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Materials Letters 59 (2005) 2759 – 2764

materials letters

www.elsevier.com/locate/matlet

Influence of the solution pH on the morphological, structural and electrical properties of $Bi_{3.50}La_{0.50}Ti_3O_{12}$ thin films obtained by the polymeric precursor method

A.Z. Simões[a,*], A. Ries[a], F. Moura[a], C.S. Riccardi[a], E. Longo[b], J.A. Varela[a]

[a]*Chemistry Institute, Universidade Estadual Paulista (UNESP), Araraquara-SP, CEP, 14801-970, Brazil*
[b]*Chemistry Department, Universidade Federal de São Carlos (UFSCAR), São Carlos-SP, CEP, 13565-905, Brazil*

Received 19 January 2005; accepted 31 March 2005
Available online 31 May 2005

Abstract

Lanthanum-doped $Bi_4Ti_3O_{12}$ thin films (BLT) were deposited on Pt/Ti/SiO_2/Si substrates using a polymeric precursor solution. The spin-coated films were specular, crack-free and crystalline after annealing at 700 °C for 2 h. Crystallinity and morphological evaluation were examined by X ray diffraction (XRD) and atomic force microscopy (AFM). The stability of the formed complex is of extreme importance for the formation of the perovskite phase. Films obtained from acid pH solution present elongated grains around 200 nm in size, whereas films obtained from basic solution present a dense microstructure with spherical grains (100 nm). The dielectric and ferroelectric properties of the BLT films are strongly affected by the solution pH. The hysteresis loops are fully saturated with a remnant polarization and coercive voltage of P_r=20.2 μC/cm^2 and V_c=1.35 V and P_r=15 μC/cm^2 and V_c=1.69 V for the films obtained from basic and acid solutions, respectively.

Keywords: Crystal structure; Dielectrics; Ferroelectrics; Thin films

1. Introduction

Ferroelectric thin films have received considerable attention in recent decades for the potential applications in nonvolatile random access memories [1]. Among related materials of interest, lead zirconate titanate ($PbZr_xTi_{1-x}O_3$, PZT) is probably the most extensively studied. PZT films have favourable characteristics, including high polarization, a low processing temperature, and remaining apparently fatigue-free when used as conducting oxide electrodes [2,3]. Nevertheless, environmental safety issues concerning the Pb-containing formula may ultimately prevent it from being used in many applications. Layer-structured perovskite like strontium bismuth tantalate ($SrBi_2Ta_2O_9$, SBT) has also been studied [4]. Although SBT is a fatigue-free material, the practical application of SBT is limited, primarily due to its small polarization ($2P_r$=4–16 μC/cm^2) and high processing temperature of over 750 °C.

Recently, polycrystalline La-substituted bismuth titanate ($Bi_{4-x}La_xTi_3O_{12}$, BLT) films have attracted attention because of their possible application to ferroelectric random access memories due to their high fatigue endurance as well as low deposition temperature [5]. Compared with another well-known fatigue-free ferroelectric material $SrBi_2Ta_2O_9$ (SBT) which is also a Bi-layered perovskite oxide, BLT has many attractive properties, such as low processing temperature and large values of remnant polarization. However, pure bismuth titanate ($Bi_4Ti_3O_{12}$, BIT) is prone to fatigue. Two reasons for the fatigue-free behaviour of BLT have been found. One is the charge-compensating role of the (Bi_2O_2) layers. Another is the suppression of oxygen vacancies after substituting some La atoms for Bi atoms, since the oxygen ions near Bi ions in BIT are likely to be

* Corresponding author. Tel.: +55 16 2016712; fax: +55 16 2227932.
E-mail address: alezipo@yahoo.com (A.Z. Simões).

0167-577X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2005.03.051

less stable than those near Sr ions in SBT due to the high volatility of bismuth oxide [6–8].

It is well known that the phase formation is directly related with the purity of the precursor, processing method, as well as of the time and temperature of the reaction. Any change in these parameters can induce the formation of the undesired phases [9], as it was already observed in the process of preparation of PZT [10] by the polymeric precursor method. This chemical method involves the formation of a chelate through the reaction of the citric acid with the metallic cation, followed by polyesterification with ethylene glycol. Even so, this reaction presents a chemical memory, in which the metallic cations responsible to form the net can be separated. The key for the obtaining of perovskite phase is intimately related with the structure originating from the chemical memory.

