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Reduced leakage current and large polarization of $Na_{0.5}Bi_{0.5}Ti_{0.98}Mn_{0.02}O_3$ thin film annealed at low temperature

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Abstract

$Na_{0.5}Bi_{0.5}Ti_{0.98}Mn_{0.02}O_3$ (NBTMn) thin films were fabricated on indium tin oxide/glass substrates via chemical solution deposition and annealed at various temperatures from 450 to 600 °C and the influence of annealing temperature on their crystallization and electrical properties was investigated. X-ray diffraction measurement reveals that the film can be crystallized at an annealing temperature as low as 500 °C. The leakage current shows a decreasing tendency with a low and stable leakage current density of 10^{-7} A/cm^2 as the annealing temperature increases to 550 °C. However, the electrical properties degrade at 600 °C, which may be due to the recrystallization effect together with ions volatilization. The NBTMn thin film annealed at 550 °C exhibits the higher ferroelectricity with a large remanent polarization (P_r) of 38 μC/cm^2, which is nearly to the value of NBT ceramics.

Keywords: A. Films; B. Surfaces; C. Ferroelectric properties

1. Introduction

In view of environment protection, it is desired to use lead-free piezoelectric or ferroelectric materials in place of lead-based compounds, represented by $Pb(Zr,Ti)O_3$, $Pb(Mg,Nb)O_3$ in electric industry [1,2]. Among lead-free materials, $Na_{0.5}Bi_{0.5}TiO_3$ (NBT)-based materials are considered to be the potential candidates, in which Bi^{3+} has the electronic configuration similar to Pb^{2+} in $PbTiO_3$ [3,4]. NBT shows the superior ferroelectricity with a relatively large remnant polarization (P_r) of 38 μC/cm^2. It has a high Curie temperature of 320 °C, and depoles at 200 °C due to the phase transition from ferroelectric to antiferroelectric [5,6].

However, for NBT thin film, its intrinsic performance is difficult to be measured because of low resistivity [7]. A variety of methods have been taken to overcome this drawback [8–15]. Among them, site engineering is one of the best available ways. By co-doping (La, Ce) into $(Na_{0.5}Bi_{0.5})_{0.94}$-$Ba_{0.06}TiO_3$ thin film obtained at 650 °C, its ferroelectric properties are obviously enhanced with P_r of 29.5 μC/cm^2 [16]. With 2 at% Mn doping, the leakage current density for $Bi_{0.5}(Na_{0.76}K_{0.2}Li_{0.04})_{0.5}TiO_3$ thin film annealed at 800 °C is reduced by more than two orders of magnitude [7]. For $(Na_{0.85}K_{0.15})_{0.5}Bi_{0.5}TiO_3$ thin film fabricated at 700 °C, as Mn doping content increasing in the range of 0–6 at%, the P_r value tends to be improved from 14.2 to 19.2 μC/cm^2 [17].

It is widely known that the crystallization process is affected by variable such as annealing temperature. And, it has been demonstrated that decreasing annealing temperature can reduce volatilization in thin film with volatile elements which would induce the formation of oxygen vacancies ($V_O^{\bullet\bullet}$) [18,19]. In addition, for the A-site complex NBT thin film, it is more difficult to control the complicated composition exactly along with ion substitution. Precise stoichiometry is of necessity to improve the local and global homogeneity of film. As chemical solution deposition (CSD) has the advantages of high chemical homogeneity in molecular level and easily controllable

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stoichiometry [20], it would be of high efficiency in obtaining exact composition for ion-doped NBT-based thin film. Therefore, for the ion-doped NBT film, we can deduce that the performance can be further enhanced by lowering annealing temperature using the CSD method.

In this experiment, we report on the crystallization, leakage characteristic and ferroelectric properties of $Na_{0.5}Bi_{0.5}$-$Ti_{0.98}Mn_{0.02}O_3$ (NBTMn) thin films annealed at various temperatures from 450 to 600 °C. The pure NBT thin film annealed at 550 °C is fabricated for comparison. NBTMn can be well crystallized at the annealing temperature as low as 500 °C. More importantly, the NBTMn film annealed at 550 °C shows improved ferroelectricity with a larger P_r of 38 μC/cm^2 which is closely related to its reduced leakage current density than that of NBT film.

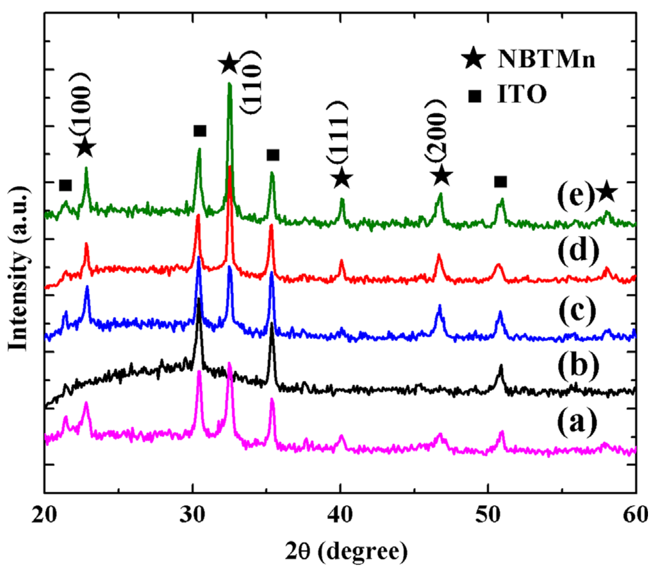

Fig. 1. XRD patterns of (a) NBT annealed at 550 °C and (b)–(e) NBTMn films annealed at 450 °C, 500 °C, 550 °C and 600 °C.

