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Preparation and characterization of $SrBi_2Nb_2O_9$ thin films made by polymeric precursors

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A polymeric precursor solution was employed in preparing $SrBi_2Nb_2O_9$ (SBN) powder and thin films dip coated onto Si(100) substrate. XRD results show that the SBN perovskite phase forms at temperatures as low as 600 °C through an intermediate fluorite phase. This fluorite phase is observed for samples heat-treated at temperatures of 400 and 500 °C. After heat treatment at temperatures ranging from 300 to 800 °C, thin films were shown to be crack free. Grazing incident angle XRD characterization shows the occurrence of the fluorite intermediate phase for films also. The thickness of films, measured by MEV, was in the order of 80–100 nm.

I. 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 nonfatigue nature and the possibility of low polarization switching voltage, which were major drawbacks for other materials such as lead zirconate titanate (PZT).[1,2]

Several deposition techniques have been used to obtain thin films of these compounds, such as pulsed laser ablation,[3–5] chemical vapor deposition (CVD),[6,7] metallorganic decomposition (MOD),[8,9] and sol-gel.[10,11] However, these methods require heat treatment at high temperatures, what is seriously deleterious to the Si-wafer properties.

In this paper, we report the preparation of SBN thin films by the polymeric precursor method, dip coated onto Si(100) and $Pt/Ti/SiO_2/Si(100)$. The polymeric precursor method was proposed by Pechini[12] 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.[13,14] As far as we know, no polymeric precursor solutions have been reported for SBN production.

II. EXPERIMENTAL

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 polyestherification reaction. The molar ratio among 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). Figure 1 shows a flowchart for preparing $SrBi_2Nb_2O_9$ precursor solution. This solution was used for direct deposition of thin film, and after partial decomposition of the organic polymer, to prepare the SBN powder. Partially decomposed solid resin was ground in a mortar and calcined at temperatures ranging from 400 to 800 °C for 2 h.

Prior to coating, the substrates were cleaned by immersion in a sulfochromic solution followed by rinsing several times in de-ionized water. The dip coating was conducted by immersion of the clean substrates in the polymeric solution followed by controlled withdrawal at a speed of 1 cm/min. After deposition, substrates were dried on a hot plate (~ 150 °C) followed by a two-step heat treatment. In this first step, the temperature was raised to 300 °C and kept at this temperature for 2 h, for elimination of the organic material. 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. The polymeric precursor solution viscosity was adjusted by

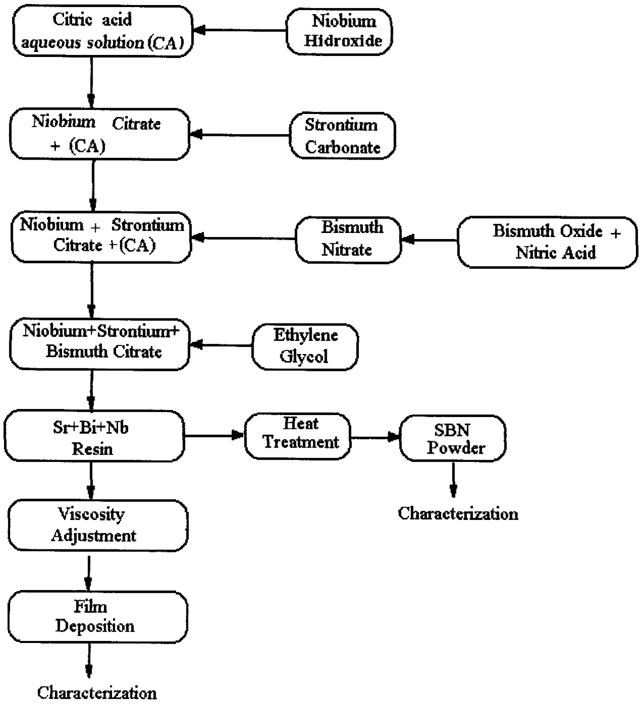

FIG. 1. Flowchart of polymeric precursor preparation.

