Structural and optical characteristics of bismuth oxide thin films

L. Leontie a,*, M. Caraman b, M. Alexe c, C. Harnagea c

a Faculty of Physics, "Al. I. Cuza" University, 11 Carol I Blvd., R-6600 Iasi, Romania
b Bacau University, 157 Marasesti Blvd., R-5500 Bacau, Romania
c Max Planck Institute of Microstructure Physics, Weinberg 2, D-06120 Halle, Germany

Abstract

The formation of different phases of Bi–O system during oxidizing process of Bi films from the viewpoint of structure characteristics and optical properties, is investigated. As revealed by structure and surface investigations, the thermal oxidation, in air, of Bi films on glass results in polycrystalline and multiphase bismuth oxide films. At substrate–film interface an amorphous oxide layer forms up, to whom surface the growth processes of crystallites belonging to diverse phases, with different geometric shapes occur. For nanometric up to submicronic thicknesses, BiO is predominant phase, while in case of micronic films, α-Bi₂O₃ and Bi₂O₃ are the main phase components. From absorption curves the band gap values, ($E_\text{g} = 2.29–3.31 \text{ eV}$), for direct transitions, have been determined and an energy gap of $\sim 2 \text{ eV}$ for amorphous phase was found. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Atomic force microscopy; X-ray scattering, diffraction, and reflection; Growth; Oxidation; Surface thermodynamics (including phase transitions); Bismuth; Inorganic compounds; Polycrystalline surfaces

1. Introduction

Bismuth oxide (Bi₂O₃) in thin films is an interesting material characterized by a significant band gap, high refractive index and dielectric permittivity, as well as marked photoconductivity and photoluminescence [1–5].

A characteristic feature of bismuth oxide consists of its polymorphism: five modifications, known as α-, β-, γ-, δ-, and ω-Bi₂O₃, were reported [6–8]. Two of them, the low-temperature α and the high-temperature δ phases, are stable; the others are high-temperature metastable phases [7,8]. Each polymorph possesses distinct crystalline structures and physical properties (electrical, optical, photoelectrical, etc.). For example, at 300 K, the band gap of monoclinic α-Bi₂O₃ is equal to 2.85 eV, while that of tetragonal β phase is 2.58 eV [1,3].

Owing to their peculiar characteristics, bismuth oxides are used in various domains, such as microelectronics [9], sensor technology [10], optical coatings [11], transparent ceramic glass manufacturing [12], etc.

The phase relations in case of Bi–O system, as well as the chemical bonding in Bi₂O₃ polymorphs,
that play a key role in understanding the oxidation processes of Bi, were tackled in some recent papers [13–15].

Due to both experimental and theoretical relevance, the optical properties of bismuth oxides have been investigated in [1–4,16–19].

In the present paper, the formation of different phases belonging to Bi–O system during thermal oxidization of Bi films is investigated by means of atomic force microscopy (AFM) and X-ray diffraction (XRD) techniques, and of optical absorption study.

2. Experimental

Thin films of Bi (99.999% purity), with thickness between 0.035 and 1.150 μm, have been deposited in vacuum (~10⁻⁵ Torr) onto glass substrates, maintained at room temperature.

They were submitted to a thermal oxidizing treatment, in air [4,5], consisting of a quick heating (with a rate of 10 K/min), followed by an annealing for 15 min at a temperature 773 K, and finally a quick cooling (over 10 K/min) to the room temperature.

The thickness of the obtained films, as measured by a TENCOR P-2 Long Scan profiler, ranged between 0.059 and 1.635 μm.

The crystalline structure and surface morphology of the films were studied by XRD method (using a PHILIPS X'PERT system), and AFM (Nanosensors, NCH-W type apparatus), respectively.

The transmission and reflection spectra in the spectral range (300–1000) nm were recorded by means of a VASE ellipsommetr, at room temperature.

The calculation of absorption coefficient, \( \alpha \), was made taking into account the relation [20]:

\[
\alpha = \frac{1}{d} \ln \left\{ \frac{(1 - R)^2}{2T} + 1 \sqrt{\left[ \frac{(1 - R)^2}{2T} \right]^2 + R^2} \right\}.
\]  

3. Results and discussion

It was established in our previous works [4,5], that thermal oxidation of Bi films in air leads to polycrystalline films containing different phases of Bi–O system: BiO, \( \alpha \)-, \( \beta \)-Bi₂O₃, as well Bi₂O₂₃, Bi₂O₂₇₅, and unoxidized Bi.

