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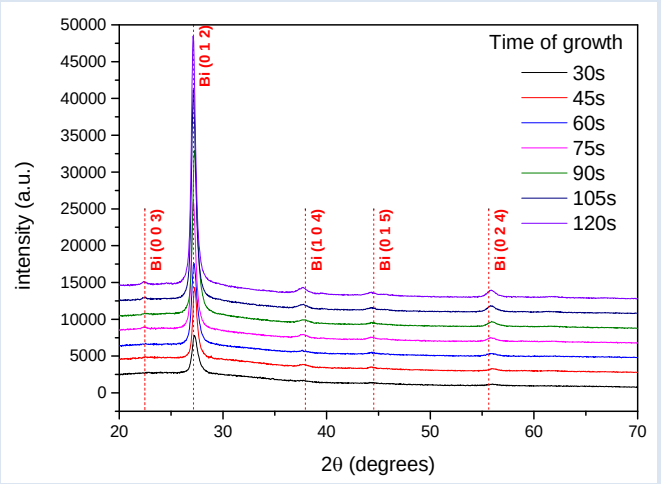
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STRUCTURAL AND MORPHOLOGICAL PROPERTIES OF BI(X)SI(Y)O(Z) THIN FILMS PREPARED VIA UNBALANCED MAGNETRON SPUTTERING

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ABSTRACT

Bismuth-silicon-oxygen-based thin films were prepared via an unbalanced magnetron sputtering system in a reactive atmosphere with a mixture of argon and oxygen at room temperature. It is clear that this technique is highly environmentally friendly and does not produce toxic products or gases during or after the process. These films exhibited high homogeneity and constant thickness around 200 nm. The structural properties of the films were analyzed by means of X-ray diffraction, which mainly showed the presence of bismuth and bismuth oxide. As for the morphological properties, con-focal microscopy measurements showed good homogeneity over the surface as well as low average roughness, which indicates good thickness uniformity.

Keywords: Bismuth-silicon-oxygen, UBM, X-ray diffraction, thin films.

PROPIEDADES ESTRUCTURALES Y MORFOLOGICAS DE PELICULAS DELGADAS DE BI(X)SI(Y)O(Z) PRODUCIDAS POR LA TECNICA DE UNBALANCED MAGNETRON SPUTTERING

RESUMEN

Se produjeron películas delgadas de bismuto-silicio-oxigeno por medio de un sistema de deposición física de vapores asistido por plasma y con un magnetrón desbalanceado (UBM por sus siglas en inglés) con atmósfera reactiva de argón y oxígeno, y a temperatura ambiente. Las películas mostraron alta homogeneidad y espesor constante de aproximadamente 200 nm. Las propiedades estructurales de las películas fueron analizadas mediante difracción de rayos X en donde se evidencia la alta presencia de bismuto y óxido de bismuto. En cuanto a lo que tiene que ver con las propiedades morfológicas se hicieron medidas de microscopía con-focal donde se evidencia la buena homogeneidad de las películas sobre la superficie y la baja rugosidad promedio que a su vez indica buena uniformidad del espesor.

Palabras Claves: Bismuto-silicio-oxígeno, UBM, difracción de rayos X, películas delgadas.

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1. INTRODUCTION

In recent years, the development of bismuth based compounds and the study of their properties has attracted interest because of the interesting behavior that they exhibit in different areas. Some gas sensors for combustion exhaust control, for which NO and NO2 are the main components, are made with the commonly-used semiconductor oxides, but there is a problem related to lack of selectivity. Bismuth oxide Bi2O3 is a good alternative for selectively detecting NO [1]. The rapid determination of trace phenolic compounds is of great importance for evaluating the total toxicity of contaminated water, and the use of common electrochemical tyrosinane biosensors combined with bismuth nanoparticles for this kind of detection seems to be promising because of the low cost and the speed of response [2].

It is known that physical vapor deposition processes do not produce toxic residues. They involve very clean techniques, and not only do the results concerning homogeneity and thickness have very good reproducibility, but a variety of materials can be produced, especially in the shape of thin films [3, 4]. A magnetron is used to increase the rate of collisions near the target, and this enhances the homogeneity of the coatings, but in order to achieve high ion rates near the substrate, the magnetic field must be unbalanced, and thus some field lines pass through the substrate. This is called the unbalanced magnetron sputtering technique (UBM), and it achieves better performance than conventional sputtering systems [5]. The level of unbalance of a magnetron can be estimated using a coefficient of geometrical unbalance KG, according to [6]:

$$K_0 = \frac{Z(B_{z=0})}{2R} \qquad (1)$$

where R is the average radius of the erosion zone "race-track" and Z(Bz=0) is the distance from the target surface to the point on the axis of the magnetron where the magnetic field changes its direction, that is where the Bz component is zero.

