

STRUCTURAL AND OPTICAL CHARACTERIZATION OF THERMALLY OXIDIZED BISMUTH FILMS

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Structural and optical analysis of bismuth oxide thin films was studied. The vacuum thermal evaporation was used to prepare bismuth films onto glass substrates maintained at different temperatures. Subsequently, their thermal oxidation in air was performed for 1 and 2 hours time, respectively. The optical measurements consisted in recording the transmission and reflection spectra of the films at an UV/VIS Spectrometer. The structural characteristics of the films were deduced from the XRD spectra obtained at a DRON 3 diffractometer (Cu-K α line). The computer-assisted analysis of the optical and XRD spectra allowed the study of the oxidation process and revealed the presence of more than one phase of the bismuth oxide, depending on the temperature of the substrate.

INTRODUCTION

The potential applications of bismuth oxide Bi₂O₃ discovered during the last years led to the intensification of its research, since it has large energy bandgap, high photoconductivity and significant photoluminescence. Up till now five polymorphic forms were found for Bi₂O₃, each of them with its specific properties: two stable polymorphs, namely the α and δ phases (α -Bi₂O₃ is monoclinic; δ -Bi₂O₃ is face-centered cubic) and three metastable phases: β , γ and ω , respectively (β -Bi₂O₃ is tetragonal; γ -Bi₂O₃ is body-centered cubic; ω -Bi₂O₃ is triclinic).

Several deposition methods were used to obtain thin films of bismuth oxide, such as electrodeposition, thermal evaporation under vacuum, sol-gel, pulsed laser deposition, etc.¹⁻¹⁰ Thermal oxidation of the deposited bismuth films is another method that has recently proved its advantages when preparing bismuth oxide films, since it is inexpensive and rather easy to be controlled.^{1,3,5} When the thermal oxidation is performed in short successive stages, sandwich heterostructures of Bismuth oxide/Bismuth (semiconductor/semimetal) can be obtained, which

can exhibit interesting properties and useful practical applications.

This article presents the results of the studies on the structural and optical properties of such Bismuth oxide/Bismuth overlapped structures, obtained by partial thermal oxidation of bismuth films deposited by classic thermal evaporation under vacuum at more than one substrate temperature. Polymorphism and structural changes were noticed and studied for each of the two oxidation stages (one hour each) that were performed on the Bismuth films.

EXPERIMENTAL

As we mentioned before, classic vacuum thermal evaporation was used to obtain the initial Bismuth thin films. High purity (99.999 %) Bismuth powder was vaporized at around $5 \cdot 10^{-5}$ torr pressure, in a standard vacuum unit, onto chemically-cleaned glass slides. The temperature of the substrate during the vacuum depositions was maintained at different values, in order to study its influence on the properties of the obtained films. This article discusses the results for only two such substrate temperatures, namely for 300 K (room temperature) and 373 K, respectively. Except for the substrate temperature, the rest of the deposition parameters were maintained constant for each individual Bismuth film deposition.

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After cooling, the Bismuth films were submitted to thermal oxidation in air, in two stages of one hour each, separated by several days one from the other, by using a home-built device. The temperature was gradually increased up to around 683 K, for the first oxidation hour and then the temperature was risen at around 543 K during the next hour of oxidation.

Transversal SEM images at lower magnification (100 x - 300 x) were obtained by means of a Quanta 200 Electron Microscope, by placing the films almost vertically and thus sending the electron beam almost perpendicularly to the glass slides cross-section. This SEM arrangement allowed for the in-depth layer-by-layer imaging of the films, being useful to prove the partial oxidation of the initial bismuth thin films, subsequent to only short thermal oxidation durations.

A DRON-3 diffractometer with a Cu-K α line ($\lambda = 1.5418 \text{ \AA}$) was used to get the X-ray diffraction spectra of the oxidized Bismuth films.

