

Optical properties of δ -Bi₂O₃ thin films grown by reactive sputtering

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The optical properties of δ -Bi₂O₃ thin films were investigated using spectroscopic ellipsometry and optical absorption spectrum. δ -Bi₂O₃ thin films were grown on Si and quartz substrates under different oxygen flow ratios (OFR) by radio frequency reactive magnetron sputtering. The Tauc-Lorentz dispersion method was adopted to model the optical dispersion functions of the thin films. The optical bandgap was obtained by three different methods. It was found that refractive index and extinction coefficient decrease, and the optical bandgap has a slight blue shift with increasing the OFR. Factors influencing the optical constants and optical bandgap are discussed.
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The interest in the bismuth oxide (Bi₂O₃) is mainly motivated by its excellent optical properties such as large energy band gap, high refractive index and dielectric permittivity as well as remarkable third-order optical nonlinear properties, ion conductivity and photoluminescence,¹⁻⁵ and by its potential applications in the fields such as optical communication devices, optoelectronics, optical coatings, oxide electrolyte fuel cell, and gas sensors.⁶⁻⁸

Bismuth oxide has five main polymorphic forms that are known as: α , β , γ , δ ⁸ and ω -Bi₂O₃ phase.⁹ Each polymorph possesses distinct crystalline structure and properties. Most previous studies of the optical properties have focused primarily on the α -Bi₂O₃ phase due to its stability at low temperature.^{1,2,10} The δ -Bi₂O₃, one of the best oxygen ion conductors, is stable only between 729 °C and 825 °C (the melting point of bismuth oxide), and could be stabilized to room temperature (RT) by doping with different transition metal oxides or rare earth oxides. The pure δ -Bi₂O₃ thin films have not been obtained at RT for a long time. The electric properties of the doped δ -Bi₂O₃ have been investigated intensively for many years,^{8,11,12} but up to now only few studies concerning the optical properties of the δ -Bi₂O₃ have been reported.¹³

In this paper, we report the study of the optical properties of the δ -Bi₂O₃ thin films prepared by radio frequency (rf) reactive sputtering at various O₂ flow ratios (OFRs).

The substrates used to grow the thin films were Si (100) slices and quartz glass. Bi targets with the purity of 99.99% were used as the starting materials. The chamber was firstly pumped down to a pressure better than 5×10^{-5} Pa, and then the working gas, mixture of Ar (5N) and O₂ (5N), was introduced into the chamber until the pressure stabilized at 0.5 Pa. The sputtering was carried out with the power of 30 W for 30 min at substrates temperature of 200 °C. The OFR [=O₂/(O₂+Ar)] in the gas mixture was 5%, 10%, and 20%, respectively, by adjusting the relative flux of oxygen and argon.

Figure 1(a) shows the XRD (θ - θ scan, Philips X'Pert Pro MPD, Cu K α radiation) patterns of the thin films on Si (100) substrate deposited at different OFRs. One can see that the

diffraction peaks for these three samples situate at the same position and can be indexed as δ -Bi₂O₃ except the change of the peak intensities. The decrease in the diffraction intensity with OFR is probably due to the decrease in the thickness of the thin films derived from the different sputtering rates at various OFRs. δ -Bi₂O₃ has a defective-fluorite structure with a very high level of deficiency in oxygen sublattice.¹⁴ Crystals with the fluorite structure of space group Fm3m (O_h^5) are characterized by a simple vibrational structure with only one Raman active phonon of T_{2g} symmetry at $k=0$.¹⁵ The laser Raman spectra ($\lambda=514.5$ nm) of the thin films are shown in Fig. 1(b). Indeed, there is only one wide peak at 618 cm⁻¹, which is close to the reported value.¹⁴ (The peak located at 519.2 cm⁻¹ corresponds to the first-order optical phonon mode of c -Si substrate.) This confirms the formation of a disordered Bi₂O₃ fluorite modification at RT, which is coincident with the XRD results.