2. EXPERIMENTAL PART

Thin films of bismuth-silicon oxides were produced with an unbalanced magnetron sputtering system with a 4-inch-high pure (99.999%) bismuth target. This bismuth target was used as the source material, and it was deposited on glass substrates. Over the target is the "race-track", a zone with a high rate of erosion that functions in metallic mode (without oxides over the target [7,8]) on which squares of silicon were located in four different configurations, 1, 5, 9, and 17, as can be seen in Figure 1. The distance between the target and the substrates was kept at 50 mm. All the thin films were produced at room temperature.

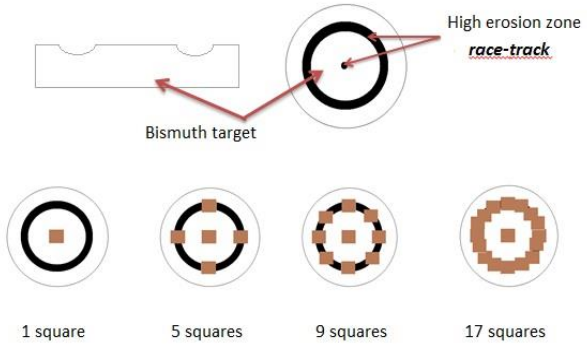


Figure 1. Location scheme of Si squares on the race-track.

Silicon squares of 7*7 mm and 3 mm in height were cleaned with isopropanol and acetone in an ultrasonic cleaner and then dried with pressurized air. The glass substrates were previously cleaned with water, then were immersed in a sulfochromic mixture (H2CrO4 + H2SO4) for one week [9-11] in order to eliminate insoluble organic residues, and after that were cleaned with doubly distilled de-ionized and de-mineralized water and rinsed with ultrasound for 10 minutes with isopropanol and finally with acetone. The sputtering process was carried out in a reactive atmosphere of 80% argon and 20% oxygen flowing at 9 sccm. The base pressure of the deposition chamber was below $9*10^{-4}$ Pa and the working pressure around $3.5*10^{-3}$ Pa. All the specimens were prepared with a sputtering power of 40 watts, and the time ranged from 30 to 120 seconds, which resulted in thicknesses around 100 to 200 nm.

The morphology of bismuth silicon oxide films was observed with a scanning electron microscope (FEI Quanta 200), and surface topographies were measured using a confocal microscope (Carl Zeiss LSM 700). The films' microstructure was determined with an X-ray diffraction system (Phillips X-Pert Pro Panalytical) in the conventional Bragg-Brentano (Θ-2Θ) geometry and CuKα radiation with λ=1.540998.The X-ray diagrams were taken for a 2θ range between 10 and 90 degrees in

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steps of Δ2θ=0.02.

3. RESULTS AND DISCUSSION

The influence of sputtering time and quantity of Si over the target on crystalline structures of as-grown thin films was investigated by means of an X-ray diffraction system in Bragg-Brentano mode. The diffraction diagram shown in Figure 2 refers to thin films produced with 1, 5, 9, and 17 squares of Si for 60 seconds of sputtering process, and they were analyzed by consulting the international center for diffraction data (ICSD) cards supported by the X'Pert High Score Plus software provided with a diffractometer, at the Universidad Nacional de Colombia.

