

Structural and morphological behavior of bismuth thin films grown through DC-magnetron sputtering

Comportamiento estructural y morfológico de películas delgadas de bismuto obtenidas a través de sputtering con magnetrón DC

Claudia Milena Bedoya-Hincapié¹ Jhonattan de la Roche¹ Elisabeth Restrepo-Parra¹
José Edgar Alfonso² Jhon Jairo Olaya-Florez²

Recibido 28 de abril de 2014, aceptado 28 de agosto de 2014
Received: April 28, 2014 Accepted: August 28, 2014

ABSTRACT

Bismuth thin films were grown onto glass substrates through the DC magnetron sputtering technique. The effects of substrate temperature on the microstructure of the films were evaluated. The structural behavior was analyzed via X-ray diffraction, and it showed a marked influence of the substrate temperature on the crystallite size and the micro-stress. The morphologies evaluated through Electron Probe Micro-analyzer images indicated a slight difference in the grain size with an increase in temperature as well as a significant increase in surface roughness, according to profilometer measurements.

Keywords: Bismuth, thin film, thermal effects, sputtering, microstructure.

RESUMEN

En este trabajo se depositaron películas delgadas de bismuto sobre sustratos de vidrio mediante la técnica de sputtering con magnetrón DC y se evaluaron los efectos de la temperatura del sustrato en la microestructura de las películas. El comportamiento estructural se analizó mediante difracción de rayos X, mostrando una notable influencia de la temperatura del sustrato en el tamaño de cristalito y microestrés. La morfología evaluada por medio de imágenes de la microsonda electrónica, presentó una leve diferencia en el tamaño de grano con el incremento de la temperatura así como un significativo incremento de la rugosidad superficial, según medidas de perfilometría.

Palabras clave: Bismuto, película delgada, efectos térmicos, sputtering, microestructura.

INTRODUCTION

Bismuth (Bi), a typical semimetal, has a unique set of properties, such as large Fermi wavelengths [1], strong diamagnetism, and very high magnetoresistance [2]. Recently, bismuth nanostructures have attracted much attention because of their quantum transport and finite-size effects and their potential application for magnetic field sensors, optical devices, catalysts and thermoelectric coolers or power generators [3-7].

At the same time, with increasing environmental concerns and the need for green reagents, interest in bismuth and its compounds has increased tremendously during the last decade [8]. Up to now, many papers on bismuth nanostructures synthesized by means of various techniques have been reported, such as thin films [9], nanowires [10], nanotubes [11], nanoplates [12], and nanobelts [13]. In particular, bismuth thin film deposition is complicated due to its melting point, which leads to

¹ PCM Computational Applications. Laboratorio Física del Plasma. Universidad Nacional de Colombia-Sede Manizales. E-mail: cmbedoyahi@unal.edu.co; jdey@unal.edu.co; erestrepopa@unal.edu.co

² Grupo de Ciencia de Materiales y Superficies. Departamento de Física. AFIS Análisis de Fallas, Integridad y Superficies. Universidad Nacional de Colombia-Sede Bogotá. Bogotá, Colombia. E-mail: jealfonsoo@unal.edu.co; jjolayaf@unal.edu.co

higher crystallization rates and low vapor pressure. They have been deposited using several deposition techniques, including pulsed laser deposition (PLD) [14-15], molecular beam deposition method [16], rf sputtering [17], thermal evaporation [18] and electro-deposition [19]. Some of the advantages of using sputtering techniques are the possibility of evaporating materials with different natures and the good adherence of the thin film. Recently, Dong-Ho Kim and co-workers [17] have successfully prepared bismuth thin films through rf-magnetron sputtering, demonstrating the effects of deposition temperature on surface morphology and their electrical transport properties. They found that homogenous thin films cannot be obtained above 175 °C, and the onset of the coalescence of grains is around 100 °C, where movement of grains and surface diffusion of atoms are enhanced. Also, Latha Kumari, S.-J. Lin, J.-H. Lin, Ma, Lee and Liou [18] deposited bismuth thin films onto (100) Si through thermal evaporation at various substrate temperatures (30, 100 and 200 °C), observing the formation of coalescence grains and highly textured crystallographic thin films at low temperatures, while for a high temperature (200 °C) there is no uniform growth, due to grain segregation, island formation, and random-oriented polycrystalline structure. However, there have been few reports up to now about the effect of substrate temperature on the microstructure of Bi thin films deposited via dc magnetron sputtering.

