Effect of forming technique $Bi_xSi_yO_z$ coatings obtained by sol- gel and supported on 316L stainless steel

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Abstract. $Bi_xSi_yO_z$ type coatings via sol-gel synthesized from bismuth nitrate pentahydrate, and tetraethyl orthosilicate as precursors; glacial acetic acid and 2-ethoxyethanol as solvents, and ethanolamine as complexing. The coatings were supported on AISI 316L stainless steel substrate through dip-coating and spin-coating techniques. The study showed that the spin-coating technique is efficient than dip-coating because it allows more dense and homogeneous films.

1. Introduction

Bismuth silicon $Bi_{12}SiO_{20}$ (BSO), belong to the sillenite family, with the general formula $Bi_{12}MO_{20}$ (M= Si, Ge, Ti, Pb, Mn, $B_{1/2}$, $P_{1/2}$). BSO is a stoichiometric sillenite with a fully occupied oxygen sublattice that meets all the major criteria for application as a low sintering temperature (Ts=850°C) [1].

Sol-gel synthesis is a very promising, since it offers potential advantages over traditional solid-state synthesis methods. The sol-gel method allows a precise control over the composition, the homogeneity and deposition over a large area. The most important advantage of sol-gel synthesis in comparison with other coating methods is the ability to tailor the microstructure of the deposited film by varying the concentration, the pH and the viscosity of the sol. [1art]. The key aspect of any sol-gel thin film process is the chemical stability of solution that directly determines properties of the films [2].

Spin coating has been shown to be an effective approach for the fabrication of inorganic films or membranes with controlled structure and crystal orientation [3]. Spin coating is a well-established technology which in the past has been used in the manufacture of photoresists and oxide coatings for screens [4,5]. There is a substantial scientific literature on the spin-coating process and useful reviews on the subject are given by [6,7].

The dip-coating process was first commercially used to produce thin films in a sol–gel technology in 1939 [8]. It has also been used to produce thin films in other technologies, such as photoresists films [9] and lubricant layers for magnetic hard disks [10]. Dip coating is a simple process for depositing a thin film of solution onto a plate, cylinder, or irregular-shaped object. The fact that the geometry of the substrates can vary widely is a distinguishing feature of the dip-coating technique. The process involves immersing a substrate into a reservoir of solution for some time thereby ensuring that the substrate is completely wetted, and then withdrawing the substrate from the solution bath. The liquid film formation is achieved by two main mechanisms, i.e. gravity draining of liquid solution and evaporation of solvent. An early dip-coating analysis was presented by Landau and Levich [11]. This

model is a 1-D model derived purely from hydrodynamics of a Newtonian fluid flow, ignoring solvent evaporation [12].

2. Experimental

For the deposition of the BSO thin films, the sols were prepared using bismuth nitrate $Bi(NO_3)_3{\cdot}5H_2O$ (Alfa Aeser, 98%) and $Si(OC_2H_5)_4$ TEOS (Aldrich, 98%) as the precursors, 2-ethoxyethanol (Aldrich, 99%) and glacial acetic acid (Aldrich, 99%) as the solvents, and ethanolamine (Aldrich, 99%) as the complex agent [1]. First, the bismuth nitrate was drying at a temperature of 65°C/96h. Next, bismuth nitrate (10g) was dissolved in the acetic acid (25ml) under constant stirring for 3h at room temperature. Second, the TEOS (0.38ml) was then diluted with 2-ethoxyethanol to the concentration from 0.9M under constant stirring for 0.5h at room temperature. Finally, was mixing together solutions forming the sol. Ethanolamine was added to control pH=4. Sol with a concentration from 0.9M, was deposited onto 316L stainless steel substrate using the spin-coating method at 2500 and 4000rpm for 10s and dip-coating method at 13.2cm/min.

Films sintering were carried out at heating rate of 1°C/min. permitting removal in a controlled manner, the organic component of the films. This process seeks to avoid pore formation and the difference in thermal expansion present in the metal-coating interface, does not favour the formation of cracks in the coatings. Then the heating program employed for this study relates: Initial temperature of 20ºC to 300ºC and stabilized at this temperature for one hour. Heating was restarts to 400ºC and equilibrated for half an hour.

