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$SrBi_2Nb_2O_9$ Thin Films Deposited by Dip Coating Using Aqueous Solution

S. M. Zanetti,[a]* E. R. Leite,[a] E. Longo[a] and J. A. Varela[b]

[a]Departamento de Química - UFSCar, PO Box 676, 13560-905 São Carlos, SP, Brazil
[b]Instituto de Química - UNESP, PO Box 355, 14801-970 Araraquara, SP, Brazil

Abstract

A new approach for $SrBi_2Nb_2O_9$ (SBN) thin films synthesis using aqueous solution was successfully experienced. The deposition solution was prepared from Sr–Bi–Nb mixed-citrate solution, requiring no special atmosphere and using common reagents. Films were deposited by dip coating onto $Pt/Ti/SiO_2/Si(100)$ substrates and heat treated at temperatures ranging from 300 to 700°C. The process of formation and crystallization of $SrBi_2Nb_2O_9$ thin films, prepared by the aqueous solution method, have been studied with particular emphasis on the microstructure of crystallized films. Crystalline phases formation were followed by grazing incident X-ray diffraction (GIXRD), microstructure characterization was evaluated by scanning electron microscopy (SEM) and surface roughness were observed using atomic force microscopy (AFM). To reach the desired thickness, substrates were dipped in the deposition solution twice, forming double-layered films. The thickness of each layer ranged from 80 to 100 nm.

Keywords: films, sol–gel processes, niobates, perovskites.

1 Introduction

Recently, ferroelectric thin films for nonvolatile memory applications have attracted great interest, in particular, those ferroelectric materials belonging to the layered perovskite family, such as $SrBi_4Ti_4O_{15}$ (SBIT), $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2Nb_2O_9$ (SBN). Due to their non-fatigue nature and the possibility of low polarization switching voltage, which were major drawbacks for other materials such as lead zirconate titanate $Pb(Zr,Ti)O_3$ (PZT),[1,2] these kind of ferroelectric materials have potential technological application. Lead zirconate titanate has been widely studied for application to nonvolatile memory devices. However, PZT films on Pt electrode present serious problems of degradation due to oxygen vacancies created at the interface. In addition, PZT capacitors do not maintain good electrical properties when PZT layer is <100 nm. To overcome these obstacles, new thin-film materials containing elements other than Pb and Ti, have been investigated.[3] Among ferroelectric materials belonging to the layered perovskite family, $SrBi_2Nb_2O_9$ (SBN) have been considered for thin film processing due to their potential application as ferroelectric nonvolatile memories with low-voltage operation.

Several deposition techniques have been used to obtain thin films of those compounds, such as pulsed laser ablation,[4–6] chemical vapor deposition (CVD),[7–9] metallorganic decomposition (MOD)[10–12] and sol–gel.[13,14] However, these methods require heat treatment at high temperatures, which can cause damage on a Si wafer.[1] Physical methods require sophisticated equipment, what may be considered as a disadvantage under the point of view of industrial application.

Although sol–gel method is considered very good in terms of stoichiometric control and introduction of dopants, it requires free-water atmosphere for synthesis and deposition. Moreover, sol–gel methods present a serious problem of solution aging, which may alter the film microstructure, causing ferroelectric losses.[15]

In this paper, we report the preparation of SBN thin films, dip coated onto $Pt/Ti/SiO_2/Si(100)$, using the polymeric precursor method. The polymeric precursor method was proposed by Pechini[16] and has been widely utilized to synthesize mixed oxides. The advantage of this method is the possibility of precise stoichiometric control, besides utilization of simple and cheaper reagents as precursors.[17,18] As far as we know, no polymeric precursor solution has been reported for SBN production.