In this paper, we study the effect of the substrate temperature on the structural and morphological behavior of bismuth thin films deposited via dc-magnetron sputtering onto a glass substrate.

EXPERIMENTAL DETAILS

Bismuth monolayers were deposited via the dc magnetron sputtering technique using a bismuth target (99.99%) 2 inches of diameter. Coatings were deposited on glass substrates, varying the substrate temperature from 100 to 160 °C. The substrates were ultrasonically cleaned in acetone solution for 15 minutes and underwent a pretreatment through a plasma cleaning process that was carried out for 15 minutes before the deposition. The deposition parameters used for the growth of the thin films were: base pressure of 10^{-4} Pa, work pressure of 6×10^{-3} Pa, 1 W/cm² for power density, argon gas flow of 20 sccm and a deposition time of 20 minutes.

Structural characterization was performed with a Bruker AXS D8 advanced X-Ray diffractometer (XRD), using parallel beam geometry and a grazing incidence angle $\phi = 1.5^\circ$ with Cu- α radiation ($\lambda = 1.5406 \text{ \AA}$) ranging between 20-80° with steps of 0.02° . Cross section and morphological surface analyses were carried out using the JEOL JXA-8530F Field Emission Electron Probe Microanalyzer (EPMA) with 10 keV of energy and a magnification of 50.000X. Also, thickness and roughness measurements of the thin films were determined with a Veeco Dektak 150 surface profilometer, using a 2.3 mm length and a measuring range of 6.5 μm .

RESULTS AND DISCUSSION

XRD patterns of bismuth monolayers deposited at different substrate temperatures are shown in Figure 1. The identified and indexed XRD peaks for all the samples belong to a hexagonal structure ($a=b=4.547$, $c=11.8616 \text{ \AA}$, $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$) matching PDF 44-1246, being consistent with a hexagonal primitive cell, which is regularly used to describe a bismuth lattice [20-21]. Furthermore, Bi can take the form of a rhombohedral cell and can also be assimilated into a slightly deformed pseudo-cubic cell [15]. XRD patterns exhibited no presence of preferred orientation, indicating randomly oriented polycrystalline thin films. The width of the peaks related to crystallite size and micro-stress revealed the influence of the substrate

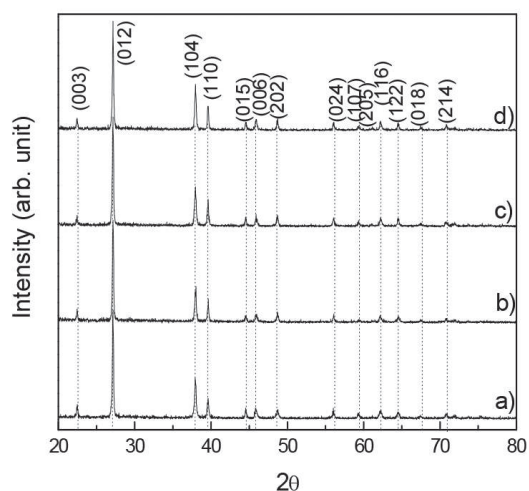


Figure 1. XRD patterns of Bi thin films grown at various substrate temperatures: a) 100, b) 120, c) 140 and d) 160 °C.

temperatures. Average crystallite size and micro-stress were estimated using the Williamson-Hall method, fitting the profiles with a Lorentzian function, by employing the following equation, which includes the main contributions (crystallite size, micro-stress and instrumental error) to the width of the peak:

$$\beta = \frac{0.9\lambda}{D \cos \theta} + 4\varepsilon \tan \theta + \beta_0 \quad (1)$$

where β is the Full Width at Half Maximum, λ is the X-ray wavelength, β_0 is the instrumental error, D is the crystallite size and ε is the micro-stress.

