region are gradually reduced, while the absorptivity gradually increases, which may be attributed to an evolution of the crystalline structure and the surface morphology of the films.

Keywords: Ag_2O film, radio-frequency reactive magnetron sputtering, optical properties, microstructure

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1. Introduction

When heated or irradiated by a focused laser beam to a temperature above a critical value, silver oxide (Ag_xO) film can be decomposed into Ag nanoparticles because of its thermodynamic instability. Using the surface plasmon of the produced Ag nanoparticles, the diffraction intensity of the Ag_xO film is strengthened at the short wavelength. Since the 1990s, Ag_xO film has attracted much attention due to its promising applications in optical and magneto-optical disks.[1−4] Fuji *et al.*[1] and Kim *et al.*[3] pointed out that the Ag_xO film could be used as a readout layer in a new near-field optical disk and as a mask layer in a new magneto-optical disk. Using the Ag nanoparticles produced by the thermal decomposition of Ag_xO film can not only produce the near-field light, but also enhance the short-wavelength storage density and the signal-to-noise ratio of optical and magneto-optical disks.

Ag_xO film has a wide range of the energy band gap (1.2 eV–3.4 eV) due to its dependences of stoichiometry, crystalline phase and property on deposition technique.[5−8] The reported forms of Ag_xO include the AgO, Ag_2O, Ag_3O_4, Ag_4O_3 and Ag_2O_3 phases, of which Ag_2O is most stable thermodynamically.[9] The Ag_xO films deposited by magnetron sputtering technique usually are biphased (AgO+Ag_2O).[10,11] The critical values of the thermal decomposition of Ag_2O and AgO phases are near 300 °C and 200 °C, respectively. However, the biphased Ag_xO film cannot be fully decomposed into

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Ag nanoparticles, only when heated to a temperature over 400 °C,[10] which is attributed to the film biphased structure. This has become a bottleneck for the application of the Ag_xO film to optical and magneto-optical storage. Recently, Gao *et al.*[12,13] have successfully prepared the single-phased Ag_2O film by using the direct-current reactive magnetron sputtering method and have intensively studied the thermodynamic instability and the thermal decomposition process of the film by using the rapid thermal processing technique. The critical value of the thermal decomposition temperature for the film is approximately 200 °C.[13] This result is important for the application of the film to optical and magneto-optical storage. In addition, the relationships between microstructure and optical constants and optical properties are also studied by using the spectroscopic ellipsometry and the single-oscillator model.[12,14] The substitution of the biphased Ag_xO film by the single-phased Ag_2O film may effectively cope with the bottleneck in the application of the film to the short-wavelength optical and magneto-optical storages.

Although the effects of the flow rate ratio of oxygen to argon, sputtering power and deposition pressure on the microstructure and the optical properties of the biphased Ag_xO films have been intensively studied,[15–18] the effect of substrate temperature (T_s) on the relevant properties of the single-phased Ag_2O film has not been reported yet. We address the effect of the T_s on the microstructure and the optical properties of the single-phased Ag_2O film deposited by radio-frequency (RF) reactive magnetron sputtering method by using the X-ray diffactometry, scanning electron microscopy and spectrophotometry in hopes of obtaining an optimal value of T_s.

2. Experimental procedure

A group of the single-phased Ag_2O films were deposited on glass substrates by RF reactive magnetron sputtering method at different values of T_s. A mixture of the high-purity (99.99%) oxygen and argon gas with their flow ratio of 2:3 was used as a reactive gas, while a high-purity (99.995%) rectangular silver plate with a size of 220 mm (long) ×80 mm (wide) ×5 mm (thick) was used as a sputtering target. During the deposition, the deposition pressure and the RF deposition power were maintained to be 0.2 Pa and 200 W respectively. The distance between electrode and substrate was 35 mm and the deposition time was 20 min. Prior to the deposition, the glass substrate was rinsed separately with acetone and alcohol in an ultrasonic bath for 10 min, put into an ultrahigh vacuum chamber with a base pressure lower than 6×10^{-4} Pa and then heated to 300 °C sequentially.

The film structure was measured via the X-ray diffractometry (Philips PANA-lytical X'pert) and the cold-field SEM (JEOL-JSM-6700F). Cu Kα (λ = 1.540598 nm) was used as the X-ray source and a grazing angle of 5° was used for the XRD measurements. The optical reflectivity and transmissivity of the films were measured by the ultraviolet–visible–near infrared spectrophotometry (Shimadzu UV-3150). The film thickness was determined by using the spectroscopic ellipsometry and the general oscillator model. All the measurements above were conducted at room temperature.