*To whom correspondence should be addressed. Fax: +55-16-261-5215; e-mail: psmz@iris.ufscar.br

2 Experimental Procedure

2.1 SBN Synthesis

Strontium carbonate, $SrCO_3$ (Merck), niobium ammonium oxalate, $NH_4H_2[NbO–(C_2O_4)_3]\cdot 3H_2O$ (CBMM, Araxá, Brazil) and bismuth oxide, Bi_2O_3 (Aldrich) were used as reagents to synthesize $SrBi_2Nb_2O_9$ (SBN). Niobium hydroxide was formed by dissolution of the niobium ammonium oxalate in water and precipitated as $Nb(OH)_5$ by addition of NH_4OH. After filtration, niobium hydroxide was dissolved in an aqueous solution of citric acid to form niobium citrate. The content of Nb was gravimetrically determined as Nb_2O_5. To this niobium citrate solution were added stoichiometric amounts of $SrCO_3$ as salt and Bi_2O_3 dissolved in water with HNO_3. Ethylenediamine was added dropwise into the solution with constant stirring until the pH reached 7–8. After homogenization of the solution, ethylene glycol was added to promote polymerization of mixed citrate by polyesterification reaction. The procedure for deposition solution preparation is presented in the flowchart in Fig. 1. The molar ratio between strontium, bismuth and niobium was 1:2:2, the citric acid/metal molar ratio was fixed at 3.95 and the citric acid/ethylene glycol ratio was fixed as 60/40 (mass ratio). The viscosity of the deposition solution was adjusted by water evaporation until reach 15 mPas.

2.2 Films preparation and characterization

Films were dip coated from SBN deposition solution onto $Pt/Ti/SiO_2/Si$ substrate. After deposition, substrates were dried on a hot plate (~150°C) followed by two-step heat treatment. In this first step, the

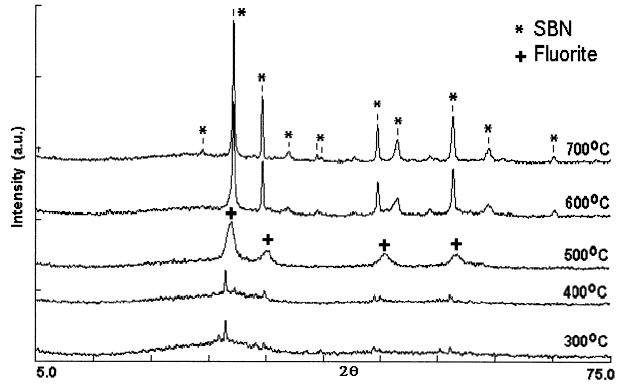

Fig. 2. XRD results for powder samples heat-treated at 300, 400, 500, 600, and 700°C for 2 h.

