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Effect of Gas Flow Ratio on the Chemical and Electrochemical Properties of Bismuth-Oxygen Films Deposited in Reactive Phase Sputtering

Giovany Orozco-Hernandez ^{1,2} , Jhon Jairo Olaya-Flórez ¹, Jose Edgar Alfonso-Orjuela ³ , Daniel Alejandro Pineda-Hernandez ⁴ and Elisabeth Restrepo-Parra ^{4,*}

¹ Departamento de Ingeniería Mecánica y Mecatrónica, Universidad Nacional de Colombia, Sede Bogotá, Bogotá 111311, Colombia; gorozcoh@ecc.edu.co (G.O.-H.); jolayaf@unal.edu.co (J.J.O.-F.)

² Postgraduate Department, Universidad ECCI, Bogotá 111311, Colombia

³ Grupo de Ciencia de Materiales y Superficies, Departamento de Física, Universidad Nacional de Colombia, Sede Bogotá, Bogotá 111311, Colombia; jealfonsoo@unal.edu.co

⁴ Laboratorio de Física del Plasma, Universidad Nacional de Colombia Sede Manizales, Manizales 170003, Colombia; dapinedah@unal.edu.co

* Correspondence: erestrepopa@unal.edu.co

Abstract: In this work, the study of chemical, physical, and electrochemical behavior of bismuth and oxygen-based thin films, produced through an unbalanced magnetron sputtering (UMS) technique in reactive phase, is presented. The main aim of this investigation is to analyze the influence of Ar/O₂ gas flow on the microstructure, chemical composition, and corrosion properties of bismuth and oxygen-based thin films. Coatings were grown keeping the power at 50 W with a mixture of Ar:O₂ (80/20) as constants, while the gas flow rate was varied taking values of 12, 15, 20, 25, and 30 sccm. X-ray diffraction (XRD) analyses were carried out showing that films exhibited a polycrystalline Bi phase and no crystalline bismuth oxide phases. For elemental composition analysis, the Rutherford backscattering spectroscopy (RBS) technique was used. The results suggested that film compositions were a mixture of metallic bismuth and amorphous bismuth oxide; moreover, chemical elemental distribution was studied using proton-induced X-ray emission (PIXE) measurements determining that before the corrosion analysis, samples exhibited a uniform distribution of Bi and O. Finally, the influence of the gas flow on the films anticorrosive properties was discussed. Potentiodynamic polarization technique results revealed that the corrosive behavior highly depends on the sample production parameters; samples grown at 20 and 30 sccm showed the best corrosion resistance represented in lower corrosion current density. This behavior is probably due to the thickness of these films.

Keywords: XRD; RBS; SEM; PIXE; corrosion resistance



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1. Introduction

Because of their special characteristics, bismuth oxide-based materials have been widely used in several fields, such as microelectronics, sensors and actuators, optical coatings, transparent ceramic glass manufacturing, among others. For this reason, bismuth oxide exhibits high oxide ionic conductivity, and good electronic properties. They have been included in applications as good electrolyte materials for solid oxide fuel cells (SOFC) [1,2]. The versatility of the material has been studied in several cases, such as the work reported by T.P. Gujar et al. [3] who studied the electrical resistivity that exhibited an n-type semiconductor. These kinds of studies of bismuth oxides have been used specially in optical and semiconductor applications because its band gap takes values between 2 and 3.6 eV approximately, depending on the technique of production [4]. The versatility of the applications of bismuth oxide is due to several polymorphic forms that

