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Materials Letters 61 (2007) 2457–2459
materials letters
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Preparation and electric characteristics of gadolinium-substituted bismuth titanate ferroelectric thin films

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Received 4 July 2006; accepted 18 September 2006
Available online 4 October 2006

Abstract

Gadolinium-substituted bismuth titanate ($Bi_{4-x}Gd_xTi_3O_{12}$, BGT) thin films were deposited on the (111)Pt/Ti/SiO_2/(100)Si substrates by a modified Sol–Gel process. With the aid of X-ray diffraction (XRD), the structure and appropriate Gd-substituted content x of BGT thin films were detected. The surface quality of the films was measured by means of an atomic force microscope (AFM) in tapping mode. The surface of BGT thin films was smooth and the phase was homogeneous. The ferroelectric properties of the films were investigated. When the Gd-substituted content x was equal to 0.75, the remanent polarization was the largest. The remanent polarization 2Pr value was equal to 15.4 μC/cm^2 and the coercive field Ec value was 54.17 kV/cm.

Keywords: Ferroelectric thin films; Layered perovskite; $Bi_4Ti_3O_{12}$; Sol–Gel

1. Introduction

Ferroelectric thin films have been mainly utilized for nonvolatile random access memories (NVRAMs) and dynamic random access memories (DRAMs) applications. The leading candidate is lead zirconate titanate $PbZr_{1-x}Ti_xO_3$ (PZT), which has a high Curie temperature and large remanent polarization [1,2]. As we all know that some serious problems in PZT films, including polarization fatigue, reduction of remanent polarization due to repetitive switching, and so on, limit their applications. Recently, the issues with fatigue and concerns of environmental safety have been paid to bismuth layer-structured ferroelectrics (BLSFs) as ferroelectric materials, such as bismuth strontium tantalate $SrBi_2Ta_2O_9$ (SBT) and bismuth titanate $Bi_4Ti_3O_{12}$ (BTO) instead of conventional lead (Pb)-based ferroelectrics because of their excellent fatigue properties, quick response of polarization switching and Pb-free chemical composition. It has been demonstrated that Pt/SBT/Pt capacitors exhibit essentially no polarization fatigue up to about 10^{12} switching cycles and good retention characteristics [3]. The ferroelectric properties of the SBT system have been widely studied in both bulk materials and thin films. However, the high post-annealing temperatures, which do not match the conventional very large scale integrated processing and the low remanent polarization of SBT thin films are two major barriers for their application to random access memories [4]. Other layered perovskite ferroelectric materials, BTO single crystals have exhibited spontaneous polarization (Ps) values the along a axis and c-axis that reach ~50 μC/cm^2 and ~4 μC/cm^2, respectively. Nevertheless, polycrystalline BTO thin films exhibit relatively high leakage current, domain pinning and small remanent polarizations (2Pr) [5], which make it difficult to use BTO directly for real device applications. To improve its relatively low remanent polarization and fatigue properties, some of the trivalent elements such as La, Nd etc. were used to substitute Bi at A-site [6,7]. The structure of Ln-substituted (Ln=La, Nd, etc.) BTO thin films consists of a layer structure of $(Bi_2O_2)^{2+}$ and $[(Bi_{2-x}Ln_x)Ti_3O_{12}]^{2-}$ pseudoperovskite layers stacked along the c-axis direction. The $(Bi_2O_2)^{2+}$ layers act as

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doi:10.1016/j.matlet.2006.09.037