The investigations of film structure, performed by XRD method, corroborated to SEM and optical polarizing microscopy techniques, confirmed that as prepared bismuth oxide films are polycrystalline and multiphase.

The crystalline structure of bismuth oxide films strongly depends on the nucleation and growth processes at film–substrate interface and is mainly determined by the crystalline structure of the substrate. If this is amorphous, then a bismuth oxide layer of the same nature is expected to form up at the structure’s interface. A homogenous germination of different crystalline phases of Bi–O system takes place on the newly formed amorphous layer and among them the phase with lowest free energy will be predominant.

In case of thermal oxidation of metal films, the formation of crystallites within liquid phase can represent the initial growth stage [21]. In this process, different types of surface irregularities and structural defects for both substrate surface layer and new amorphous layer behave as growth centers.

The crystallization process at the interface layer can go on as a result of (i) formation of 3D germs which, by adding oxide molecules from metal-oxide solution, continue the growth process, or via (ii) formation of 2D monomolecular layers leading to appearance of 3D germs.

A criterion for the predominance of 2D or 3D germination is usually the correlation between surface enthalpies for substrate, \( S_s \), growing crystal, \( S_c \), and interface layer, \( S_I \) [22]. If \( S_s < S_c + S_I \),
3D germs are to show up on the support surface; in the opposite case, \( S_c > S_i + S_s \), growth processes based on the 2D germination take place.

The growth rate, \( v \), for the crystallization centers corresponding to 2D or 3D germination, is given by the relationship [21]:

\[
v = \frac{kT}{h} \exp \left( -\frac{A + \Sigma}{kT} \right), \tag{3}
\]

where \( k \) and \( h \) are the Boltzmann’s and Planck’s constants, respectively, \( T \) is absolute temperature, \( A \) represents the work required for the build of a center with critical dimensions, and \( \Sigma \) is the molecular activation energy of the transition into crystalline phase. The parameters \( A \) and \( \Sigma \) to a great extent depend on the geometric shape of crystallization center.

The amorphous phase is characterized by high density of defects, with large spectrum of activation energies, \( \Sigma \). Consequently, at film–substrate interface, the formation of both crystallization germs belonging to different phases of Bi–O system, and of a discontinuous amorphous structure are to take place.

In case of nanostructured films (Fig. 1a), the oxidation process leads to high surface density of crystallization centers, with different growth directions and rates. This results in nanocrystallites of different dimensions and geometric shapes, with the basis laying on the film surface. Among them a number of well-outlined crystallites, in form of cones with rounded apex can be evidenced. The mentioned high density of growth germs is in concordance with previous supposition concerning the formation of an amorphous layer at substrate–film interface.

When the film thickness increases about three times (Fig. 1b), a sudden separation of growth rates takes place. Most germs possess small growth rates, probably due to their dimensions, below critical values. During the oxidation process these crystallites dissolve, stimulating by this the growth of larger crystallites with dimensions exceeding the critical values. The mentioned supposition is also supported, as one can see from Fig. 1b, by the presence of an uniform (by thickness) layer around larger crystallites.

For micronic films \( (d \sim 1.5 \mu m) \), the surface density of germs overtaking the critical dimensions enlarges and, as results from Fig. 1c, the amount of crystallites with larger growth rates is increased. But the shape of the respective crystallites essentially differs from those registered for previous submicronic thicknesses.
In order to establish the phase composition of investigated films, XRD patterns (Fig. 2) of respective samples have been analyzed, by appealing to ICDD database [23].

In case of thinnest film (\(d \approx 60 \text{ nm}\)), the diffraction patterns evidence an intense peak located at \(2\theta \approx 28^\circ\), as well three weak lines lying between \(15^\circ\) and \(60^\circ\). These reflections belong respectively to BiO, the main phase component, as well to \(\beta\)-Bi\(_2\)O\(_3\) modification and to Bi\(_2\)O\(_3\). Besides, one evidences a continual field in the range \(2\theta \approx (15-40)^\circ\), with a poorly outlined maximum at about \(25^\circ\), which attests the presence of an amorphous phase into the film—this is exactly the amorphous layer from substrate–film interface.

