Pulsed laser deposition and characterization of Bi$_{3.25}$Nd$_{0.75}$Ti$_3$O$_{12}$ thin films buffered with La$_{0.7}$Sr$_{0.3}$MnO$_3$ electrode

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Abstract

Bi$_{3.25}$Nd$_{0.75}$Ti$_3$O$_{12}$ (BNT) ferroelectric thin films with a thickness of ~0.5 μm, on substrates of Pt/Ti/SiO$_2$/Si, (100) SrTiO$_3$ and (100) MgO, with a 0.4-μm-thick La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) layer as bottom electrode, were deposited via pulsed laser deposition. The multilayer thin films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrical measurement. The LSMO layers on Pt/Ti/SiO$_2$/Si were polycrystalline, while those on SrTiO$_3$ and MgO single crystal substrates were highly c-axis oriented. The BNT films were polycrystalline on LSMO covered Pt/Ti/SiO$_2$/Si and MgO, and c-axis oriented on LSMO/SrTiO$_3$. Dielectric constant and loss tangent (at 1 kHz) of the BNT thin films on LSMO buffered Pt/Ti/SiO$_2$/Si, STO and MgO substrates were 224, 263 and 204, and 0.03, 0.04 and 0.05, respectively. They had a remnant polarization of 25.4, 29.5 and 19.1 μC/cm$^2$, and a coercive field of 133, 176, 134 kV/cm, respectively. No fatigue was found for all the three BNT thin films up to $3 \times 10^{10}$ switching cycles.

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1. Introduction

Nonvolatile ferroelectric random access memory has been acknowledged to be one of the many promising applications of ferroelectric materials. Lead zirconate titanate (PbZr$_{1-x}$Ti$_x$O$_3$, or PZT) has some of the best ferroelectric characteristics, such as large polarization and lower processing temperature, as compared to other ferroelectric candidates. However, PZT thin films suffer from serious fatigue and imprint problems, as Pt was employed as electrode [1–3]. Although the problems could be suppressed by using various oxide electrodes, the oxide electrodes would result in lower polarization density and processing complexity [4–6]. In this respect, it was necessary to develop new ferroelectric materials to replace PZT. About 10 years ago, SrBi$_2$Ta$_2$O$_9$ (SBT) thin film was found to be a candidate with good fatigue endurance [7–9]. The critical disadvantages of SBT thin films in terms of practical memory applications were their relatively small remnant polarization and high processing temperature. Another promising ferroelectric thin film after SBT was lanthanum doped bismuth titanate (Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$, or BLT) [10]. BLT had important advantages of larger polarization and lower processing temperature over SBT. Besides the extensive studies on BLT, quite a few of attempts of substitution for bismuth ion with other trivalent rare-earth cations were also made by the ferroelectric research community. It was found that, among many rare-earth elements, Pr, Nd, Sm and Gd fitted the requirements of the ionic radius, stable Curie temperature and phase stability of the layered perovskite structures [11]. Nd doped bismuth titanate (Bi$_{4-x}$Nd$_x$Ti$_3$O$_{12}$ or BNT) had the best electrical properties compared to other candidates [12].

It was reported that Bi$_{3.25}$La$_{0.75}$Ti$_3$O$_{12}$ (BLT) films with LaNiO$_3$ electrode had better electrical properties (larger remanent polarization, lower coercive field and better fatigue resistance) than those with Pt electrodes [13]. Similar results were reported by others for Bi$_{3.25}$Nd$_{0.75}$Ti$_3$O$_{12}$ (BNT), where SrRuO$_3$ was used as oxide electrodes. Also, BNT thin films have been prepared mostly by sol–gel process [11,12]. In this paper, deposition of BNT thin films,
on single crystal substrates (SrTiO$_3$/STO and MgO) deposited by pulsed laser deposition (PLD) technique, will be reported. In the present study, La$_{0.7}$Sr$_{0.3}$MnO$_3$ layer was employed as the bottom electrode. BNT film were also deposited on Pt/Ti/SiO$_2$/Si substrate as a comparison. It has been found that the BNT thin films deposited on the single crystal substrates were epitaxial, while that on the silicon substrate was of polycrystalline characteristic. The BNT thin films produced in the present work had dielectric, ferroelectric, fatigue properties comparable with those widely reported in open literature [10,11].

