Preparation and characterization of bismuth nanostructures deposited by pulsed laser ablation

L Escobar-Alarcón¹, J G Morales-Mendez², D A Solís-Casados³, S Romero¹, M Fernández¹, E Haro-Poniatowski²

¹ Departamento de Física, Instituto Nacional de Investigaciones Nucleares, Apdo. Postal 18-1027, México DF 11801, México.
² Departamento de Física, Universidad Autónoma Metropolitana Iztapalapa, Apdo. Postal 55-534, México, D.F., México.
³ Centro Conjunto de Investigación en Química Sustentable UAEM-UNAM, Carretera Toluca-Atlacomulco Km 14.5, Unidad San Cayetano, Toluca, Estado de México, 50200, México.

E-mail: luis.escobar@inin.gob.mx

Abstract. Bismuth nanostructures, from nanoparticles to quasi-percolated films, were deposited by pulsed laser ablation (PLA) on different substrates using the 355 nm line of a Nd:YAG laser. The morphology and size distribution of the obtained nanostructures were investigated, as a function of the number of ablation pulses, by high resolution electron microscopy (HRTEM) and atomic force microscopy (AFM). Deposits with a small number of pulses, 50, are formed of separated isolated particles with diameters in the range from 5 to 20 nm. Further increase in the number of pulses (>100) results in coalescence of individual particles with the formation of dendritic structures and finally, for 500 pulses, quasi-percolated Bi films are obtained. Additionally, the nanostructures formed were characterized by XPS, and Raman spectroscopy in order to determine the physical and chemical properties of the deposited material.

1. Introduction

Nanostructured materials have attracted great interest because their physical properties are different from those of the same bulk material. The differences arise owing to the nanoscale dimensions of nanostructures that favour quantum effects due to spatial confinement of the carrier charges and corresponding modification of their density of states (DOS) [1]. It is worth mentioning that not only the size but also the shape of the nanostructures determine some important materials properties. Therefore investigating preparation techniques that allow the control of size and shape of nanostructures is a key issue in this field. It has been shown that pulsed laser ablation at low pressure can produce bismuth nanostructures in an easy way. In particular, the solid–liquid-solid transitions of nanocrystalline bismuth, embedded in amorphous germanium, prepared by PLA in vacuum have been studied [2]. Furthermore, the optical properties of nanocomposite films consisting of Bi nanostructures embedded in Al₂O₃ prepared by the same technique have been investigated [3] in detail. Bismuth is a semimetal which has unusual electronic properties resulting from its highly anisotropic Fermi surface, low carrier concentration, small effective mass and long mean free path of the charge carriers [3]. As a consequence, Bi nanostructures have been considered good candidates for nano-sized materials with novel physical, chemical and thermal properties. Therefore there are a number of research
efforts looking to synthesize bismuth and bismuth-based compounds at the nanoscale controlling the properties of the deposited material.

2. Experimental Procedure
The nanostructures were produced by laser ablation in a vacuum chamber (Intercovamex) at low pressure, close to $2 \times 10^{-5}$ Torr, ablating a high purity bismuth target. A Nd:YAG laser (Spectra Physics) emitting at the third harmonic (355 nm) with 10 ns pulse duration was used as energy source. The laser energy per pulse and the spot size were 5 mJ and 1.5 mm respectively, which correspond to a laser fluence of 300 mJ/cm$^2$. The deposits were performed at room temperature on different substrates: glass, TEM carbon-coated copper grids and pieces of silicon (100) wafers. The morphology and size distribution of the nanostructured films was investigated as a function of the number of pulses used to ablate the target. The substrates were placed 5 cm away and in front of the Bi target.

