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THE INFLUENCE OF SUBSTRATE TEMPERATURE ON THE STRUCTURE AND ON THE OPTICAL REFLECTION SPECTRUM OF BISMUTH THIN FILMS

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Thin films of pure bismuth were deposited by vacuum thermal evaporation onto glass substrates maintained at different temperatures: 27 deg. C, 50 deg. C, 100 deg. C, 150 deg. C and 200 deg.C, respectively. The structure of the obtained films was analyzed by means of X-ray Diffractometry, with a Shimadzu diffractometer, which operates with a Cu target. The XRD patterns corresponding to a wide angular range proved the polycrystallinity of the bismuth films. Peak indexation was also performed, revealing changes in films' structures with changing substrate temperature. Grains sizes were estimated by using Scherrer's formula. The substrate temperature during the initial deposition also influenced the profile and the values of the optical reflection spectra, which were taken by means of a Perkin Elmer UV-VIS spectrometer, operated between 9000 and 52000 cm^{-1}. Correlations between the optical behavior and the structural changes were inferred.

INTRODUCTION

Among the chemical elements, semimetals draw attention because they exhibit high temperature and magnetic field dependence of the electrical resistance (known as magnetoresistance), making semimetals useful for magnetic field sensing applications.[1] Bismuth is a group V element, whose semimetal behavior in the bulk state is due to the overlap of the conduction and valence bands.

Along with other materials having low Fermi energy and small electron/hole effective mass, bismuth exhibits anomalous transport properties in thin film state as compared with the bulk state. This is considered to be due to a quantum size effect arising from the quantization of the component of the electron momentum, normal to the film plane, which leads to a decrease and even to the disappearance of the overlap between the valence and the conduction bands. The band separation depends on the film thickness. It was also found so far that there is a minimum in the variation of the electrical resistance of bismuth films with changing temperature, the position and magnitude of this minimum being a function of the substrate temperature during deposition. [2]

Bismuth is a semimetal with extremely high magnetoresistance, in the single-crystal state the electrical resistance increasing by a factor of 10^5 in a 7 Tessla magnetic field. This kind of behavior recommends bismuth for excellent magnetic field sensors. [3]

Another reason for studying bismuth is that it proves to be a nontoxic substitute for mercury electrodes.[4] The superconducting transition of vacuum-deposited amorphous bismuth films was also studied. [5]

Finally, bismuth films are worth studying and obtaining since they can rather easily be thermally

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oxidized in air in order to form bismuth trioxide, Bi_2O_3, the latter having large energy band gap, high photoconductivity, high refractive index and high oxide ionic conductivity, which recommend it for solar cells building, fuel cells, optical coatings, oxygen sensors, etc. [6-8]

Bismuth films were deposited on a rather large variety of substrates, such as: amorphous carbon, resine, [9] glass[2, 10] or mica[11] by using different kinds of deposition methods.

This article presents the results of the studies on the structural and optical properties of bismuth films deposited on glass substrates by classical thermal evaporation under vacuum at 5 different substrate temperatures.

EXPERIMENTAL

High purity (99.999 %) bismuth powder was thermally-vaporized in a standard vacuum unit, at $5 \cdot 10^{-5}$ torr pressure, from a quartz ampoule surrounded by tantalum wire run by electric current of 10 A. The substrates were chemically-cleaned, high-quality microscope glass slides, cut in 16 mm width parts, inserted in groups of four pieces into a home-made holder.

The temperature of the glass substrates during the vacuum depositions was maintained at room temperature (27 deg. C), 50 deg. C, 100 deg. C, 150 deg. C and 200 deg. C, respectively, in order to study the temperature's influence on the properties of the obtained films. The temperature of the glass substrates was monitored by a digital thermocouple. The other parameters during the depositions were kept unchanged.

The structure of the prepared bismuth films was studied by means of X-ray Diffractometry (XRD), by using a 6000 Shimadzu diffractometer, operating with a Cu target (λ=1.5418 Å). The scanning range was wide, between 15 and 80 degrees, with a scanning speed of 2 deg. /min. The XRD peaks were identified according to literature.