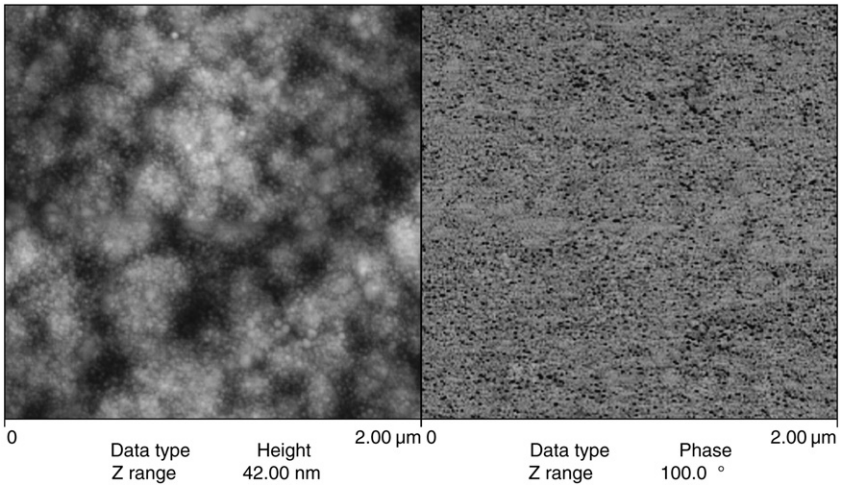

Fig. 1. AFM images of $Bi_{3.25}Gd_{0.75}Ti_3O_{12}$ thin films annealed in a RTA furnace at 650 °C for 5 min in an O_2 atmosphere.

insulating layers [8] and largely control the electronic response, while the ferroelectricity arises mainly from the pseudoperovskite blocks [9,10]. The improved ferroelectricity is primarily because the rotation of TiO_6 octahedra in the *a*–*b* plane is accompanied with a shift of the octahedron along the *a* axis which is largely enhanced by the substitution element such as La and Nd for Bi in the pseudoperovskite [11–13]. Considering that the substitution with smaller cation could cause relatively larger shift along the *a* axis and more internal stress, which might result in a larger remanent polarization. We attempted here to use Gd as the candidate to substitute A-site Bi^{3+}. With this purpose, $Bi_{4-x}Gd_xTi_3O_{12}$ (x=0.5, 0.75, 1, 1.5, 2 and 3) thin films were deposited by Sol–Gel process.

2. Experimental

Sol–Gel technique along with both spin-coating and rapid thermal annealing (RTA) techniques was applied to prepare BGT thin films. The thin films were prepared according to the formula $Bi_{4-x}Gd_xTi_3O_{12}$ with 15 mol% excess Bi. The starting materials used to prepare precursor were bismuth nitrate pentahydrate [$Bi(NO_3)_3{\cdot}5H_2O$], gadolinium nitrate hexahydrate [$Gd(NO_3)_3{\cdot}6H_2O$] and tetrabutyl titanate [$Ti(OC_4H_9)_4$] for Bi, Gd and Ti, respectively. No chelating agent was used in our system. A volatile temperature of Bi component was relatively low with a melting temperature of 272 °C under atmospheric pressure. Therefore, it was generally seen that the excessive Bi component was incorporated in the raw materials in order to compensate for the loss of this volatile component in the film during the annealing process. Bismuth nitrate pentahydrate (15 mol% excess) and gadolinium nitrate hexahydrate were dissolved in 2-methoxyethanol at room temperature, respectively and were mixed together. Then, tetrabutyl titanate was mixed with Bi–Gd solution and the mixture was stirred for 30 min at room temperature to obtain the transparent and stable BGT precursor. The concentration of the precursor was adjusted to 0.1 mol l^{-1}. The spin-coating technique was employed to deposit the precursor solution on the Pt/Ti/SiO_2/Si substrates at 4000 rpm for 30 s. The wet films were dried at 400 °C in air on hot plate for 5 min and this procedure was performed several times to achieve the desired film thickness. The thickness of the films was about 300 nm. The films used were annealed at 650 °C for 5 min in a rapid thermal annealing furnace in an oxygen atmosphere. For electrical property measurements, the Pt top electrodes with a diameter of 0.2 mm were sputter deposited through a mask on the surface of BGT-coated Pt/Ti/SiO_2/Si.

3. Results and discussion

An atomic force microscope (AFM) in tapping mode was used to observe the sample's surface morphology. As shown in Fig. 1, the surface was smooth and the phase was homogeneous. The typical surface roughness values root-mean-square (Rq), roughness (Ra) and valley to peak (Rmax) were 3.30 nm, 2.63 nm and 25.0 nm, respectively. The scan area was 2 µm × 2 µm.

