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Bilayered $Pb(Zr,Ti)O_3/(Bi,Nd)_4Ti_3O_{12}$ thin films

Chow Hong Sim · Xing Sen Gao · Zhao Hui Zhou · John Wang

Abstract Bilayered thin films consisting of $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) and $(Bi_{3.15}Nd_{0.85})Ti_3O_{12}$ (BNT) layers are successfully deposited on Si(100)/SiO_2/Ti/Pt substrate by a combined process involving sol-gel and RF-sputtering. Their dielectric properties cannot be described by the simple rule of mixture on the basis of the series connection model. There occurs a dielectric layer of lower dielectric permittivity in the bilayered thin film, which degrades the polarization behaviors. The bilayered film gives rise to an improvement in fatigue resistance up to 10^{10} switching cycles. Moreover, the domain pinning effect after polarization switching is reduced greatly as compared to that of single layered PZT and BNT thin films.

Keywords Bilayered thin films · PZT · BNT · Series connection model · Rayleigh law

1 Introduction

Ferroelectric thin films are being extensively studied for their technological applications in various electronic, microelectronic, nonvolatile ferroelectric random access memory (NVFRAM) and microelectromechanical (MEM) systems [1, 2]. In NVFRAM, application of an electric field polarizes the film into two stable states that could be used to designate the binary Boolean algebra in a computer memory. The attractive characteristic lies on the retention of this memory stored after the removal of power supply. A promising ferroelectric thin film for device applications should possess the following properties: a relatively low processing temperature, a high enough remanent polarization (P_r), a low coercive electric field (E_c), a low enough leakage current, together with the required high fatigue endurance. Among the thin film systems that have been widely investigated, $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) thin films have attracted a considerable degree of attention owing to their excellent ferroelectric properties [3, 4]. However, their applications are largely limited by their poor fatigue endurance. On one hand, although various approaches have been taken to enhance their fatigue resistance, there is a fundamental understanding on the phenomena involved [5]. On the other hand, considerable effort has been focused on alternative ferroelectric systems. For example, layered perovskite $Bi_4Ti_3O_{12}$ (BIT) has been demonstrated to exhibit excellent fatigue endurance up to 10^{10} cycles [6]. It is generally believed that the high fatigue endurance is related to the $(Bi_2O_2)^{2+}$ layers that compensate the space charges and stabilize the oxygen vacancies [6, 7]. Unfortunately, the material exhibits a rather low P_r value of $<10\ \mu C/cm^2$, which is indeed too low for several technologically demanding applications [7].

In an attempt to realize thin films with desirable ferroelectric behaviors and high fatigue endurance, bilayered thin film consisting of PZT and $(Bi_{3.15}Nd_{0.85})Ti_3O_{12}$ (BNT) layers were fabricated. In this paper, we report on the synthesis of bilayered PZT/BNT films deposited on Si(100)/SiO_2/Ti/Pt substrates, together with their ferroelectric and dielectric properties.

2 Experimental details

Sol-gel processing, assisted by spin-coating, and magnetron sputtering were used to deposit the PZT and BNT layers respectively. The PZT sol solution with concentration of 0.4 M was prepared from $Pb(CH_3COO)_2{\cdot}3H_2O$, $Zr[OCH(CH_3)_2]_4$

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and $Ti[OCH(CH_3)_2]_4$ in a solvent containing 3 parts of ethylene glycol monomethyl ether and 1 part of acetic acid. The starting materials for BNT sputtering target are Bi_2O_3, Nd_2O_3 and TiO_2 powders. Excess 5 mol% of PbO and Bi_2O_3 were added in the respective starting compositions to compensate for the likely loss of these two volatile oxides. Firstly, PZT sol solution was spin-coated on $Si(100)/SiO_2/Ti/Pt$ substrate at 3000 rpm for 30 seconds. The film was dried under 300°C for 5 minutes and baked under 500°C for 20 minutes before thermal annealing at 650°C for 30 minutes in air. The BNT layer was then sputtered on the as-annealed PZT layer at a base pressure of 10^{-6} Torr, deposition pressure of 20 mTorr of Ar and rf power of 100 W. The bilayered thin film was subsequently thermally annealed at 700°C using rapid thermal process chamber.