are known as α , β , γ , and δ [5,6]. These polymorphs exhibit different crystal structures, generating different optical, electrical, and mechanical properties, with some of them being stable at low temperature (monoclinic α -phase and high temperature face-centered cubic δ -phase). In contrast, δ - Bi_2O_3 crystalizing in other forms is only stable between 729 °C and 825 °C [7]. For this reason, it is of great importance to perform a deep structural and compositional characterization since the stoichiometry and presence of vacancies also influence the stability and the physical properties of these materials. In this work, we used several methods such as X-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS), and proton-induced X-ray emission (PIXE), that allow the identification of phases and elemental composition; furthermore, it is important to determine the homogeneity of the coatings, which can be analyzed using depth profiles, and these different properties need to be considered for technological applications such as anticorrosive protection. Some previous works have been reported. Fabio Leonardo Alf rez Vega et al. [8] showed that the corrosion resistance of SiO_2 - TiO_2 - ZrO_2 - Bi_2O_3 coatings deposited by means of spin-coating on $\text{Ti}_6\text{Al}_4\text{V}$ alloys improved the corrosion resistance caused by the bismuth oxide due to the protective oxide layer's behavior preventing the electrolyte migrating to the substrate. Growth of bismuth oxide on 316L stainless steel substrates can be used for corrosion protection in biomedical applications. Not many reports can be found regarding corrosion resistance of Bi_2O_3 ; nevertheless, BiO is non-toxic and exhibits excellent chemical inertness and biocompatibility [9].

On the other hand, as a thin film, bismuth oxide has been produced mainly using a magnetron sputtering technique, according to several reports [10,11]. The unbalanced magnetron sputtering technique is a modification of traditional magnetron sputtering that acts as an electron trap, localizing the ionization region near the sputtering cathode, increasing the sputtering rate [12]. It allows the production of high purity, well-adhered, and uniform coatings on large area substrates. Moreover, a better control on surface properties is obtained through the appropriate combination of process variables [13–15]. These variables include unbalanced grade of the magnetron, ion energy, ionic current density, plasma density, gas flux, discharge power (current–voltage), substrate temperature, sample–target distance, sample rotation velocity, and total pressure, among others. Controlling these process parameters allows the modification of the coating's properties such as the microstructure, chemical composition, hardness, mechanical, optical, electric, and magnetic characteristics. As is expressed before, the gas flow has a strong effect on the coating's properties as texture and microstructure, surface morphology, porosity, among others [16]. The novelty of the work lies in the detailed investigation of the chemical, physical, and electrochemical behavior of bismuth and oxygen-based thin films, produced using the reactive phase unbalanced magnetron sputtering technique. The study demonstrates that varying the Ar_2 gas flow significantly impacts the anticorrosive properties of the films, highlighting the formation of an amorphous bismuth oxide phase that had not been previously identified by XRD, which directly influences the corrosion resistance of the coatings.

The main aim of this investigation was to analyze the influence of Ar/O_2 gas flow on the microstructure, chemical composition, and corrosion properties of bismuth and oxygen-based thin films. This study is of great interest to understand the corrosion resistance of the films and establish the relationship between corrosion resistance and structural characteristics.

2. Materials and Methods

Bismuth and oxygen-based thin films were deposited by means of an unbalanced DC magnetron sputtering technique from a 4 in bismuth (99.999% pure) metal target. To eliminate atmospheric gas inside the reaction chamber, the base pressure reached was 5.0×10^{-4} Pa by using mechanical and turbo molecular pumps. A mixture of argon and oxygen gas (80:20 percent ratio, respectively) was introduced into the chamber reaching a work pressure between $(3.4 \text{ and } 3.6) \times 10^{-1}$ Pa depending on the gas flow variation, taking values of 12, 15, 20, 25, and 30 sccm. The films were deposited on glass substrates and

AISI 316L stainless steel substrates previously prepared to a mirror-like finish; then, as well as the glass substrates, they were cleaned with isopropanol and acetone just before being introduced in the reaction chamber. The experiments were run at room temperature, with 50 W of power applied to the target and a deposition time of 4 min.

Crystallinity properties of the films were examined by a diffractometer (Phillips Panalytical, Bogotá, Colombia) at room temperature working in the conventional Bragg–Brentano geometry with Cu K α radiation ($\lambda = 1.540998 \text{ \AA}$). XRD patterns were taken from 10° to 90° with a step size of 0.02° .

The scanning electron microscopy technique was used for observing the films' morphology. In this case, an FEI Quanta 200 microscope (Bogotá, Colombia) with acceleration voltages between 20 kV and 30 kV was employed. Moreover, an energy dispersive X-ray spectroscopy (EDS) method coupled to the SEM equipment was used for evaluating the elemental composition on the films.

