CHARACTERIZATION OF BISMUTH OXIDE THIN FILMS DEPOSITED VIA UNBALANCED MAGNETRON SPUTTERING


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ABSTRACT

Bismuth oxide thin films (250 nm) were deposited via unbalanced DC magnetron sputtering on Ti-6Al:4V, and common glass substrates. After being deposited, the films were heated (annealed) for 1 h between 473 and 1073 K in steps of 100 K. The morphology was characterized via scanning electron microscopy (SEM), the micro-structure was analyzed through x-ray diffraction (XRD), and the electrochemical behavior was analyzed with the potentiodynamic polarization test. Additionally, a proton-induced X-ray emission (PIXE) test was done on one of the samples in order to check the chemical distribution of the elements in the surface. The SEM and XRD analyses showed that the post-annealing process affects both the morphology and the structure of the films for all the samples. Finally, the electrochemical tests showed that films grown at 773 K have the highest degree of corrosion resistance.

Keywords: Unbalanced magnetron, thin films, post annealing, electrochemical test, ion-beam analysis, PIXE, bismuth oxide.

CARACTERIZACIÓN DE PELÍCULAS DELGADAS DE OXIDO DE BISMUTO DEPOSITADAS MEDIANTE SPUTTERING CON MAGNETRON DESBALANCEADO

RESUMEN

Películas delgadas de óxido de bismuto (250 nm) fueron depositadas mediante sputtering DC con magnetrón desbalanceado sobre sustratos de Ti-6Al:4V y vidrio común. Después de ser depositadas, las películas fueron calentadas (tratamiento térmico) durante 1 h entre 473 y 1073 K en pasos de 100 K. La morfología fue caracterizada mediante microscopía electrónica de barrido (MEB), la micro estructura se analizó por difracción de rayos x (DRX), y el comportamiento electroquímico se analizó con la prueba de polarización potencio-dinámica. Además, se realizó una prueba de emisión de rayos x inducida por protones (PIXE) en una de las muestras para comprobar la distribución química de los elementos en la superficie. Los análisis MEB y DRX mostraron que el tratamiento térmico posterior afecta a la morfología y la estructura de las películas para todas las muestras. Finalmente, los ensayos electroquímicos mostraron que películas crecidas a 773 K tienen el más alto grado de resistencia a la corrosión.

Palabras Claves: magnetrón desbalanceado, películas delgadas, tratamiento térmico, ensayos electroquímicos, análisis de haces de iones, PIXE, oxido de bismuto.
1. INTRODUCTION

Bismuth oxide based materials exhibit high ionic conductivity and have been proposed as suitable materials for electrolyte in solid oxide fuel cells (SOFC’s) and oxygen sensors. SOFC’s are promising materials for the future of greener and more efficient energy sources [1]. Additionally, bismuth oxides exhibit interesting properties, such as high refractive index, high electric permittivity, and photoluminescence [2, 3]. For these reasons, this material has been widely used in applied fields like gas sensors, optical layers, and the production of ceramic glasses [4, 6]. Furthermore, bismuth oxides have shown to be excellent photo-catalysts in water dissociation and decontamination under visible light radiation [5]. Bismuth containing hetero-metallic oxides is a potential candidate for a wide variety of applications in the microelectronics industry due to the high mobility of charge carriers, and the large mean free path for electrons [9, 10]. A low fusion point (576.2 K) and catalyst-free synthesis are some of the other advantages of bismuth compared with other semiconductor materials [7, 8]. Recently it has been demonstrated theoretically that bismuth is an attractive material because of its low-scale thermo-electricity due to its anisotropy [10], and moreover a low value of effective mass and the large mean free path allow a magneto-resistance effect, observed in bismuth as a bulk [11], nanowires [12], and thin films. In addition, semi-metal bismuth thin films become a semiconductor at a critical thickness of around 30 nm [9, 10].