A MII-4 Linnik interferential Microscope was used to measure the thickness of the films by the multiple-beam Fizeau fringe method,¹¹ at reflection of monochromatic light.

The optical transmission and reflection spectra of the oxidized bismuth films were obtained with a Perkin Elmer Lambda 35 UV/VIS Spectrometer operated at room temperature, in the 270–1100 nm spectral range, at normal incidence. Corrections were applied for the contribution of the glass substrates to the transmission spectra.

RESULTS AND DISCUSSION

The transversal SEM images at lower magnification, obtained as described above, were conclusive for the partial oxidation subsequent to each of the two short oxidation stages, since three different layers were observed this way, namely the glass substrate, the Bismuth remaining film and the Bismuth oxide surface layer, as it is shown in Fig. 1. The SEM microscope gives the possibility to measure horizontal sizes. Still, such measurements cannot be considered accurate in the case of almost transversal SEM images, such as the one in Fig. 1, because of the slight inclination of the film with respect to the vertical axis, which induces a magnification of the actual widths of the overlapped layers when projecting them onto the imaging detector. This is why the scale of the SEM image from Fig. 1 is not shown there.

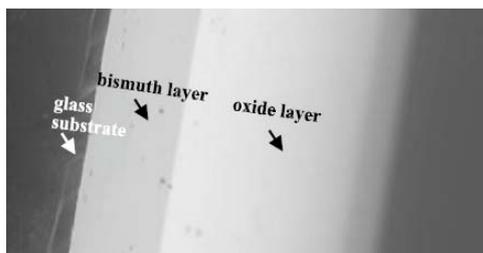


Fig. 1 – Transversal SEM image for a Bismuth oxide/Bismuth structure, at $T_s = 373 \text{ K}$, after the 1st oxidation stage (130 x magnification).

This kind of almost transversal SEM images have only qualitative value, namely to observe the existence of more than one layer in an object's marginal cross-section. Only comparisons between the widths of different overlapped layers can be done as quantitative evaluations. Thus, the oxidation degree of the bismuth films after each oxidation stage could be evaluated by comparing the widths of the overlapped layers from the almost transversal SEM images (not shown here). An increase of the width of the top layer, namely the Bismuth oxide, and a corresponding decrease of the middle layer, namely the remaining film Bismuth unoxidized are a clear indication of an increase of the oxidation degree for longer oxidation duration (from one to two hours of heating). When analyzing the transversal SEM image, one has to pay attention that there is a vague blur of the transversal SEM image at its right side, that is also due to the deviation of the film's position with respect to the vertical axis (which corresponds to the direction of propagation of the incident electron flux inside the microscope). This blur cannot be considered as another solid layer in the SEM image.

The XRD patterns of the oxidized bismuth films are shown in Figs. 2 and 3, in pairs.

The two XRD spectra from Fig. 2 belong to the Bismuth oxide/Bismuth structures, with 300 K substrate temperature (during the initial Bismuth deposition by thermal evaporation), for each of the two oxidation stages of one hour each. In the same way, the XRD spectra from Fig. 3 correspond to the two oxidation stages of the initial Bismuth film deposited at 373 K substrate temperature.

As it can be noticed, each XRD spectrum presents several clear individual peaks, whose attribution to corresponding Bismuth oxide phases and polymorphic forms was identified by comparison with the data from the literature.^{1-8, 10, 12-15} As a result, it was found out that the Bismuth oxide/Bismuth overlapped layers were multiphase and polycrystalline. The oxidized Bismuth films also have a rather pregnant tendency to become texturized, with a specific preferential orientation of the crystallites after a certain crystalline plane, since each XRD pattern contains a peak which is significantly higher than the other peaks.

