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Characterization of ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films prepared by metal organic decomposition method

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Abstract

Ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films were prepared using the spin-coating method onto Pt/Ti/SiO_2/Si substrate by the metal organic decomposition. Crystallographic properties of BLT films were characterized as a function of annealing temperature. The effect of excess Bi content on the microstructure and ferroelectric properties was also investigated. X-ray diffraction (XRD) results show that predominant $Bi_4Ti_3O_{12}$ phase can be obtained at 550 °C, while the films keep randomly oriented structure up to 750 °C. An increase in grain size of BLT films with increasing annealing temperature was observed by the field emission scanning electron microscopy (FE-SEM). The hysteresis loops of BLT films were found to be well defined for temperatures above 600 °C. The remanent polarization decreased when more than 10% of excess Bi has been used in the precursor solution. The films with both Bi deficiency and Bi excess over 10% in the BLT precursor solution annealed at 650 °C showed poor fatigue properties. This was attributed to the structure defects and to the presence of a secondary phase. The films prepared with the Bi content in excess of 10% and annealed at 650 °C exhibited an outstanding hysteresis behaviors with the remanent polarization ($2P_r$) of 25.66 as well as fatigue-free behavior up to 3.5×10^9 bipolar cycles.

Keywords: BLT; Thin Film; MOD; FeRAM; Ferroelectric properties

1. Introduction

Ferroelectric materials based on layered perovskite structures have attracted great attention for the ferroelectric random access memories (FeRAM) due to their superior properties, such as high fatigue resistance during electric field cycling with a Pt electrode [1–3]. These material have the general formula $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$, where A=Ca^{2+}, Ba^{2+}, Sr^{2+}, Bi^{3+}, etc., B=Fe^{3+}, Ti^{4+}, Nb^{5+}, Ta^{5+}, etc., n is the number of BO_6 octahedra in the pseudoperovskite block (n=2, 3, 4, and 5) [4,5]. Among them, $SrBi_2Ta_2O_9$ (SBT) and $Bi_4Ti_3O_{12}$ (BTO) thin films have been intensively investigated. However, SBT films have some serious drawbacks for the FeRAM applications, such as the high processing temperatures (above 800 °C) and the low remanent polarization of about 20 μC/cm^2 [2]. In the case of BTO thin films, it is known that BTO single crystals have a large spontaneous polarization (P_s) of 45 μC/cm^2 [6]. This value is three times larger than for the SBT. On the other hand, BTO thin films suffer from low remanent polarization (0.6–4 μC/cm^2), high leakage current density, and fatigue failure. Recently, Park et al. [7] have reported on the new $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films fabricated by a pulsed laser deposition method at 650 °C. They have proposed that the fatigue failure characteristics of BTO films can be improved by using the low deposition temperature as well as by the substitution of some bismuth ions near the Ti–O octahedron layers with the lanthanum ions.

In this paper, we investigated the phase formation, microstructure, and ferroelectric properties of BLT thin films as a function of annealing temperature and excess Bi content. The characteristics of BLT thin films were examined by X-ray diffraction (XRD), high-resolution transmission electron

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microscopy (HR-TEM), and depth-profiling from Auger electron spectroscopy (AES).

2. Experimental details

The BLT thin films were deposited on the Pt/Ti/SiO_2/Si substrates by the metal-organic decomposition (MOD) technique. The BLT thin films were synthesized according to the formula $Bi_{4-x}La_xTi_3O_{12}$ (x=0.75) with 0–30% excess Bi. The precursor materials used in the MOD method were bismuth acetate [$Bi(CH_3CO_2)_3$], lanthanum–acetate hydrate [$(CH_3CO_2)La\cdot xH_2O$], and titanium *iso*-propoxide {$Ti[OCH(CH_3)_2]_4$}. The solvents for the precursor were acetic acid [CH_3CO_2H] and 2-methoxyethanol [$CH_3OCH_2CH_2OH$], respectively. Initially, the solid-state bismuth acetate and lanthanum acetate were dissolved in the acetic acid and deionized water. Then, these solutions were mixed to obtain a (Bi, La) stock solution followed by stirring for 12 h. Subsequently, the titanium *iso*-propoxide was dissolved and magnetically stirred in 2-methoxyethanol under the N_2 atmosphere for 12 h. Finally, both solutions were mixed to prepare the stoichometric, transparent and stable BLT precursor. The mixture of two solutions was stirred for 24 h at room temperature. The concentration of the BLT precursor was adjusted to 0.33 M.

