Spectroscopic ellipsometric study of the optical properties of Ag_2O film prepared by direct-current magnetron reactive sputtering*

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The Ag_2O film, as-deposited by direct-current magnetron reactive sputtering at a substrate temperature of 150 °C, clearly shows a preferential orientation (111), and is capable of lowering the threshold value of the thermal decomposition temperature to about 200 °C, which is helpful to its application in optical and magneto-optical storage. This paper fits its optical constants in terms of a general oscillator model by using measured ellipsometric parameters. The fitted oscillator energy 2.487 eV is close to the optical direct interband transition energy value of the Ag_2O film determined by Tauc equation; whereas, the fitted oscillator energy 4.249 eV is far from the fitted plasma oscillator energy 4.756 eV by single-oscillator energy. The photoluminescence spectrum centred at about 2.31 eV indicates a direct-energy gap photoluminescence mechanism of the Ag_2O film.

Keywords: Ag_2O film, spectroscopic ellipsometry, general oscillator model, single-oscillator model
PACC: 0760F, 7865P, 4270Q, 3360F

1. Introduction

Silver oxide ($Ag_\chi O$) films have attracted much interest due to their unique physical properties.[1−4] In particular, since the 1990s, $Ag_\chi O$ films have been widely studied due to their potential application in optical and magneto-optical storage. As previously reported,[2,5,6] the $Ag_\chi O$ film could act as a readout layer for a new optical disk or a mask layer for a new magneto-optical disk owing to its thermal instability. Radiated by a focused laser, $Ag_\chi O$ film is able to rapidly decompose into silver particles and oxygen. The produced Ag particles aggregate and produce a metallic probe as a non-transparent aperture, where near-field light is produced. Near-field light reduces the spot size and increases the storage density of optical and magneto-optical disks. Conversely, the produced silver particles enhance the signal-to-noise ratio of new optical and magneto-optical disks subsequent to scattering by the silver particle. Whether applied to optical or magneto-optical storage, the decomposition reaction to create silver particles is involved in the data read-in and read-out process. In addition, Peyser *et al.*[7] reported dynamic fluorescence from individual silver nano-clusters in a very thin silver oxide film structure indicating that $Ag_\chi O$ film was able to act as a storage material.

The $Ag_\chi O$ films can be prepared by chemical-bath deposition,[3] thermal-evapouration combined with glow discharge,[8] and magnetron reactive sputtering.[9−11] Among the film deposition techniques, magnetron reactive sputtering with a silver target and a gas mixture of argon and oxygen is widely used with the advantage of easily controlling the composition ratio of oxygen. However, a threshold value of the thermal decomposition temperature (TDT) of approximately 400 °C for $Ag_\chi O$ films has been a potential bottleneck for large-scale applications in optical and magneto-optical storage. As previously reported,[9] the $Ag_\chi O$ film as-deposited by direct-current magnetron reactive sputtering (DC-sputtering) at room temperature demonstrated an amorphous composite structure composed of Ag_2O and AgO. The TDT of the AgO and the Ag_2O phases was approximately 200 °C and 300 °C, respectively. Chiu *et al.*[6] also reported that AgO began to decompose into Ag_2O and O_2 at approximately 160 °C, while Ag_2O began to decompose into Ag clusters and

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O_2 at approximately 380 °C. The higher TDT may be attributable to the coexistence of the AgO and Ag_2O phases in the as-deposited $Ag_\chi O$ film. An Ag_2O film may sharply lower the TDT.

Although the optical properties of the $Ag_\chi O$ film composed of AgO and Ag_2O has been intensively studied,[9−12] the optical properties of an Ag_2O film has not been reported because the Ag_2O film is difficult to prepare by DC-sputtering. In this work, the optical constants of the Ag_2O film deposited by DC-sputtering at a substrate temperature of 150 °C were fitted in terms of the general oscillator model (a model combined with three Gaussian oscillator models) by using the measured ellipsometric spectra to extract the information on the interband transitions. Additional analysis of the photoluminescence (PL) spectrum was used to verify the results obtained by spectroscopic ellipsometry (SE). In addition, the TDT of the Ag_2O film was determined by x-ray diffractometry of the annealed Ag_2O film by rapid thermal processing (RTP) at 200 °C and 250 °C for 5 min.

