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Effect of lanthanides-substituted on ferroelectric properties of bismuth titanate thin films prepared by metalorganic decomposition

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Abstract

The effect of lanthanides (A = La, Eu, Ce, Dy, Yb)-substitution on the ferroelectric properties of bismuth titanate ($Bi_{3.25}A_{0.75}Ti_3O_{12}$, BAT) thin films has been investigated. The structure and morphology of the films were analyzed using X-ray diffraction and scanning electron microscopy, respectively. After annealing at 700 °C, the BAT films exhibited a polycrystalline structure. As a increasing the ionic radius of the lanthanides element (Eu, Ce) with a smaller ionic radius than La in the pseudoperovskite layer, the BAT thin films showed well saturated *P–E* curves and the remanent polarization ($2P_r$) values increased from 8.08 and 44 $\mu C/cm^2$ at an applied voltage of 10 V. The BAT thin films exhibited no significant degradation of switching charge at least up to 5×10^9 switching cycles at a frequency of 100 kHz. Moreover, the BAT film capacitors have appeared good retention properties after 3×10^4 s at room temperature.
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Keywords: Ferroelectric properties; Dielectric properties; Ionic radius; Lanthanides substitutions

1. Introduction

The bismuth layer-structured ferroelectrics which belong to the compounds of the Aurivillius family have the general formula, $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$, where A can be Ca^{2+}, Ba^{2+}, Sr^{2+}, and Bi^{3+}, among others; B can be Fe^{3+}, Ti^{4+}, Nb^{5+}, and Ta^{5+}; and n is the number of BO_6 octahedra in the pseudo-perovskite block (i.e., n = 2, 3, 4, 5) [1–3].

Many researchers have studied candidate ferroelectric materials for application in non-volatile random access memories (NVRAMs) [4–8]. Among these, PZT thin films exhibit a high dielectric constant and a high Curie temperature, but have some serious drawbacks for commercial use, such as fatigue, imprint, and leakage current [9]. In recent years, some Bi-layered oxide perovskites, such as $SrBi_2Ta_2O_9$ (SBT) and $Bi_{4-x}La_xTi_3O_{12}$ (BLT), have been intensively studied for use in NVRAMs, because with simple Pt electrodes and repeated polarization reversals with electric field cycling, they show low leakage current, low coercive field, and lack of fatigue [3,10]. The fatigue of the ferroelectric thin films is exhibited in the loss of switchable polarization with repeated switching cycles. This loss of switchable polarization limits the lifetime of the ferroelectric device, where the write and read cycles both rely on ferroelectric switching [11]. Data retention is the time-dependent change in the polarization state of a ferroelectric thin film, and it has been reported that because of this effect, stored data can be lost over time, even at room temperature [4]. A typical logic state retention test scheme would be to write to the capacitor using a pulse of one polarity, and subsequently read from it using two pulses of opposite polarity, thereby simulating a logic “0” state and a logic “1”state read operation. The delay between the write and read pulses is the retention time. The fatigue-free behavior of SBT and BLT thin films is due to the charge compensating effect of the Bi_2O_2 layers, resulting in the reduction of space charges, and from the unpinning of domain walls that occurs as rapidly as domain wall pinning [12]. However, SBT and BLT thin films have a disadvantage for high-density integration in NVRAMs in that they have a low remanent polarization

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($2P_r$ for SBT = 20 μC/cm^2, and for BLT = 27 μC/cm^2, respectively) [3]. Recently, Chon et al. reported the fatigue-free and large remanent polarization of Sm-substituted $Bi_4Ti_3O_{12}$ (BIT) ($2P_r$ of BSmT = 49 μC/cm^2) [13]. Noguchi et al. reported that TiO_6 octahedra in the pseudo-perovskite blocks show the shift of the octahedron along the a-axis, which is largely enhanced due to the substitution of lanthanides (e.g. La, Pr, Nd, Sm, Eu, etc.) for Bi in the pseudo-perovskite blocks [14].

In this paper, we report on the fabrication of lanthanides (A = La, Eu, Ce, Dy, Yb)-substitution in BIT thin films, and on the effect of A-substitution in BITthin films on the ferroelectric properties, such as the remanent polarization, fatigue, and retention characteristics.