Rutherford backscattering spectroscopy (RBS) was performed with a 2 mm diameter collimated beam of 2.0 MeV ^4He from a Van Der Graff accelerator (Cape Town, South Africa). The detector with resolution of 20 keV, solid angle of 1.3×10^{-3} steradians and a scattering angle of 165° were used and allowed analysis of the depth distribution and elemental composition of the samples, as well as the layer's thickness. Also, to measure the thickness of the films produced, a physical step was implemented that would later allow profilometry measurements to be carried out. For this, a Veeco brand contact profilometer, model Dektak 150, with a $2.5 \text{ }\mu\text{m}$ radius tip was used, applying a force of 1 mgf in the crests and valleys mode, over a distance traveled of 2300 μm and that crossed the step area. This measurement was taken in 3 different areas of each sample and an average was made for the thickness of each film.

With the purpose of determining the elemental chemical distribution in the samples, proton-induced X-ray emission (PIXE) measurements were performed by means of a nuclear microprobe with a proton beam of 3 MeV energy and current of $\sim 100 \text{ pA}$, focused into a $2 \times 2 \text{ }\mu\text{m}$ spot. PIXE spectra were registered with an Si (Li) detector positioned at a take-off angle of 135° with a 125 μm -thick Be absorber to shield the detector from backscattered protons. Quantitative results were obtained using GeoPIXE software (version 6.1).

Once the coatings were deposited, an electrochemical study was carried out using a Gamry Instruments Potentiostat/Galvanostat Reference 600 to obtain potentiodynamic polarization curves. An aqueous solution of NaCl at 3.5% was employed as an electrolyte that interacts with a sample exposed area of 0.159 cm^2 . Three electrodes were used, one for reference (calomel saturated—SCE), an auxiliary platinum electrode, and the surface of the sample acting as a third electrode. Once immersed, the stabilization time was 60 min. The measurements were carried out in a full range between -0.3 and 0.3 V with respect to open circuit potential (OCP) with a scan rate of 0.5 mV/s .

3. Results and Discussion

The XRD results are shown in Figure 1 for samples grown varying the gas flow rate, taking values of 12, 15, 20, 25, and 30 sccm. In these results, for all the films, the presence of only metallic bismuth peaks (ICDD 00-044-1246) with a rhombohedral polycrystalline phase and 316L SS substrate can be identified, while only one peak for bismuth oxide signals is present at $2\theta = 22.2^\circ$. Peaks with greater intensity identified were $\{012\}$ families of crystalline planes. The low crystallinity of the films can be due to (i) the fact that the oxygen atom is included in interstitial positions of the bismuth lattice supporting the shift in the diffraction peaks; (ii) the bismuth oxide phases can be formed as an amorphous phase at high flow rates [17]. Moreover, the presence of other crystallographic planes was observed in samples grown at 20 and 30 sccm. As was explained later, the increase in the gas flow generates an increase in the thickness and this influences the preferential orientation and the crystallographic planes formation. The preferred orientation of the films can be explained in terms of the energy E_{hkl} which is the sum of the surface energy (S_{hkl}) and the strain energy (U_{hkl}). The surface bombardment of increasingly energetic particles increase the

strain accumulation in films as a function of the gas flow increase, which also increases the velocity of gas particles. It should be noted that the surface energy is independent of film thickness, whereas the strain energy increases linearly with the thickness of the film. The increase in the film thickness results in increasing the strain accumulation and hence a decrease in (012) texture coefficient, and corresponding presence of (115) and (306,024) planes, which help to release stress, since they are planes with lower atomic density. In that case, (012) preferred orientation is expected to have a low particle energy (lower gas flow as 12 and 15 sccm). At comparatively larger particle velocity, other planes can be favored, corresponding to lower surface free energy [18]. However, it was observed that there was not a completely continuous trend. Films grown at 20 and 30 sccm exhibited higher polycrystallinity than the coating grown at 25 sccm. This failure of continuous trend may be due to competition between surface energies and strain energy.