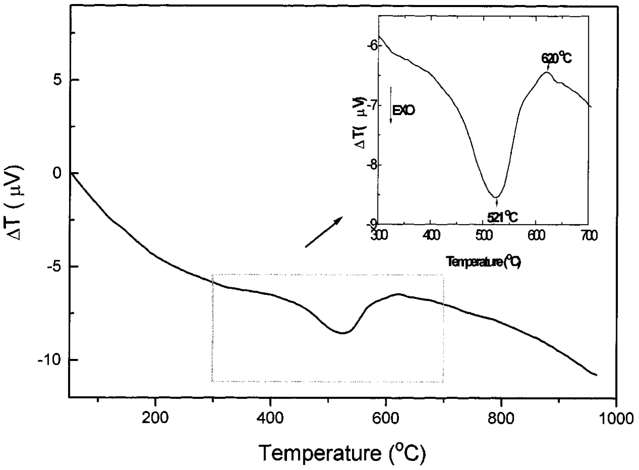

FIG. 2. DTA curve of polymeric precursor heat-treated at 400 °C for 2 h.

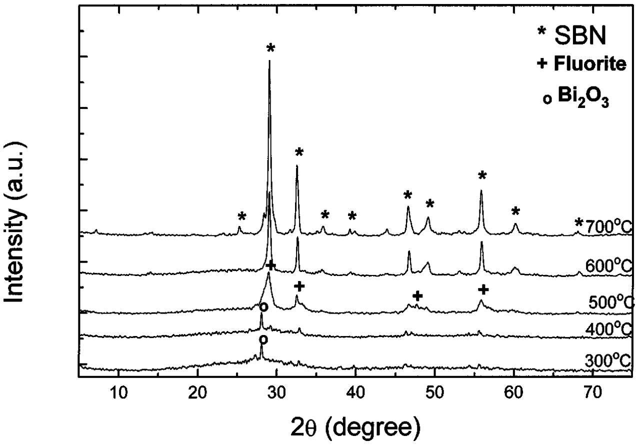

FIG. 3. XRD results for powder samples heat-treated at 300, 400, 500, 600, and 700 °C for 2 h.

adding water to the polymeric solution and measured using a viscometer (Brookfield, DV-III) at 25 °C until a value of 14 mPa·s was reached. The (Sr, Bi, Nb) polymeric precursor was characterized by simultaneous thermal analysis, TG/DTA (Netzsch, STA409), in synthetic air (50 cm^3/min) using a constant heating rate of 5 °C/min from room temperature to 1000 °C. The powder calcined at different temperatures was characterized by x-ray diffraction (XRD) (Siemens, D5000) with Cu K_α radiation and a graphite monochromator. The lattice parameters were measured using the least-squares method, using SiO_2 as standard. The phase evolution of films was followed by grazing incident x-ray diffraction (GIXRD) (Siemens, D5000), using an incident angle of 2°(θ) and a LiF(100) monochromator. The microstructure evolution and thickness were characterized by a scanning electron microscope (SEM) (Zeiss, DSM940A).

The thermogravimetric results showed weight loss in several temperature ranges for the polymeric precursor. For temperatures higher than 580 °C, no more weight loss was observed. Figure 2 shows DTA results of the polymeric precursor powder heat-treated at 400 °C for 2 h. A broad exothermic peak centered at 521 °C, related to an intermediate phase crystallization phenomenon, followed by a small endothermic peak at 620 °C, probably related to the perovskite SBN phase formation, was observed.

Figure 3 shows the phase evolution characterized by XRD. The powder sample heat-treated at 300 °C shows a poorly crystallized Bi_2O_3 phase. As the temperature increased, this Bi_2O_3 phase originated a nonindexed phase. This phase is likely related to an intermediate fluorite phase. As observed in the XRD pattern (Fig. 3), the perovskite phase (SBN) originates from this fluorite phase, as observed by Boyle *et al.* for $SrBi_2Ta_2O_9$ (SBT).[15,16] These results suggest that the peak observed by DTA at 521 °C is due to the fluorite phase crystallization. Lattice parameters measured for the SBN phase calcined at 1000 °C for 2 h showed $a = b = 5.507$ Å and $c = 25.05$ Å values. These values are in agreement with those reported by Subbarao[17] if considered a tetragonal structure.