Thus, in Fig. 2, the XRD spectrum taken after the 1st hour of thermal oxidation presents 8 clear peaks. The assignation of the XRD peaks from Fig. 2 is given in Table 1, according to literature.^{1, 2, 13-15}

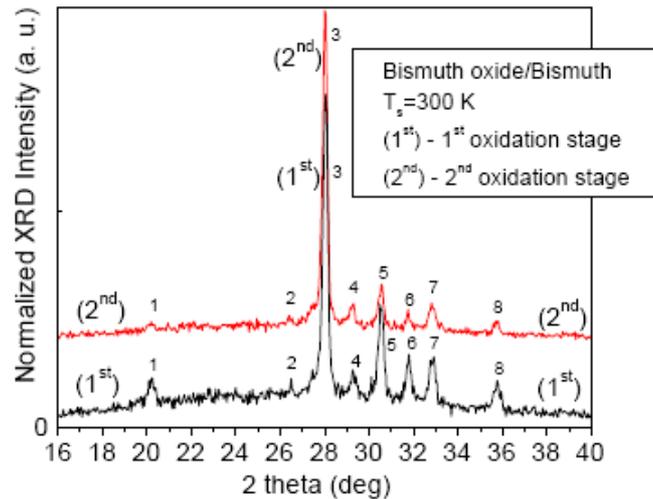


Fig. 2 – XRD patterns for Bismuth oxide/Bismuth structures deposited onto glass maintained at $T_s=300$ K, for two oxidation stages, one hour each.

Table 1

Attribution of the XRD peaks from Fig. 2

Substrate temperature (K)	Oxidation stage	Peaks Nos.	Bismuth Oxide attribution of peaks	Observations
300	1 st	1, 4	$\text{Bi}_2\text{O}_{2,33}$	-
		3	BiO	Highest peak
		2, 8	$\alpha\text{-Bi}_2\text{O}_3$	-
		5, 6	$\beta\text{-Bi}_2\text{O}_3$	-
		7	$\gamma\text{-Bi}_2\text{O}_3$ or $\beta\text{-Bi}_2\text{O}_3$	-
		2 nd	1, 4	$\text{Bi}_2\text{O}_{2,33}$
	2 nd	2, 8	$\alpha\text{-Bi}_2\text{O}_3$	-
		3	BiO	Highest peak
		5, 6	$\beta\text{-Bi}_2\text{O}_3$	-
		7	$\gamma\text{-Bi}_2\text{O}_3$ or $\beta\text{-Bi}_2\text{O}_3$	-

It can be noticed that the partially-oxidized Bismuth films contain both the stable oxide of Bi_2O_3 (Bismuth trioxide), but there are also present some intermediate oxides, such as BiO and $\text{Bi}_2\text{O}_{2,33}$.² The analyzed films also contain a mixture between the α , β and γ forms of Bismuth trioxide.^{1,13,15} The highest peak, namely peak no. 3, from $2\theta=28.05^\circ$, belongs to BiO. Peak no. 7 seems to be given by the $\gamma\text{-Bi}_2\text{O}_3$ phase, even though it can be also assigned to the $\beta\text{-Bi}_2\text{O}_3$ phase.¹⁴

The same peaks are also found after the 2nd oxidation stage, but their intensities are slightly changed. The peak from $2\theta=28.05^\circ$ becomes even more intense than the other peaks, which means that the texture becomes more pregnant. Peaks nos 5 and 6 decrease for the 2nd spectrum, which

indicates a decrease of the presence of the $\beta\text{-Bi}_2\text{O}_3$ phase in the film.

For the pair of XRD patterns shown in Fig. 3, which correspond to 373 K temperature of the glass substrate, things are behaving differently. Thus, if after the first hour of oxidation the XRD spectrum presents 6 peaks, with peak no. 3, at $2\theta=25.50^\circ$, being more intense than the others, after the 2nd oxidation stage, there are 7 clear peaks, some of them at totally different diffraction angles, with peaks 2 and 4 being now more intense. The attribution of the individual peaks from the XRD patterns in Fig. 3 is given in Table 2, according to literature.^{1, 2, 13, 14}