Spectroscopic ellipsometry (SE) is a nondestructive and powerful technique to investigate the optical response of materials, and in particular, to measure simultaneously the thickness and the optical constants of a multilayer system.¹⁶ In this study, SE (UVISEL Jobin-Yvon) has been employed to investigate the optical characteristics of the δ -Bi₂O₃ thin films at RT in the spectral range 0.75–5.50 eV with a step of 0.05 eV and at an incident angle of 70°. A dispersion model capable of describing the interband absorption of thin films is

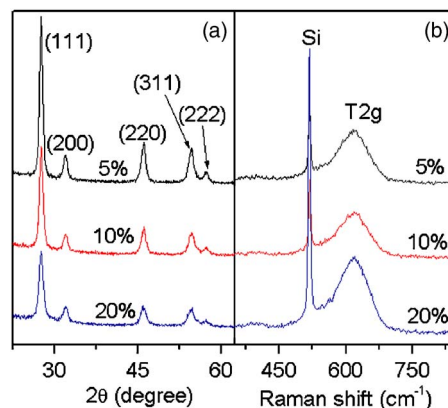


FIG. 1. (Color online) XRD patterns (a) and Raman shift (b) of δ -Bi₂O₃ thin films deposited at various O₂ flow ratios.

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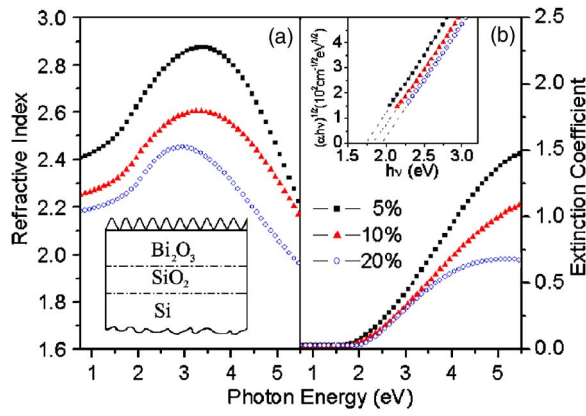


FIG. 2. (Color online) Refractive index (a) and extinction coefficient (b) of δ - Bi_2O_3 thin films deposited with different O_2 flow ratios based on the TL model. The inset in (a) shows the BEMA model used to simulate. The inset in (b) is the determination of optical band gap based on the absorption coefficient $\alpha=4\pi k/\lambda$, where λ is the wavelength of a photon and k is the extinction coefficient.

essential for data analysis. We adopted the Tauc-Lorentz (TL) model¹⁷ to describe the dispersion of the δ - Bi_2O_3 thin films as expressed in the following:

$$\varepsilon_i(E) = \begin{cases} \frac{AE_0C(E-E_g)^2}{(E^2-E_0^2)^2+C^2E^2} \cdot \frac{1}{E}, & (E > E_g) \\ 0, & (E \leq E_g) \end{cases}, \quad (1)$$

$$\varepsilon_r(E) = \varepsilon_\infty + \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi. \quad (2)$$

The TL dispersion model was obtained from the Tauc joint density of states and the standard quantum mechanical or Lorentz calculation for ε_i (the imaginary part of the complex dielectric function) of a collection of noninteracting atoms. Above equations as functions of the photon energy E are uniquely defined by five parameters A (transition matrix element, which is proportional to the magnitude of ε_i , related to the film density¹⁸), E_0 (peak transition energy, corresponds to the Penn gap which represents an average separation between valence and conduction bands¹⁹), C (broadening term, which can be related to the degree of disorder in the material¹⁸), E_g (optical band gap), which all have the energy unit, and ε_∞ (high frequency dielectric constant), where P stands for the Cauchy principal part of the integral. The TL dispersion function has been successfully employed in many materials in a wide energy range.^{16,20,21}

To extract the optical constants of the thin films, a four-layer model is used: Si (100) substrates, SiO_2 interfacial layer, homogeneous δ - Bi_2O_3 films and surface rough layer which was assumed to consist of void and Bi_2O_3 (certain volume percentage of Bi_2O_3 : $f_{\text{Bi}_2\text{O}_3}$) based on the Bruggeman effective medium approximation (BEMA).²² Schematic

structure of the four-layer model was shown in the inset in the Fig. 2(a). The variables in the fitting include the thickness of all of the layers, the volume fraction of the δ - Bi_2O_3 present in the surface rough layer, and all the dispersion relation describing the optical properties of the δ - Bi_2O_3 films.