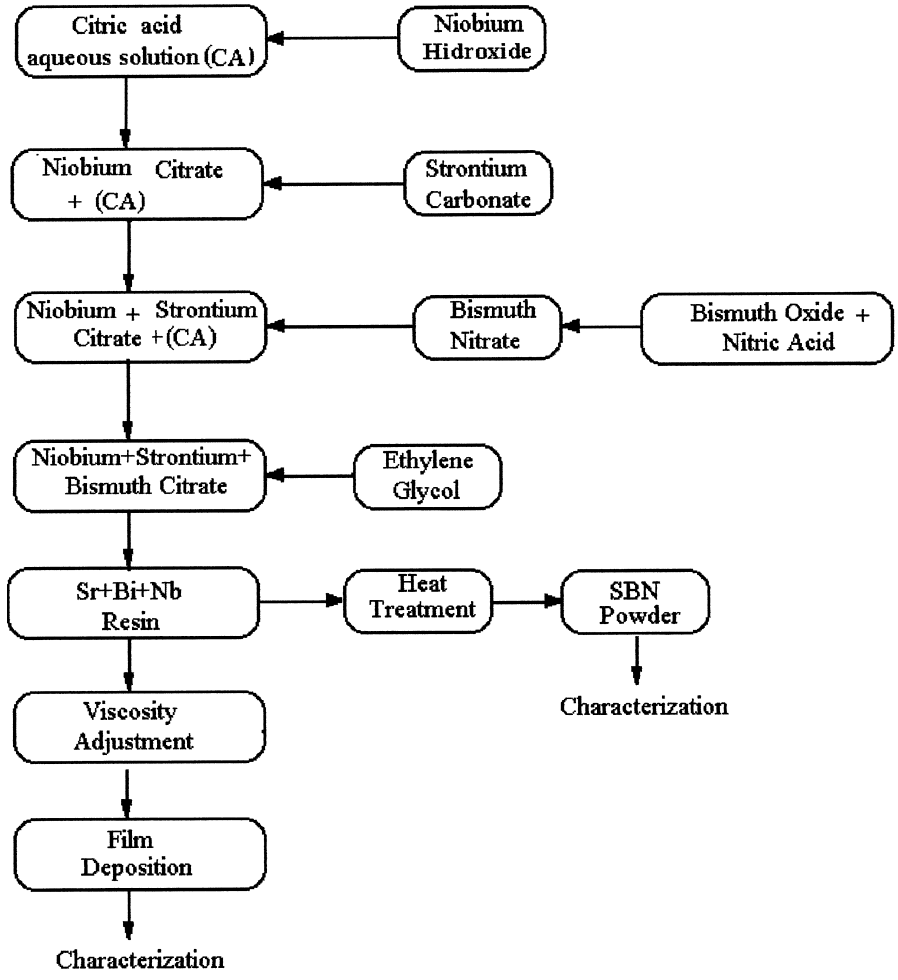

Fig. 1. Flowchart of polymeric precursor preparation.

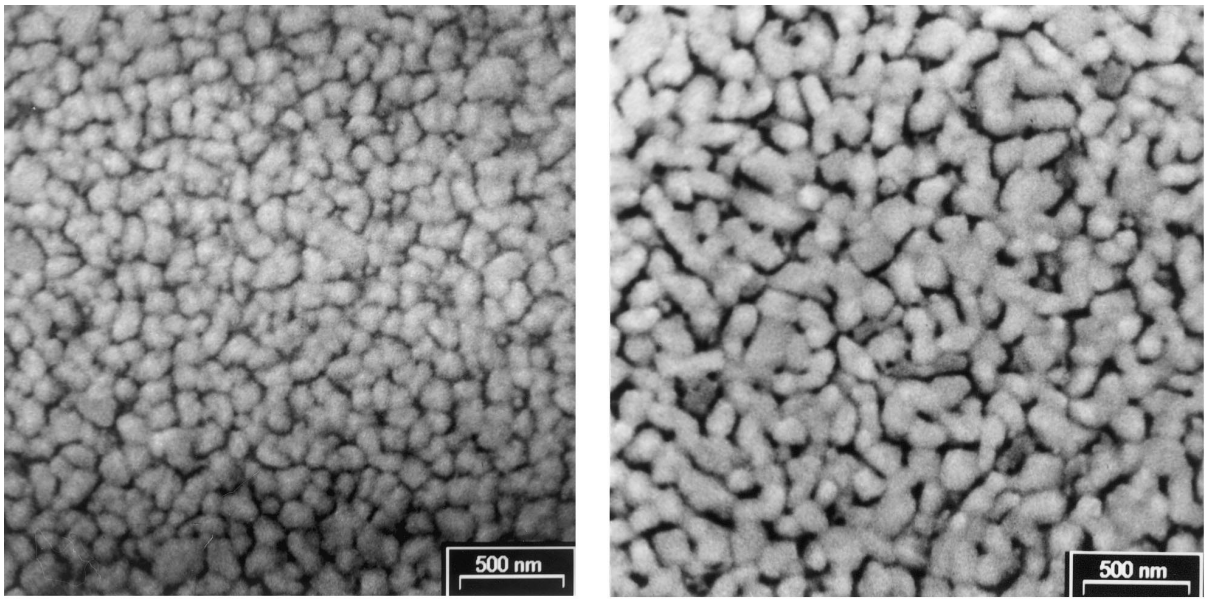

Fig. 3. SEM micrographs of films heat-treated at 700°C: (a) mono-layered; (b) double-layered.

temperature was raised to 300°C and kept at this temperature for 2 h, for elimination of the organic material of each layer. In a second step, films were heat-treated at the desired temperature and soaked for 2 h at temperatures ranging from 300 to 800°C. Heating and cooling rates were 1°C min.

Films were characterized by grazing incident X-ray diffraction (GIXRD) (Siemens, D5000), using Cu k_α radiation and an incident angle of 2°(α) and a LiF100 monochromator. Scanning Electron Microscopy (SEM) (Zeiss, DSM940A), Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM) (Digital, NanoScope 3A), were used for microstructure characterization. Surface roughness (RMS) was examined by AFM, using tapping mode.