2. Experimental

Bi$_{3.25}$Nd$_{0.75}$Ti$_3$O$_{12}$ (BNT) and La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) targets with a diameter of about 2.5 cm, were prepared using commercial Bi$_2$O$_3$, Nd$_2$O$_3$, TiO$_2$, SrCO$_3$, La$_2$O$_3$ and MnO$_2$ powders, via the conventional ceramic processing. A LSMO layer was first deposited on Pt/Ti/SiO$_2$/Si, (100) SrTiO$_3$ (STO) and MgO single crystal substrates. On top of the LSMO layer, BNT thin film was deposited. The deposition was carried out for 60 min at a substrate temperature of about 550 °C and a chamber oxygen pressure of 0.2 mbar, using a KrF excimer laser at 2 Hz repetition frequency, with an energy of 250 mJ/pulse. The distance between substrate and target was 4.5 cm. Before the deposition of BNT film, LSMO layer on Pt/Ti/SiO$_2$/Si was annealed at 800 °C and those on STO and MgO were annealed at 900 °C, both for 30 min. The deposited BNT film was post-annealed at 750 °C for 30 min.

Phase composition and crystallization of the BNT/LSMO thin films were examined by X-ray diffraction (XRD), using a Philips PW 1729 type X-ray diffractometer with Cu K$_a$ radiation. Surface morphology was observed by scanning electron microscopy (SEM), using a JEOL JSM-6340F type field emission scanning electron microscope. Film thickness was determined from cross-sectional SEM images.

Dielectric properties of the BNT thin films were measured using a sandwich structure. Top electrode was Au dots with a diameter of about 0.2 mm, deposited via a vacuum evaporation. An HP 4194 LCR meter was used to record capacitance and dielectric loss as a function of frequency. Polarization-electric field (P-E) hysteresis loops of the samples were recorded using Radiant Technology RT6000 type ferroelectric tester system. All measurements were performed at room temperature. Fatigue resistance of the BNT thin films was measured at 200 kV/cm electric field up to $3 \times 10^{10}$ switching cycles, using 1 MHz bipolar square waves.

3. Results and discussion

Fig. 1 shows the XRD patterns of the LSMO layers on different substrates. It is found that the LSMO layer on Pt/
layer on the platinized silicon substrate exhibits a typical polycrystalline microstructure, where nearly round grains are randomly distributed (Fig. 3a). In contrast, an array-like grain arrangement is readily observed in the LSMO layer deposited on STO substrate (Fig. 3b). The LSMO grains are of a much regular shape than that on Pt/Ti/SiO₂/Si substrate. The array-like grain distribution and regular grain shape become much pronounced in the oxide layer on MgO (Fig. 3c). This observation is in good agreement with the XRD results shown in Fig. 1.

The BNT thin films also demonstrate different surface profiles. The film deposited on the LSMO/Pr/Ti/SiO₂/Si substrate is characterized by well-developed grains with a relatively wide grain size distribution (Fig. 3d). The sample on the LSMO/STO substrate consists of both elongated and equiaxed grains (Fig. 3e), while that on the LSMO/MgO exhibits well-shaped grains and a relatively narrow grain size distribution (Fig. 3f). The difference in microstructures of the BNT thin films on the different substrates is believed to be...
closely related to the difference in morphologies of the LSMO layers. It is necessary to notice that, how the substrate characteristic affected the microstructure and orientation of the LSMO layer and subsequently the microstructure and electrical properties of the BNT thin films, was not within the scope of the present work.

The thicknesses of the LSMO layers and the BNT films, estimated from the cross-sectional SEM image of the sample on silicon substrate as shown in Fig. 4, are about 0.5 and 0.4 μm, respectively. Fig. 5 shows the representative P–E hysteresis loops of the BNT thin films deposited on the three substrates. The BNT thin films, on the LSMO-covered Pt/Ti/SiO₂/Si, STO and MgO substrates, have a remnant polarization of 25.4, 29.5 and 19.1 μC/cm², and a coercive field of 133, 176, 134 kV/cm, respectively. These electrical properties of the BNT thin films are comparable with the values for those prepared by other methods in the literature [10,11]. However, the remnant polarizations of the BNT thin films in the present work are all lower than that reported by Chon et al. [12], where the BNT thin films were deposited on Pt/Ti/SiO₂/Si substrates via a sol–gel process. Since the properties of thin films produced by PLD are essentially dependent on deposition parameters, there is still room to improve the electrical properties of the BNT thin films by optimizing the processing parameters. The deposition parameters in the present study are only arbitrarily selected.