The as-prepared bismuth nanostructures onto the TEM carbon-coated grids were observed in a JEOL 2100 transmission electron microscope in order to analyze their shape, size and structure. Determination of the elements presents in the deposits as well as their bonding features were done by X-ray Photoelectron Spectroscopy (XPS) using a Jeol JPS 9200 XPS. Raman spectroscopy (RS) was used to study the vibrational features of the deposits using an HR LabRam 800 system equipped with an Olympus BX40 confocal microscope and a Nd:YAG laser (532 nm). The amount of Bi deposited on silicon substrates was estimated from Non-Rutherford Backscattering Spectroscopy (NRBS). Measurements were performed in a Tandem Van de Graff accelerator using a proton beam of 2.8 MeV and a detection angle of 165°. AFM images were acquired with an Asylum Research microscope operating in the non-contact mode.

3. Results and Discussion
3.1 Transmission Electron Microscopy (TEM)
In order to investigate, and eventually control, the morphology and size of the Bi nanostructures and therefore the properties of the obtained materials, the number of pulses used to ablate the Bi target was varied from 50 to 500. Representative TEM images of Bi nanostructures as well as their corresponding size distributions at different number of pulses (50, 100, 200, 300 and 500) are shown in figure 1. As it is observed in figure 1a, the sample prepared using 50 pulses consists of nearly spherical nanoparticles with a mean diameter close to 6 nm and a size distribution from 5 to 16 nm. The sample deposited using 100 pulses (figure 1b) is formed by well-separated nanoparticles (characteristic of a nucleation stage of growth) with bigger sizes, around 12 nm, and with wider size distribution. In this case, it is clearly observed that nanoparticles exhibit faceted irregular shapes and the covered area was increased. When 200 pulses are used, the mean diameter increases to 25 nm with a size distribution from 5 to 70 nm (figure 1c). This broad and asymmetric distribution is indicative of coalescence processes between the individual particles as a result of a larger covered area that favors their interaction. The deposit obtained with a number of laser shots greater than 300 shows a quasi-percolated state in which nanostructures with mean diameter of 33 nm are observed (figure 1d). At the highest number of pulses used in this work (500) a quasi-percolated film is observed leaving channels of uncovered substrate (figure 1e), with Feret’s diameters (defined as the measured distance between parallel lines that are tangent to the particle’s profile and perpendicular to the ocular scale) close to 60 nm. The HRTEM image of this sample shows the presence of nanocrystals with sizes ranging from approximately 10 to 20 nm. From this image the measured interplanar distances are 3.3 and 2.2 Å that agree well with the values of Bi (012) plane (3.3 Å) and (110) plane (2.2 Å) according to the data reported in the JCPDS database (00-044-1246). This result reveals the polycrystalline nature of the deposited Bi nanostructures. Figure 1 f) shows the plot of the Feret’s diameter of the Bi nanostructures in the deposits, as a function of the number of laser pulses. As is clearly observed, the mean Feret’s diameter increases with the number of laser shots following a linear relation. This is an interesting result because it allows the control of the mean size of the nanostructures in a straightforward way.
Figure 1. TEM images of Bi nanostructures and their corresponding size distributions at different number of pulses, a) 50, b) 100, c) 200, d) 300, e) 500 and the Feret’s diameter as a function of the number of laser pulses.

3.2 Atomic Force Microscopy
Figure 2 shows, as an example, the AFM images obtained for the nanostructures deposited using 50 pulses (figure 2a) and 200 pulses (figure 2b). The images show that the nanostructures shape and size change with the number of laser pulses. Individual nanoparticles with a quasi-spherical shape and diameters of about 5 to 35 nm are observed for the sample deposited using 50 pulses. In contrast, nanostructures with sizes ranging from 15 to 45 nm, arranged in a rod-like shape, are observed in the case of the sample deposited with 200 pulses. These results agree reasonably with the TEM measurements. In general terms, in the case of a lower number of pulses the nanostructures preferentially grow with a quasi-spherical shape; whilst a higher number of pulses leads to larger nanostructures with more complex shapes covering completely the surface. It is worth noting that these nanostructures result from aggregation processes and seem to be formed actually by individual smaller nanoparticles. In some sense, these results reveal the early mechanisms that control the deposition of Bi thin films; starting with the arrive of incident atoms on surface defects that act as nucleation centres for nanoparticle growth followed by their agglomeration resulting in islands and finally promoting the formation of a continuous film.