Figure 2 shows the calculated crystallite grain size and the micro-stress as a function of the substrate temperature. Crystallite size exhibited a linear behavior with an increase in substrate temperature, indicating an enhanced crystallite quantity, seen by the increase in the intensity of the peaks, while the micro-stress diminished at higher temperatures, helping to relax and release the stress in the thin film.

The average thickness values of the thin films measured with profilometry equipment were in the range 600-900nm. No significant differences in thickness between the films were observed with variation of substrate temperature.

In order to establish the temperature effect in bismuth thin films over a wide range, an XRD analysis of temperature in the range from 100 to 300 °C in situ was carried out on the film grown at 120 °C in air atmosphere, with temperature steps of 50 °C. These results are shown in Figure 3. Bismuth

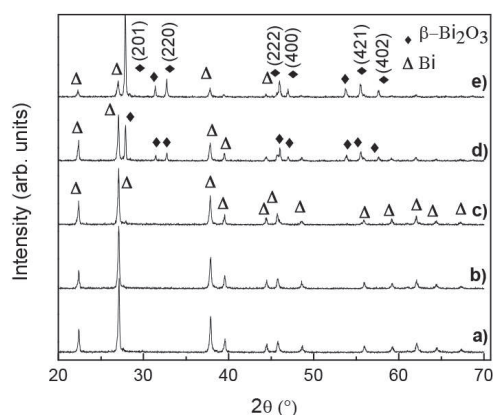


Figure 3. XRD patterns of bismuth thin film annealed in air atmosphere at different temperatures: a) 100, b) 150, c) 200, d) 250 and e) 300 °C.

diffraction peaks appear at low temperatures up to approx. 200 °C, and its decrease is associated with the bismuth oxide $\beta\text{-Bi}_2\text{O}_3$ (PDF 27-0050), a formation that is clearer above 250 °C. This indicates the change from hexagonal to tetragonal structure, and also a shift to a yellow-plated color surface. An example of this is the research developed by Dong-Ho Kim, S.-H. Lee, J.-K. Kim and G.-H. Lee [17], who deposited Bi thin films at room temperature which were then annealed for 1 h at over 250 °C, showing XRD patterns of bismuth oxide.

An EPMA cross-section image of the bismuth thin films is shown in Figure 4. Columnar growth with large irregular particles occurs in the films, which

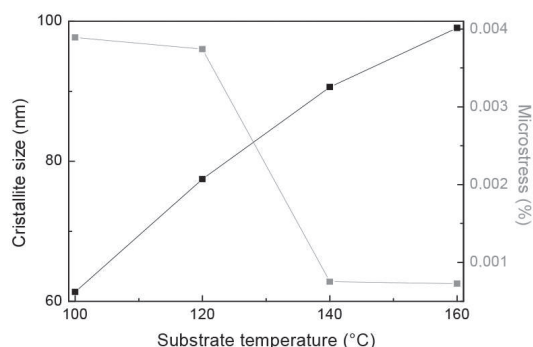


Figure 2. Crystallite grain size and micro-stress as a function of substrate temperature in Bi thin films.

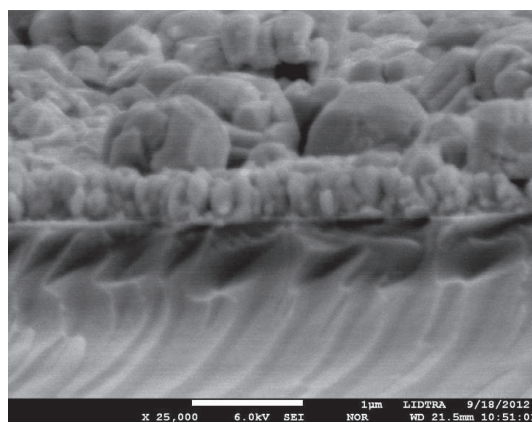


Figure 4. EPMA Cross-section image of Bi thin films' growth morphology.

has been also reported for Bi films produced through dc sputtering [22, 23], rf sputtering [17] and PLD techniques [14]. The typical columnar growth in the thin films, as well as the low melting point of Bi and a rapid solidification process, can be observed, due to the high mobility of the adsorbed species on the heated surface [18]. According to the Thornton diagram [24], the structural model for thin films obtained through PVD techniques depends on the pressure and the relation between the substrate temperature and melting temperature (T/T_m). Bi has a low T_m , equal to 271 °C [14], so T/T_m takes values of 0.68, 0.72, 0.76 and 0.79, clearly locating the thin film morphology in zone 2, ascribed to a dense columnar growth.