3. Results and discussion

3.1. Microstructure

Figure 1 shows the X-ray diffraction patterns of the single-phased Ag_2O films deposited at different values of T_s. Clearly, each of the Ag_2O films deposited at the values of $T_s \leq 200$ °C shows a $\langle 111 \rangle$ preferential orientation, which may be due to the smallest surface free energy of its (111) crystalline face. Simultaneously, the film crystallization becomes poor as the value of T_s increases from 100 °C to 225 °C. Notably, the Ag_2O film deposited at $T_s = 225$ °C loses the $\langle 111 \rangle$ preferential orientation.

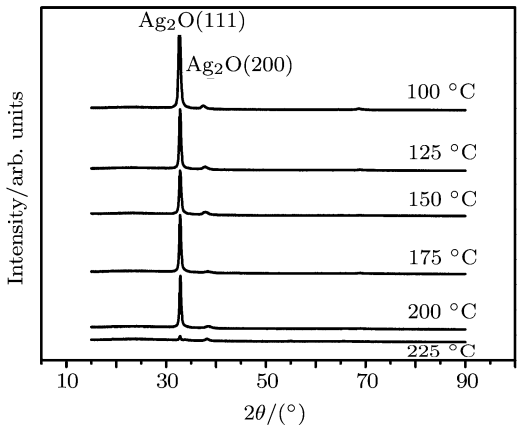


Fig. 1. X-ray diffraction patterns of the Ag_2O films deposited at different substrate temperatures.

Figure 2 indicates both the deviation of 2θ from the standard value of the (111) diffraction peak and

the average grain size along ⟨111⟩ orientation for the deposited Ag_2O films. Clearly, the value of the 2θ deviation first increases and then decreases with the increase of T_s, indicating an obvious transition of the stress from compressive to tensile. Generally speaking, the smaller the 2θ deviation, the better the crystallization is. It seems that the crystallization of the Ag_2O film deposited at $T_s = 225$ °C is best. However, the conclusion is very different from that from the XRD result. Hence, the crystallization quality is not judged in terms of the 2θ deviation alone. The grain size of the film is also an important judgment indicator. The average grain size of the film is calculated in terms of the following Scherrer formula:[19]

$$D = 0.9\lambda/(\beta \cos\theta), \tag{1}$$

where D is the average grain size, λ is the wavelength of incident X-ray (for Cu Kα, $\lambda = 0.154056$ nm), β and θ are the full width at half maximum of the intensity and Bragg angle, respectively. Clearly, with the value of T_s increasing, the average grain size along ⟨111⟩ orientation largely increases from 17.79 nm to 30.60 nm. The result indicates that the grain ingredient (i.e. the crystallinity) reduces with T_s increasing even though the average grain size along ⟨111⟩ orientation increases considerably. This results in the fact that the diffraction of the (111) crystalline face of the Ag_2O film deposited at $T_s = 100$ °C is the strongest and that the film crystallization becomes poor as T_s increases.

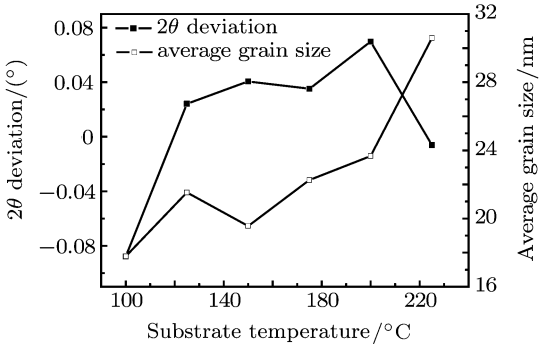


Fig. 2. Deviations of 2θ from the standard value of the (111) diffraction peak and the average grain size along ⟨111⟩ orientation for the deposited Ag_2O films.

Figure 3 shows the surface morphologies of the single-phased Ag_2O films deposited at different values of T_s. The film surface morphology obviously evolves from a uniform and compact surface structure to a loose and gullied surface structure. The evolution of the film surface structure may be attributed to both the increase in the mobility of the atoms or molecules in the film surface and the probability of the escaping from substratum surface as T_s increases. This can well explain the result that the Ag_2O film deposited at $T_s = 225$ °C shows an obviously loose and gullied surface without the ⟨111⟩ preferential orientation.