2. Experimental

The $Bi_{3.25}A_{0.75}T_3O_{12}$ (BAT, A = La, Eu, Ce, Dy, Yb) thin films were prepared by the MOD method, and were spin-coated onto a Pt (150 nm)/Ti (50 nm)/SiO_2/Si substrate. The precursor materials used in the material preparation were bismuth acetate [$Bi(CH_3CO_2)_3$], lanthanides acetate hydrate [$A(CH_3CO_2)_3{\cdot}xH_2O$] (cerium acetate hydrate, europium acetate hydrate, lanthanum acetate hydrate, dysprosium acetate hydrate, ytterbium acetate hydrate), and titanium isopropoxide {$Ti[OCH(CH_3)_2]_4$}, and the solvents used were acetic acid [CH_3CO_2H], and 2-methoxyethol [$CH_3OCH_2CH_2OH$]. An excess of 10% bismuth acetate was used to compensate for the Bi loss that occurs during annealing. Stock solutions with a mole ratio of Bi:A:Ti of 3.25:0.75:3 were spun onto the Pt/Ti/SiO_2/Si substrate, and then pre-baked on a hot plate at 400 °C for 10 min. The pre-baked film was annealed at 700 °C for 1 h under an oxygen atmosphere for crystallization to occur. The final thickness of the BAT film was 200 nm. Top electrodes of 300 μm in diameter were fabricated by depositing a 150-nm-thick Pt film at room temperature using dc magnetron sputtering.

The crystalline structures of the BAT thin films were analyzed using X-ray diffraction (XRD) on a Rigaku-D/MAX diffractometer with Cu Kα radiation. The surface and cross-sectional microstructures of the films were examined using a JOEL JSM-6300 field-emission scanning electron microscope (FE-SEM). The thickness of the annealed BAT films was estimated using a SEM and TEM. The ferroelectric properties were examined using a precision workstation ferroelectric tester (Radiant Technologies, USA) equipped with a micrometer probe station. The electrical fatigue properties of BAT films were tested using 100 kHz bipolar pulses at an applied voltage of 5 V. The fatigue testing was measured at room temperature, and a data retention test was carried out at both room temperature and at higher temperatures. The read and write pulses were performed using a signal in amplitude of 5 V and in pulse width of 2 ms. The dielectric constant and the loss factor were measured using an HP 4192 impedance analyzer.

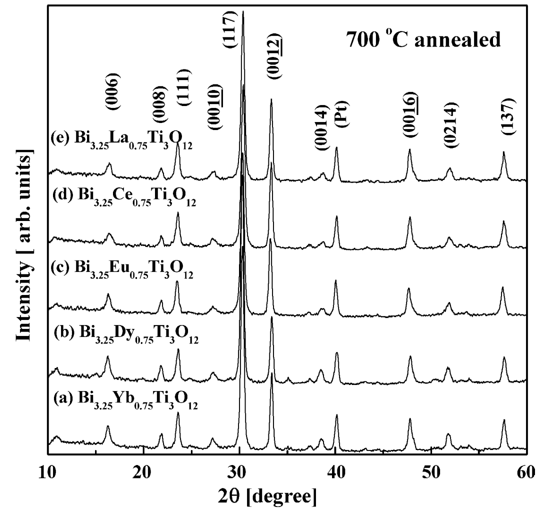

Fig. 1. X-ray diffraction patterns of BAT thin films.

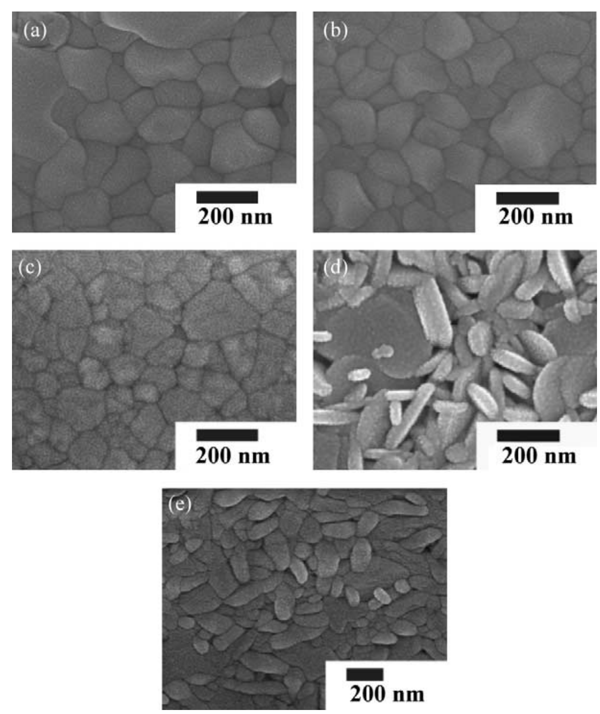

Fig. 2. Surface morphology of (a) BYbT, (b) BDyT, (c) BEuT, (d) BCeT and (e) BLaT thin films deposited on Pt (150 nm)/Ti (50 nm)/SiO_2/Si substrates.

3. Results and discussion

Fig. 1 shows the XRD patterns of the BAT thin films. For BAT thin films annealed at 700 °C, they showed the typical XRD patterns seen for BIT [15,16]. The obtained BAT thin films exhibited a polycrystalline structure, and no

Table 1
Ionic radius of the lanthanides elements

Lanthanides elements	Bi	Yb	Dy	Eu	Ce	La
Ionic radius (Å)	0.93	0.86	0.92	0.98	1.01	1.14

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