Bilayered thin films with three different thickness ratios of PZT:BNT were fabricated in this study: 1:2 (150 nm-PZT/300 nm-BNT, coded as *150PZT/300BNT*), 1:1 (225 nm-PZT/225 nm-BNT, coded as *225PZT/225BNT*) and 2:1 (300 nm-PZT/150 nm-BNT, coded as *300PZT/150BNT*). The total thickness of the bilayered thin films was controlled at 450 nm. For comparison purpose, single layered PZT and BNT films of the comparable thickness were also deposited, by following the same deposition process as described above.

The thin film samples were studied for texture and morphology by using x-ray diffractometer (Bruker D8 Advanced XRD) and secondary electron microscope (Philips XL30 FE-SEM). A ferroelectric analyzer (Radiant Technologies) and impedance analyzer (Solartron SI 1260) were utilized to investigate their electrical properties, where Au dots of 0.1 mm in radius were sputtered on the films as top electrodes.

3 Results and discussions

Figure 1 shows the x-ray diffraction (XRD) patterns of bilayered thin films of different thickness combinations. Both PZT and BNT layers in the bilayered thin films were crystallized into the desired perovskite and layered perovskite structures, respectively. No pyrochlore phase was detected. Apparently, the constituent PZT and BNT layers are well retained as discrete phases, where interfacial interactions are undetectable. According to PDF, randomly oriented PZT has (110) as the strongest peak while the intensity of (100) and (200) are only 12 and 15% of the (110) peak intensity respectively. However, PZT films in our study have the peak intensities of (100) and (200) very close to that of (110), therefore it is more (100) than randomly oriented. All BNT layers in bilayered films are randomly oriented. Figure 2 shows cross-section of the *225PZT/225BNT* bilayered film. The upper BNT layer appears to be grainy while lower PZT layer has columnar structure. Both layers are densely packed with discrete interface.

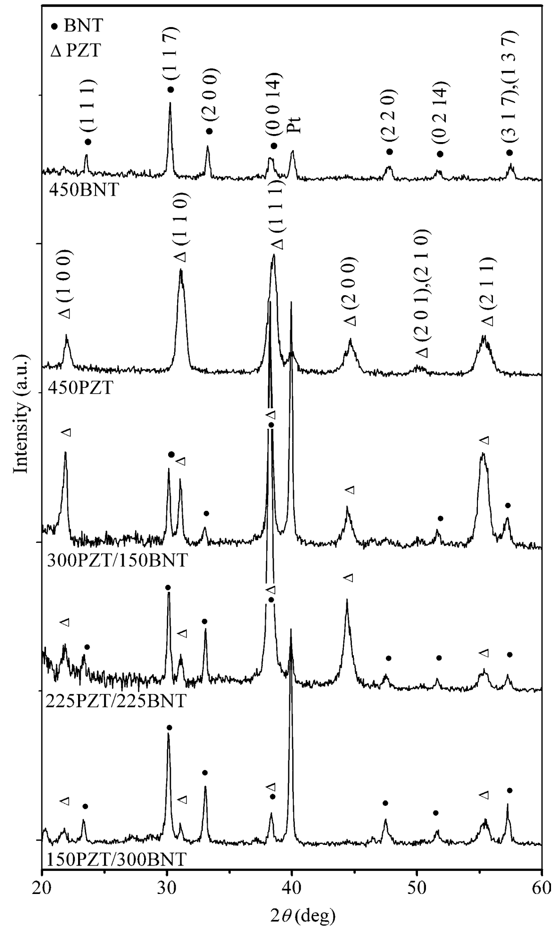

Fig. 1 XRD patterns of bilayered PZN/BNT thin films

Figure 3 shows the remanent polarization (P_r), measured at an applied electric field of 500 kV/cm, as a function of layer thickness ratio of PZT to the total thickness of the bilayered thin films (d_{PZT}/d). Undoubtedly, BNT layer lowers the polarization of the bilayered film, which is partially related to the fact that BNT exhibits a much lower P_r than that of PZT.