2. Experiments

The Ag_2O film was deposited on a glass substrate by using a DC-sputtering technique at a substrate temperature of 150 °C under a mixture of argon and oxygen (both of 99.99 % purity). Before film deposition, the glass substrate was rinsed sequentially with acetone and alcohol in an ultrasonic bath for 10 min, and was subsequently put into an ultrahigh vacuum chamber previously evacuated to a base pressure below 4×10^{-4} Pa and heated to 300 °C. During film deposition, a working pressure of 1.5 Pa and an oxygen flux ratio of 0.5 were maintained, respectively. After film deposition, the film SE parameters sensitive to surface properties were measured in time by variable-angle spectroscopic ellipsometry (J.A. Woollam), even though Ag_2O film is stable at room temperature. The film thickness was about 1290.804 nm as fitted by SE, near the film thickness value of approximately 1300 nm calculated by reflectance spectra. The film optical constants were acquired in terms of general oscillator model by using the measured SE parameters. The film crystalline structure was characterised by x-ray diffractometry (Philips PANA-lytical X'pert). All the measurements were conducted at room temperature.

3. Results and discussion

Advantages of using a rotating-compensator ellipsometer vs a rotating-polariser (analyser) ellipsometer include the following abilities to assess: (i) the degree of polarisation of the light reflected from samples; (ii) the full range ($0 < \Delta < 360°$) of ellipsometric parameters. The ability to estimate the degree of polarisation is particularly important when a high degree of surface roughness induces light scattering upon light reflection because light scattering changes ellipsometric spectra significantly if the degree of polarisation is not taken properly into account. In terms of the two-layer model, the surface roughness, film thickness, and film optical constants were extracted from measured SE spectra.

3.1. Structural properties

Figure 1 illustrates the x-ray diffraction pattern of the Ag_2O film as-deposited. As observed in Fig. 1, the Ag_2O film demonstrated a sharp and strong Ag_2O-(111) diffraction peak and two weak Ag_2O-(220) and (311) diffraction peaks. Clearly, the Ag_2O film was (111) oriented. Figure 2 demonstrates the Ag $3d_{5/2}$ x-ray photoelectron spectroscopy (XPS) of the Ag_2O film as-deposited. The Ag $3d_{5/2}$ XPS peak was decomposed into two peaks for Ag_2O and AgO, respectively. The content ratio of Ag_2O and AgO in the Ag_2O film as-deposited was approximately 94:6 as determined by the ratio of these two integrated peak intensities. The XPS confirmed that the as-deposited film sample as-deposited was Ag_2O film, which was in good agreement with x-ray diffraction result. To determine the TDT, the Ag_2O film as-deposited was annealed by RTP at 200 °C and 250 °C for 5 min under a protection of high-purity nitrogen. The sketch of the thermal processor was described elsewhere.[13] The RTP can shorten the solid-phase recrystallization time up to several minutes in comparison with traditional furnace annealing. The quantum-optical effect is generally argued to play an important role in addition to a thermal effect.[14] Figure 3 demonstrates the x-ray diffraction patterns of the annealed Ag_2O film by RTP. Clearly, the Ag_2O film annealed at 200 °C began to exhibit Ag characteristic diffraction peak, while the annealed Ag_2O film at 250 °C exhibited strong Ag diffraction peaks. As verified by Fig. 3, the as-deposited Ag_2O film was able to effectively lower the TDT to approximately 200 °C, which was important

to its application in optical and magneto-optical storage.