The microstructure development was investigated with Scaning Electron Microscopy (SEM) (Tescan vega3 Bruker probang EDS with 15keV power) and Confocal Laser Microscopy (CLM) (LSM 700 Carl Zeiss).

3. Results and discussion

Figures 1 and 2 shows the BSO coatings obtained by dip-coating. Very porous, cracked and low adhesion coatings are observed. According to these results, the dip-coating technique is not recommended for films BSO system. This behaviour is most likely due to high viscosity of the sol. When removing the stainless steel substrate of the sol, abrupt dehydration of solvents that make it up is not presented, this makes the film drains and does not adhere to the substrate. After the sintering process, the coatings obtained are very thick, because the difference between the thermal expansion coefficients of the film and the substrate of poor quality coatings are obtained.

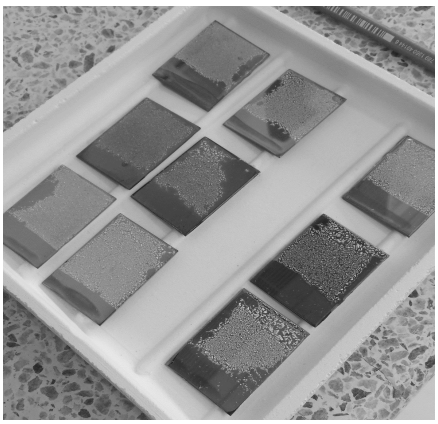


Figure 1. BSO films by dip–coating technique.

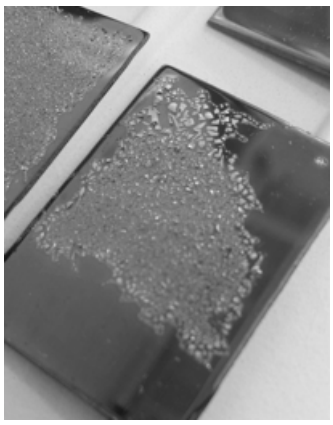
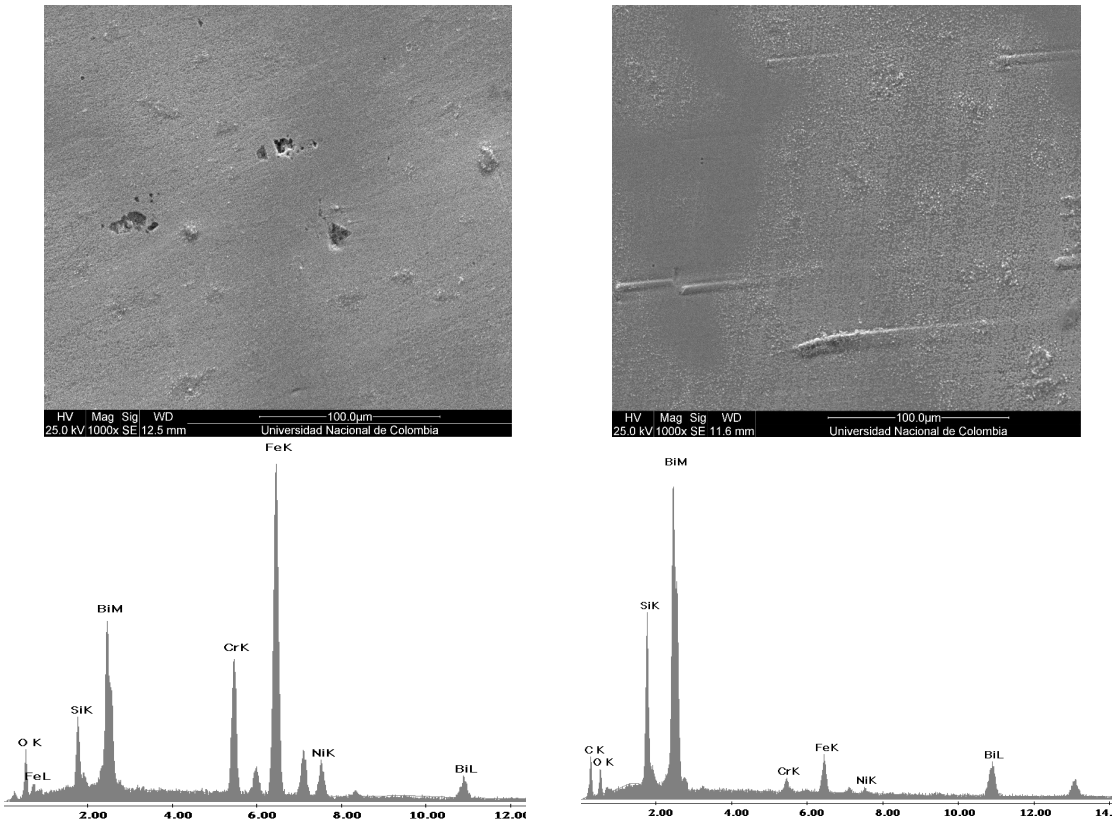