Ferroelectric films have been fabricated by rf sputtering [11], pulsed laser deposition [12], electron cyclotron resonance plasma sputtering [13] and metalorganic chemical vapor deposition [14]. In this work, we report the preparation of BLT thin films on platinum-coated silicon substrates by the polymeric precursor method. Compared with other techniques, the polymeric precursor method has the advantages of easier composition control, better homogeneity, low processing temperature (compatible with Si processing), easier fabrication of large areas and low cost [15]. In this work, BLT thin films were prepared by the polymeric precursor method. The effects of solution pH on the structural, morphological and electrical properties of BLT thin films were investigated.

2. Experimental procedure

Titanium isopropoxide (Hulls AG), hydrated lanthanum carbonate (Aldrich) and bismuth nitrate (Aldrich) were used as raw materials. The precursor solutions of bismuth, titanium and lanthanum were prepared by adding the raw materials to ethylene glycol and concentrated aqueous citric acid under heating and stirring. Appropriate quantities of solutions of Ti, Bi and La were mixed and homogenized by stirring at 90 °C. The solution pHs were adjusted at values of 3 and 9. To obtain the basic pH, ethylenediamine was added to the solution until a complete complexation of the cations was present in the system. The molar ratio of metal:citric acid:ethylene glycol was 1:4:16. The viscosity of the resulting solution was adjusted to 20 cP by controlling the water content using a Brookfield viscosimeter. Films were spin-coated from $Bi_{4-x}La_xTi_3O_{12}$ ($x=0.50$) deposition solution onto Pt/Ti/SiO_2/Si substrate. It was observed from a previous work that BLT films were completely crystallized at 700 °C for 2 h; so this was the temperature at which films were heat-treated [16]. Multilayered films were obtained by spinning 5 times (pH=3, [M]=0.1 mol L^{-1}) and 10 times (pH=9, [M]=0.05 mol L^{-1}) the deposition solution on the surface of the platinum-coated silicon substrate previously cleaned with Extran solution and ethanol. The films were heat-treated at 400 °C for 2 h with a heating rate of 3 °C/min in a conventional furnace and immediately crystallized at 700 °C for 2 h, before the next deposition. All films were heat-treated in static air. In this work, an excess of 5.0 wt.% of Bi was added to the solution aiming to minimize the bismuth loss during the thermal treatment. Without this additional bismuth the pure phase could not be obtained as it has been reported in the literature [17]. Phase analysis of the films was performed at room temperature by X-ray diffraction (XRD) using a Bragg–Brentano diffractometer (Rigaku 2000) and CuKα radiation. The morphology of the annealed films was studied using scanning electron microscopy. The thicknesses were measured from the transversal section by using back-scattering electrons (Topcom SM-300). The thickness results obtained from SEM represent an average value of three measurements. Surface roughness (RMS) was examined by AFM, using tapping mode technique. Next, a 0.5-mm diameter top Au electrode was sputtered through a shadow mask at room temperature. After deposition of the top electrode, the film was subjected to a post-annealing treatment in a tube furnace, at 300 °C with a constant heating rate of 1 °C/min, in oxygen atmosphere for 1 h. Here, the desired effect is to decrease eventually present oxygen vacancies.

The relative dielectric constant ε_r and dissipation factor ($\tan\delta$) were measured versus frequency using an impedance analyser (model 4192 A, Hewlett Packard). The capacitance–voltage characteristic was recorded in the MFM configuration using a small AC signal of 10 mV at 100 kHz. The AC signal was applied across the sample, while the DC was swept from positive to negative bias. Ferroelectricity was investigated using a Sawyer–Tower circuit attached to a computer-controlled standardized ferroelectric test system (Radiant Technology 6000 A). The leakage current–voltage (I–V) characteristic was determined with a voltage source measuring unit (Radiant Technology 6000 A). All measurements were performed at room temperature. For the fatigue measurements, internally generated 8.6 μs wide square pulses or externally generated square pulses were used. After the end of each fatigue period, the polarization characteristics of the films were measured over a range of frequencies.

3. Results and discussion

It is well known that the thickness of the layer is a function of viscosity, ionic concentration of the solution and spinning speed. It is important to control the thickness of the layer due to its strong influence on the grain size, dielectric and ferroelectric properties. It was observed that for thinner films interfacial “dead layers” could appear at the interface between films and substrate. These layers possess poor dielectric properties influencing the performance of the device [18]. These dead layers are originated from oxygen interdiffusion, chemical reaction, or structural defects at the