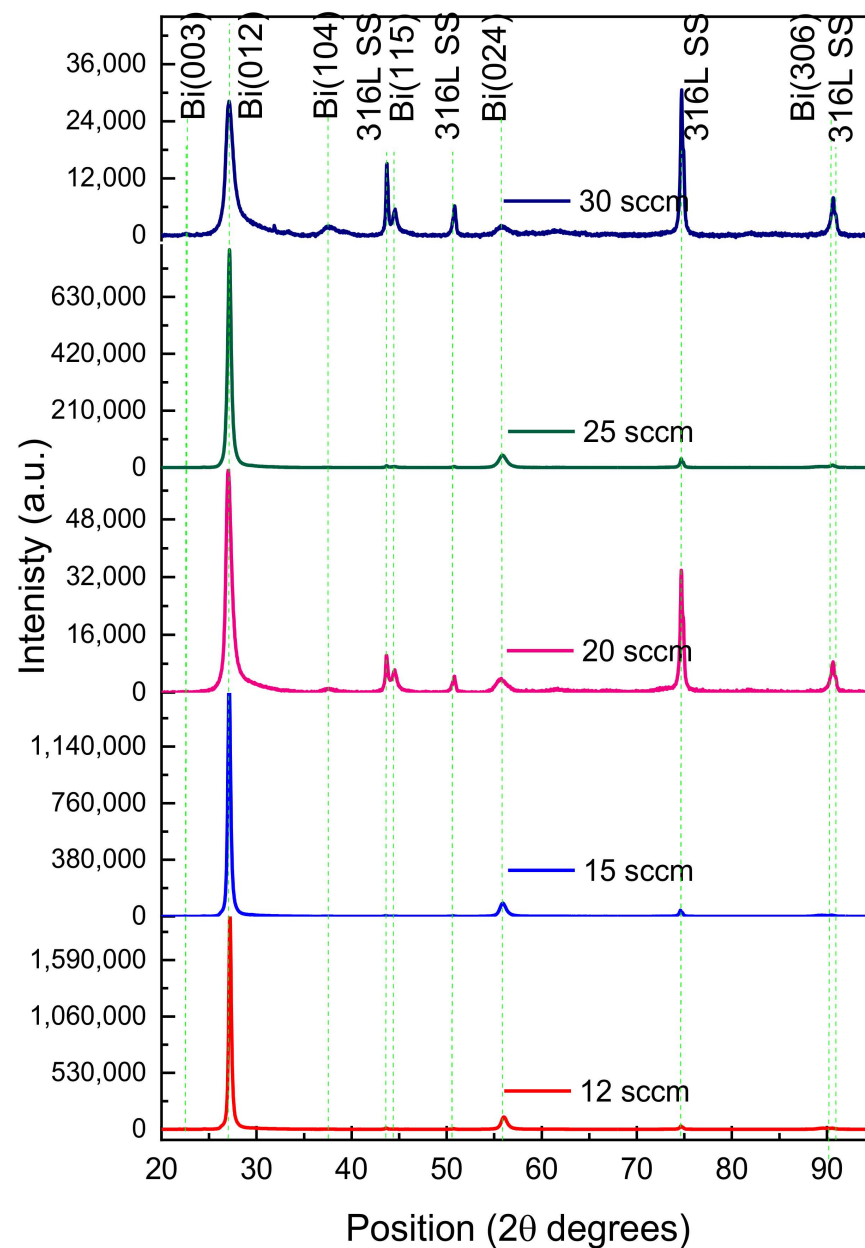


Figure 1. XRD patterns of samples grown on AISI 316L SS substrates, varying the gas flow rate.

Figure 2a shows RBS spectra over the samples produced varying gas flow rate and grown on glass substrates, where the oxygen and bismuth presence can be identified. Figure 3 presents the thickness calculated from these spectra. No relationship between thickness and flow rate was observed [19]. On the other hand, in these spectra, signals belonging to oxygen and bismuth can be identified. A depth profile carried out on samples grown at 20 sccm and 50 W, as an example of the results, shown in Figure 2b, allows ensuring the presence of both oxygen, and bismuth in the film thickness, corroborating the presence of the bismuth oxide formation, although in XRD results, it was not identified; this means that the compound was formed in an amorphous phase [20]. An approximation of the thickness trend as a function of the gas flow, calculated from the RBS results, is included in Figure 3. From these results, it can be seen that there is no appreciable influence of the gas flow on the thickness of the thin films produced. The thickness of the thin films produced by varying the gas flow was measured by means of the profilometry technique, exhibiting values between 200 ± 50 nm and 600 ± 50 nm.