Figure 2. 2M2 film detail by dip-coating technique.

The spin-coating technique allows obtaining dense coatings with good adhesion. The results obtained with the spin-coating technique are shown in Figure 3 and Figure 4. Figure 3 shows the

results of SEM for coatings BSO. Figure labelled 2M2, corresponding to a monolayer coating obtained at a speed of 2500rpm and corresponds to a monolayer 2M3 obtained speed of 4000rpm. Figures 3 and 4 show the EDS analysis which verifies the existence of the film BSO. In Figure 3(a) coating failure detailed with the appearance of pores.

In Figure 3(b) shows the coating 2M3, corresponds to a monolayer obtained at a speed of 4000rpm by spin coating. A denser coating without pores and trails that are characteristic of the forming process by spin-coating at high speed (4000rpm) is observed.



(a) (b)

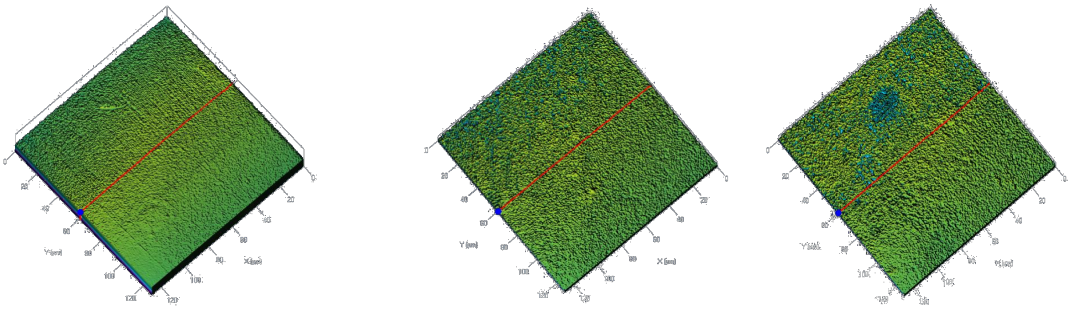
Figure 3. Representative SEM photomicrograf and EDS analysis of samples. (a) 2M2 film and (b) 2M3 film.

In Figure 4, the micrographs for determining the roughness values shown. Regarding the roughness values of the films 2M2 and 2M3 0.029 m difference. The films are rougher than the substrate, the 2M3 samples are a little rough due to the formation of contrails in the coating and that emerges from the SEM micrograph of Figure 3(b).

Table 1 registers the roughness values obtained for the substrate and the films obtained by spin-coating.

Table 1. Rugosity Values.

Sample	Rugosity (m)
Substrate	0.072
2M2	0.228
2M3	0.257



(a) (b) (c)

Figure 4. Representative CLM photomicrograf analysis of samples. (a) substrate, (b) 2M2 film and (c) 2M3 film**.**

4. Conclusions

A sol–gel dip/spin coating method was proposed to prepare BSO films, and this was demonstrated for fabricating films. According to SEM the best results were obtained coatings speeds 4000rpm. According to these results, the dip-coating technique is not recommended for films BSO system

Acknowledgement

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