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Synthesis of Bismuth Oxide Thin Films Deposited by Reactive Magnetron Sputtering

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In this work Bi_2O_3 thin films were deposited onto the Si (111) and soda lime glass substrates by the reactive direct current magnetron sputtering system using pure Bi as a sputtering target. The dependences of electro-optical characteristics of the films on the substrate type and temperature were investigated. Transmittance and reflectance of the Bi_2O_3 films were measured with ultraviolet and visible light spectrometer. It was found that the substrate temperature during deposition has a very strong influence on the phase components of thin films. The results indicate that the direct allowed transitions dominate in the films obtained in this work. For the direct allowed transitions the band gap energy is found to be about 1.98 eV and 2.2 eV. The reflectance of thin bismuth oxide film depends on the substrate. Small transparency of thin films grown on glass is more related to large reflectance than absorption. The reflectance spectra of the bismuth oxide thin films deposited on the Si substrates show higher quality of optical characteristics compared to the samples deposited on glass substrates.

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1. Introduction

Bismuth oxide Bi_2O_3 has been investigated extensively due to its optical and electrical properties such as large energy gap (from 2 to 4 eV) [1], refractive index and high oxygen ion conductivity at high and medium temperatures [2]. These properties make bismuth oxide one of the most perspective candidates for application in optoelectronics, solar cells and solid oxide fuel cells (SOFCs) to replace now commonly used yttrium stabilized zirconium (YSZ) [2].

Bismuth oxide has a few main polymorphic forms that are known as α, β, γ, δ [3, 4]. All polymorphs have different crystal structure and various optical, electrical and mechanical properties. Only two of them, the low temperature monoclinic α-phase and high temperature face-centered cubic δ-phase are stable. The other phases are metastable. There is a great interest in δ-Bi_2O_3 due to its high oxide ion mobility arising from numerous oxygen vacancies in the crystal structure [5, 6]. But the δ-Bi_2O_3 phase is only stable between 729 ℃ and 825 ℃ (the melting point) [5]. Upon cooling, δ-Bi_2O_3 phase transforms to α-phase and the ionic conductivity drops by some orders of magnitude.

Magnetron sputtering is a widespread method because of high deposition rate, dense and highly adhesive films, and possibility of using commercially available large area deposition systems.

In this paper, the growth and characterization of Bi_2O_3 thin films prepared by reactive DC magnetron sputtering is reported, and the structural and optical properties of the films are investigated and discussed.

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2. Experiment

Bi_2O_3 thin films were deposited onto the soda lime glass substrates and Si (111) by the direct current magnetron sputtering system in $Ar+O_2$ atmosphere. Thin films were grown at room temperature and on heated substrates. Before deposition, the substrates were degreased ultrasonically using acetone for 10 min. At the end the substrates were cleaned with deionized water and dried in air. The target was a metallic Bi. The deposition conditions of the films are summarized in Table.

TABLE

Summary of deposition conditions.

Magnetron	Disk
area of cathode (target) [cm^2]	70
target material	Bi, 99.999%
discharge voltage [V]	350–450
discharge current [mA]	100–500
working gases	$Ar+O_2$
initial pressure in chamber [Pa]	5×10^{-3}
partial pressure of active gas (O_2) [Pa]	0.1
total pressure in the chamber [Pa]	0.3
distance between the cathode and the substrate [cm]	6
substrate temperature [℃]	20–200

The crystallographic structure of the thin films was investigated by the X-ray diffraction (XRD) studies using Bruker D8 Discover diffractometer with the monochromatic Cu K_α radiation ($\lambda = 0.15418$ nm). The analysis of XRD peak broadening β was made using the Scherrer method, which is frequently applied for determination of crystallite size D. The transmittance and reflectance spectra were collected using an Ocean Optics USB4000 spectrophotometer equipped with a CCD detector.

3. Results and discussion

The influence of the substrate temperature on the crystalline structure of the thin films was investigated with a constant partial pressure of oxygen. The XRD patterns (Fig. 1) show that the thin film deposited on Si substrates at room temperature (20 ℃) has a monoclinic structure of α-Bi_2O_3 phase. The heating of the substrate up to the temperature of 200 ℃ leads to the formation of a mixture of α-Bi_2O_3 and cubic δ-Bi_2O_3. The average grain size of the thin films is about 30–50 nm as estimated from the Scherrer equation.

