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Journal of Alloys and Compounds 458 (2008) 500–503

Journal of ALLOYS AND COMPOUNDS

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Structural and electrical properties of $SrBi_2(Ta_{0.5}Nb_{0.5})_2O_9$ thin films

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Received 10 January 2007; received in revised form 4 April 2007; accepted 5 April 2007
Available online 12 April 2007

Abstract

$SrBi_2(Ta_{0.5}Nb_{0.5})_2O_9$ (SBTN) thin films were obtained by polymeric precursor method on Pt/Ti/SiO_2/Si(1 0 0) substrates. The film is dense and crack-free after annealing at 700 °C for 2 h in static air. Crystallinity and morphological characteristic were examined by X-ray diffraction (XRD), field emission scanning electron microscopy (FEG-SEM) and atomic force microscopy (AFM). The films displayed rounded grains with a superficial roughness of 3.5 nm. The dielectric permittivity was 122 with loss tangent of 0.040. The remanent polarization (P_r) and coercive field (E_c) were 5.1 μC/cm^2 and 96 kV/cm, respectively.

Keywords: Ferroelectric; Chemical synthesis; Thin films; Nanostructures

1. Introduction

$SrBi_2(Ta_{0.5}Nb_{0.5})_2O_9$ (SBTN) thin films have been intensively studied as capacitor material for ferroelectric random access memory (FeRAM) devices [1,2]. This material belongs to the ferroelectric bismuth-layered perovskite structure, first described by Aurivillius. In this material, the perovskite $(A_{m-1}B_mO_{3m+1})^{2-}$ structure is sandwiched between the $(Bi_2O_2)^{2+}$ layers, where A is a relatively large divalent or trivalent cation such as Bi^{3+}, Ba^{2+}, Sr^{2+} or K^+, and B a small, highly charged cation such as B is Ti^{4+}, Ta^{5+}, Nb^{5+}, Mo^{6+} or W^{6+} [3].

Much attention has been paid to $SrBi_2Ta_2O_9$ (SBT) thin films for their applications in nonvolatile memory devices due to the fadique absence, as opposed to $Pb(Zr,Ti)O_3$ (PZT) films, which present serious problems of degradation when deposited on Pt electrodes [4]. However, the main problem for the application of SBT as FeRAM is the high temperature required for good crystallization, around 800 °C, added to the fine microstructure with small grain size, which affects the ferroelectric performance [5]. To overcame this difficulty, the niobium can decrease the processing temperature in SBT based material besides to promote the increasing of the grain size, which is desirable to obtain good ferroelectric properties [6,7]

Several deposition techniques have been used to obtain SBTN thin films, such as metalorganic chemical vapor deposition (MOCVD), sol–gel, radio frequency magnetron, ion beam sputtering and laser ablation [8–12]. Normally, physical methods have the disadvantage of requiring sophisticated and expensive equipment. Although the sol–gel method is considered excellent in terms of stoichiometric control and introduction of dopants, it required free-water atmosphere for synthesis and deposition. Moreover, sol–gel method presents a serious problem of solution aging, which alters the film microstructure, causing significant ferroelectric losses [13].

In this paper, we reported our first studies in the preparation of SBTN thin films, spin coated onto Pt/Ti/SiO_2/Si(1 0 0) substrate, by the polymeric precursor method (PPM). The PPM is based on the Pechini method [14] and has been widely utilized to synthesize mixed oxides. The main advantage of this method is the possibility of precise stoichiometric control, besides utilization of simple and cheaper reagents as precursor [15]. As far as we know, no polymeric precursor solution has been reported for the preparation of SBTN thin film.

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0925-8388/$ – see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.jallcom.2007.04.039

2. Experimental procedure

Strontium carbonate, $SrCO_3$ (Merk), niobium ammonium oxalate, $NH_4H_2[NbO\text{-}(C_2O_4)_2]\cdot 3H_2O$ (CBMM, Araxá, Brazil), bismuth oxide, Bi_2O_3 (Aldrich), tantalum ethoxide, $Ta(OC_2H_5)_5$ (Alfa Aesar) were used as raw materials. The molar ratio among Sr^{2+}, Bi^{3+}, Ta^{5+} and Nb^{5+} was 1:2:1:1. Niobium hydroxide was formed by dissolution of niobium ammonium oxalate in water and precipitated as $Nb(OH)_5$. After filtration, niobium hydroxide was dissolved in aqueous solution of citric acid to form niobium citrate. The pH was adjusted to 7–8 adding ethylenediamine. In the preparation of tantalum citrate, tantalum ethoxide was dissolved in ethylene glycol under heating and stirring and then, citric acid was added. $SrCO_3$ and Bi_2O_3 were dissolved in nitric acid and then added in the appropriate amount of niobium and tantalum citrate. Ethylenediamine was added into the solution until the pH reached 8–9. The citric acid/ethylene glycol ratio was fixed as 60/40 (mass ratio). The viscosity of the resulting solution was adjusted to 20 cP by controlling the water content using a Brookfield viscosimeter. The SBTN thin film was spin coated on $Pt/Ti/SiO_2/Si(1\,0\,0)$ substrates by spinner (spin coater KW-4B, Chemat Technology) operating at 5000 revolutions/min for 30 s. In previous work, we demonstrated that SBTN powders free of secondary phases can be formed at 700 °C [16]. Therefore, in this work the film was annealed at 400 °C for 2 h with heating rate of 3 °C/min and spinned again, until the seven layers were reached. All layers were crystallized at the same time at 700 °C for 2 h.