Bismuth oxide thin films has been deposited by some techniques like physical vapor deposition (PVD) which are excellent options for producing coatings [8]; especially unbalanced magnetron sputtering (UBM) technique has been increasing its popularity because of its benefits for the final product in terms of the homogeneity and stoichiometry. Some researchers have shown that the use of UBM in the production of bismuth allows the presence of unusual electronic properties due to the highly anisotropic Fermi surface of bismuth [9]. In this paper we deal with the correlation between the chemical composition of the bismuth oxide thin films and the corrosion resistance of the samples.

2. EXPERIMENTAL SETUP

Substrates of common glass (15*15 mm) and Ti-6Al:4V alloy (cylinders of 13.5 mm in diameter and 3 mm in thickness) were used. These alloy cylinders were polished with waterproof abrasive paper with different grain sizes and then with a cloth impregnated with alumina (grains diameter around 1 μm), the final average roughness of the alloy substrates was 41 nm ± 5 nm. Finally, the surfaces were cleaned using acetone and the ultrasound bath technique in order to eliminate contaminants.

The bismuth oxide coatings were grown through the unbalanced magnetron sputtering technique using a 4-inches bismuth target (99.999 % pure). Deposition of bismuth oxide thin films was done in a stainless steel chamber with conditions: substrate-target distance was kept constant at 50 mm; the working pressure was around 3.3x10⁻¹ Pa and the base pressure was close to 8x10⁻⁴ Pa; power supplied to the target 40 W, argon–oxygen mixture (80:20) flux of 9.0 sccm; 4 minutes of deposition time and room temperature. Under these conditions, thin films with thicknesses around 250 nm were produced. After that, thermal treatments were applied to the bismuth oxide produced films in a Barnstead Thermolyne reference 1300 furnace from 473 to 1073 K in steps of 100 K for one hour at each temperature, and then they were slowly cooled until they reached room temperature.

The microstructure of the films was analyzed via X-ray diffraction (XRD) technique using a X’Pert Pro Panalytical diffractometer with Cu Kα radiation (λ=1.5306 Å) in the Bragg-Brentano mode from 20 to 80° 20 degrees and a step of 0.02°. The morphological analysis was done using a FEI Quanta scanning electron microscope, equipped with dispersive x-ray (EDX) microprobe working at 20 kV. The micrographs were taken at 200X, 800X, and 6000X.

In order to check the electro-chemical properties of the thin films deposited on Ti-6Al:4V alloy, potentiodynamic polarization tests were done with a Gamry R600 potentiostat and the corrosion rate (CR) was calculated via the Tafel extrapolation technique. The samples were immersed in an aqueous solution of 0.6M NaCl at 3.5%, acting as an electrolyte that interacts with an exposed area of the sample of 0.159 cm². A three-electrode cell arrangement was used: one for reference (saturated calomel - SCE), an auxiliary platinum electrode, and...
the surface of the sample acting as a third electrode. The samples were immersed for 1 hour before starting potentiodynamic polarization testing. The measurements were carried out in a full range between -300 mV and 300 mV with respect to open circuit potential ($E_{ocp}$) with a scan rate of 0.5 mV/s. All these experimental conditions are in agreement with those used by other researchers [13, 14]. Assuming that corrosion is uniform over all the exposed area, corrosion rate ($CR$) can be calculated in millimeters per year ($mpy$) from Faraday’s equation, Equation 1, where $K_1$ is a constant that takes a value of 0.1288, $j_{corr}$ is the corrosion current density, $EW$ is the equivalent weight of the corroding species in grams, and $\rho$ is the density of the corroding material in g/cm$^3$ [15]:

$$CR = K_1 \frac{j_{corr}}{\rho} EW$$

In order to analyze the composition and chemical distribution of the elements on the sample surface, proton-induced X-ray emission (PIXE) measurements were performed by using the nuclear microprobe installed at the zero-degree beam-line of the 5.5 MV CN Vand der Graaff accelerator located at iThemba LABS, Faure, South Africa. A proton beam of 3.0 MeV energy was used with current of ~100 pA focused onto a 4 µm$^2$ spot produced. PIXE spectra were registered with a PGT Si (Li) detector positioned at a take-off angle of 135° with a 125 µm-thick Be absorber interposed between Si(Li) detector and target to shield the detector from backscattered protons. The sample surface was analyzed using a scanned area of 83×83 µm. Beam was ratered over the square area using a data matrix of 128×128 pixels, with a total dwell time of 10 ms per pixel. These PIXE experimental conditions are quite similar to those widely used in this kind of research [16, 17]. Following data collection, evaluation of the event-by-event files were quantitative analyzed with the GeoPIXE software package using the Dynamic Analysis method [18].

3. RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy analysis

The morphology of the films was analyzed by scanning electron microscopy (SEM), the images were taken on the films grown onto Ti-6Al:4V and common glass substrates. Figure 1 shows morphology evolution of the film surface as a function of the Ti-6Al:4V substrate temperature. These micrographs were taken in same size areas. In all the samples some droplets structures are pointed out (circled in order to highlight a few) and are formed due to agglomeration of bismuth particles without melting, however there is an increase in the droplets size and number as can be seen in Figure 2 of the samples grown on glass substrates; moreover, in Fig 1 (a) and Fig 1 (b) some patches are shown (pointed to by blue arrows) that indicates inhomogeneity and are possibly formed due to coalescence processes between some droplets that move from its sites in order to form bigger droplets like the ones on Fig 1 (c). Fig 1 (a) shows a smooth and homogeneous surface with low roughness, while Fig 1 (b) shows an increase in the quantity of patches (inhomogeneity) and droplets. Finally, Fig 1 (c) shows a surface with high porosity and bigger droplets, these droplets could be formed due to coalescence process or recrystallization process that take place at higher temperatures [19]. The coatings grown on common glass exhibit a similar behavior, i.e., they are homogeneous at low temperatures and porous at high temperatures.

Figure 2 shows the surface micrographs taken at 6000X of the samples surfaces on glass substrates without thermal treatment and annealed at 573 K, 673 K and 873 K. Porosity can clearly be seen in the samples with thermal treatments as well as the droplets (red circled), which are uniformly distributed over the surface. Size and number of droplets on the surface was analyzed through ImageJ free software and we calculated that size of droplets increases with the annealing temperature, as well as the number of the droplets. The Table 1 shows the values of the droplets size and number as a function on annealing temperature. As reported by Sterzer et.al. the number and mainly the size of the droplets increase as a function of temperature because of coalescence processes [19]. Moreover, Iljinas and Marcinauskaus studied the morphology evolution of bismuth oxide films as a function of temperature, they concluded that the change of temperature influences the morphology of the films and also its crystal structure; in our case, surface roughness increased with the annealing temperature from 0.2 to 1 µm ± 5nm [20].
The EDX analysis was done on the surface and also on some droplets of the films grown at low temperature and showed that their chemical composition is metallic bismuth for droplets and also for the smooth film (see Fig. 3a), while the same analysis on samples grown at high temperatures showed oxygen in their chemical composition in the smooth surface, droplets still are metallic bismuth (see Fig. 3b). This chemical behavior can be explained if we take into account the high power (40W) applied to the target. This power probably results in bismuth ions with high kinetic energy.
when reaching the substrate surface, and thus the formation time is not sufficient for the formation of the Bi$_2$O$_3$ phase at room temperature. But not only that, the difference of atomic masses between bismuth (208 u) and oxygen (16 u) could allow bismuth ions to displace the oxygen ions, because of their large mass, under the experimental conditions used. This can also explain the absence of bismuth oxide in the samples without thermal treatment because its chemical composition is only metallic bismuth and confirm the XRD results for the samples at room temperature. Also the presence of oxygen in the sample annealed on the smooth surface, supports the possibility of the growth of bismuth oxide compounds at high temperatures, as can be seen by XRD in the next section.