Figure 2 shows the refractive indices and extinction coefficients of the δ - Bi_2O_3 thin films deposited with different OFRs extracted from the best-fitted results shown in Table I. All the parameters listed in Table I have a confidence limit better than 90%. Within the OFR range used in this study, it was found that high oxygen flow results in a low refractive index and extinction coefficient. Similar results were found in many materials such as TiO_2 , ZnO , Al_2O_3 , SiO_2 , and ZrO_2 , etc.^{23–26} It is well known that the refractive index is closely related to the density of materials, being lower at lower density. Two factors affect the density of the thin films: (1) The excess oxygen in the vacuum chamber might be absorbed in the films during sputtering duo to the low reaction rate between Bi and O ions; (2) the higher the oxygen partial pressure, the lower the energy of the arriving species of the Bi and O ions on the substrates (because of the poison effect on the target), the lower the mobility of the condensed particles. The low surface mobility favors the three-dimensional (3D) island growth leading to the growth of a large number of small crystallites; while the high surface mobility favors the two-dimensional (2D) manner leading to the formation of large grain size, and thus the dense packing structure was formed at low OFR and the loose structure was formed at high OFR.²⁷ It is worth noting that, the parameter A and $f_{\text{Bi}_2\text{O}_3}$ in TL model decrease with increasing the OFR (see Table I). The highest A value corresponds to the δ - Bi_2O_3 thin film deposited at OFR of 5%. In this case, the E_0 have the lowest value. This result suggests that the thin films with relative dense structure could be obtained at low OFR. The parameter C related to the disorder in the films increases with increasing OFR. Above analysis indicates that the decrease in the packing density is the main reason responsible for the decrease of the refractive index. Other factors, such as unoxidized or sub-oxidized species also have an important effect on the refractive index of the films. Our XPS analyses revealed that all the thin films grown at different OFRs (5%, 10%, even 80%) have a narrow Gauss-shaped $\text{Bi}4f_{7/2}$ and $\text{Bi}4f_{5/2}$ peaks centered, respectively, at 158.5 and 163.8 eV (the full width at half maximum of about 1.35 and 1.36 eV, respectively). There are no significant differences for the thin films deposited at different OFRs. Both the relative looser microstructure and slightly improved stoichiometric composition of the δ - Bi_2O_3 films might account for the decrease of the extinction coefficients with increasing OFR.

The k spectra [Fig. 2(b)] have been used to derive the absorption coefficient by means of $\alpha=4\pi k/\lambda$. The optical gap has been derived from a plot of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) as shown in the inset in Fig. 2(b). For the indirect allowed transition, the band gap energy is found to be

TABLE I. Parameters of the TL model for fitting the optical functions of the δ - Bi_2O_3 films.

O_2 (%)	$t_{\text{Bi}_2\text{O}_3}$ (nm)	t_s (nm)	$f_{\text{Bi}_2\text{O}_3}$ (%)	E_g (eV)	A (eV)	E_0 (eV)	C (eV)	ε_∞
5	297.4	18.7	55.26	1.63	74.66	5.12	5.23	1.58
10	280.0	16.3	34.79	1.74	67.54	5.47	6.78	1.79
20	260.5	14.7	29.20	1.85	65.52	5.52	6.90	1.82

