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Mixed grains and orientation-dependent piezoelectricity of polycrystalline Nd-substituted $Bi_4Ti_3O_{12}$ thin films

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ABSTRACT

Polycrystalline $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ (BNT) thin films were prepared on Pt/Ta/glass substrates by a pulsed laser deposition method. X-ray diffraction measurements revealed that the BNT thin films were preferentially oriented along the (117) direction although they possessed a polycrystalline structure. Good ferroelectric properties of the BNT thin film were observed with a remnant polarization of 13 μC/cm^2 (2 P_r ~26 μC/cm^2). The fatigue resistance test exhibited that the ferroelectric polarization of the BNT thin film degraded significantly after around 10^9 switching cycles, which can be attributed to its crystal structure. We investigated the surface morphology and ferroelectric domain structure by atomic force microscopy (AFM) and piezoresponse force microscopy (PFM), respectively. Interestingly, mixed grains consisting of long and circular shapes were observed on the BNT film surface, which corresponded to *a*- and *c*-axes orientations of crystal growth, respectively. The PFM study revealed that the piezoelectric coefficient (d_{33}) of the long grains was much larger than that of the circular grains.

1. Introduction

Lead-free ferroelectric materials such as $Bi_4Ti_3O_{12}$, $BiFeO_3$, $BaTiO_3$, and $SrBi_2Ta_2O_9$ are considered alternatives to replace the lead zirconium titanate ($Pb(Zr,Ti)O_3$, PZT) system [1–7]. However, lead-free ferroelectric materials unfortunately possess worse physical properties such as ferroelectric polarizations and piezoelectric coefficients compared to the PZT system, even though they exhibit excellent endurance against ferroelectric fatigue in the ferroelectric switching process over 10^{12} cycles [2,8]. For these reasons, one of main issues of lead-free ferroelectric materials is to maximize the ferroelectric polarizations and piezoelectric coefficients [9,10]. For example, La substitution or La and Nb co-doping of multiferroic $BiFeO_3$ thin films led to improvement of the ferroelectric properties [11–13]. In addition, La doping enhanced the magnetic moment and reduced the leakage current [11,13]. The enhanced physical properties in lead-free ferroelectric materials originate from the structural distortions of octahedrons caused by the substitution of transition metals [14]. Similar to the substitution of transition metals, the strain effects induced by lattice misfit of the film and substrate materials also causes enhanced ferroelectricity [15,16]. In particular, the compressive stress induces tetragonally-strained $BiFeO_3$ and $BaTiO_3$ thin films on $LaSr_{0.5}Mn_{0.5}O_3/LaAlO_3$ substrates, leading to an increased remnant polarization [17,18].

Meanwhile, the use of silicon or single crystalline substrates for device applications is not preferred due to their high cost. Although it may be necessary to employ buffer layers when using glass substrates, glass substrates have advantages that make them worthy of consideration as an alternative. In this work, we investigated the ferroelectric properties of neodymium-substituted bismuth titanate ($Bi_{3.15}Nd_{0.85}Ti_3O_{12}$, BNT) thin films grown on glass substrates by pulsed laser deposition (PLD). We conducted atomic force microscopy (AFM) and piezoresponse force microscope (PFM) studies of the BNT thin films. The polycrystalline BNT thin films showed a mixed crystal structure of *a*- and *c*-oriented grains and good ferroelectric properties with a remanent polarization of 13 μC/cm^2. Furthermore, the crystal orientation effect of the grains on the piezoelectric coefficients was investigated by PFM. We also confirmed the polarization fatigue and leakage current characteristics of the polycrystalline BNT thin films for application in non-volatile memory devices.

