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Low temperature synthesis and ferroelectric properties of La substituted $Bi_4Ti_3O_{12}$ thin films by sol–gel

H. Wang *, M.F. Ren

Department of Information Material Science and Engineering, Guilin University of Electronic Technology, Guilin 541004, China

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Abstract

$Bi_{4-x}La_xTi_3O_{12}$ (BLT) thin films were prepared on p-Si substrates by using sol–gel method. The effect of La content and annealing temperature on structure, morphology, dielectric and ferroelectric properties of BLT films were investigated. Even at low temperatures ranging from 500 to 650 °C, the BLT thin films were uniform and crack free as well as exhibited no preferred orientation analyzed by X-ray diffraction and atomic force microscope. La content and annealing temperature affect greatly on the preferred orientation and ferroelectric properties of BLT thin films. The $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films annealed at as low as 600 °C showed excellent dielectric and ferroelectric properties with a dielectric constant of 288, a dielectric loss of 1.57%, a remanent polarization of 17.5 μC/cm^2 and a coercive field of 102 kV/cm, which are better than those of $Bi_4Ti_3O_{12}$ thin films prepared using the same processing. The low processing temperature and the large remanent polarization of BLT are favorable for device application.

Keywords: La substituted; BLT; Ferroelectric thin film; Sol–gel

1. Introduction

Nonvolatile memories are taking an increased share of the growing memory market and becoming an indispensable component of memory circuits [1,2]. Bismuth layered structure ferroelectrics (BLSFs) thin films have been widely investigated aimed at applications in nonvolatile ferroelectric random access memories (FRAMs). The reason is that this family of compounds has superior properties, such as a high fatigue resistance during electric field cycling with a Pt electrode [3,4]. BLSF materials can be described as the intergrowth structure of fluoritelike $(Bi_2O_2)^{2+}$ units and perovskitelike $(A_{n-1}B_nO_{3n+1})^{2-}$ slabs, where $n = 2$–5. The 12-fold perovskite A-sites can be occupied by cations like Ba^{2+}, Ca^{2+}, Sr^{2+}, Bi^{3+} and rare earth elements, and the six-fold B-sites are usually occupied by smaller cations like Ti^{4+}, Ta^{5+}, Nb^{5+} and W^{6+}. Among BLSFs, $SrBi_2Ta_2O_9$ (SBT) and $Bi_4Ti_3O_{12}$ (BIT) have attracted a dominant attention. However, the SBT films have some serious drawbacks, such as high processing temperatures (above 800 °C) and low remanent polarization of 4–10 μC/cm^2, which is insufficient for the high-density integration of FRAM [3,5]. In the case of BIT thin films, *a*-axis-orientation BIT thin film has a large spontaneous polarization of 45 μC/cm^2, which is three to four times higher than that of SBT. Nevertheless BIT thin films are *c*-axis-orientation with the increase of annealing temperature *c*-axis oriented [6], the spontaneous polarization is much lower than that of *a*-axis oriented BIT films due to the polarization axis lies on the *a*–*c* plane with closing to the *a*-axis.

Recently, it was reported that the La substituted $Bi_4Ti_3O_{12}$ (BLT) have larger P_r and larger E_c than those of pure BIT. It was found that although the La substitution modifies the structure of BIT thin films, the BLT showed the characteristics similar to BIT thin films. Many processing techniques, such as sol–gel [7], metalorganic vapor phase epitaxy [8] and chemical solution deposition [9] have been employed to synthesis BLT thin films, but the problem of low polarization due to *c*-axis-oriented has not been intensively investigated so far.

High annealing temperature is another problem of BLT thin films applied in Si integration devices (for example, in

* Corresponding author.
E-mail address: wh65@gliet.edu.cn (H. Wang).

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FRAMs). However, in previous works, several researches reported that the temperature of 700–750 °C or higher is required to produce perovskite layered BLT thin films [7–9]. In present paper, the synthesis of $Bi_{4-x}La_xTi_3O_{12}$ thin films annealing at low temperature, microstructure, dielectric and ferroelectric properties of $Bi_{4-x}La_xTi_3O_{12}$ thin films deposited on p-Si were reported.

2. Experimental procedure

2.1. Fabrication of $Bi_{4-x}La_xTi_3O_{12}$ thin films

$Bi_{4-x}La_xTi_3O_{12}$ films were prepared on p-Si(1 0 0) substrates by sol–gel method. This processing was selected due to its low cost, easy control of stoichiometry, simplicity and the potential commercial application to deposit uniform films over large areas. Moreover, this processing has previously been successfully applied to deposit BIT thin films.