**Table 1.** Size and number of droplets of the bismuth oxide thin films deposited on glass substrates and different annealing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of droplets</th>
<th>Average size of droplets [µm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al:4V RT</td>
<td>17</td>
<td>0.271 ± 0.001</td>
</tr>
<tr>
<td>Ti-6Al:4V 573 K</td>
<td>20</td>
<td>0.329 ± 0.001</td>
</tr>
<tr>
<td>Ti-6Al:4V 673 K</td>
<td>26</td>
<td>0.397 ± 0.001</td>
</tr>
<tr>
<td>Ti-6Al:4V 873 K</td>
<td>30</td>
<td>0.434 ± 0.001</td>
</tr>
</tbody>
</table>

### 3.2 X-ray Diffraction analysis

Figure 4 shows the XRD patterns for the samples at room temperature and annealed at 573, 873 and 1073 K. In the figure, peaks corresponding to the Ti-6Al:4V substrate (red dots) according to the ICSD 98-008-4715 reference pattern are clearly seen [21, 22]; for the samples at room temperature, the XRD pattern shows mainly metallic bismuth peaks (ICDD 01-085-1331) marked in blue [23]. However, in the sample annealed at 573 K, a mixture of phases can be seen: metallic bismuth peaks and peaks of oxygen-deficient bismuth oxide Bi$_2$O$_{2.33}$ marked in the figure (ICDD 01-074-1374 and ICDD 00-027-0051 respectively); this oxygen-deficient phase has a tetragonal crystal system and can be formed due to the annealing temperature. For the samples annealed at higher temperatures 873 K and 1073 K the XRD results showed the presence of the alpha phase of bismuth oxide (α-Bi$_2$O$_3$) (ICSD 98-006-6293) [24] and also some peaks of the oxygen-deficient bismuth oxide phase Bi$_2$O$_{2.33}$ as in the case of the 573K film. This alpha phase crystallizes in a monoclinic structure and is stable up to 1003K [25 - 27]; at this temperature other compounds appeared like VO$_2$ and TiO$_2$ and a mixture of phases is clear, this can be attributed to the high temperature that also affects the substrate microstructure. These results show the influence of the annealing temperature on the formation of different bismuth oxide phases and affects clearly the microstructure of the film and also the substrate itself at high annealing temperatures.

![Figure 3. EDX spectrum of surface of the sample on titanium alloy substrates, (a) sample without heat treatment and (b) sample with heat treatment at 873K.](image)

### 3.3 Micro-PIXE analysis

PIXE analysis was done on the sample annealed at 773 K. Figure 5 shows the PIXE spectrum of the sample collected in a specific square area of 6889 µm$^2$. Detection of bismuth x-ray peaks corresponding to the M and L shells were identified as well as the K-lines of Al, Ti and V which are the main components of the Ti-6Al:4V alloy substrate. Small amounts of Fe in the ppm range were detected and appear to be part of the substrate. In this particular area of the sample, a two-dimensional elemental map performed by micro-PIXE (Figure 6)
revealed the presence of the bismuth L x-ray shell lines. In general, the map shows a homogenous distribution of bismuth in the film with some exceptions (agglomerates of enriched Bi encircled in red and some Bi un-enriched patches encircled in blue) that depends on the thermal treatment temperature. In the case of agglomerates (highlighted by red circles) with enriched Bi, the concentration given by the color-coded scale bar at the right of the map points at the weight percent concentration of bismuth in a Bi₂O₃ phase, which is close to 89%. The agglomerates of bismuth that are highlighted can be correlated to the droplets seen via SEM in Figures 1 and 2. It is important to say that in PIXE spectrum of the figure 5 there is no evidence of some chloride peak that would represent the presence of this element on the surface of the film, that fact suggests that the chemical reaction of the electrolyte (NaCl) and the film surface is not occurring on the electrochemical tests and that supports the low corrosion rate exhibited by this sample.

Figure 4. XRD pattern of thin films grown at room temperature and heat treated at 573 K, 873 K and 1073 K.