2. Experimental

BNT thin films were prepared on Pt/Ta/fused silica glass substrates by PLD. As an adhesion layer, a 5 nm thick Ta film was deposited on glass using radio frequency (RF) magnetron sputtering at an RF power of 100 W with 10 mTorr Ar gas at 500 °C. Subsequently, a 50 nm thick Pt electrode film was deposited on the Ta/glass substrate by RF magnetron sputtering at an RF power of

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50 W and a pressure of 10 mTorr at 600 °C. A KrF eximer laser with a wavelength of 248 nm and an energy density of 0.5 J/cm^2 was focused onto the BNT target. The distance between the target and substrate was ~4 cm. After the base pressure reached ~5×10^{-7} Torr, the substrate temperature was set at 800 °C with an oxygen partial pressure of 100 mTorr. After deposition, the thin film was immediately cooled down to room temperature under oxygen ambient at 300 Torr. The structure of the BNT thin film was investigated by X-ray diffraction (XRD, CuKα1 radiation, λ = 1.542 Å). The surface morphology and roughness of the BNT thin film were evaluated by AFM. In addition, its ferroelectric domain structure was investigated by PFM. RF magnetron sputtering was used to fabricate the Pt top electrode (diameter of 100 μm and thickness of 100 nm) on the BNT thin film. The Pt top electrode was annealed at 450 °C for 30 min prior to obtaining the ferroelectric hysteresis loops, which were measured by a RT66A (Radiant Technologies, Inc.) test system. The leakage current was measured using a Keithley 4200 semiconductor parameter analyzer (Keithley Instruments, Inc.).

3. Results and discussion

The configuration of the BNT thin film on the (111) Pt/Ta/glass substrate is schematically depicted in Fig. 1a. The 5 nm thick Ta layer was used as an adhesion layer between the Pt bottom electrode and the glass substrate. First, we investigated the crystal structure of the 100 nm thick BNT thin films by XRD measurements. Fig. 1b shows the XRD pattern of the BNT thin film grown on the Pt/Ta/glass substrate. The Pt bottom electrode film on the Ta adhesion layer exhibits the highest intensity of the (111) peak. Along with the Pt (111) peak, (008), (111), (0010), (117), (0014), and (220) peaks of the BNT thin film were observed. These peaks indicate that the BNT thin film has a mixed crystal structure of *a*- and *c*-oriented grains, which demonstrates its polycrystalline nature.

To measure the ferroelectric properties of the BNT thin film, the hysteresis loop of the Pt/ BNT/Pt capacitor was obtained at a measurement frequency of 2 kHz. Fig. 2a shows the ferroelectric hysteresis loop of the BNT thin film on the Pt/Ta/glass substrate. Note that asymmetric feature is observed in the ferroelectric hysteresis curve. Asymmetric behavior in ferroelectric hysteresis can be generated by difference of the work function between top and bottom electrodes, defect charges, and interfacial charges [19,20]. In the present study, different temperature in electrode deposition may give rise to the asymmetric feature. Namely, the Pt bottom electrode was deposited at much higher temperature than the Pt top electrode. This might produce higher charge density at the interface between BNT thin film and Pt bottom electrode where the Schottky barriers at the interfaces of the BNT thin film would be asymmetric [20]. The capacitor exhibits a relatively high remanent polarization of 13 μC/cm^2 ($2P_r$ ~26 μC/cm^2) with a coercive electric field of approximately 190 kV/cm. This value is much higher than that ($2P_r$ ~4.8 μC/cm^2) of a *c*-axis epitaxial $Bi_4Ti_3O_{12}$ (BTO) thin films fabricated by pulse laser deposition [21]. It is also higher than that of a *c*-axis epitaxial Nd-substituted BTO thin film on a (001) $LaAlO_3$ single-crystalline substrate (2Pr ~17.6 μC/cm^2) [22]. However, compared to the (104)-oriented ferroelectric Nd-substituted BTO film on a (100) Si substrate ($2P_r$ ~37.8 μC/cm^2) [23], our BNT sample has a small Pr value. Although the BNT has a polycrystalline structure, its remnant polarization is a comparable value. We believe that the high remnant polarization can be attributed to the mixed crystal structures consisting of *a*- and *c*-oriented grains as well as Nd substitution.