Figure 4 shows the phase evolution characterized for films using GIXRD. In contrast to results shown for powder samples, a diffuse XRD pattern is observed for films heat-treated at 300 and 400 °C, indicating that the precursor is amorphous. Films heat-treated at 500 and 600 °C presented the fluorite phase, in agreement

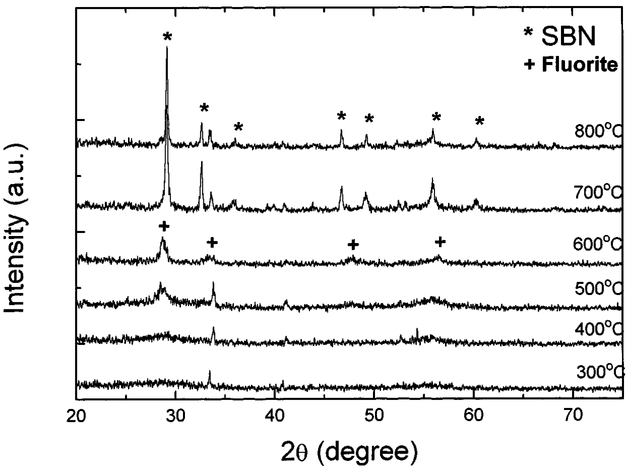

FIG. 4. GIXRD results for films heat-treated at 300, 400, 500, 600, 700, and 800 °C for 2 h.

with results obtained for powder samples. After thermal treatment at 700 °C, only peaks related to the SBN phase are observed. These results suggest that the SBN phase is formed at temperatures between 600 and 700 °C. Lattice parameters calculated for films heat-treated at 800 °C for 2 h were $a = b = 5.497$ Å and $c = 24.01$ Å. These results are different from those obtained for the powder; in films, the c parameter is smaller, indicating, probably, diffusion and reaction between film and silicon wafer or compression stress.

Crack-free films with an area of 1.0 × 1.0 cm were obtained after heat treatment at several temperatures. The scanning electron micrograph of Fig. 5 shows a microstructure evolution as a function of heat-treatment temperature. Films heat-treated at 600 °C [Fig. 5(a)] are crack free, with a smooth surface and no defined grain structure. A defined grain structure can be observed for films heat-treated at 700 °C [Fig. 5(b)]. Thickness, evaluated by SEM, ranged from 80 to 100 nm.

Figure 6 presents the SBN film deposited onto $Pt/Ti/SiO_2/Si(100)$ substrate. It can be observed that the XRD data [Fig. 6(a)] show a monophasic film, with a preferential orientation in the ⟨215⟩ direction and a homogeneous and dense microstructure [Fig. 6(b)], with well-defined spherical type grains. Electrical measurements of films deposited onto Pt are in progress.

III. CONCLUSIONS

Polymeric precursors method allows one to synthesize $SrBi_2Nb_2O_9$ (SBN) phase at temperatures as low as 600 °C. This is an improvement in the synthesis of this compound once the traditional solid state reaction requires temperatures above 1200 °C. XRD data show that the SBN perovskite phase crystallizes through an intermediate fluorite phase. The experimental results show that crack-free SBN thin films can be formed by dip coating onto Si(100) substrate using polymeric precursors method. The SBN phase crystallizes at temperatures between 600 and 700 °C in films.