Figure 5. Experimental PIXE spectrum of Bi₂O₃/Ti6Al4V irradiated with 3.0 MeV 1H¹⁺ of approximately 100 pA current and a total charge of 57 nC collected over 3333 seconds. This irradiation was done on an area of 6889 µm² (p = pile up).
3.4 Potentiodynamic polarization analysis

Figure 7 shows the polarization curves for the coatings of bismuth oxide deposited on the titanium alloy substrates and annealed at different temperatures. This figure shows that the interception of the Tafel slopes with the anodic and cathodic branches is produced at higher currents, i.e., in the coatings that were heat treated at 473 K. For these coatings, the degradation obtained was calculated as 1.424 mpy, this value is in the order of magnitude of the film without heat treatment and means a poor anti-corrosive effects protection. On the other hand, a lower current occurs in the sample with heat treatment at 773 K. In this sample, the degradation was calculated as 2.42E-04 mpy, making this sample the best of the set for resistance against a corrosive environment. These results may be related to the appearance of the Bi$_2$O$_3$ poly-crystalline phase at high annealing temperatures, as can be seen in the XRD analysis. In addition, it is known that these oxide films passivate the surface. In this case, the presence of bismuth oxide on the surface can explain the fact that the curves show a rapid passivation on the independent anode side. The formation of the layer causes a chemically non-reactive behavior under severe attack, which reduces material degradation. Corrosion current density ($j_{corr}$), corrosion potential ($E_{corr}$), and corrosion rate ($CR$) obtained during the electrochemical test are presented in Table 2. As can be seen in PIXE results, the samples with higher annealing temperatures, for example the sample annealed at 773 K behaves better against corrosive processes among all the samples and the lack of chloride signals supports this behavior, despite the fact of the existence of pores like SEM micrographs probed.

Table 2. Electrochemical parameters of the bismuth oxide thin films deposited on Ti-6Al:4V substrates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$j_{corr}$ [A/cm$^2$]</th>
<th>$E_{corr}$ [V]</th>
<th>CR [mpy]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-6Al:4V RT</td>
<td>1.20E-05</td>
<td>-0.386</td>
<td>3.578</td>
</tr>
<tr>
<td>Ti-6Al:4V 473 K</td>
<td>4.76E-06</td>
<td>-0.543</td>
<td>1.424</td>
</tr>
<tr>
<td>Ti-6Al:4V 573 K</td>
<td>1.74E-06</td>
<td>-0.353</td>
<td>5.21E-01</td>
</tr>
<tr>
<td>Ti-6Al:4V 673 K</td>
<td>9.47E-09</td>
<td>-0.196</td>
<td>2.83E-03</td>
</tr>
<tr>
<td>Ti-6Al:4V 773 K</td>
<td>8.11E-10</td>
<td>-0.19</td>
<td>2.42E-04</td>
</tr>
<tr>
<td>Ti-6Al:4V 873 K</td>
<td>1.05E-08</td>
<td>-0.413</td>
<td>3.14E-03</td>
</tr>
<tr>
<td>Ti-6Al:4V 973 K</td>
<td>1.58E-09</td>
<td>0.00181</td>
<td>4.73E-04</td>
</tr>
<tr>
<td>Ti-6Al:4V 1073 K</td>
<td>1.53E-09</td>
<td>0.214</td>
<td>4.56E-04</td>
</tr>
</tbody>
</table>
4. CONCLUSIONS

Thin films of bismuth oxide were grown on Ti-6Al:4V alloy substrates at room temperature by means of unbalanced DC magnetron sputtering, and thermal treatments were applied to them. The results obtained through XRD and PIXE tests show that at high annealing temperatures (773K) the α-Bi$_2$O$_3$ phase is present along with other bismuth phases, and that fact decreases the degradation of the material by about 4 orders of magnitude compared with the sample without annealing process, which is a very interesting result for application in coatings used for anticorrosive purposes. The PIXE spectrum does not have any signal of the presence of chloride and that result support the potentiodynamic electrochemical test result of the sample annealed at 773K, this sample was the one which exhibited the best behavior of the set against corrosive processes.

Number and size of droplets increase as a function of annealing temperature, this phenomenon is explained due to coalescence and recrystallization processes, these effects have an increment with the temperature, for that reason also the surface roughness of the films increases as well with temperature.

5. ACKNOWLEDGEMENT

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6. REFERENCES