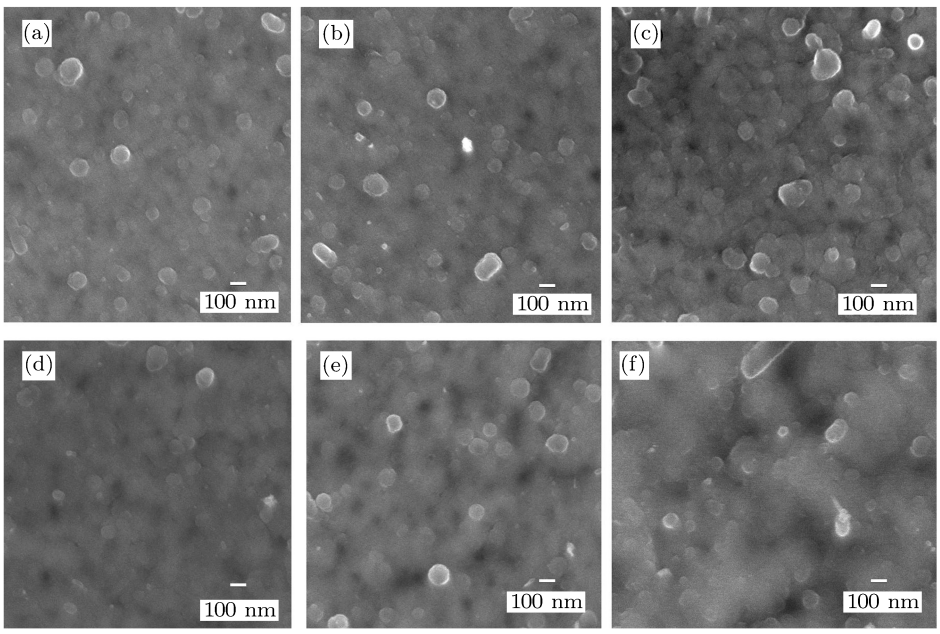


Fig. 3. Surface morphologies of the single-phased Ag_2O films deposited at substrate temperatures of (a) 100 °C, (b) 125 °C, (c) 150 °C, (d) 175 °C, (e) 200 °C, (f) 225 °C.

3.2. Optical properties

Figure 4 exhibits the absorptivity spectra of the Ag_2O films deposited at different T_s values. It is noted that a red shift of the film absorption edge (i.e. from 3.5 eV to 2.4 eV) clearly takes place with T_s increasing. And the film absorptivity increases as T_s increases.

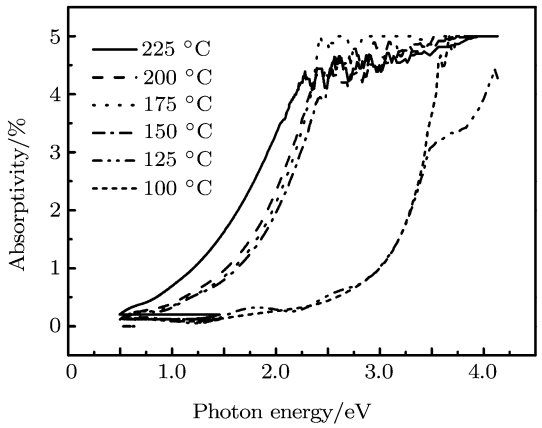


Fig. 4. Absorptivity spectra of the Ag_2O films deposited at different substrate temperatures.

Figures 5 and 6 show the reflectivity and transmissivity spectra of the films, respectively. Clearly,

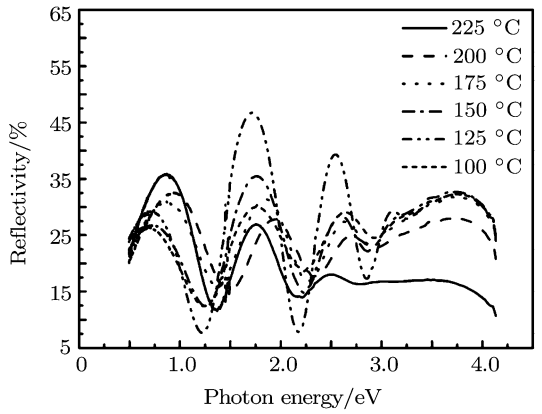


Fig. 5. Reflectivity spectra of the Ag_2O films deposited at different substrate temperatures.