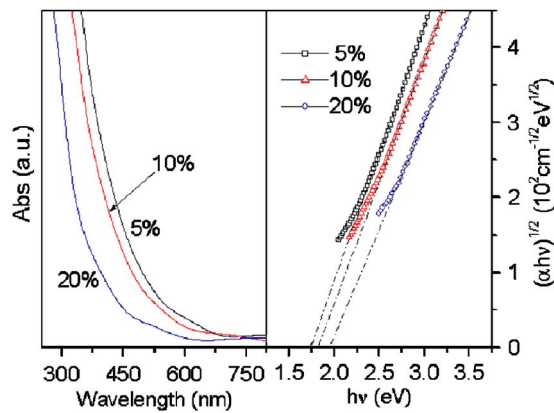


FIG. 3. (Color online) Absorption spectra of δ - Bi_2O_3 thin films deposited at different O_2 flow ratios, and $(\alpha h\nu)^{1/2}$ vs $h\nu$ plot for α larger than 10^4 cm^{-1} .

about 1.73 eV for the δ - Bi_2O_3 thin films deposited at 5% OFR, and moves, respectively, to 1.83 and 1.95 eV for the films at 10% and 20% OFRs, a smaller blue shift occurs. These data are slight higher than the values obtained from the best-fitted results tabulated in Table I. However, the optical band gap obtained from the k spectra is found to be consistent well with the results obtained from the optical absorption spectra (model CARY-5E apparatus) of the films deposited on quartz with different OFRs (see Fig. 3). The quantum confinement effect is considered the main factor that leads to the slight blue shift of the optical band gap of the δ - Bi_2O_3 thin films with increasing OFR, since the grain sizes decrease obviously with increasing the OFRs as observed by field-emission scanning electron microscopy (FE-SEM) (Sirion 200 apparatus) shown in Fig. 4. From the fitted parameter in Table I, one can find that the thicknesses of the rough layer of the Bi_2O_3 thin films slightly decrease, while the volume percentages of the Bi_2O_3 decrease greatly with increasing the OFR. This result is in good agreement with the decreased particle sizes and loose microstructures of the film prepared at high OFRs.

In summary, Bi_2O_3 thin films were deposited at different oxygen flow ratios by RF reactive magnetron sputtering. The as-deposited thin films belong to δ - Bi_2O_3 polymorph at room temperature. The refractive index and extinction coefficient decrease with increasing the oxygen flow ratio due to the

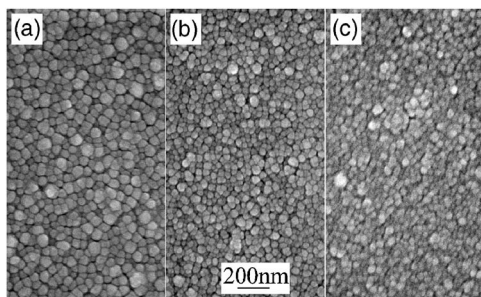


FIG. 4. FE-SEM images of δ - Bi_2O_3 thin films deposited on Si (100) at different O_2 flow ratios: (a) 5%, (b) 10%, and (c) 20%.

decreased packing density in the δ - Bi_2O_3 thin films. The optical band gap of the δ - Bi_2O_3 thin film obtained by Tauc-Lorentz dispersion method is in good agreement with that obtained by optical absorption spectrum and has a slight blue shift with increasing the oxygen flow ratio. It is considered that the quantum confinement effect is responsible for the blue shifts. These results suggest that the compact δ - Bi_2O_3 thin film deposited at low OFRs hold promise for application in optoelectronic devices.

