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Microstructure and ferroelectric properties of Nb-doped $Bi_4Ti_3O_{12}$ thin films prepared by sol–gel method

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Abstract

The effects of Nb doping on the ferroelectric properties of $Bi_4Ti_3O_{12}$ (BIT) thin films were investigated. Ferroelectric Nb-doped $Bi_4Ti_3O_{12}$ (BTN) thin films were prepared by a sol–gel spin-coating method and annealed at several temperatures in an oxygen atmosphere. From analyzing X-ray diffraction patterns, it could be determined that a randomly oriented film was obtained by doping Nb ion into BIT thin film. The BTN film consisted of more disordered plate-like grains whereas the plate-like grains in the BIT film were more parallel to the substrate. The remanent polarization ($2P_r$) and coercive field ($2E_c$) of the BTN thin film that annealed at 700 °C were about 39.8 μC/cm^2 and 136.7 kV/cm at a sweep electric field of 175 kV/cm. The pulse polarization ($P_{sw}-P_{ns}$) and the shape of the hysteresis loops did not change significantly before and after the 1.5×10^{10} switching cycles.

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1. Introduction

Ferroelectric thin films have attracted much attention for use in nonvolatile ferroelectric random access memory (FeRAM) devices [1,2]. Among these ferroelectrics, $Bi_4Ti_3O_{12}$ (BIT) is known as a promising candidate material for FeRAM applications because of its large spontaneous polarization. BIT is a member of the Aurivillius family of the bismuth layer structure perovskites which have the general formula of $(Bi_2O_3)^{2+}(A_{x-1}B_xO_{3x+1})^{2-}$, where A can be Ca, Ba, Sr, Pb, Bi, etc., B represents Ti, Nb, Ta, etc., and x is the number of BO_6 octahedra in the pseudo-perovskite block (i.e. $x = 2, 3, 4$) [3,4]. For

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BIT, A = Bi, B = Ti, and $x = 3$. In order to improve the ferroelectric properties of BIT, a doping technique has been adopted [5]. Park et al. [4] reported that the La-doped BIT thin film, where La was substituted for Bi, exhibited a large remanent polarization and fatigue-free behavior. Noguchi and Miyayama [6] prepared the V-doped BIT thin film (where V was substituted for Ti) whose remanent polarization was superior to $SrBi_2Ta_2O_9$ and $Sr_{0.8}Bi_{2.2}Ta_2O_9$. In addition, Watanabe et al. [7] investigated the codoping effect of La and V into the BIT thin films.

There are several different methods used to prepare doped and nondoped BIT thin films. These include sputtering [8], laser ablation [9], chemical vapor deposition (CVD) [10] and the sol–gel method [11,12]. Among these, the sol–gel method offers many advantages such as highly homogeneous thin films, large area coating, low cost, and high flexibility.

In this work, we prepared the Nb-doped BIT, $Bi_{4-x}(Ti_{1-x}Nb_x)_3O_{12}$ ($x = 0.02$) thin films (where Nb^{5+} was substituted for Ti^{4+}) on a $Pt/Ti/SiO_2/Si$ substrate by the sol–gel method, and investigated the ferroelectric properties of the films fabricated in a capacitor form.

2. Experimental procedure

Bismuth nitrate pentahydrate [$Bi(NO_3)_3 \cdot 5H_2O$] (Aldrich), titanium isopropoxide [$Ti(OC_3H_7)_4$] (Aldrich), and niobium ethoxide [$Nb(OC_2H_5)_5$] (Aldrich) were used as starting materials. Titanium isopropoxide and niobium ethoxide were dissolved in 2-methoxyethanol and then acetylacetone was added to the solution as a chelating agent. The solution was stirred for 2 h for homogeneity. At the same time, bismuth nitrate pentahydrate (10 mol% excess) was dissolved in 2-methoxyethanol and acetic acid in a volume proportion of 3:1 and stirred for 2 h. Acetic acid ensured that the solution was more stable. The two solutions were mixed by continuous stirring to obtain a starting solution where the concentration was adjusted to 0.1 M. The $Bi_{4-x}(Ti_{1-x}Nb_x)_3O_{12}$ ($x = 0.02$) (BTN) thin films were coated 2 days after the starting solution was prepared.

The starting solution was dropped onto a $Pt/Ti/SiO_2/Si$ ($15 \times 15 \times 1$ mm) substrate and rotated at 3000 rpm for 30 s. The substrate was cleaned in an ultrasonic bath with acetone, ion-exchanged water, and ethanol, successively. After spin-coating, the wet films were dried at 350 °C for 10 min on a hot plate which evaporated the solvent and decomposed the organic molecules. The procedure from spin-coating to drying was repeated three times and the films were then pre-annealed in an electric furnace at 500 °C for 10 min. The above process (spin-coating, drying, and pre-annealing) was repeated until the desired thickness was obtained. Finally, the films were annealed at several temperatures for 30 min in an oxygen atmosphere for full crystallization.

The structural characterization and surface morphology of the thin films were analyzed using an X-ray diffractometer (XRD) (MAC Science, M03X-HF) with CuKα radiation operated at 30 kV and 30 mA, and a scanning electron microscope (SEM) (JEOL, JSM-5400), respectively. For electrical measurements, gold was coated by thermal evaporation on the surface of the films using a mask to provide the top electrodes with an area of 5×10^{-4} cm^2. Then, the films with the gold electrodes were heated up to 400 °C for 10 min. Hysteresis loops and fatigue characteristics of the films were measured using a ferroelectric tester (Radiant Technologies, RT66A).

3. Results and discussion

Fig. 1 shows the XRD patterns for the BTN thin films annealed at several temperatures ranging between 400 and 700 °C. The secondary phase was not found in the patterns at any of the temperatures and there were not any peaks indicating the crystallization of the BTN film at 400 °C (maybe an amorphous state). As the annealing temperature increased to 500 °C, the (1 1 7) and (0 0 12) peaks appeared, so it could be determined that the BTN film began to crystallize under 500 °C. The peaks in the XRD patterns became sharper and the full-width at half-maximum (FWHM) decreased with the annealing temperature, indicating high crystallinity and grain growth.