2. Experiment

NBTMn thin films were deposited on ITO/glass substrates at annealing temperatures ranging from 450 to 600 °C via CSD. The precursor solution of NBTMn was prepared by dissolving sodium acetate (CH_3COONa, Alfa Aesar, 99%), bismuth nitrate [$Bi(NO_3)_3 \cdot 5H_2O$, Aladdin, 99%], manganese acetate ($C_4H_6MnO_4$, Aladdin, 99%), tetrabutyl titanate [$Ti(OC_4H_9)_4$, Aladdin, 99%] in the mixture of acetylacetone, ethylene glycol and acetic acid. The precursor solution was deposited onto substrate by spin coating. The wet film was pyrolyzed on a hot plate at 250 °C for 5 min and annealed layer by layer at various temperatures (450 °C, 500 °C, 550 °C and 600 °C) for 10 min in O_2 atmosphere by the rapid thermal process. The deposition and post-annealing procedure were repeated several times to obtain a desired thickness. Au top electrodes were deposited on the films using a sputtering system to form a structure of Au-NBTMn-ITO. The crystallization of the films was characterized using an X-ray diffractometer (XRD) (Bruker D8). The surface morphology and cross-sectional image were detected with a scanning electron microscope (FeSEM, Hitachi S-4200). The insulating and ferroelectric properties were measured by a standard ferroelectric tester (Radiant Technologies).

3. Results and discussion

Fig. 1 shows the XRD patterns of pure NBT thin film annealed at 550 °C and NBTMn thin films annealed at 450–600 °C. All the film samples, except for the NBTMn annealed at 450 °C, show a single phase of perovskite structure with polycrystalline diffraction peaks, matching well with the distorted rhombohedral *R3c* structure. No diffraction peaks of NBTMn can be detected in the film annealed at 450 °C, meaning that the film is amorphous. When the annealing temperature increases to 500 °C, the evident crystalline diffraction peaks of NBTMn thin film being observed, which is among the lowest heat treatment temperature in the

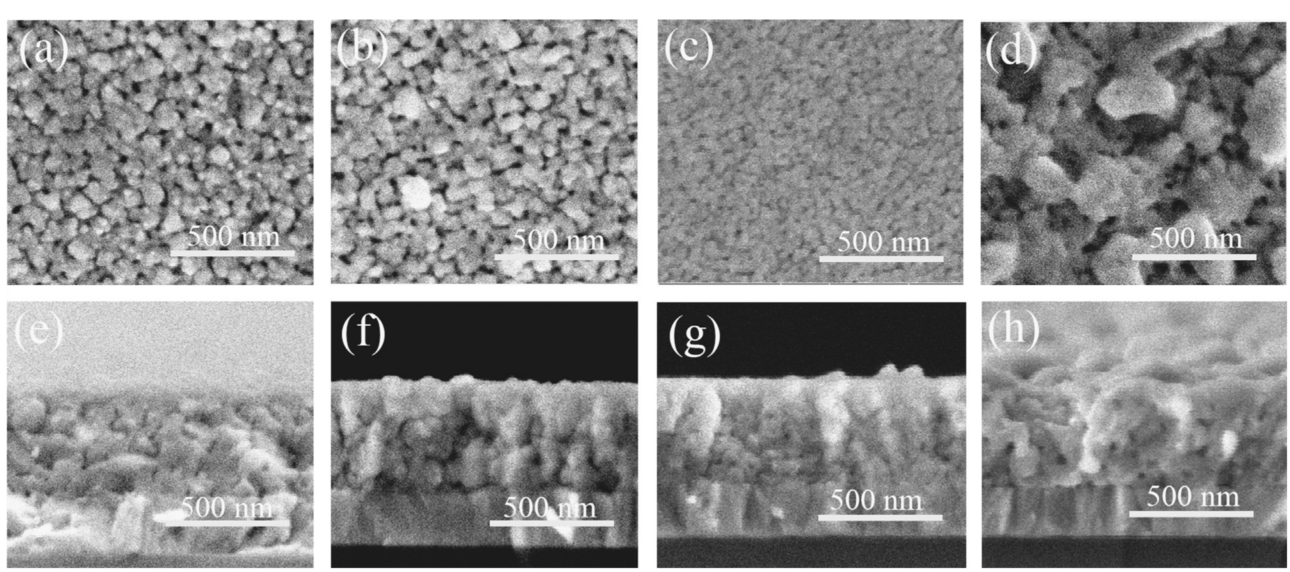

Fig. 2. Surface morphologies and cross-sectional images of NBT (a) and (e) annealed at 550 °C, and NBTMn films annealed at (b) and (f) 500 °C, (c) and (g) 550 °C, (d) and (h) 600 °C.