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On the optical properties of bismuth oxide thin films prepared by pulsed laser deposition

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Abstract

The optical properties of bismuth oxide films prepared by pulsed laser deposition (PLD), absorption in the photon energy range 2.50–4.30 eV and optical functions (n, k, ε_1, and ε_2) in the domain 3.20–6.50 eV, have been investigated. As-prepared films (d=0.05–1.50 μm) are characterized by a mixture of polycrystalline and amorphous phases. The fundamental absorption edge is described by direct optical band-to-band transitions with energies 2.90 and 3.83 eV. The dispersion of the optical functions provided values of 4.40–6.25 eV for electron energies of respective direct transitions. In the spectral range 400–1000 nm, bismuth oxide films show a normal dispersion, which can be interpreted in the frame of a single oscillator model.

Keywords: Bismuth oxide; Ellipsometry; Optical properties; Reflection spectra

1. Introduction

Bismuth oxide plays a significant role within the class of semiconducting oxide materials, due to a variety of physical properties determined by its numerous polymorphs [1–4]. This semiconductor is characterized by significant values of bandgap, refractive index and dielectric permittivity, as well remarkable photosensitivity and photoluminescence [5–7].

Depending on preparation technology, which favors the predominance of certain phases, its electrical conductivity may vary by over 5 orders of magnitude, while its energy gap may change from about 2 to 3.96 eV [5–9].

Bismuth oxide is relevant for a number of applications in present solid-state technology: it is widely used in opto-electronics, optical coatings, as well as in transparent and superconductor ceramic glass manufacturing [10–16].

Some technological applications of this material in thin film form are based on the distribution of surface states, which determines its photocatalytic properties and the capture of polar gases in gas sensors [17–20].

Due to both experimental relevance and theoretical interest, the study of optical properties of bismuth oxide thin films has been reported by a number of authors [3,5,6,11,12,22,23].

In a series of previous papers [7,9,21], we studied the optical, photoelectrical and photoluminescence properties of bismuth oxide films prepared by thermal oxidation of bismuth thin films.

In the present paper we investigate the optical properties of bismuth oxide films, prepared by pulsed laser deposition (PLD).

2. Experimental details

Bismuth oxide films under study were prepared by pulsed laser deposition (PLD) method (see Table 1), at a chamber pressure p=0.2 mbar, from high-purity

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Table 1
Deposition conditions of PLD films

Pulse energy (mJ)	Deposition time (min)	Thickness (μm)
600	5	0.08
600	15	1.50
300	5	0.06
300	7	0.09
300	9	0.11
300	11	0.14
300	13	0.16

Substrate temperature: T_S=300 K, distance between target and substrate: 6 cm, O_2 concentration: 20/SCCM, chamber pressure: p=0.2 mbar, vacuum inside chamber: 10^{-5} Torr, KrF excimer laser with fluence on the target: 0.1–7.0 J/cm^2, pulse frequency: f=1 Hz, and pulse length: τ=25 ns.

(99.9998%) Bi_2O_3 hot-pressed or sintered pellets. A KrF excimer laser was used (wavelength 248 nm), providing pulses with a duration of 25 ns, at a frequency of 1 Hz. The fluence on the target could be varied from 0.1 up to 7.0 J/cm^2. The film thickness (measured by a TENCOR P-2 Long Scan profilometer) ranged between 0.05 and 1.50 μm. Glass maintained at about 300 K was used as substrate.

The crystalline structure and growth mechanism were investigated by means of X-ray diffraction (XRD) (using Cu Kα radiation) and atomic force microscopy (AFM) techniques. The AFM inspections (see Fig. 1) show that the films have a crystallite-like surface morphology. The presence of pinholes in the studied films was not observed. The typical AFM image from Fig. 1 evidences crystallites with nanometric dimensions, for both in-plane projections and that perpendicular to film surface. As revealed by X-ray diffraction analyses [21], corroborated by polarizing microscopy technique, the use of PLD method resulted in bismuth oxide films with mixed structure: polycrystalline (consisting of Bi_2O_3 nanocrystallites) and amorphous.