For the fabrication of BLT thin films, the BLT precursor solution was syringed through a 0.2-μm acrodisc syringe filter (Gelman Science, Ann Arbor, MI, USA) on the Pt (120 nm)/Ti (30 nm)/SiO_2/Si substrate. The films were deposited by the spin-coating method at 4000 rpm for 30 s. After the spin-coating procedure, the films were kept on hot plate at 400 °C for 10 min to remove the organic ingredients. The coating/drying circles were repeated 10 times. The prebaked films were annealed at temperatures between 550 and 750 °C for 1 h under an oxygen atmosphere to promote crystallization. The final thickness of BLT films measured using transmission electron microscope (TEM) was about 180 nm. To investigate the ferroelectric properties of BLT thin films, a top Pt electrode of 150 nm thickness and 300 mm in diameter was formed using a shadow dot mask by radio-frequency sputtering.

The annealed BLT films were analyzed by XRD using the Rigaku-D/MAX diffractometer (CuK_α 30 kV, 200 mA). The surface morphologies of BLT thin films were examined using the JEOL 6330F field emission scanning electron microscope (FE-SEM). The cross-sectional microstructure of BLT films was examined using the JEOL JEM-2000EXII transmission electron microscope (TEM). The compositional depth profile between the BLT film and the Pt electrode was investigated using the Perkin-Elmer l660 Auger electron spectroscopy (AES). The AES operation conditions such as the type of ion used for the sputtering, the sputtering rate, the electron accelerating voltage, and the operating pressure were Ar^+, 303 Å/min for SiO_2, 10 kV, and 5×10^{-10} Torr, respectively. The chemical compositions of BLT thin films with the Bi excess were examined using the JEOL JXA-890 electron probe microanalysis (EPMA). The ferroelectric properties of BLT films were measured using a precision workstation ferroelectric tester (Radiant Technologies, USA).

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of BLT films annealed at temperatures ranging from 550 to 750 °C. It can be seen that the XRD peak corresponding to the (117) reflection appears at 550 °C. This fact gives the evidence that the crystallization to the layered perovskite structure begins close to this temperature. For the temperatures above 550 °C, all BLT films show typical XRD patterns of the BTO-layered perovskite polycrystalline structure and no pyrochlore phase (cubic Bi_2O_3). The secondary phase as well as the preferred orientation was also not observed. The reason may be that the La^{3+} ions in the BLT films do not form pyrochlore phase but can be dissolved into the pseudoperovskite structure. Therefore, it seems that the La^{3+} ions can easily substitute for the Bi^{3+} ions [8] in pseudoperovskite structure. This partial substitution of the La^{3+} for the Bi^{3+} ions in the BTO influences the structural properties of the Bi layer. With a furthermore increase in the annealing temperature, all XRD diffraction peaks become sharper, while the full width at a half maximum (FWHM) decreases. These results indicate that the grain size increases with increasing annealing temperature. It is important to note that, in the Bi-layered ferroelectrics, there is the possibility of formation of the face-centered fluorite cubic crystal structure existing as an intermediate phase between the amorphous and perovskite structures. It is known also that, generally, the fluorite structure shows the Bi-deficient properties compared with the perovskite structure [9]. However, the XRD results plotted in Fig. 1 indicate the absence of the fluorite structure for all the range of the investigated annealing temperatures.

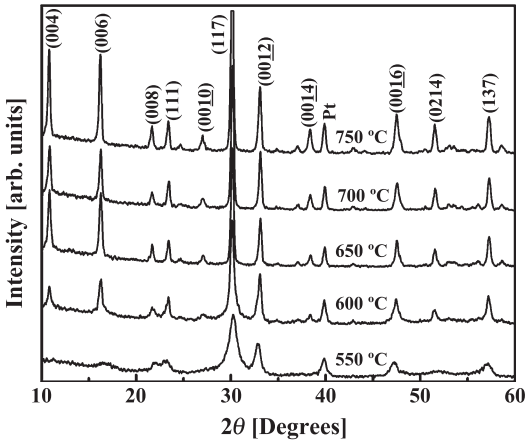

Fig. 1. X-ray diffraction patterns of BLT films as a function of annealing temperature.