Bismuth nitrate $Bi(NO_3)_3{\cdot}5H_2O$, titanium isopropoxide $(C_4H_9O)_4Ti$ and lanthanum nitride $La(NO_3)_3{\cdot}6H_2O$ were selected as precursors. Excess 5% Bi precursor was added to compensate Bi evaporation during annealing. Acetic acid and 2-methoxyethanol were used as solvent. Bismuth nitrate and lanthanum nitride were initially dissolved in glacial acetic acid, respectively. Titanium isopropoxide was added to this mixture with constant stirring. Finally, the wine-colored clear solution thus formed was diluted with 2-methoxyethanol to adjust the viscosity and concentration of the solution. (1 0 0)p-type silicon wafers with a resistivity of 6–9 Ω cm were cleaned by a standard process. The spin-on technique was employed to deposit solution on silicon substrates. After spinning onto substrates, wet films were kept on a hot plate in air at 250 °C for 10–15 min to remove solvents and other organics, then the dry films were annealed for 30 min at various temperatures in oxygen atmosphere. The desired thickness of $Bi_{4-x}La_xTi_3O_{12}$ films was achieved by multiple spin-bake processes. In this work, all the films prepared were about 400 nm thick. The composition was determined by electron probe microanalysis.

2.2. Characterized of the samples

The structure and the surface morphology of the films were analyzed by X-ray diffraction (XRD) and examined by atom force microscope (AFM), respectively. The dielectric constant and dielectric loss were measured using an HP4284A impedance analyzer. Ferroelectric properties of the $Bi_{4-x}La_xTi_3O_{12}$ thin films were measured using a RT66A standardized ferroelectric tester (Radiant Technologies, USA). Before electrical measurements, the Ag/BLT/Ag thin film capacitors were postannealed by RTA at their respective crystallization temperature for 60 s. The Ag electrode, with a thickness of 50 nm and a diameter of 0.4 mm, was patterned by a shadow-mask-process.

3. Results and discussion

3.1. Structure and surface morphology of $Bi_{4-x}La_xTi_3O_{12}$ thin films

The structure of $Bi_{4-x}La_xTi_3O_{12}$ thin films was analyzed by X-ray diffraction. The pyrolyzed films dried at 250 °C were found to be amorphous, and post-deposition annealing was required to develop crystallinity. The effects of annealing temperature on the structure and properties of the $Bi_4Ti_3O_{12}$ and $Bi_{4-x}La_xTi_3O_{12}$ thin films deposited on p-Si(1 0 0) substrates were studied. Fig. 1 shows the XRD patterns of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films annealed at 500, 550, 600 and 650 °C in oxygen, while the annealing time is kept in 30 min. The peaks show a consistent pattern of $Bi_4Ti_3O_{12}$, which is shown in Fig. 2 ($x = 0$). The bismuth layered perovskite structure appears after annealed at 500 °C for 30 min, but the characteristic peaks shown in 500 °C patterns are weak and broad. As the annealing temperature increase, annealing results in sharp peaks with high intensity, indicating better crystallinity and an increase in grain size. The coincidence of diffraction peaks of $Bi_{4-x}La_xTi_3O_{12}$ with those of $Bi_4Ti_3O_{12}$ implies that the La substitution does not affect the layered perovskite structure of $Bi_4Ti_3O_{12}$. But the lattice parameters, both *a*-axis and *c*-axis parameters, are found to be a little shorter than the lattice parameters of $Bi_4Ti_3O_{12}$ thin films

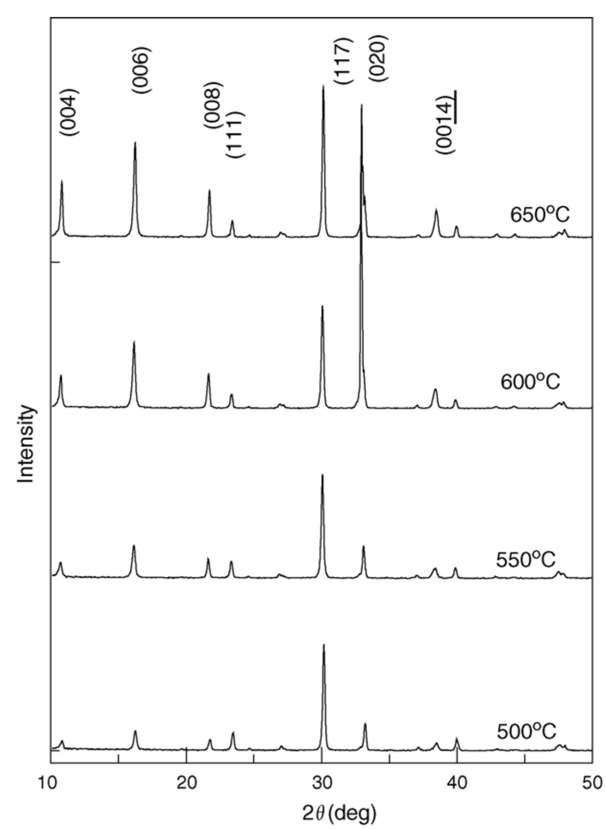

Fig. 1. X-ray diffraction patterns of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films on p-Si substrates annealed at various temperatures for 30 min.