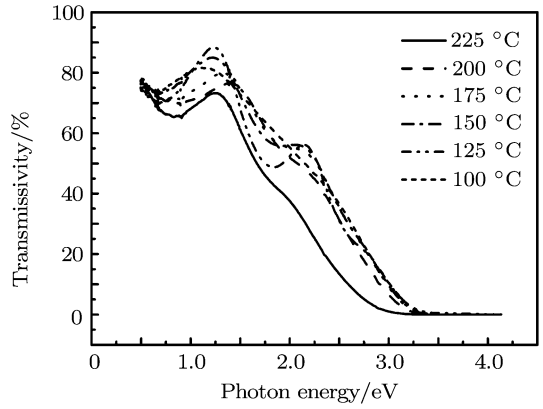


Fig. 6. Transmissivity spectra of the Ag_2O films deposited at different substrate temperatures.

the specular reflectivity and transmissivity in the transparent region gradually decrease with the increase of T_s, indicating the increasing surface roughness and the enhanced absorption in the transparent region. The enhanced absorption essentially arises from the evolution of the film microstructure.

Figure 7 is the fitted optical energy gap of the deposited Ag_2O films in terms of the following Tauc formula:

$$(ah\nu)^2 = B(h\nu - E_{g,opt}), \tag{2}$$

where a and $E_{g,opt}$ denote the absorption coefficient and the optical energy gap of the film, respectively; $h\nu$ and B are the incident photon energy and the film structure-dependent constant, respectively; the a near the absorption edge can be given by the following equation:

$$a = 1/d \ln((1-R)^2/T), \tag{3}$$

with R, T and d denoting the optical reflectivity, transmissivity and thickness of the film, respectively. The film thicknesses fitted by using the spectroscopic ellipsometry and the general oscillator model are 195.6 nm, 211.4 nm, 226.3 nm, 140.9 nm, 136.8 nm and 149.1 nm at substrate temperatures of 100 °C, 125 °C, 150 °C, 175 °C, 200 °C and 225 °C respectively. Clearly, the film thickness largely increases (below 150 °C) and then decreases (above 150 °C) with T_s increasing. This changing trend can be explained by considering the effect of T_s on the molecule nucleation density: because the changing trend of the molecule nucleation density with the increase of T_s according to the nucleation thermodynamic theory[20] is similar to that of the film thickness.

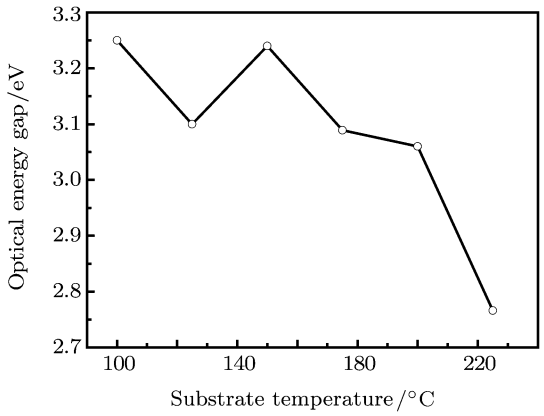


Fig. 7. Fitted optical energy gaps of the deposited Ag_2O films by the Tauc formula.

As seen from Fig. 7, the film $E_{g,opt}$ fitted by Eqs. (2) and (3) largely decreases from 3.25 eV to 2.77 eV as T_s increases. The result basically accords with the absorptivity result, indicating that the Ag_2O film is a direct and wide energy gap material. The deposited Ag_2O films each have a wide energy gap range, which is due to the different microstructures (i.e. different stoichiometries, crystalline phases and properties arising from different deposition parameters).

4. Conclusion

The preferentially $\langle 111 \rangle$ oriented Ag_2O films are deposited on glass substrates by RF-sputtering technique at $T_s \leq 200$ °C, which is attributed to the smallest surface free energy of the film (111) crystalline face. The film crystallization becomes poor with the T_s increasing, especially, the Ag_2O film deposited at $T_s = 225$ °C, loses the $\langle 111 \rangle$ preferential orientation. The film grain ingredient (i.e. the crystallinity) reduces with the increase of T_s even though the film average grain size along the $\langle 111 \rangle$ orientation considerably increases from 17.79 nm to 30.60 nm, which results in the poor crystallization. A well-crystallized Ag_2O film is prepared preferably at lower T_s, while a polycrystalline Ag_2O film is easy to prepare at high T_s. The crystallization quality of the film is not judged by 2θ deviation alone. The average grain size is also an important judgment indicator. The transmissivity and the reflectivity in the transparent region gradually reduce, while the absorptivity gradually increases as T_s increases from 100 °C to 225 °C , which may be attributed to the evolution of the crystalline structure and the surface morphology from a uniform and compact surface structure to a loose and gullied surface structure. The film $E_{g,opt}$ fitted in terms of the Tauc formula largely decreases from 3.25 eV to 2.77 eV with T_s increasing. The result is in agreement with the absorptivity result, indicating that the Ag_2O film is a direct and wide energy gap material.

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