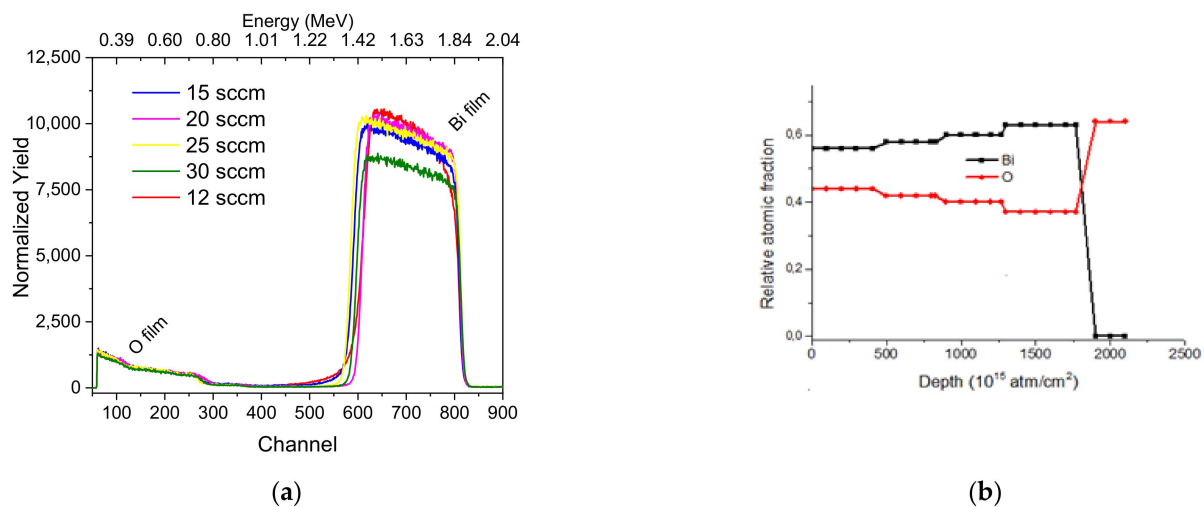


Figure 2. (a) RBS spectra of samples grown at different Ar:O₂ gas flux, at a power of 50 W, and (b) RBS depth concentration profile of bismuth and oxygen in the sample grown at 20 sccm and 50 W.

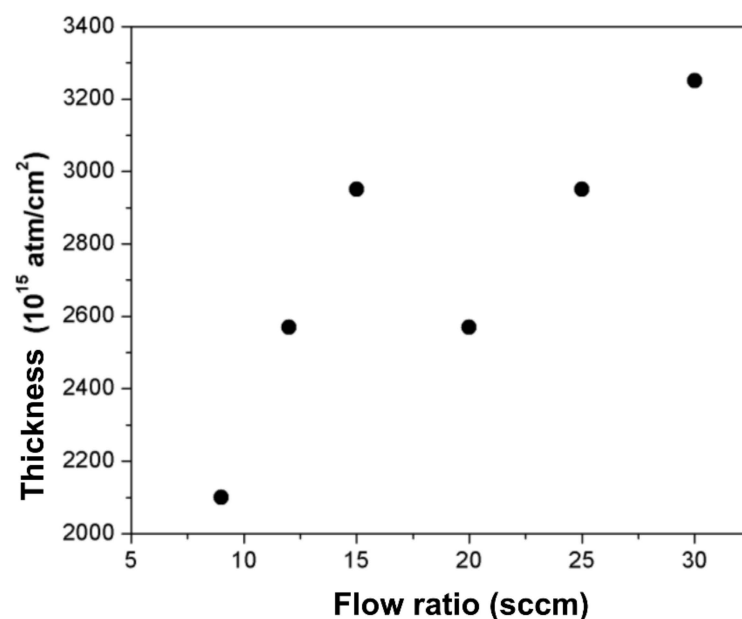


Figure 3. Thickness of the films as a function of gas flow rate.