For an increased, submicronic film thickness (Fig. 2b), generally reflections registered at smaller thicknesses maintain, but weak lines are seen to intensify. By comparing Fig. 2a and b, it can be observed that the main phase component remains BiO, while the amount of \(\beta\)-Bi\(_2\)O\(_3\) and Bi\(_2\)O\(_3\) does not substantially modify. At the same time, the presence of a new, nonstoichiometric phase, Bi\(_2\)O\(_{2.75}\), as well of unoxidized Bi, is pointed out for these films.

In case of micronic films, \(d \sim 1.5 \text{ \(\mu\)m}\) (Fig. 2c), the diffraction patterns are more complex. \(\alpha\)-Bi\(_2\)O\(_3\) and Bi\(_2\)O\(_3\) are now the main phase components, while the amount of BiO diminishes—the magnitude of respective pick, by \(28^\circ\), is about half of first two. By comparison with the other, thinner films, presence of \(\alpha\) phase, as well as of a new component, the nonstoichiometric phase Bi\(_2\)O\(_{2.33}\), is registered. Besides, in thicker bismuth oxide films, the amount of unoxidized Bi (the line located at \(\sim 27^\circ\)) is evidently increased, reflecting an incomplete oxidation of respective films.

Also, by comparing Figs. 1c and 2c, with Figs. 1a and 2a, one can state that polymorph \(\alpha\)-Bi\(_2\)O\(_3\) preponderantly growths in form of needles with maximum surface density, while BiO phase growths in form of cones with large bases.

Additionally information concerning phase formation in Bi–O system for as prepared films can be obtained by analyzing the optical absorption by red border of the fundamental absorption band.

In Fig. 3, the absorption spectra, e.g. dependence \((zhv)^2 = f(hv)\), corresponding to the same typical samples, are shown. By extrapolation to \(x = 0\) of linear abrupt parts, the value of band gap for direct transitions can be determined. In this way, one can evaluate from curve 1 the optical gap of BiO (predominant phase) at about 3.31 eV, at \(T = 293 \text{ K}\). For photon energies \(h\nu < 3.20\ \text{ eV}\), the absorption spectrum can be described by a linear plot of \((zhv)^{1/2} = f(hv)\) dependence, which is characteristic to amorphous phase. By extrapolating the last curve to background, one can evaluate the band gap of amorphous bismuth oxide, at \(\sim 2\ \text{ eV}\).

The red tile of absorption spectrum, which is more pronounced for thinner films, attests once again presence of the above-mentioned interface amorphous layer, where the growth processes are initiated.
The presence of $\beta$-Bi$_2$O$_3$ and of Bi$_2$O$_{2.75}$ leads, in case of films with intermediate, submicronic thickness (curve 2), to a red shift of the absorption edge, at about 3 eV.

For micronic films (curve 3), the slow increase of absorption coefficient in the photon energy range (1.40–2.60) eV can be explained by the phase mixture (Bi$_2$O$_3$, BiO, Bi$_2$O$_{2.33}$, Bi$_2$O$_{2.75}$), with different amounts and band gaps laying between ~2.5 and 3.3 eV. The extrapolation of linear part of curve 3 to $\alpha = 0$ gives $E_g$ value for $\alpha$-Bi$_2$O$_3$ (the predominant phase in case of micronic films), of about 2.3 eV. The obtained results show that the band gap of $\alpha$ phase is significantly inferior to that of BiO.

4. Conclusions

Bismuth oxide films prepared by thermal oxidation, in air, of vacuum evaporated Bi films on glass are polycrystalline and multiphase.

In case of nanometric (up to ~60 nm) and submicronic films ($d \sim 0.15$ μm), BiO, with a band gap $E_g \sim 3.3$ eV is preponderant.

The principal phase components in case of micronic films ($d \sim 1.6$ μm) are $\alpha$-Bi$_2$O$_3$, Bi$_2$O$_3$, BiO, and unoxidized Bi.

The phase mixture leads, in case of submicronic and micronic films, to a red shift of the absorption edge, from 3.31 to 2.29 eV.

At film–substrate interface an amorphous oxide layer forms, to whom surface predominant growth of BiO or $\alpha$-Bi$_2$O$_3$ occurs. The band gap of amorphous bismuth oxide is about 2 eV.

References