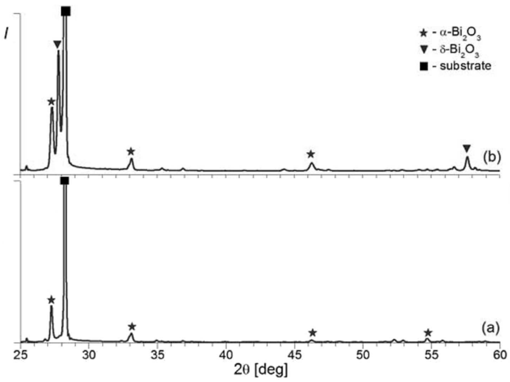

Fig. 1. X-ray diffraction patterns of thin films deposited on Si substrates at (a) 20 ℃ and (b) 200 ℃, respectively.

The transmittance spectra of bismuth oxide films deposited on glass substrates are presented in Fig. 2. The small transparency and the lack of interference oscillations of the spectra may indicate that a large fraction of the material deposited on the glass substrate has amorphous structure. The small transparency of thin films grown on the glass sometimes can be also related with larger reflectance or scattering than absorption. The reflectance spectra of the Bi_2O_3 samples deposited at 20 ℃ and 200 ℃ on glass substrates are presented in Fig. 3a and b. As follows from the figures, the interference oscillations are weaker for the film deposited on the unheated substrate.

The reflectance spectra of the Bi_2O_3 samples deposited at 20 ℃ and 200 ℃ on the Si substrates are presented in Fig. 4a and b. As can be seen from them the reflectance spectra of the bismuth oxide thin films deposited on Si substrate show higher quality of optical characteristics compared to those of the samples deposited on the glass substrates, since the surface of the Si substrate is polished better than the glass surface and therefore the surface roughness is smaller and interference character of the spectra is stronger.

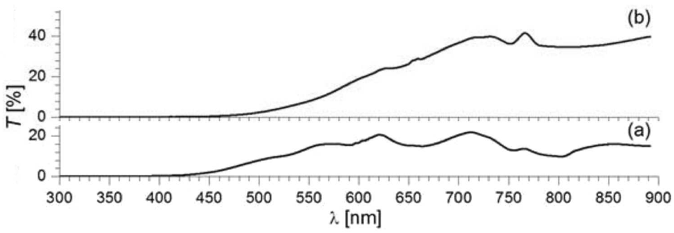

Fig. 2. Transmittance spectra of bismuth oxide films deposited on glass substrates at (a) 20 ℃, (b) 200 ℃.

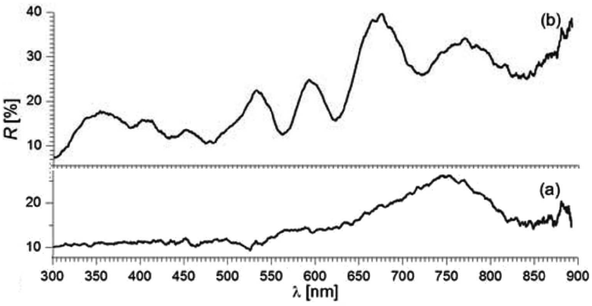

Fig. 3. Reflectance spectra of bismuth oxide films deposited on glass substrates at (a) 20 ℃, (b) 200 ℃.

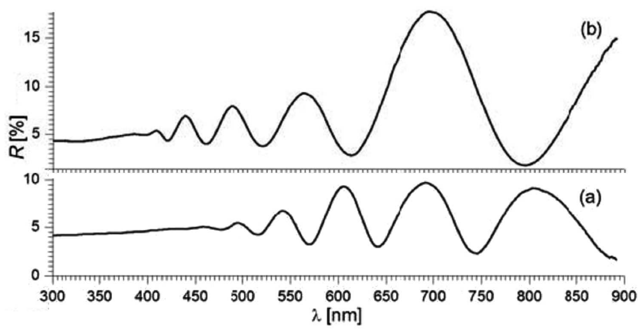

Fig. 4. Reflectance spectra of bismuth oxide films deposited on Si substrates at (a) 20 ℃, (b) 200 ℃.