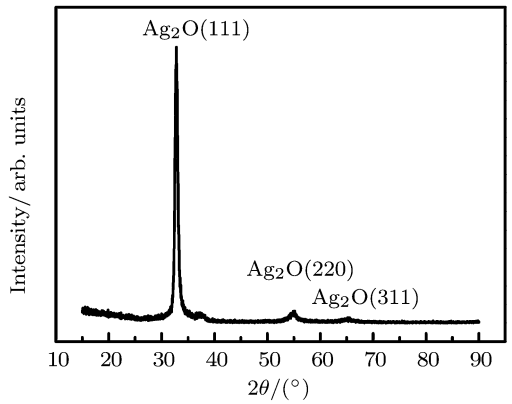


Fig. 1. The x-ray diffraction pattern of the as-deposited Ag_2O film.

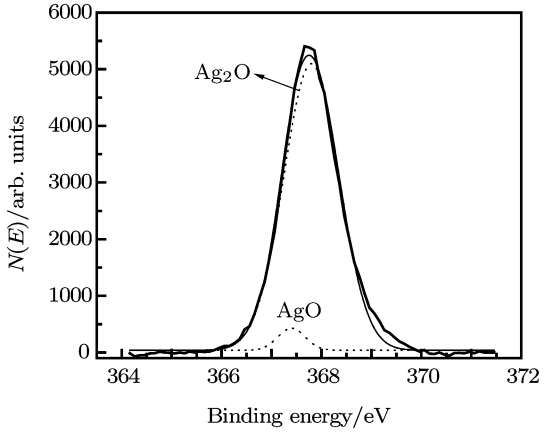


Fig. 2. The Ag $3d_{5/2}$ x-ray photoelectron spectroscopy of the as-deposited Ag_2O film.

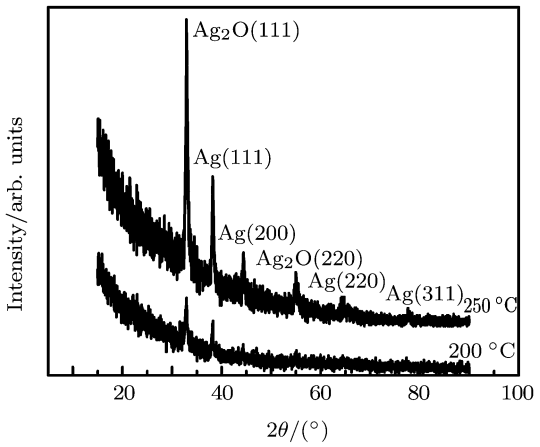


Fig. 3. The x-ray diffraction pattern of the annealed Ag_2O film by RTP.

3.2. Optical properties

The optical constants of the as-deposited Ag_2O film were fitted in terms of the general oscillator model by using SE spectra. In the SE measurement, the SE parameters Ψ and Δ, related to the film optical and structural properties, are defined as[15–17]

$$\rho = \tan(\Psi)\exp(\mathrm{i}\,\Delta) = R_\mathrm{p}/R_\mathrm{s}, \tag{1}$$

where R_p and R_s are complex reflection coefficients of polarised light parallel and perpendicular to the plane of incidence, respectively. In the SE analysis, the modeling parameters of interest, i.e., optical constants and layer thickness, were varied to achieve the best fit between calculated and experimental SE parameters by minimizing the weighted estimator below 5%. The measured SE spectra were analysed by a two-layer model to extract the optical constants of the as-deposited Ag_2O film because there always exists surface roughness layer. The used two-layer model is shown in Fig. 4.[18]

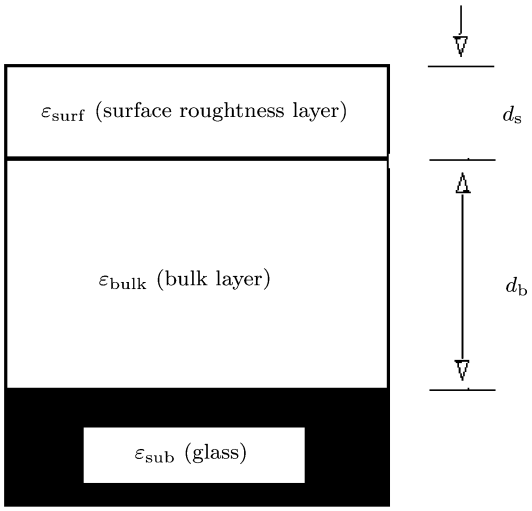


Fig. 4. Sketch of the two-layer model used in SE analysis.