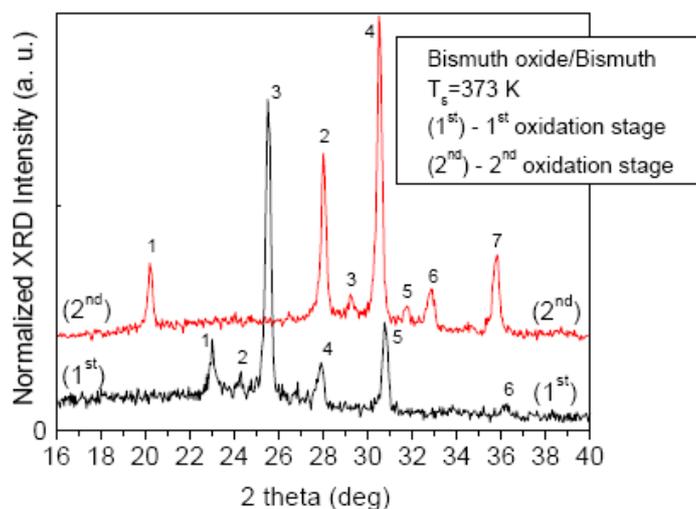


Fig. 3 – XRD patterns for Bismuth oxide/Bismuth structures deposited onto glass maintained at $T_s=373$ K, for two oxidation stages, one hour each.

Even in the case of 373 K substrate temperature, the oxidized Bismuth films contain a mixture of Bismuth oxides and more than one of the Bi_2O_3 polymorphic forms. Another intermediate oxide, namely $\text{Bi}_2\text{O}_{2.75}$ appears for 373 K substrate temperature.¹ Peak no. 4 from the 2nd XRD spectrum in Fig. 3 probably belongs to β - Bi_2O_3 phase,¹⁴ but, according to some authors,¹⁵ it can also belong to pure unoxidized bismuth film. The peak no. 1 from $2\theta=23^\circ$ found after the first hour of thermal oxidation disappears after the 2nd oxidation stage. Instead, other peaks, namely peaks nos. 2 and 4, from $2\theta=28^\circ$ and 30.50° , become more intense after the 2nd oxidation. These changes noticed in the XRD spectra indicate that there is a significant change in the films oxidation degree, structure and texture for longer thermal oxidation of the initial bismuth film deposited at 373 K glass substrate temperature.

The optical transmission and reflection spectra in pairs (as explained above, for the XRD patterns) are presented in Figs. 4 and 5, respectively.

The optical transmission spectra reveal that the films have a good transparency in the investigated spectral range. While for the films deposited at 300 K substrate temperature, the transmission factor decreases with increasing duration of thermal oxidation from one hour (1st oxidation stage) to two hours (2nd oxidation stage), things behave oppositely for the films deposited at 100 degrees more ($T_s = 373$ K) for the temperature of the same kind glass substrate.

The reflection spectra from Fig. 5 present a similar behavior with the transmission spectra above, with a more prominent change of the values of the reflection factor for $T_s = 373$ K substrate temperature when passing from the first to the second oxidation stage than for $T_s = 300$ K. The change of the temperature T_s of the glass substrate induces an increase with a few percents of the values of the transmission and reflection factors.

Table 2

Attribution of the XRD peaks from Fig. 3

Substrate temperature (K)	Oxidation stage	Peaks Nos.	Bismuth Oxide attribution of peaks	Observations
373	1 st	1	$\text{BiO}_{2.33}$	-
		2, 3, 6	α - Bi_2O_3	Peak 3 – the highest
		4	α - Bi_2O_3	-
		5	β - Bi_2O_3	-
		1, 3	$\text{Bi}_2\text{O}_{2.33}$	-
	2 nd	2	α - Bi_2O_3	-
		4, 5	β - Bi_2O_3	Peak 4 – the highest
		6	γ - Bi_2O_3 or β - Bi_2O_3	-
		7	$\text{Bi}_2\text{O}_{2.75}$	-