The optical reflection spectra of the bismuth films were obtained with a Perkin Elmer Lambda 35 Spectrometer operated at room temperature and at normal incidence, in the 9000 - 52000 cm^{-1} spectral range, *i.e.* in the near-Infrared, Visible and Ultraviolet domains.

RESULTS AND DISCUSSION

Figures denoted as 1 and 2 present the XRD patterns for each of the Bi films deposited at 27 deg. C, 50 deg. C, 100 deg. C, 150 deg. C and 200 deg. C, respectively, having the interplanar distance as variable on the horizontal axis. Peak indexation is shown in the inset of each XRD patterns. Along with the complete XRD pattern, the highest XRD peaks are also depicted into the same figures, as they are fitted very well with the Gauss function and from which the mean bismuth grain size was estimated, according to Scherrer's formula:

$$\langle D \rangle = \frac{0.94 \cdot \lambda}{\beta \cdot \cos\theta} \quad (1),$$

where λ is the wavelength of the X-rays used to obtain the XRD spectra, θ is the X-ray diffraction angle corresponding to the highest XRD peak, number 0.94 is used for spherically-assumed crystallites and β is the width estimated as **FWHM** – full width at half maximum – of the highest XRD peak of each complete XRD pattern.

Table 1 reunites the parameters necessary in order to estimate the mean grain size for each of the obtained Bi films, according to Scherrer's formula, where the magnitudes represent: the position of the highest peak's maximum, $\mathbf{2\theta_{highest\ peak}}$, the corresponding interplanar distance, $\mathbf{d_{highest\ peak}}$, the crystalline plane $(hk\ell)$ giving rise to those highest XRD peaks, the **FWHM** of the chosen XRD peaks, expressed both in degrees and in radians and, finally, the estimation of the mean grain size, **<D>**, calculated according to Scherrer's formula (1) and expressed in nanometers.

The investigation of the crystalline structure of the Bi films, done by XRD, proves that the deposited films are polycrystalline, with a tendency of getting texturized, *i. e.* with a specific preferential orientation after a certain crystalline plane. Except for the film deposited at 100 deg. C, whose highest XRD peak is given by to the (012) plane, all the other Bi films, deposited at 27 deg. C, 50 deg. C, 150 deg. C and 200 deg. C, respectively, have the most prominent (highest) XRD peak given by the (003) crystalline plane, with insignificant fluctuations of the XRD peak position, when passing from one substrate temperature to the other. Still, one can notice important decrease of the number of XRD peaks for the film deposited at 200 deg. C, as compared to the others. There is also a high background in the XRD pattern corresponding to t_s= 200 deg. C (t_s – substrate temperature). This is probably due to the amorphization of the films because of the beginning of oxidation of Bi with the oxygen either left in the vacuum chamber or with the one in the air, after the deposition.

The average size of the crystalline grains obtained from the fitting of the highest XRD peak ranges between 14.58 and 22.09 nm, being the highest for t_s= 150 deg. C, as one can notice from Table 1. The film deposited at 27 deg. C presents low background and smaller number of XRD peaks than the other analyzed Bi films, except for the film deposited at 200 deg. C that, instead, has an obvious amorphous phase present, together with some families of crystalline planes. Thus, it can be concluded that the film with t_s=27 deg. C has the highest order of atoms of all the analyzed films. This is why its crystalline grains are the biggest.