In the two-layer model, the surface roughness layer was assumed to be composed of 50% Ag_2O particles and 50% voids. The dielectric function, $\varepsilon_\mathrm{surf}$, is calculated in terms of the Bruggerman effective medium approximation (EMA) model due to the best fit in surface roughness.[19] The dielectric function of the glass substrate, ε_sub, was previously fitted according to the measured SE spectra of the glass substrate. Although the Caughy and Sellmeier models were used to analyse the $Ag_\chi O$ film and obtained a better fit, the unknown and hidden information related to optical origin was difficult to obtain by Caughy and Sellmeier models alone. Hence, the unknown dielectric functions of the Ag_2O film were analysed by general

oscillator model due to the strong interference oscillation. The general oscillator model is described as

$$\varepsilon_{\rm n} = \varepsilon_{\rm n1} + {\rm i}\,\varepsilon_{\rm n2}, \tag{2}$$

$$\varepsilon_{\rm n1} = 2P/\pi \int_0^{\infty} \zeta\varepsilon_{\rm n2}(\zeta)/(\zeta^2 - E^2){\rm d}\xi, \tag{3}$$

$$\varepsilon_{\rm n2} = A_{\rm n}(\exp(-((E - E_{\rm n})/\sigma)^2) - \exp(-((E + E_{\rm n})/\sigma)^2),$$

$$\sigma = B_{rn}/(2\sqrt{\ln 2}), \tag{4}$$

where P is the Cauchy principal part of the integral, $E_{\rm n}$ is the optical transition energy at a given energy position, $A_{\rm n}$ is another fitting constant, and $B_{\rm rn}$ is the spectral broadening parameter. In order to express a total film thickness, we define a film mass thickness, $d_{\rm f}$. The value of $d_{\rm f}$ in the two-layer model is calculated by $d_{\rm b} + 0.5d_{\rm s}$ because a frequency of 50 vol.% of voids is assumed for $d_{\rm s}$ in the SE analysis. In the SE measurement, a high-accuracy mode is chosen to avoid the influence of the inhomogeneity with thickness on fitted result. Additionally, two incident angles of 60° and 70° are used to avoid the influence of structure anisotropism on the fitted result. In addition, the backside of the glass substrate is sanded in order to avoid backside reflectance. The SE parameters with high reliability are finally acquired by using these measurement methods. Figure 5 shows the measured and calculated SE parameters of the Ag_2O film as-deposited at an incident angle of 70° and 60°, respectively.

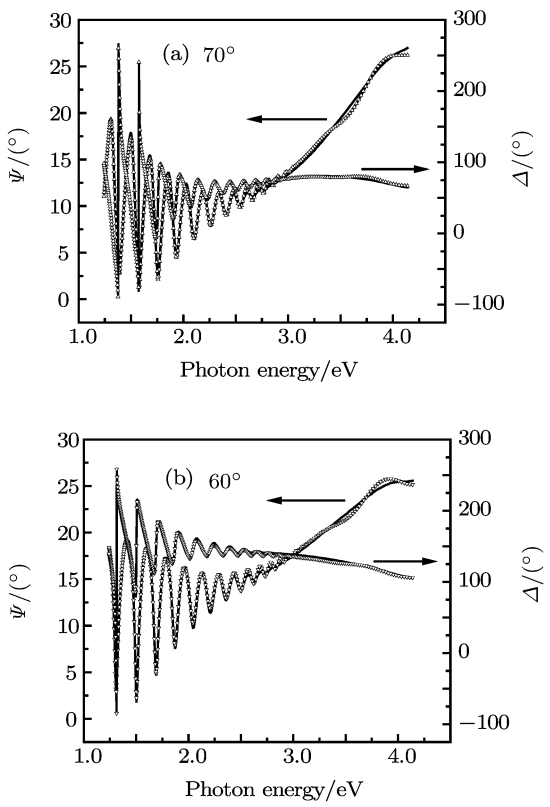


Fig. 5. Measured and calculated SE parameters of the as-deposited Ag_2O film at an incident angle of (a) 70°, (b) 60°, respectively. The symbols and the solid line indicate the fit obtained in the analysis using the two-layer model.