3.3 Non-Rutherford Backscattering spectroscopy (NRBS)
The NRBS spectra of the same samples (not shown) reveal an increment of the signal associated to bismuth as the number of pulses increases. From these spectra, the number of atoms per unit area was estimated. It was found that the amount of Bi atoms varies monotonically, from about $3.8 \times 10^{15}$ atoms/cm$^2$ to $1.5 \times 10^{16}$ atoms/cm$^2$ as the number of pulses is increased from 50 to 500 respectively. It is clearly that the deposition rate of Bi depends on the number of pulses, decreasing as the number of pulses increases. This could be attributed to a reduction in the sticking coefficient and/or to sputtering processes.
3.4 Raman characterization

The Raman spectra of all samples showed peaks at 71 and 97 cm\(^{-1}\) as is presented in figure 3. These signals correspond to the \(E_g\) and \(A_{1g}\) first order Raman modes characteristic of rhombohedral bismuth [5] and reveal the crystalline state of the formed nanostructures. It is worth mentioning that the signal around 125 cm\(^{-1}\), that could be attributed to the Bi—O stretches of \(\beta\)-Bi\(_2\)O\(_3\) [6], was observed only in the sample prepared using 500 pulses, suggesting a partial oxidation of the Bi nanostructures due to exposure to the environmental moisture and/or laser induced oxidation.

Figure 3. Raman spectra of the samples prepared using different number of pulses.

3.5 X-ray photoelectron spectroscopy (XPS)

Figure 4a shows the high-resolution XPS spectrum of the Bi 4f region of the sample prepared with 500 pulses. It is worth mentioning that the XPS spectra of all samples were very similar. The two peaks at 162.4 eV and 157.1 eV can be assigned to Bi 4f5/2 and Bi 4f7/2, respectively revealing the metallic state of the deposited nanostructures. The shoulders around 164.3 eV and 159.0 eV can be ascribed to the binding energies of Bi 4f5/2 and Bi 4f7/2 corresponding to Bi\(_2\)O\(_3\) [7]. Therefore, these results reveal that the Bi nanostructures were deposited in the form of metallic bismuth with a slight amount of Bi\(_2\)O\(_3\). Figure 4b shows the spectrum corresponding to the O 1s region. A low intensity signal suggesting a low amount of oxygen present in this
sample is observed. The presence of oxygen in the samples could be due to adsorption from the environmental moisture.

![Figure 4. High-resolution XPS spectra of the Bi 4f region (a) and the O 1s region (b) of the sample prepared with 300 pulses.](image)

4. Conclusions

Bismuth nanostructures were obtained by pulsed laser ablation under vacuum conditions. Their size and size distribution were controlled by varying the number of pulses used to ablate the Bi target following an approximately linear relation. Bi NPs with Feret’s diameter as small as 7 nm were obtained using only 50 pulses owing to the high ablation rate of Bi. Compositional and Raman analysis showed the metallic nature of the deposited material.

6. References

[1] Choi D S, Balandin A A, Leung M S, Stupian G W, Presser N, Chung S W, J. R. Heath J R, Khitun A and Wang K L 2006 Applied Physics Letters 89 141503
[2] Haro-Poniatowski1 E, Serna R, Suárez-García A, Afonso C N, Jouanne M, Morhange J F 2004 Appl. Phys. A 79 1299–1302
[3] Serna R, Jiménez de Castro M, Toudert J, Haro-Poniatowski E, García López J 2013 Appl. Phys. A 110 863-867
[4] Carotenuto G, Hison C L, Capezzuto F, Palomba M, Perlo P, Conte P 2009 J. Nanopart. Res. 11 1729
[5] Trentelman K, Raman J 2009 Spectrosc. 40 585
[6] Latha Kumari, Jin-Han Lin, Yuan-Ron Ma 2008 J. Phys. D: Appl. Phys. 41 025405
[7] Dharmadhikari V S 1982 J. Electron Spec., 25 181

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