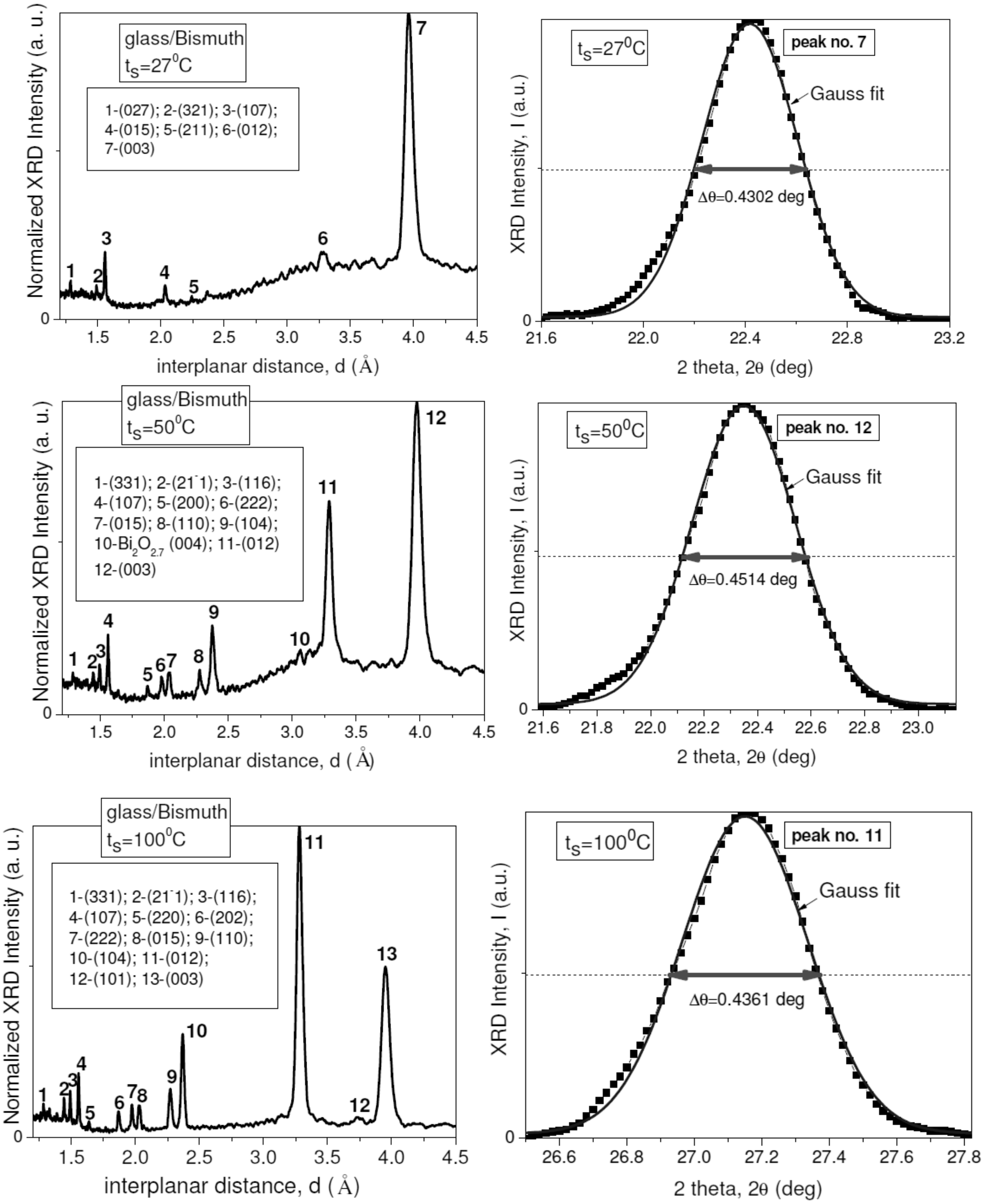

Fig. 1 – XRD patterns (left side) for the Bi films deposited at 3 different substrate temperatures and the corresponding Gauss-fitted highest XRD peaks with FWHM estimation (right side).