The symbols and the solid line indicate the fit obtained in the analysis using the two-layer model. The weighted estimator is 3.85%. Clearly, the fitted SE parameters agree quite well with the measured results. The fitted surface roughness thickness is 21.405 nm and the bulk layer thickness 1280.101 nm. The total film thickness is 1290.804 nm, near the film thickness value of approximately 1300 nm calculated by reflectance spectra. Fitted parameters used in the general oscillator model for the Ag_2O film as-deposited are listed in Table 1.

Table 1. Fitted parameters used in the General Oscillator model for the as-deposited Ag_2O.

oscillator number	$A_{\rm n}$/eV	$E_{\rm n}$/eV	$B_{\rm rn}$/eV
1	0.359	2.487	1.285
2	10.77	3.678	0.418
3	8.958	4.249	1.221

The oscillator energy of approximately 2.487 eV may correspond to the interband transition energy of the as-deposited Ag_2O film. The parametric model used here provides an explanation of some possible optical origins of the spectral feature of the dielectric function. However, as observed from the data in Table 1, the oscillator having 4.249 eV lies beyond the limits of the experimental range. Hence, there is still some uncertainty in estimating the energy band structure of the Ag_2O film by data simulation alone. In order to estimate the energy band structure of the Ag_2O film, single-oscillator model suggested by Wemple and DiDomenico is used to describe the hidden optical origin and mechanism by defining a 'dispersion-energy' parameter $E_{\rm d}$. In terms of single-oscillator model, the dispersion function in visible region[20] is formalized as

$$n^2 - 1 = E_0E_{\rm d}/(E_0^2 - E^2), \tag{5}$$

where n is refractive index, E is the photon energy, E_0 and $E_{\rm d}$ are the single oscillator energy and dispersive energy, respectively. The E_0 and $E_{\rm d}$ have a significant association with the crystalline structure and ionicity of ionic or covalent oxide materials. Figure 6 demonstrates the plot of refractive-index factor $1/(n^2 - 1)$

versus E^2 for the as-deposited Ag_2O film.

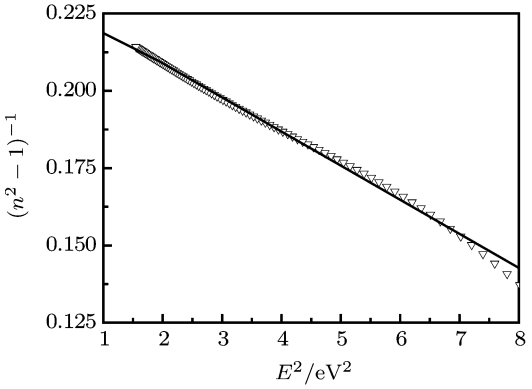


Fig. 6. Plot of refractive-index factor $1/(n^2-1)$ versus E^2 for the Ag_2O film.

The refractive index data was from the SE fitting. The resulting straight line then yields value of the parameters E_0 and E_d of 4.57 eV and 19.8 eV, respectively. In addition, in terms of single oscillator model, the band gap parameter E_a introduced by Hopfield[21] provides the connection between the single-oscillator parameters (E_0, E_d) and the Phillips static-dielectric constant parameters (E_g, $h\omega_p$), i.e

$$E_0 \cdot E_a = E_g^2,$$
$$E_a \cdot E_d = (\hbar\omega_p)^2. \quad (6)$$

The band gap parameter E_a and plasma oscillator energy $\hbar\omega_p$ calculated are 1.143 eV and 4.756 eV, respectively. Clearly, the second and third oscillator energy of 3.678 and 4.249 eV have a big difference from the fitted plasma oscillator energy $\hbar\omega_p$, which may arise from the insufficiency of the general oscillator model to explain the optical origin alone. Figure 7 illustrates the refractive index and extinctive coefficient of the as-deposited Ag_2O film.