Phase analysis of the films was performed at room temperature by X-ray diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku 2000) and Cu Kα radiation**.** The SBTN film surface was analyzed by field emission scanning electron microscopy (FE-SEM; Zeiss, Supra 35). The thickness was obtained from SEM (Topcom SM-300) represent an average value of three measurements. Surface roughness was examined by AFM, using tapping mode technique. About 0.5 mm diameter top Au electrode was sputtered through a shadow mask at room temperature.

The relative dielectric permittivity, ε_r, and dissipation factor, $\tan\delta$, were carried out at room temperature as a function of frequency in the range of 10 kHz to 1 MHz using an impedance analyzer (model 4192 A, Hewlett Packard). Ferroelectricity was investigated using a Sawyer-Tower circuit attached to a computer controlled standardized ferroelectric test system (Radiant Technology 6000 A). The hysteresis loop was measured at a frequency of 100 Hz at an applied electric field of 330 kV/cm. The leakage current–voltage (*I–V*) characteristic was determined with a voltage source measuring unit (Radiant Technology 6000 A).

3. Results and discussion

XRD pattern of SBTN film is illustrated in Fig. 1. All peaks were indexed to the perovskite phase and no secondary phases were observed. The SBTN film presents a polycrystalline nature with the maximum intensity peak at (1 1 5) direction, and exhibits very weak (0 0 *l*) peaks with the *c*-axis oriented normal to the substrate. In addition, less intense peaks along the (2 0 0) and (2 2 0) directions were observed in the pattern. Characteristic peak for platinum coated silicon (1 1 1) substrates was observed in the range of $38° < 2\theta < 44°$. These results are similar to that obtained by Zanetti et al. for SBN thin films [15].

FE-SEM image of SBTN film indicates that the microstructure is dense and the grains displayed a rodlike structure with the layered perovskite phase as shown in the Fig. 2. Chen et al. [17] observed a similar microstructure for SBT films obtained by MOD. The authors have found that elongated and bigger grains lead to better ferroelectric properties. The film thickness determined from SEM analysis is around 440 nm.

AFM micrograph on the 1 μm × 1 μm scale of SBTN thin film evidence that the film surface is dense and crack free as

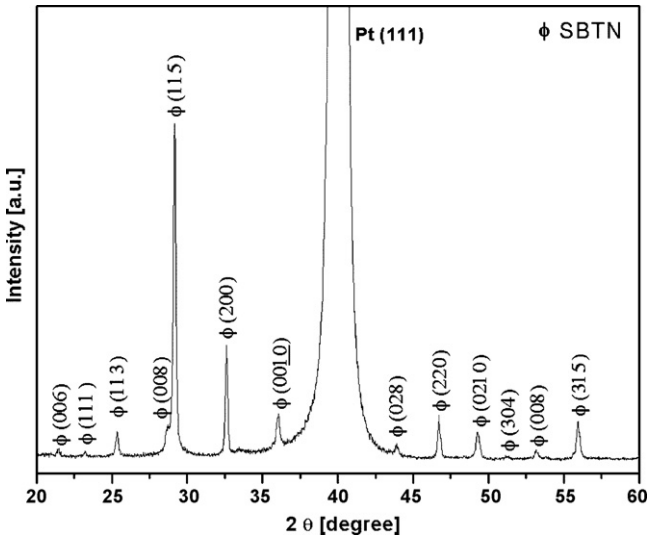

Fig. 1. X-ray diffraction for $SrBi_2(Ta_{0.5}Nb_{0.5})_2O_9$ films annealed at 700 °C for 2 h.

shown in the Fig. 3. This observation is consistent with FE-SEM measurement. Spherical grains with size around 140 nm and surface roughness of 3.5 nm were observed. This result is better compared to other chemical method (ranging from 10 to 43 nm) and similar to that obtained by physical method (nearly 4 nm) [18,19]. According to Moert el al. [20] the transformation of SBT thin films from amorphous to perovskite phase is accomplished by a strong change in the polycrystalline microstructure. The phase transformation starts at 650 °C from a smooth and fine-grained fluorite matrix to Aurivillius phase at 700 °C.

The dielectric permittivity and dissipation factor are presented in Fig. 4. The dielectric permittivity shows little dispersion with frequency indicating that our films possess low defect concentrations at the interface film-substrate. The low dispersion and the absence of any relaxation peak in $\tan\delta$ indicate that both, interfacial polarization of the Maxwell Wagner type and a polarization produced by the electrode barrier can be neglected in the film. The dielectric permittivity and dissipation

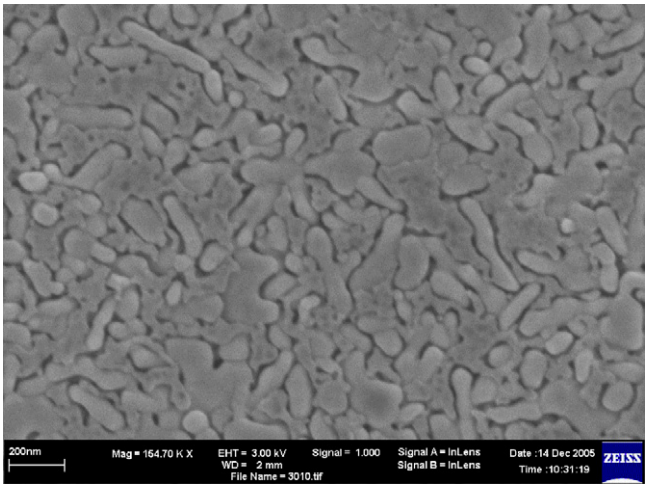

Fig. 2. FE-SEM photography for $SrBi_2(Ta_{0.5}Nb_{0.5})_2O_9$ films annealed at 700 °C for 2 h.