Figure 5 illustrates surface EPMA images of thin films for various substrate temperatures. The distribution of small grains with some large ones appears at low temperatures in the range 100–140 °C, while at 160 °C the grains tend to be slightly bigger on average. This indicates the increase of grain size due to the high growth rate at raised substrate temperatures, caused by the contribution of the thermal energy to the effects of the diffusion and the coalescence of the grains. In the range of temperatures considered in this study, segregation effects did not appear, because they become visible at higher temperatures, according reports by Dong-Ho Kim, S.-H. Lee, J.-K. Kim and G.-H. Lee [17], who suggest segregation can occur above 175 °C, or even above 200 °C [18].

Some reports indicate that the grain geometry is strongly determined by the deposition technique. The grain geometry obtained with dc- magnetron sputtering was polyhedral-like structures. Also, similar surface morphology has been found in thin films grown via the thermal evaporation method and spherical grains with pulsed laser deposition [14]. These results are in agreement with profilometer results, which suggest a strong dependence of surface morphologies on the substrate temperature, with the increases of the average roughness with temperature, as shown in Figure 6.

CONCLUSIONS

The effect of substrate temperature on the structural and morphological behavior was studied for bismuth thin films grown on glass substrates

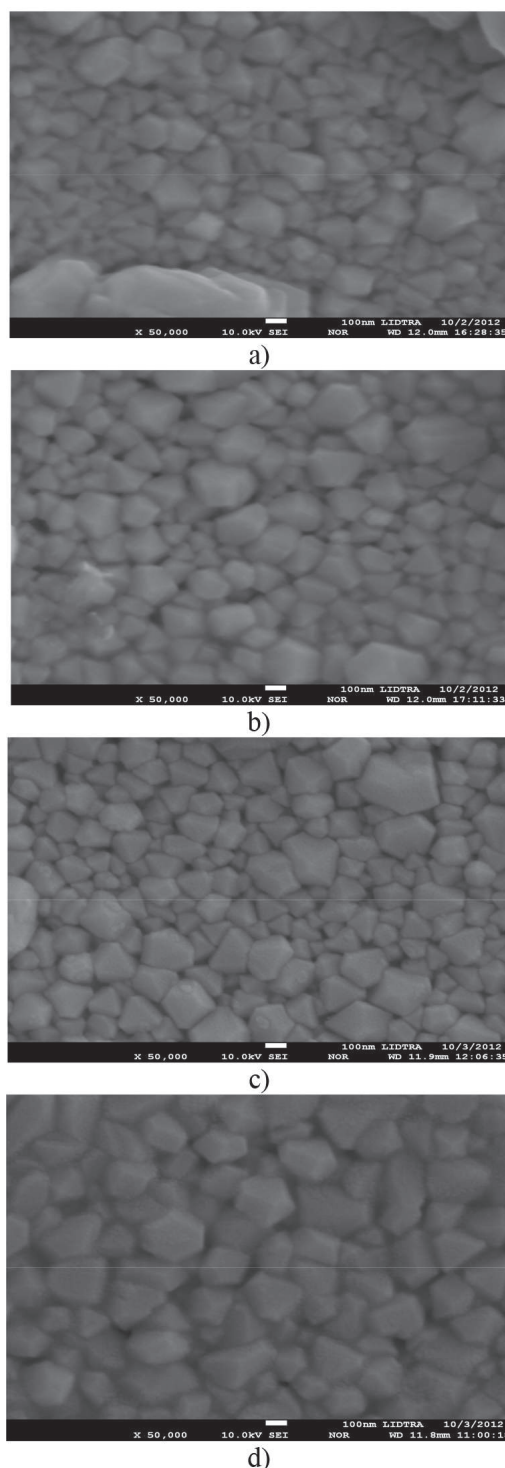


Figure 5. EPMA morphological images of Bi thin films growth at different substrate temperatures a) 100, b) 120, c) 140, d) 160 °C.