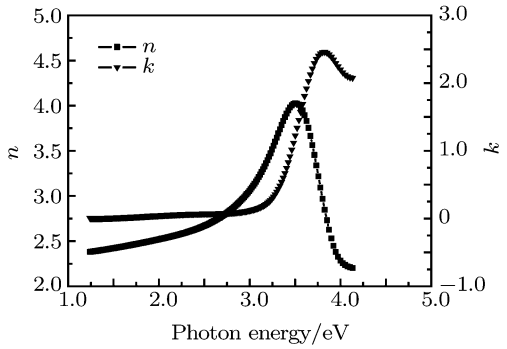


Fig. 7. Refractive index and extinctive coefficient of the Ag_2O film.

Clearly, the refractive index and extinctive coefficient monotonically change until a value of 2.48 eV is reached, implying the existence of an absorption mechanism near 2.48 eV. In particular, the refractive index and extinctive coefficient values at 1.96 eV are approximately 2.51 and 0.05, respectively, which is in agreement with that for Ag_2O film reported by Schmidt.[22]

In order to accurately provide insights on the optical properties of the Ag_2O film, the absorption coefficient spectra is presented in Fig. 8. The inset demonstrates the relationship of $(ahv)^2$ vs. the photon energy for the as-deposited Ag_2O film. The linear section shown in the curve indicates the allowed direct inter-band transition at approximately 2.35 eV, the value is close to the result of 2.487 eV given in Table 1.

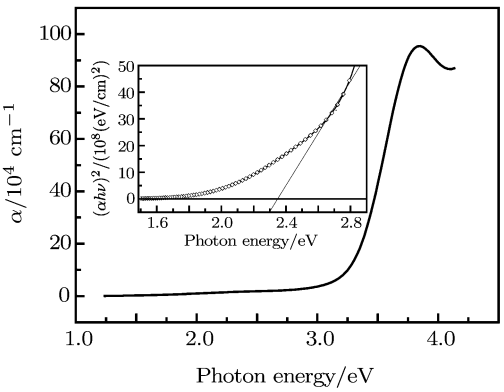


Fig. 8. Absorption coefficient spectra of the as-deposited Ag_2O film. The inset shows the relationship of $(\alpha h\nu)^2$ vs. the photon energy for the Ag_2O film

Figure 9 shows the PL spectrum of the as-deposited Ag_2O film. As observed in Fig. 9, a strong PL peak centred at approximately 2.31 eV appears which nearly agrees with the direct interband transition value mentioned above, indicating a direct-energy gap PL mechanism of the Ag_2O film.

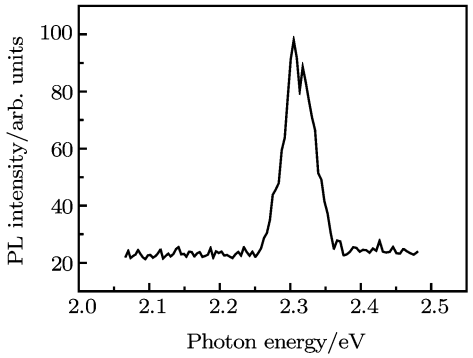


Fig. 9. PL spectrum for the as-deposited Ag_2O film.

4. Conclusions

Ag_2O film is prepared on a glass substrate by DC-sputtering at a substrate temperature of 150 °C. The annealing experiment by RTP indicates that the Ag_2O film is capable of lowering the TDT to approximately 200 °C. The optical properties of the Ag_2O film are studied by analysing the SE data with the general oscillator model. Through the analysis of absorption coefficient spectra, the Ag_2O film indicates direct interband transition structures at approximately 2.35 eV, which is very close to the value resulting from Gaussian analysis. The fitted oscillator energy of 4.249 eV is far from the plasma oscillator energy of 4.756 eV by single-oscillator model. In addition, it is concluded that the PL is related to the direct energy gap of the Ag_2O film.

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