Due to its special structure, Bi₄Ti₃O₁₂ single crystal is strongly anisotropic in all the ferroelectric properties, including saturated polarization (Pₛ), remnant polarization (Pᵣ), and coercive field (Eₑ). The polarization direction of Bi₄Ti₃O₁₂ is 4.5° off the base plane of its cell structure, thus giving rise to a much larger in-plane polarization (Pₛ = 50 μC/cm²) than c-axis polarization (Pₛ = 4.5 μC/cm²), and the Eₑ value for in-plane polarization is 50 kV/cm and the Eₑ value for c-orientation is less than 5 kV/cm [14]. For randomly oriented Bi₄Ti₃O₁₂ ceramics or thin films, both Pᵣ and Eₑ have intermediate values. Therefore, Bi₄Ti₃O₁₂ thin films with strong c-axis orientation are not desirable to have high polarization. However, high polarization in rare-

![Fig. 4. Typical cross-sectional SEM image of the BNT/LSMO on Pt/Ti/SiO₂/Si substrate.](image)

![Fig. 5. P–E hysteresis loops of the Bi₃.25Nd₀.75Ti₃O₁₂ thin films on different substrates: (a) Pt/Ti/SiO₂/Si; (b) (100) SrTiO₃; and (c) (100) MgO.](image)

![Fig. 6. Electrical fatigue characteristics of the Bi₃.25Nd₀.75Ti₃O₁₂ thin films on the LSMO/STO substrate.](image)
earth oxide doped Bi$_4$Ti$_3$O$_{12}$ (e.g., BNT) is attributed to TiO$_6$ octahedron unit adjacent to the interleaving Bi$_2$O$_2$ layer rather than by the TiO$_6$ unit of the inner central octahedron layer, thus the polarization development is along the c-axis [12]. However, large polarization ($P_r = 50 \mu$C/cm$^2$) of BNT thin films deposited on Pt/TiO$_2$/SiO$_2$/Si via a sol–gel process by Chon et al. has not been reported by Garg et al. [15] in a recent paper, where a polarization of only 6 $\mu$C/cm$^2$ was observed in the BNT thin film with the same composition, but on SrRuO$_3$ layer, deposited via a pulsed laser deposition. In this respect, the electrical properties of BNT thin films are closely related to many factors, such as substrates, electrodes, processing methods, and so on. The polarization values of the BNT thin films in the present work are just between those of Ref. [12] and Ref. [15]. The difference in the values of the BNT films deposited on the different substrates might be a reflection of the overall effect of substrates, electrodes (crystallinity, morphology and conductivity), crystalline characteristics, orientation, and so on. However, an exact explanation of this difference is really a very difficult task with the limited analytical data obtained in the present work.

Fig. 6 shows the fatigue property of BNT/LSMO/STO. No obvious fatigue is observed up to 3 $\times$ 10$^{10}$ switching cycles. Similar results are also achieved for BNT on the LSMO-covered Pt/Ti/SiO$_2$/Si and MgO substrates. The BNT films, on Pt/Ti/SiO$_2$/Si, SrTiO$_3$ and MgO substrates, have a dielectric constant of 224, 263, 204 at 1 kHz, respectively. The values are comparable with the reported data for BNT produced by other methods in the literature [10–12].

4. Conclusions

Fatigue-free Bi$_{3.25}$Nd$_{0.75}$Ti$_3$O$_{12}$ (BNT) ferroelectric thin films with a thickness of ~0.5 $\mu$m, on substrates of Pt/Ti/SiO$_2$/Si, (100) SrTiO$_3$ and (100) MgO, covered by a 0.4- $\mu$m-thick La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) layer as bottom electrode, were deposited via pulsed laser deposition. The BNT films, on the LSMO covered Pt/Ti/SiO$_2$/Si, SrTiO$_3$ and MgO substrates, had a dielectric constant of 224, 263, 204, a remnant polarization of 25.4, 29.5 and 19.1 $\mu$C/cm$^2$ and coercive field of 133, 176, 134 kV/cm, respectively. The BNT films showed very good fatigue resistance up to 3 $\times$ 10$^{10}$ switching cycles.

References