Figure 4a shows an SEM image of the sample grown at 20 sccm, as a representative micrograph of the films where the characteristic porous character of bismuth oxide coatings by the unbalanced magnetron sputtering technique can be observed. Figure 4b presents an EDS result, taken from the point (1) where the x-axis shows the energy expressed in keV and the y-axis counts in arbitrary units. The numbers placed on the SEM image represent the points where elemental composition analyses by EDS were carried out; it allowed corroboration of the uniformity of the films, since the composition does not change substantially. EDS analysis exhibited the presence of Bi and O; furthermore, C and N were identified. The latter may be due to human handling of the samples in the transport and preparation of the samples.

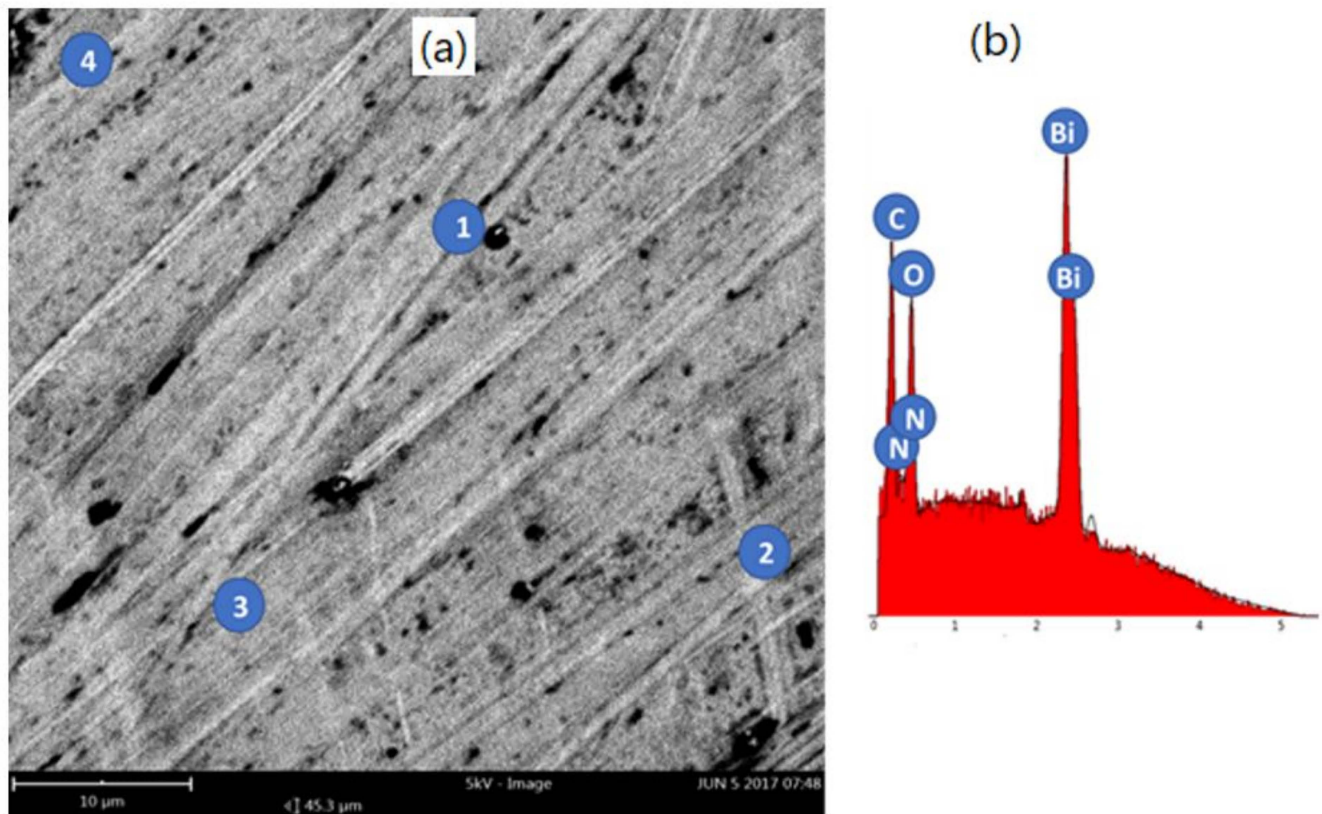


Figure 4. (a) SEM micrography of the sample grown at 20 sccm, and (b) the EDS results from the point indicated as (1) in the image of Figure 4 (a).