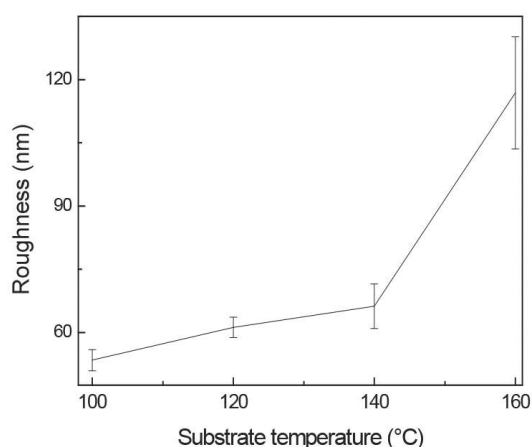


Figure 6. Roughness of bismuth thin films deposited at different substrate temperatures.

via the dc-magnetron sputtering technique. A considerable influence of the substrate temperature on the microstructure was found. The increase of crystallite size with temperature and a drop in micro-stress were observed through the Williamson-Hall method. Morphological images showed the columnar growth of the thin films and grains with a polyhedral-like geometry. Segregation in Bi thin films was not observed in the range of substrate temperatures studied, but it may appear at higher temperatures, over 170 °C.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support of the Dirección Nacional de Investigaciones of the Universidad Nacional de Colombia during the course of this research, under project 12920 “Desarrollo teórico-experimental de nanoestructuras basadas en Bismuto y materiales similares” and “Bisnano project”, and to “Universidad Nacional de Colombia” and “Cinvestav” Querétaro-México for the assistance in the measurements.

REFERENCES

[1] G.E. Smith, G.A. Baraff and J.M. Rowell. "Effective g Factor of Electrons and Holes in Bismuth". *Phys. Rev.* Vol. 135, pp. A1118-A1124. 1964.
 [2] S. Murakami. "Quantum Spin Hall Effect and Enhanced Magnetic Response by Spin-

Orbit Coupling". *Phys. Rev. Lett.* Vol. 97, pp. 236805-236808. 2006.
 [3] J. Xu, W. Zhang, M.A. Morris and J.D. Holmes. "The formation of ordered bismuth nanowire arrays within mesoporous silica templates". *Mater. Chem. Phys.* Vol. 104, pp. 50-55. 2007.
 [4] J. Heremans, C.M. Thrush, Y.-M. Lin, S. Cronin, Z. Zhang, M.S. Dresselhaus and J.F. Mansfield. "Bismuth Nanowire Arrays: Synthesis and Galvanomagnetic Properties". *Phys. Rev. B.* Vol. 61, pp. 2921- 2930. 2000.
 [5] Z. Zhang, X. Sun, M.S. Dresselhaus, J.Y. Ying and J. Heremans. "Electronic Transport Properties of Single-Crystal Bismuth Nanowire Arrays". *Phys. Rev. B.* Vol. 61, pp. 4850-4861. 2000.
 [6] D. Ma, J. Zhao, Y. Zhao, X.L. Hao and Y. Lu. "An easy synthesis of 1D bismuth nanostructures in acidic solution and their photocatalytic degradation of rhodamine B". *Chem. Eng. J.* Vol. 209, pp. 273-279. 2012.
 [7] C.M. Bedoya-Hincapié, M.J. Pinzón-Cárdenas, J.E. Alfonso-Orjuela, E. Restrepo-Parra y J.J. Olaya-Florez. "Recubrimientos De Bismuto y Óxidos de Bismuto Síntesis, Caracterización y Aplicaciones". *Dyna.* Vol. 176, pp. 139-148. 2012.
 [8] N.M. Leonard, L.C. Wieland and R.S. Mohan. "Applications of bismuth (III) compounds in organic synthesis". *Tetrahedron.* Vol. 58, pp. 8373-8397. 2002.
 [9] D.W. Song, W.-N. Shen, B. Dunn, C.D. Moore, M.S. Goorsky, T. Radetic, R. Gronsky and G. Chen. "Thermal Conductivity of Nanoporous Bismuth Thin Films". *Appl. Phys. Lett.* Vol. 84, pp.1883-1885. 2004.
 [10] Y. Hasegawa, Y. Ishikawa, T. Komine, T.E. Huber, A. Suzuki, H. Morita and H. Shirai. "Magnetoelectric Coefficient of a Bismuth Microwire Array in a Magnetic Field". *Appl. Phys. Lett.* Vol. 85, pp. 917-919. 2004.
 [11] B. Yang, C. Li, H. Hu, X. Yang, Q. Li and Y. Qian. "A Room-Temperature Route to Bismuth Nanotube Arrays". *Eur. J. Inorg. Chem.* Vol. 2003, pp. 3699-3702. 2003.
 [12] R. Fu, S. Xu, Y. Lu and J. Zhu. "Synthesis and Characterization of Triangular Bismuth Nanoplates". *Cryst. Growth Des.* Vol. 5, pp. 1379-1385. 2005.