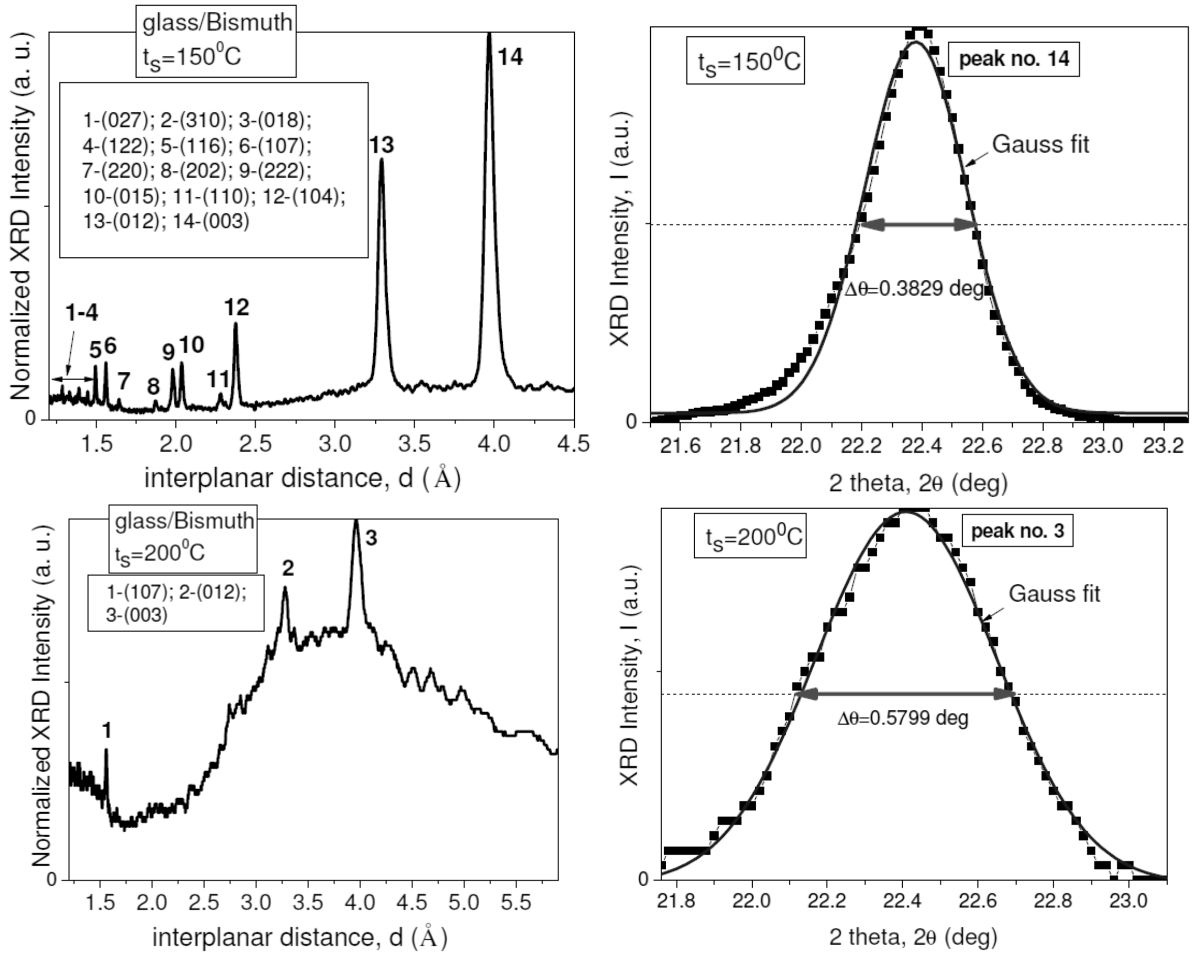

Fig. 2 – XRD patterns (left side) for the Bi films deposited at other 2 substrate temperatures and the corresponding Gauss-fitted highest XRD peaks with FWHM estimation (right side)

Table 1

Parameters of the highest peak from the XRD patterns in Figs. 1 and 2 and mean grain size estimation

t_s (deg. C)	$2\theta_{highest\ peak}$ (deg.)	$d_{highest\ peak}$ (Å)	crystalline plane $(hk\ell)$	FWHM (deg)	FWHM, β (rad)	<D> (nm)
27	22.44	3.9588	(003)	0.4302	0.0075	19.663
50	22.36	3.9728	(003)	0.45142	0.0078	18.736
100	27.16	3.2806	(012)	0.4361	0.0076	19.574
150	22.39	3.9676	(003)	0.3829	0.0067	22.090
200	22.43	3.9606	(003)	0.5799	0.0101	14.587

Fig. 3 presents the overlapped optical reflectance spectra as functions of wavenumber for all the investigated bismuth films. Comparisons between the position and the values of reflectance extrema in the corresponding spectra are given in Table 2. Thus, R_{max} and $\tilde{\upsilon}_{\text{for Rmax}}$ denote the reflectance maxima and its corresponding position over the entire investigated spectral range. The same way are the notation for the reflectance minima and for the local extrema of the reflectance spectra, noticed for all the Bi films. $\tilde{\upsilon}_{max}$ denotes the maximum available wavenumber in the spectral domain of the optical instrument and $\mathbf{R_{at}}$ $\tilde{\upsilon}_{max}$ is the value of the reflectance at this particular wavenumber of each of the deposited Bi films.