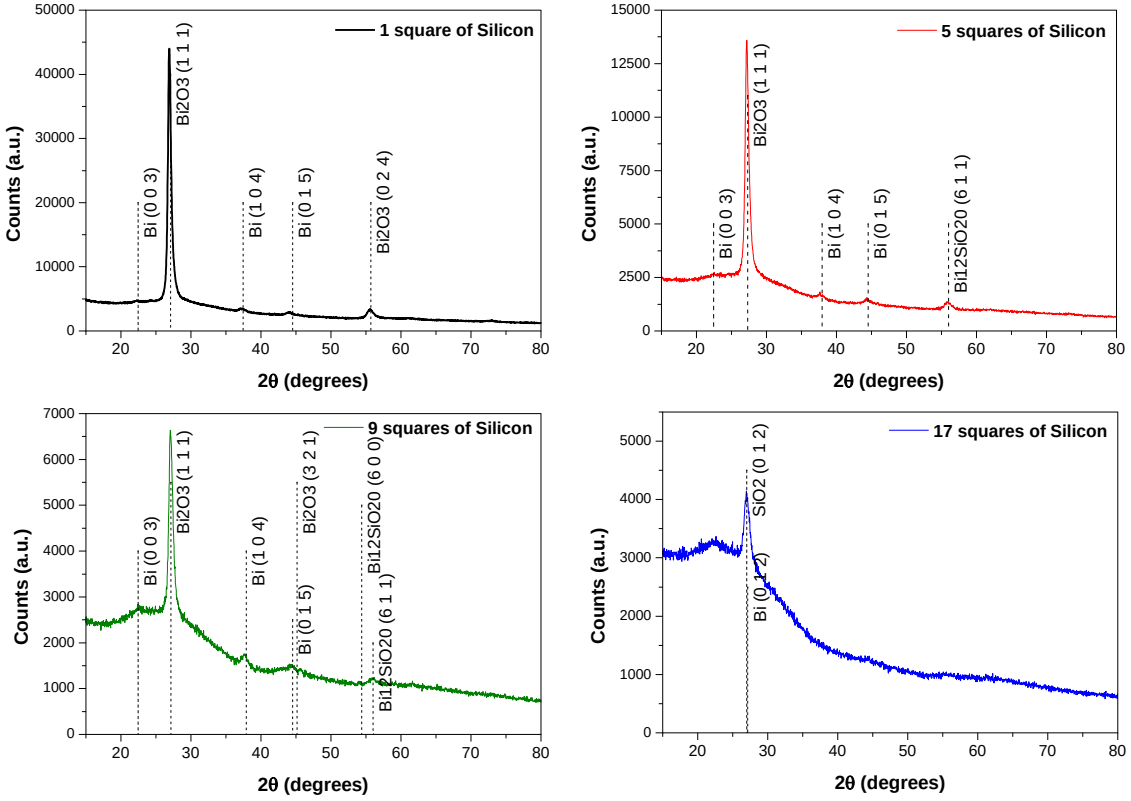


Figure 2. XRD diagrams for the specimens growth during 60 seconds

From the results of the XRD analysis, it is clear that the presence of different numbers of Si squares affects the structure of the thin films. The higher the number of Si squares, the greater the amorphous phase that appears. With 1 square of Si on the target, only Bi and BiO are present, and this is clearly shown by the 28.5° peak that is present in three of the four combinations [12,13]. When the amount of Si increases, the structure becomes amorphous, the Bi and BiO peaks disappear, and SiO begins to be dominant. To show the presence of silicon on the films, Auger electron spectroscopy measurements were done, and they are shown in Figure 3. Analyzing the auger electron energies, we found the existence of silicon with transition L3M1M1, bismuth with transition N7O4O4, and oxygen with transitions KL1L1 and KL3L3. Moreover, there was evidence of Calcium at 245.8 eV, and this is due to the composition of the substrate. The transition for this element was L3M1M1.

Using the data obtained by means of Auger electron spectroscopy, it is easy to calculate the percentage by weight according to the equation:

$$X_i = \frac{Y_i/S_i}{\sum_\alpha Y_\alpha/S_\alpha} * 100\ \% \qquad (2)$$

In this equation, X_i refers to the percentage by weight of the i element, Y_i is the full peak intensity from the peak to the valley, and S_i signifies the sensitivity factor, which is different for each element and each transition. The denominator is

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related to the sum of all the elements found in the spectrum and its sensitivities. According to this, in our specimen the percentages and elements exhibited are summed up in Table 1.

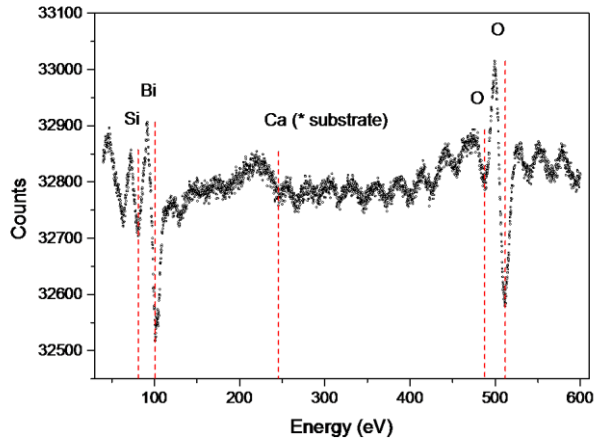


Figure 3. Auger electron spectroscopy diagram for a specimen produced with 9 squares of silicon and 60 seconds of sputtering.

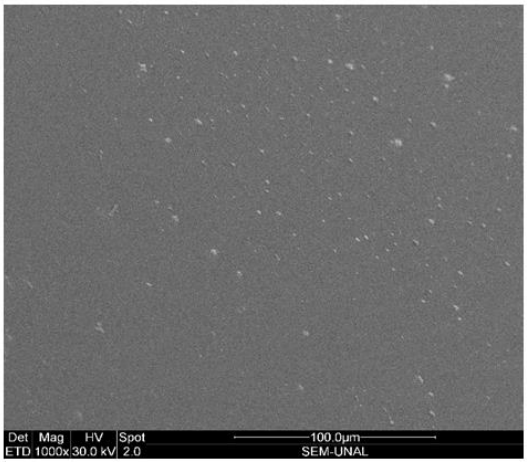
Table 1. Percentage by weight for the elements present in the sample growth at 60 seconds and with 9 squares of silicon.