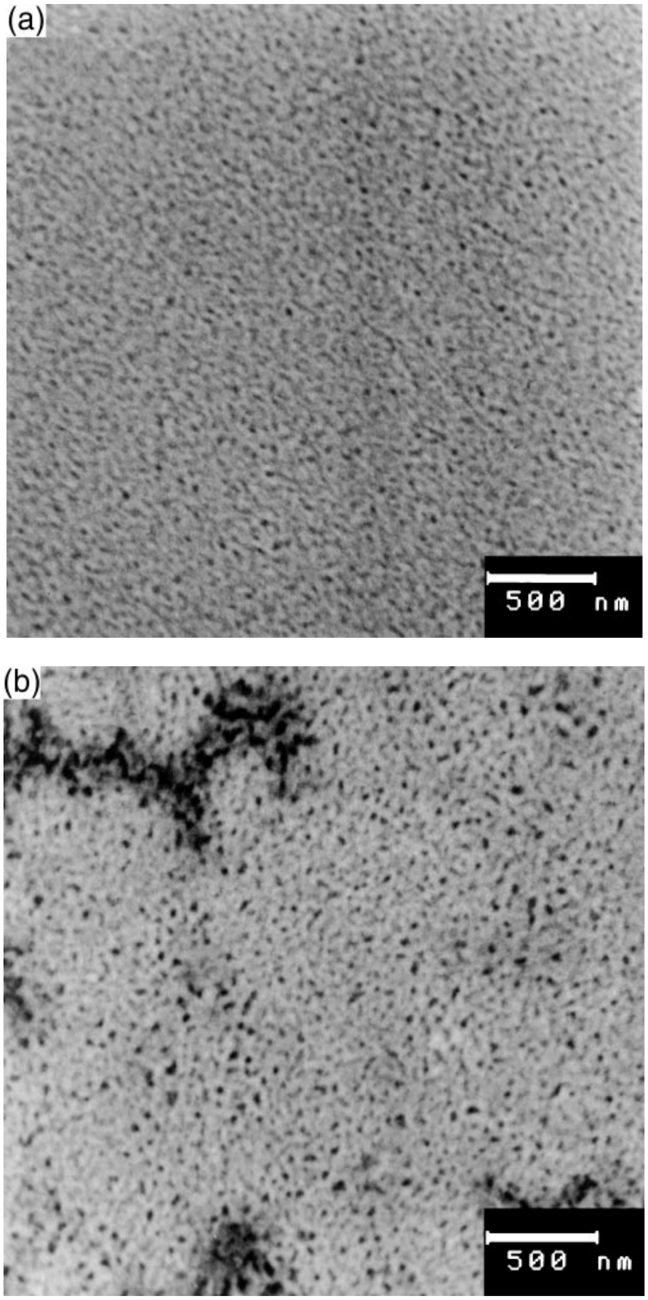

FIG. 5. Set of SEM micrographs for films with different heat treatments: (a) 600 °C and (b) 700 °C.

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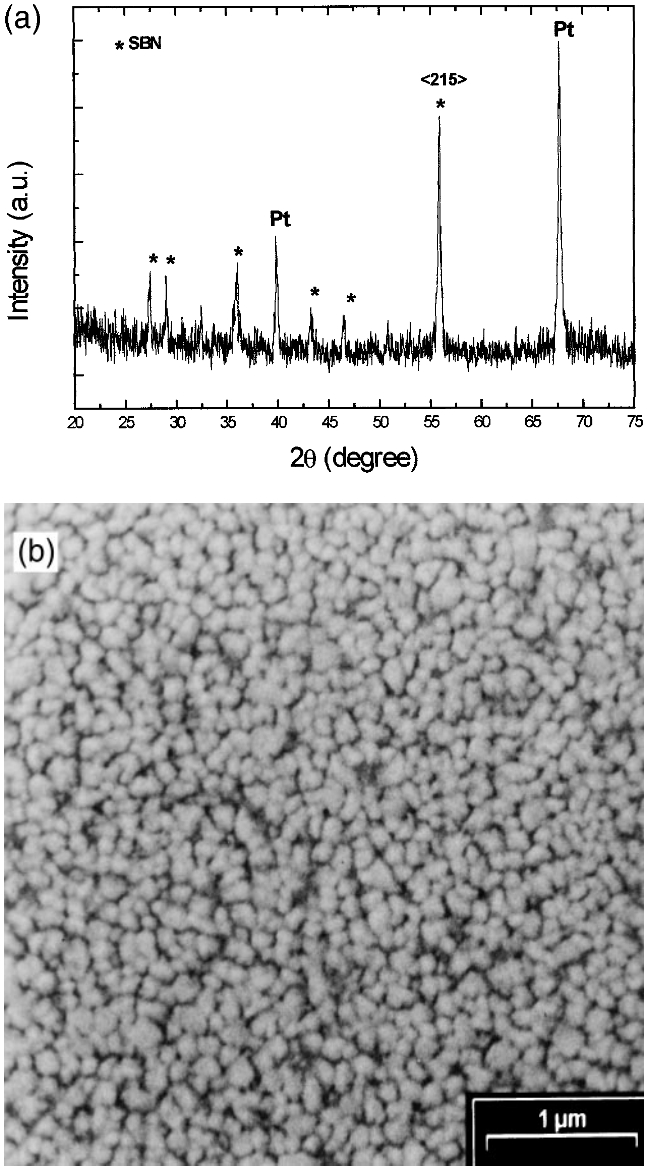

FIG. 6. SBN film deposited onto $Pt/Ti/SiO_2/Si(100)$ heat-treated at 700 °C. (a) GIXRD result; (b) SEM micrograph.

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