One can notice the maintenance of the position for the highest optical reflectance value at 11976.05 cm^{-1} for the films deposited at 27 deg. C, 100 deg. C and 150 deg. C, respectively. Still, important variations in the values of the optical reflectance factor are noticeable when passing from one substrate temperature to another, either in the maximum, minimum or local extrema values. At the highest wavenumber, *i. e.* at 52631.58 cm^{-1}, one can notice a monotonous increase in the reflectance values with increasing substrate temperature, except for t_s= 27 deg. C. The highest value of the reflectance reached for the film deposited at 27 deg. C is explained by the structural order of this film inferred from the XRD analysis, *i. e.* by the smaller number of families of crystalline planes than the other films, combined with low background, which means no amorphous phase is present within the film as deduced from the XRD analysis.

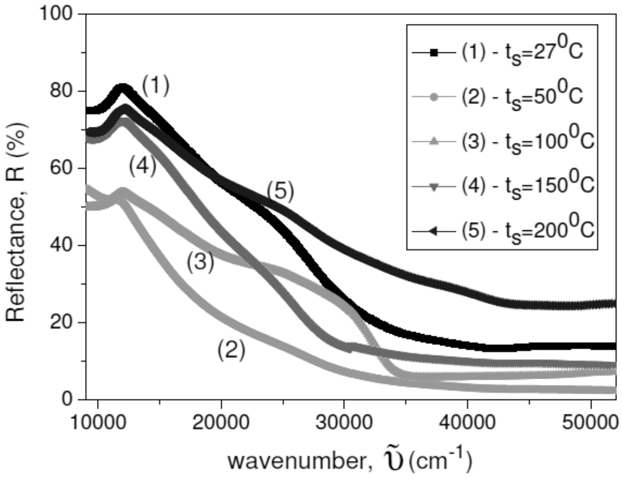

Fig. 3 – Overlapped optical reflectance spectra for all the investigated bismuth films.

Table 2

Comparisons between the positions and the values of reflectance extrema in the corresponding spectra

t_s (deg. C)	R_{max} (%)	$\tilde{\upsilon}$ for Rmax (cm^{-1})	R_{min} (%)	$\tilde{\upsilon}$ for Rmin (cm^{-1})	$\tilde{\upsilon}_{max}$ (cm^{-1})	R_{at} $\tilde{\upsilon}_{max}$ (%)	local extrema		
							type	R (%)	$\tilde{\upsilon}$ (cm^{-1})
27	81.025	***11976.05***	13.418	42553.19	52631.58	13.732	minimum	13.806	40650.41
50	54.803	9090.909	2.54	52631.58		2.54	maximum	51.724	11750.88
100	53.793	***11976.05***	5.886	36231.88		7.503	minimum	6.554	34722.22
150	72.39	***11976.05***	9.007	52631.58		9.007	minimum	13.622	30303.03
200	75.418	12048.19	24.384	48076.92		25.015	minimum	24.808	43668.12

CONCLUSIONS

Bismuth films were deposited on glass substrates maintained at 5 different substrate temperatures, by vacuum thermal evaporation. The structure of the films investigated by the XRD technique, proved to be polycrystalline and texturized, with the highest peaks fitted well by the Gauss function. The crystallites sizes were in the 14.58 nm till 22.09 nm range. At t_s=200 deg. C, there is a beginning of amorphization of the films, noticed as a high background in the XRD pattern superimposed on a small number of clear XRD peaks.

The optical reflectance properties were also studied, proving to be very sensitive to the change of substrate temperature during Bi films depositions. Thus, the substrate temperature strongly influences both the structural and the optical properties of the Bi films, being necessary to be considered whenever one wants to use them as-such or for further treatments or combinations either for theoretical or for practical uses.

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