Element	*Percentage by weight*
Silicon	2.38
Bismuth	44.64
Oxygen	9.23 37.68
Calcium (substrate)	6.1

In order to analyze the morphology of the thin films produced via the unbalanced magnetron sputtering system, scanning electron microscopy images were taken, and they are shown in Figure 4. From these micrographs, we can see the homogeneity of the thin films and some agglomerates with diameters less than 1µm (white points called droplets), which are exclusively made up of bismuth, according to the EDAX probe [14]. This kind of droplet is produced due to the high collision rates and the energy typical of UBM, as well as the low fusion temperature of bismuth. This enables the deposition of bismuth droplets that do not react with the reactive atmosphere [15, 16].

To measure the average roughness and the surface topography of the samples, confocal microscope images were taken, and they are shown in Figure 5. In (a), the surface of a specimen is shown, as well as a line along which some measurements were made. The average roughness for this area of the sample (250µm * 250µm) is 0.131 µm, and along the red line it is 0.053µm. In the same way, the analysis for the second area (250µm * 250µm) shows that the average roughness stays close to 0.121 µm and 0.060µm along the red line. This analysis allows us to conclude that the thin films that were grown have a high degree of homogeneity.

(a)



(b)

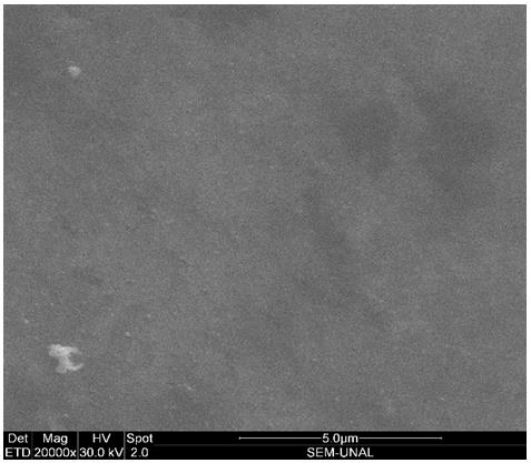


Figure 4. SEM images of 200 nm samples. (a) 1000X magnification and (b) 20000X magnification.

4. CONCLUSIONS

Bismuth silicon oxide thin films were grown with an unbalanced magnetron sputtering system with varying numbers of silicon squares on the target "race-track". The homogeneity of the films was measured by means of a confocal microscope and confirmed through SEM analysis. Due to the high collision rates near the substrate inherent to the production technique and the low fusion

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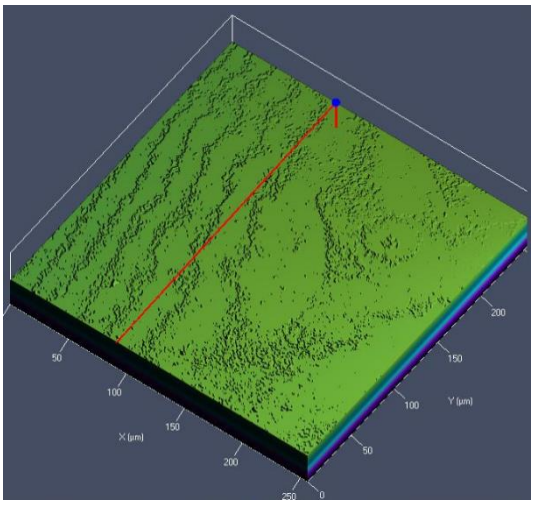
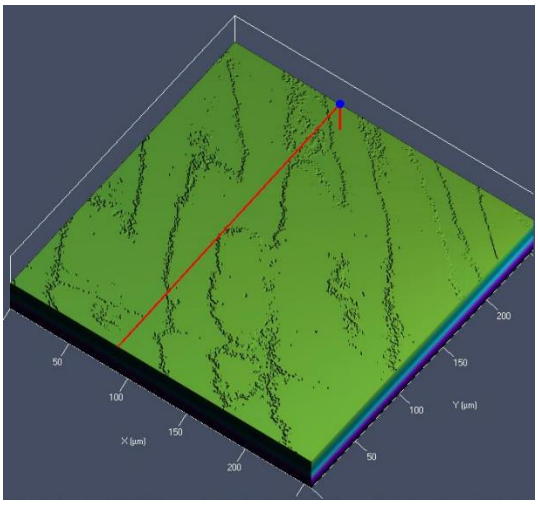
(a)   (b)

Figure 5. Confocal microscope images of the surface topography. (a) 100x magnification in area 1 and (b) 100x magnification in area 2.

temperature of bismuth, droplets of pure bismuth can be seen in the SEM images. The presence of silicon is demonstrated by the AES analysis and the XRD diagrams.

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