- [13] Z. Gao, H. Qin, T. Yan, H. Liu and J. Wang "Structure and resistivity of bismuth nanobelts in situ synthesized on silicon wafer through an ethanol-thermal method". *J. Solid State Chem.* Vol. 184, pp. 3257-3261. 2011.
- [14] M.O. Boffoué, B. Lenoir, H. Scherrer and A. Dauscher. "Pulsed laser deposition of bismuth in the presence of different ambient atmospheres". *Thin Solid Films.* Vol. 322, pp. 132-137. 1998.
- [15] A. Dauscher, M.O. Boffoué, B. Lenoir, R. Martin-Lopez and H. Scherrer. "Unusual growth of pulsed laser deposited bismuth films on Si(100)". *Appl. Surf. Sci.* Vol. 138-139, pp. 188-194. 1999.
- [16] Y. Ahn, Y.-H. Kim, S.-H. Kim and K.-H. Jeong. "Thickness dependent surface microstructure evolution of bismuth thin film prepared by molecular beam deposition method". *Curr. Appl. Phys.* Vol. 12, pp. 1518-1522. 2012.
- [17] D.-H. Kim, S.-H. Lee, J.-K. Kim and G.-H. Lee. "Structure and electrical transport properties of bismuth thin films prepared by RF magnetron sputtering". *Appl. Surf. Sci.* Vol. 252, pp. 3525-3531. 2006.
- [18] L. Kumari, S.-J. Lin, J.-H. Lin, Y.-R. Ma, P.-C. Lee and Y. Liou. "Effects of deposition temperature and thickness on the structural properties of thermal evaporated bismuth thin films". *Appl. Surf. Sci.* Vol. 253, pp. 5931-5938. 2007.
- [19] E. Bertin, S. Garbarino and D. Guay. "Formic acid oxidation on Bi covered Pt electrodeposited thin films: influence of the underlying structure". *Electrochim. Acta.* Vol. 134, pp. 486-495. 2014.
- [20] J. Chang, H. Kim, J. Han, M.H. Jeon and W.Y. Lee. "Microstructure and Magnetoresistance of Sputtered Bismuth Thin Films Upon Annealing". *J. Appl. Phys.* Vol. 98, pp. 23906-23912. 2005.
- [21] P.M. Vereecken, L. Sun, P.C. Searson, M. Tanase, D.H. Reich and C.L. Chien. "Magnetotransport Properties of Bismuth Films on P-Gaas". *J. Appl. Phys.* Vol. 88, pp. 6529-6535. 2000.
- [22] J.C.G. De Sande, T. Missana and C.N. Afonso. "Optical Properties of Pulsed Laser Deposited Bismuth Films". *J. Appl. Phys.* Vol. 80, pp. 7023-7027. 1996.
- [23] J.-H. Hsu, Y.-S. Sun, H.-X. Wang, P.C. Kuo, T.-H. Hsieh and C.-T. Liang. "Substrate dependence of large ordinary magnetoresistance in sputtered Bi films". *J. Magn. Mater.* Vol. 272-276, pp. 1769-1771. 2004.
- [24] J.A. Thornton. "Influence of apparatus geometry and deposition conditions on the structure and topography of thick sputtered coatings". *J. Vac. Sci. Technol.* Vol. 11, pp. 666-670. 1974.