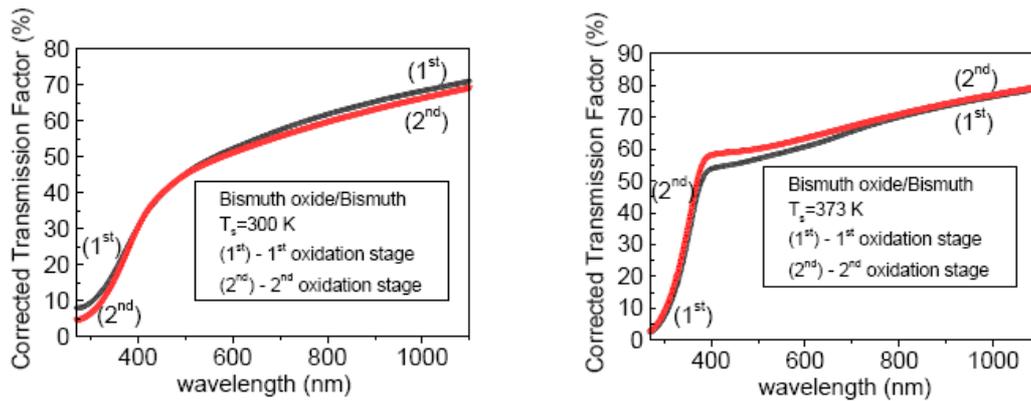


Fig. 4 – Corrected superimposed optical transmission spectra for Bismuth oxide/Bismuth structures deposited onto glass maintained at $T_s=300$ K (left) and $T_s=373$ K (right), respectively, for the two oxidation stages.

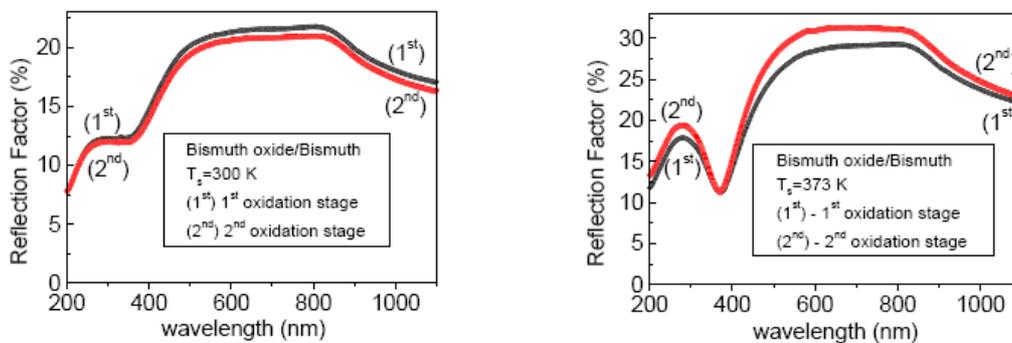


Fig. 5 – Superimposed optical reflection spectra for Bismuth oxide/Bismuth structures deposited onto glass maintained at $T_s=300$ K (left) and $T_s=373$ K (right), respectively, for the two oxidation stages.

Thus, it can be noticed that, after each oxidation stage, the interplay between the polymorphic forms of Bismuth trioxide Bi_2O_3 and also between the different intermediate Bismuth oxides influences the maximum values attained in the optical transmission and reflection spectra rather than the spectra's corresponding profiles.

The optical absorption spectra presented in Figs. 6 and 7, e.g. the dependences type $(\alpha h\nu)^2 = f(h\nu)$, where α represents the absorption coefficient, were deduced by taking into account both the transmission and the reflection data in the 270 – 1100 nm spectral range.^{1, 16} The average thickness of each sample measured at the Linnik interferential microscope was around 0.35 μm .