3 Results and Discussion

Figure 2 presents the phase evolution characterized for films using GIXRD. A diffuse XRD pattern is observed for films heat-treated at 300 and 400°C, indicating that the precursor is amorphous. Those films heat treated at 500 and 600°C presented an intermediate phase. This intermediate phase was observed for SBN powder also and can be a fluorite phase, similar to that observed for SBT powder obtained by sol–gel.[14] After thermal treatment at 700°C, only peaks related to the SBN phase are observed. These results suggest that the SBN phase be formed at temperatures between 600 and 700°C. Lattice parameters calculated for film heat-treated at 700°C for 2 h were $a = b = 5{\cdot}504$ Å and $c = 25{\cdot}045$ Å.

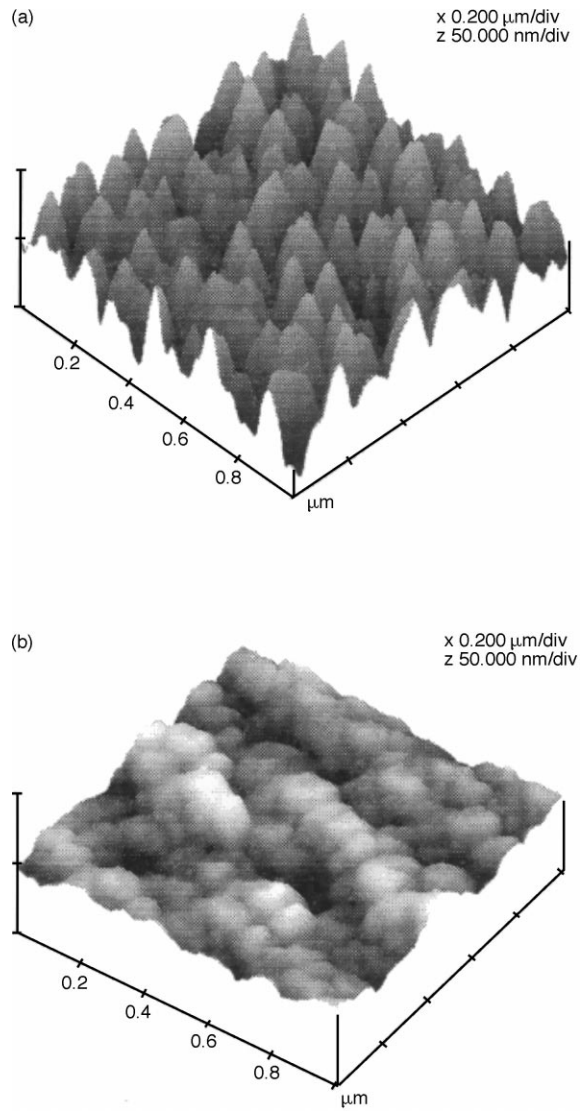

Fig. 4. AFM surface morphology of films heat-treated at 700°C: (a) mono-layered; (b) double-layered.

Figure 3 presents the SEM micrographs of the mono-layered and double-layered films heat-treated at 700°C. For mono-layered film a microstructure with defined spherical grains is observed, with average mean size around 190 nm. The double-layered film presents microstructure of elongated grains with average mean size of 230 nm. Chen *et al.*[19] observed a similar microstructure for SBT films obtained by MOD, annealed at 700°C, with 30 to 50% bismuth excess. The authors also correlated the microstructure with the ferroelectric properties, and this kind of grains (elongated and bigger than the critical size) presented the best results. Film thickness, evaluated by SEM, ranged from 80 to 100 nm for each layer.

Figure 4 presents a typical surface morphology of the films heat-treated at 700°C. The mono-layered film presents higher roughness than the double-layered one. The roughness measured by AFM ranged from 5 to 15 nm.

4 Conclusions

The results presented show that the polymeric precursors method allows one to synthesize $SrBi_2Nb_2O_9$ (SBN) as thin film deposited onto Pt/Ti/SiO_2/Si substrate. XRD data show that the SBN perovskite phase crystallizes through an intermediate fluorite phase. The SBN phase crystallizes at temperatures between 600 and 700°C in films. Double-layered films present a dense microstructure with elongated grains and roughness around 5 to 15 nm.

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