PIXE analyses applied to the sample grown at 20 sccm gas flow at a constant power of 50 W were carried out, as is shown in Figure 5a. From this figure, it is possible to identify bismuth peaks, corresponding to M and L shells and the stainless steel components like Cr, Fe, Ni, and Mo. In this sample, a map with size $198 \times 197 \mu\text{m}^2$ was generated and is shown in Figure 5b, for the bismuth L shell. This result shows the high homogeneity of the film because of the distribution of the elements in the area and the bar concentration points at the weight percent concentration of a bismuth oxide-like compound. RBS composition results indicated the presence of a deficient oxygen bismuth oxide. This fact corroborates the presence of bismuth oxide in the film, which was not possible to confirm using XRD measurements. These results suggest that the bismuth oxide grew in an amorphous phase.

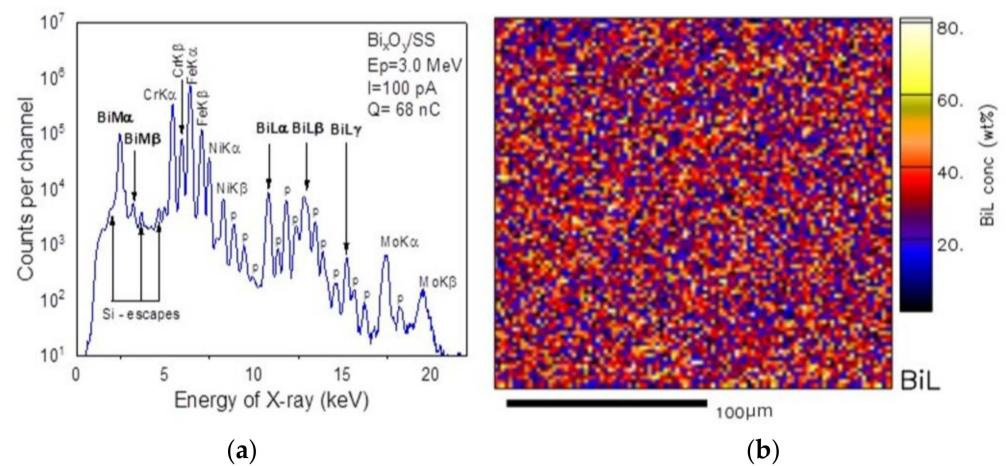


Figure 5. (a) Experimental PIXE spectrum of a Bi_xO_y/stainless steel irradiated with 3.0 MeV 1H1+ of approximately 100 pA current and a total charge of 68 nC collected over 2132 s and (b) micro-PIXE map of L bismuth shell in a sample grown at 50 W and 20 sccm.

Potentiodynamic polarization curves are shown in Figure 6. Samples grown at different flow ratios exhibited superior corrosion resistance compared to the bare substrate, as indicated by higher corrosion potential values and slightly lower corrosion current density (J_{corr}) values [21]. These observations suggest an anodic corrosion mechanism, characteristic of generalized and controlled corrosion. Additionally, the significant reduction in corrosion current density demonstrates that, overall, the bismuth oxide coatings deposited on 316L stainless steel substrates enhance corrosion resistance [22]. The quantitative values obtained from the polarization curves are presented in Table 1.