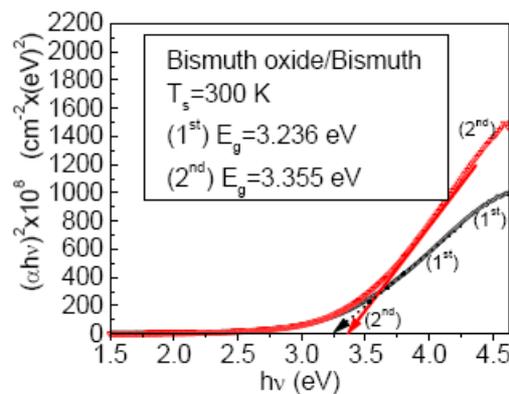


Fig. 6 – Superimposed optical absorption spectra for Bismuth oxide/Bismuth structures deposited onto glass maintained at $T_s=300$ K, for the two oxidation stages.

As it is well-known, this kind of absorption spectra (with $(\alpha h\nu)^2$ as a function of $(h\nu)$) corresponds to direct allowed transitions. From the extrapolation to $\alpha = 0$ of the linear part of the absorption spectrum, the value of the energy bandgap can be found out, as it is shown in figures 6 and 7. As done above, the absorption spectra are presented in pairs for each temperature of the glass substrate, corresponding to the two thermal oxidation stages.

It can be clearly noticed that the value of the energy bandgap slightly increases from 3.236 eV

to 3.355 eV for the pair corresponding to $T_s=300$ K, from Fig. 6, when passing from one to two hours of thermal oxidation of the initial bismuth films. Instead, for the pair of absorption spectra from Fig. 7, the energy bandgap doesn't change at all when passing from the 1st to the 2nd oxidation stage ($E_g=3.897$ eV). Still, when one compares the spectra from Fig. 7, one can notice a small decrease of the slope from the linear part of those spectra, when passing from the 1st to the 2nd oxidation stage.

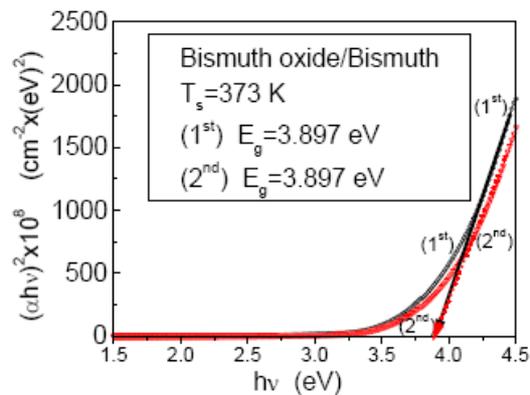


Fig. 7 – Superimposed optical absorption spectra for Bismuth oxide/Bismuth structures deposited onto glass maintained at $T_s=373$ K, for the two oxidation stages.

CONCLUSIONS

Bismuth oxide/Bismuth sandwich heterostructures were obtained by thermal oxidation of Bismuth thin films deposited by vacuum thermal evaporation. Different values of the temperature for the glass substrate were maintained during the initial Bismuth deposition, in order to study the influence on the properties of the final structures. Two separate hours of thermal oxidation in air of the Bismuth films were done, denoted as the 1st and the 2nd oxidation stages. SEM, XRD, optical transmission, reflection and absorption spectra were performed for the resulting structures and then thoroughly studied. From special transversal SEM images the partial oxidation of the films was deduced. The polycrystalline and multi-phase structure of the films was proved by the multiple peaks found and identified in the XRD spectra. High texturing degree was also deduced from the XRD patterns. The transmission and reflection spectra changed only slightly with increasing thermal oxidation time and showed a weak dependence upon the temperature T_s of the glass

substrate. On the other hand, the computed optical absorption spectra were influenced by the temperature of the glass substrate. Thus, at higher T_s , the energy bandgap didn't change with increasing duration of thermal oxidation, while at lower substrate temperature the energy bandgap increased by longer oxidation. Further investigations of the thermally oxidized bismuth films are on the way.

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