Figure 5 shows the optical absorption spectra of Bi oxides deposited on glass at 20 ℃ and 200 ℃. The absorption coefficient α is connected with the band gap energy E_g by the equation [7]

$$(h\nu\alpha)^\gamma = \beta\,(h\nu - E_g)\,, \tag{1}$$

where $h\nu$ is the energy of the incident photon, β is a parameter, γ is an index that characterizes the optical absorption process and is equal to 1/2 and 2 for indirect allowed and direct allowed transitions, respectively. E_g is determined by extrapolating the straight line portion $(h\nu\alpha)^\gamma = 0$. The plot of $(h\nu\alpha)^\gamma$ versus $h\nu$ is shown in Fig. 6. It is known from the literature that both transitions are allowed for various bismuth oxide phases

[4, 8, 9]. Spectral calculations show that the indirect allowed transitions are not allowed. For the direct allowed transitions (Fig. 6) the band gap energy is found to be about 1.98 eV and 2.2 eV. The band gaps obtained for the direct allowed transition are smaller but close to the reported values [4, 8, 9]. The results indicate that the indirect allowed transitions dominate in this bismuth oxide.

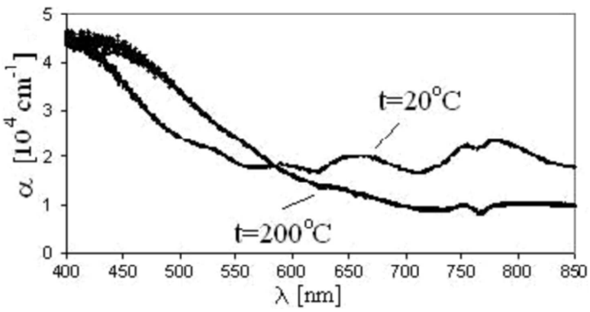

Fig. 5. Variation of absorption α with the wavelength λ of thin films deposited on glass substrates at 20 ℃ and 200 ℃, respectively.

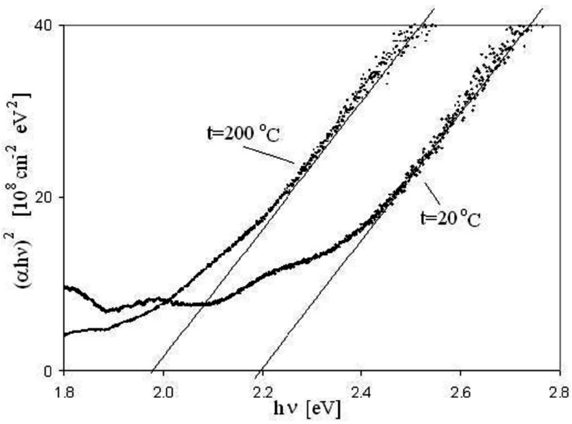

Fig. 6. Plots of $(h\nu\alpha)^2$ vs. $h\nu$ of bismuth oxide thin films deposited on the glass substrate.

As can be seen from Fig. 6, the absorption edge is shifted to the longer wavelengths for the samples deposited on the heated substrates, which may show the influence of crystalline structure onto the fundamental band gap since the XRD investigations show the formation of a mixture of α-Bi_2O_3 and δ-Bi_2O_3 phases on the heated substrate and formation of only α-Bi_2O_3 phase on the non-heated substrate.

4. Conclusion

In summary, the XRD characterization showed that the substrate temperature has great effect on the phase components of the bismuth oxide thin films. The results indicate that the direct allowed transitions dominate in these bismuth oxides. The band gap energy for the direct allowed transitions is found to be about 1.98 eV and 2.2 eV for the samples deposited on the heated and non--heated substrates, respectively. The reflectance of thin bismuth oxide films depends on the substrate type and temperature. The small transparency of the thin films grown on glass is more related with large reflectance than absorption. The reflectance spectra of the bismuth oxide thin films deposited on Si substrates show higher quality of optical characteristics compared to those of the samples deposited on the glass substrates.

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