The X-ray diffraction patterns of the $Bi_{4-x}Gd_xTi_3O_{12}$ films with x=0.5, 0.75, 1, 1.50, 2 and 3 were given in Fig. 2. The peaks were indexed according to the standard powder diffraction data of $Bi_4Ti_3O_{12}$ (BTO). Compared with the standard card of BTO, the films had a layered perovskite structure when the Gd-substituted content *x* ranged

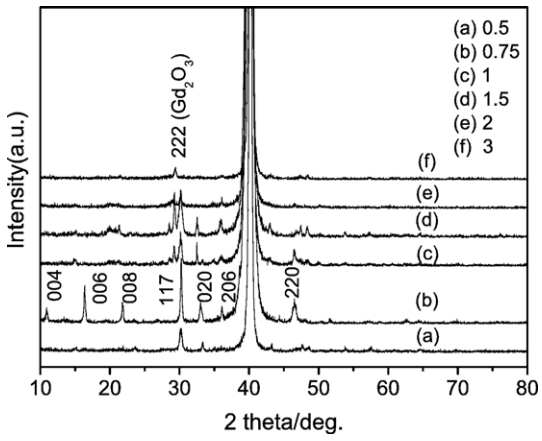

Fig. 2. XRD patterns for $Bi_{4-x}Gd_xTi_3O_{12}$ (x=0.5, 0.75, 1, 1.5, 2 and 3) thin films treated by RTA at 650 °C for 5 min in an O_2 atmosphere.

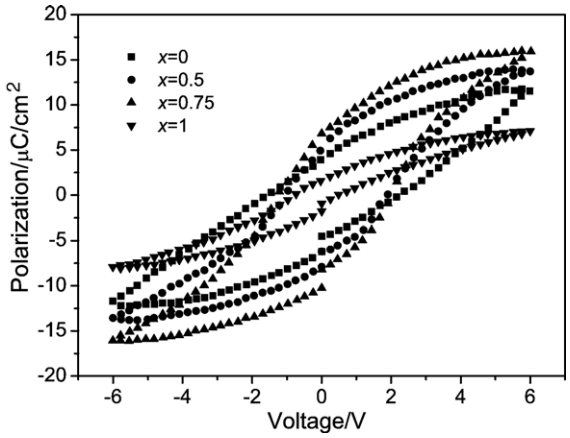

Fig. 3. *P–E* hysteresis loops of BGT films treated by RTA at 650 °C for 5 min in an O_2 atmosphere.

from 0.5 to 2 (a to e). When the content *x* was 0.5 and 0.75 (a and b), the films had a single perovskite structure. The films with predominant orientation were formed when *x* was 0.75. However, when *x* ranging from 1 to 2, the structure of the films was the layered perovskite structure but the second phase of digadolinium trioxide (222) was indexed. When *x* reached 3, the peak of layered perovskite emerged. It was concluded that the structure of the films strongly depended on the Gd-substituted content. When *x* was in the range of 0.5 to 0.75, the films had perfectly layered perovskite structure. It was difficult to obtain good crystal $Bi_{4-x}Gd_xTi_3O_{12}$ films if Gd-content *x* exceeded 2.

The *P–E* hysteresis loops of the thin films were illustrated in Fig. 3. It was observed that when the Gd-substituted content *x* was equal to 0.75, the remanent polarization was the largest. The remanent polarization 2Pr value was equal to 15.4 μC/cm^2. The coercive field Ec value was 54.17 kV/cm. The loop of the $Bi_{3.75}Gd_{0.75}Ti_3O_{12}$ thin films was asymmetric, suggesting internal bias field induced by residual internal stress.

4. Conclusions

Gadolinium-substituted bismuth titanate ($Bi_{4-x}Gd_xTi_3O_{12}$, BGT) thin films were fabricated on the (111)Pt/Ti/SiO_2/(100)Si substrates by a modified Sol–Gel process. No chelating agent was used in the BGT precursor solution. The precursor was transparent and stable. AFM showed that the surface of the films was smooth and the phase was homogeneous. The typical surface roughness values Rq, Ra and Rmax in the range were 3.30 nm, 2.63 nm and 25.0 nm, respectively. The scan area was 2 μm × 2 μm. The appropriate Gd-substituted content *x* value was 0.75 to realize the largest remanent polarization. The *P–E* hysteresis loop of the films revealed the remanent polarization 2Pr value was 15.4 μC/cm^2 and the coercive field Ec value was 54.17 k V/cm.

Acknowledgements

This work was supported by the National Natural Science Foundation (No. 10572115), People's Republic of China. The authors would also like to thank Dr. A. Li (Nanjing University) for technical assistance.

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