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- ¹L. Leontie, M. Caraman, M. Alexe, and C. Harnagea, *Surf. Sci.* **480**, 507 (2002).
- ²L. Leontie, M. Caraman, A. Visinoiu, and G. I. Rusu, *Thin Solid Films* **473**, 230 (2005).
- ³B. L. Yu, C. S. Zhu, and F. X. Gan, *J. Appl. Phys.* **82**, 4532 (1997).
- ⁴P. Zhou, G. J. You, Y. G. Li, T. Han, J. Li, S. Y. Wang, and L. Y. Chen, *Appl. Phys. Lett.* **83**, 3876 (2003).
- ⁵J. A. Switzer, M. G. Shumsky, and E. W. Bohannon, *Science* **284**, 293 (1999).
- ⁶S. W. Kang and S. W. Rhee, *Thin Solid Films* **468**, 79 (2004).
- ⁷K. Higaki, S. Kudo, and H. Ohnishi, *Electrochem. Solid-State Lett.* **1**, 107 (1998).
- ⁸N. M. Sammes, G. A. Tompsett, H. Nafe, and F. Aldinger, *J. Eur. Ceram. Soc.* **19**, 1801 (1999).
- ⁹A. F. Gualtieri, S. Immovilli, and M. Prudenziati, *Powder Diffr.* **12**, 90 (1997).
- ¹⁰L. Leontie, M. Caraman, M. Delibas, and G. I. Rusu, *Mater. Res. Bull.* **36**, 1629 (2001).
- ¹¹P. Shuk, H.-D. Wiemhöfer, U. Guth, W. Göpel, and M. Greenblatt, *Solid State Ionics* **89**, 179 (1996).
- ¹²V. V. Kharton, E. N. Naumovich, A. A. Yaremchenko, and F. M. B. Marques, *J. Solid State Electrochem.* **5**, 160 (2001).
- ¹³A. A. Agasiev, A. kh Zeinaly, S. J. Alekperov, and Y. Y. Cuseinov, *Mater. Res. Bull.* **21**, 765 (1986).
- ¹⁴N. V. Skorodumova, A. K. Jonsson, M. Herranen, M. Strømme, G. A. Niklasson, B. Johansson, and S. I. Simak, *Appl. Phys. Lett.* **86**, 241910 (2005).
- ¹⁵V. G. Keramidias and W. B. White, *J. Chem. Phys.* **59**, 1561 (1973).
- ¹⁶Z. G. Hu, J. H. Ma, Z. M. Huang, Y. N. Wu, G. S. Wang, and J. H. Chu, *Appl. Phys. Lett.* **83**, 3686 (2003).
- ¹⁷G. E. Jellison, Jr. and F. A. Modine, *Appl. Phys. Lett.* **69**, 371 (1996); **69**, 2137 (1996).
- ¹⁸A. F. I. Morral, P. R. I. Cabarrocas, and C. Clerc, *Phys. Rev. B* **69**, 125307 (2004).
- ¹⁹P. Patsalas, S. Logothetidis, L. Sygellou, and S. Kennou, *Phys. Rev. B* **68**, 035104 (2003).
- ²⁰Y. J. Cho, N. V. Nguyen, C. A. Richter, J. R. Ehrstein, B. H. Lee, and J. C. Lee, *Appl. Phys. Lett.* **80**, 1249 (2002).
- ²¹G. He, L. D. Zhang, G. H. Li, M. Liu, L. Q. Zhu, and S. S. Pan, *Appl. Phys. Lett.* **86**, 232901 (2005).
- ²²D. A. G. Bruggemann, *Ann. Phys.* **24**, 636 (1935).
- ²³H. Tomaszewski, H. Poelman, D. Depla, and D. Poelman, *Vacuum* **68**, 31 (2003).
- ²⁴E. M. Bachari, S. Ben Amor, G. Baud, and M. Jacquet, *Mater. Sci. Eng., B* **79**, 165 (2001).
- ²⁵S. Venkataraj, O. Kappertz, R. Jayavel, and M. Wuttig, *J. Appl. Phys.* **92**, 3599 (2002).
- ²⁶C. C. Lee, D. T. Wei, J. C. Hsu, and C. H. Shen, *Thin Solid Films* **290–291**, 88 (1996).
- ²⁷D. P. Zhang, J. D. Shao, Y. A. Zhao, S. H. Fan, R. J. Hong, and Z. X. Fan, *J. Vac. Sci. Technol. A* **23**, 197 (2005).