In the study of transmission and reflection spectra in the range 2.50–6.50 eV, a SPECORD M40 spectrophotometer was used, equipped for reflectance measurements at small incidence angles, $\theta \leq 8°$.

The dispersion of the refractive index, n, and of the extinction coefficient, k, in the region of the fundamental absorption edge, was calculated by means of the ellipsometric method. The ratio of reflection factors, R_p/R_s, and the phase difference between reflected and incident light, Δ, have been determined by using variable angle spectroscopic ellipsometry (VASE) technique, at room temperature.

3. Results and discussion

3.1. Basic equations

For a plan-parallel sample with thickness d, the absorption coefficient, α, in the region of fundamental absorption band, can be calculated using the following relationship [24,25]:

$$T = \frac{(1-R)^2 + 4R\sin^2\psi}{e^{\alpha d} - R^2 e^{-\alpha d} - 2R\cos 2(\delta+\psi)}, \quad (1)$$

where δ and ψ are expressed as

$$\delta = \frac{4\pi n d}{\lambda} \text{ and } \psi = \arctan\left(\frac{2k}{n^2+k^2-1}\right), \quad (2)$$

where n denotes the refraction index of the material.

In determining the absorption coefficient, α, nomograms showing the dependence of the product (αd) on the transmittance, T, for different values of reflectance, R, have been built up [25,26].

The optical constants, n and k, for wavelengths within fundamental absorption band, were calculated from the experimental spectra $R(\hbar\omega)$ ($\hbar\omega$ is the photon energy) at normal incidence, by means of equations [24]:

$$n = \frac{1-R}{1+R-2\sqrt{R}\cos\Delta}, \quad (3)$$

$$k = \frac{2\sqrt{R}\sin\Delta}{1+R-2\sqrt{R}\cos\Delta}. \quad (4)$$

In these expressions, the phase difference, Δ, considered at frequency ω_0, is determined by the Kramers–Kronig equation [24,25]:

$$\Delta_{\omega_0} = -\frac{\omega_0}{\pi}\int_0^\infty \frac{\ln R}{\omega^2-\omega_0^2}d\omega. \quad (5)$$

The optical constants, n and k, in the vicinity of the fundamental absorption band edge ($\hbar\omega < E_g$), in the spectral domain from 400 nm ($\hbar\omega_1$=3.10 eV) to 1000 nm ($\hbar\omega_2$=1.24 eV), were determined by analyzing the polarization state of

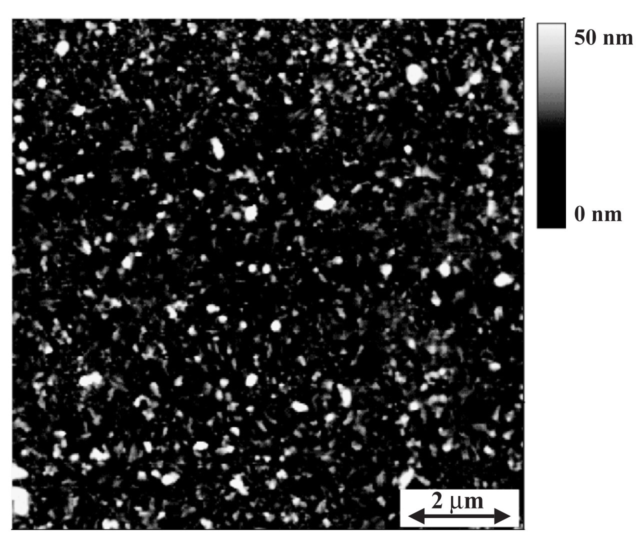

Fig. 1. AFM image of a PLD bismuth oxide film (thickness: d=0.06 μm; root mean square: RMS=9.016 nm).