Generally, a repeated polarization switching process above 10^6–10^{12} cycles causes degradation of the ferroelectric polarization. Thus, it is important to investigate polarization fatigue characteristics of ferroelectric materials for nonvolatile random access memory applications [2]. We further investigated the fatigue characteristics of the Pt/BNT/Pt capacitor. Fig. 2b shows the normalized polarization as a function of the number of switching cycles for the Pt/BNT/Pt capacitor. The fatigue endurance of the BNT capacitor is slightly degraded after 10^9 cycles of polarization switching, although Bi-layered Aurivillius compounds such as SBT and $Bi_4Ti_3O_{12}$ have demonstrated good fatigue endurance up to 10^{12} cycles of ferroelectric polarization switching [2,24]. In fact, the BNT capacitor shows better fatigue endurance than PZT capacitors previously reported despite its polycrystalline structure [25]. The ferroelectric fatigue originates from the generation of oxygen vacancies induced by repeated ferroelectric polarization switching [26]. Bi-layered Aurivillius compounds structurally have Bi_2O_2 layers that play a role in preventing the generation of oxygen vacancies in TaO_6 octahedral units [27,28]. However, the fatigue degradation observed in this work can be attributed to the fact that the BNT thin film was composed of a mixed crystal structure of *a*- and *c*-oriented grains, in which the Bi_2O_2 layers were not parallel to the bottom and top electrodes. In ferroelectrics, fatigue degradation could be greatly affected by the domain pinning effect which results in a decrease in the evolution of the switched domain [29]. The pinning effect is caused by the degraded surface,

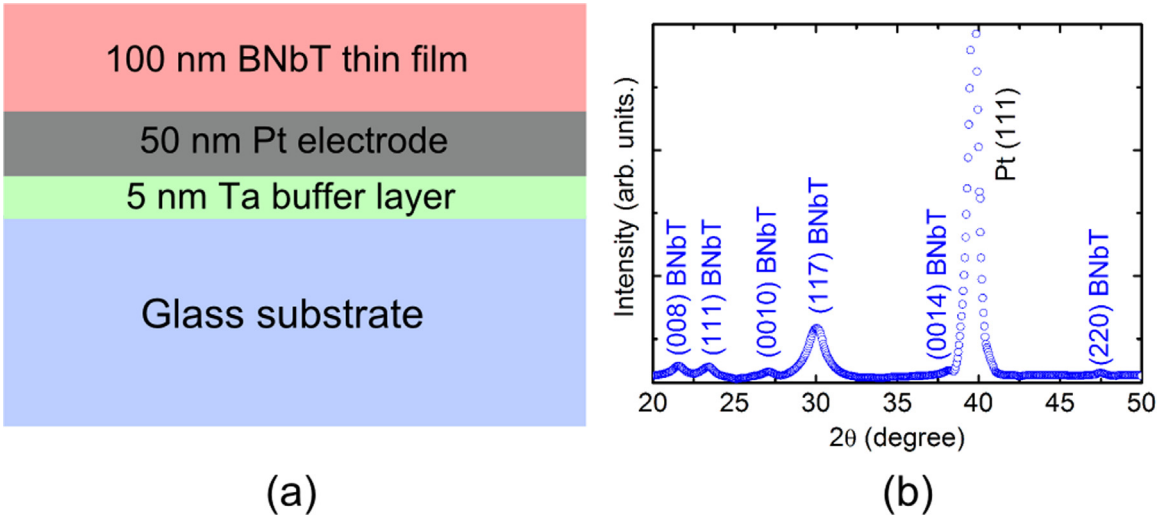

Fig. 1. (a) A schematic illustration of a BNT thin film on the Pt/Ta/glass multilayer. (b) The X-ray diffraction pattern of the BNT thin film grown on the Pt/Ta/glass substrate.