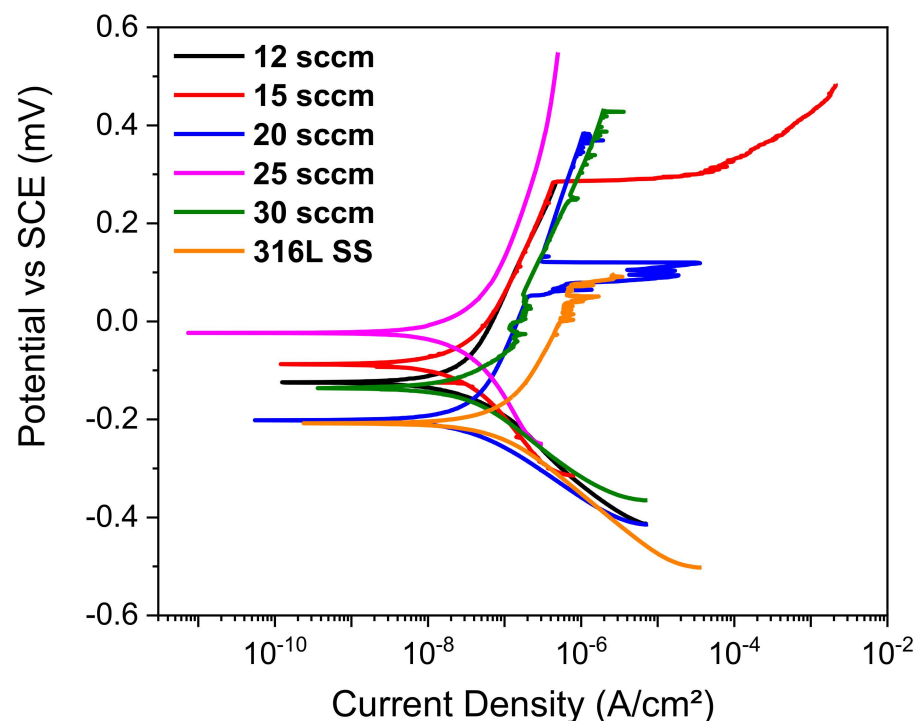


Figure 6. Potentiodynamic polarization curves for the samples grown at different gas flow ratios.

Table 1. Quantitative values extracted from the polarization curves.

Flow Rate	J_{corr} (A/cm ²)	E _{corr} (V vs. SCE)	Corrosion Rate (mm/year)	Polarization Resistance (Ohm·cm ²)
12 sccm	7.242×10^{-6}	−0.4125	2.612×10^{-7}	1500
15 sccm	8.337×10^{-7}	−0.3142	3.007×10^{-8}	2500
20 sccm	7.485×10^{-6}	−0.4142	2.700×10^{-7}	1200
25 sccm	3.157×10^{-7}	−0.2503	1.139×10^{-8}	2800
30 sccm	7.345×10^{-6}	−0.3648	2.649×10^{-7}	1100
Substrate 316	3.735×10^{-5}	−0.5020	1.347×10^{-6}	800

The analysis revealed that the samples with flow rates of 15 and 25 sccm exhibited the best corrosion resistance. These samples demonstrated the lowest J_{corr} values (8.337×10^{-7} A/cm² and 3.157×10^{-7} A/cm², respectively) and the lowest corrosion rates (3.007×10^{-8} mm/year and 1.139×10^{-8} mm/year, respectively). The corrosion rate values were calculated using Equation N. Additionally, these samples presented less negative corrosion potentials, indicating a lower tendency to corrode [23–25].

The enhanced corrosion resistance observed in all samples is attributed to the growth of amorphous bismuth oxide on the coating surface. The absence of grain boundaries eliminates the initiation points for corrosion [26,27]. In the case of the samples at 15 sccm and 25 sccm, the high corrosion resistance is explained by the homogeneity of the coatings. This is evidenced by the RBS and PIXE techniques, which show a uniform distribution of elements in the coating [28–31].

4. Conclusions

Bismuth oxide-based thin films were grown on AISI 316L stainless steel and glass substrates using an unbalanced magnetron sputtering technique varying the gas flow rate. Chemical composition was studied by ion beam analysis techniques and the presence of oxygen and bismuth were confirmed through RBS simulation analysis. These results suggest that the formation of oxygen-deficient bismuth oxide films in an amorphous phase provides a uniform and effective barrier against corrosion, markedly enhancing the corrosion resistance compared to films containing only metallic bismuth.

The analysis revealed that the samples with flow rates of 15 and 25 sccm exhibited the best corrosion resistance. This enhanced resistance is attributed to the absence of grain boundaries, which eliminates the initiation points for corrosion. Consequently, these films demonstrate superior protective properties, making them highly suitable for applications requiring robust corrosion resistance.

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