Figure 4 shows the dielectric permittivity and dielectric loss for both single layered PZT and BNT thin films and

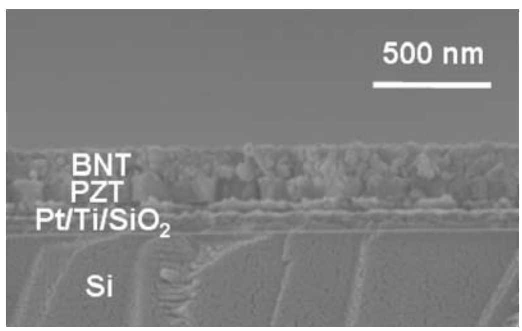

Fig. 2 SEM micrograph of the cross-section of *225PZT/225BNT* bilayered film

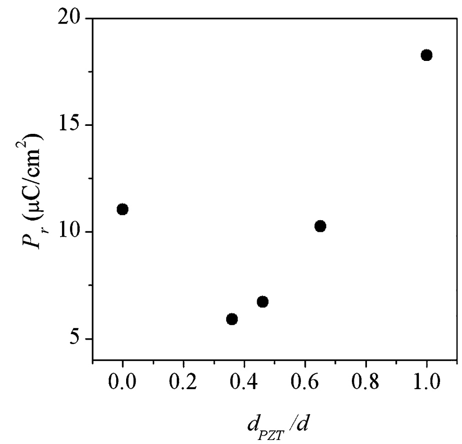

Fig. 3 P_r of bilayered and single layered thin films measured at 500 kV/cm. The ratio d_{PZT}/d is the thickness ratio of constituting PZT layer to the total thickness of the bilayered film

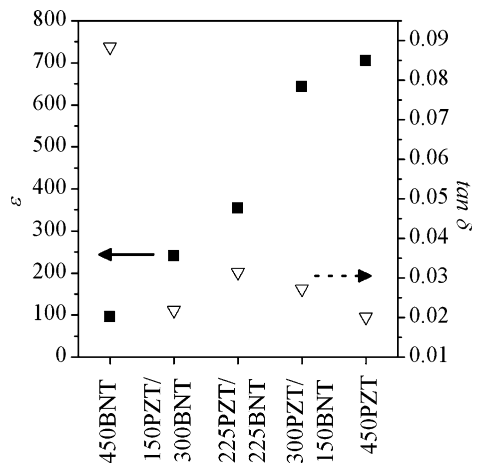

Fig. 4 Dielectric properties of the bilayered and single layered thin films at 10 kHz

bilayered thin films at 10 kHz. The dielectric permittivity increases with increasing PZT layer thickness, while dielectric loss decreases. The dielectric properties of the bilayered thin films are largely dependent on the relative thicknesses of the two constituent layers. To further investigate the interaction between the two ferroelectric layers in the bilayered films, series connection model was utilized [8]. According to the model, capacitance (C) of a bilayered thin film can be calculated on the basis of

$$\frac{1}{C_{PZT/BNT}} = \frac{1}{C_{PZT}} + \frac{1}{C_{BNT}} \tag{1}$$

Given the electrode area and dielectric permittivity remain unchanged in the same bilayered film, the expression can be written as follows

$$\frac{d_t}{\varepsilon_{PZT/BNT}} = \frac{d_{PZT}}{\varepsilon_{PZT}} + \frac{d_{BNT}}{\varepsilon_{BNT}} \tag{2}$$

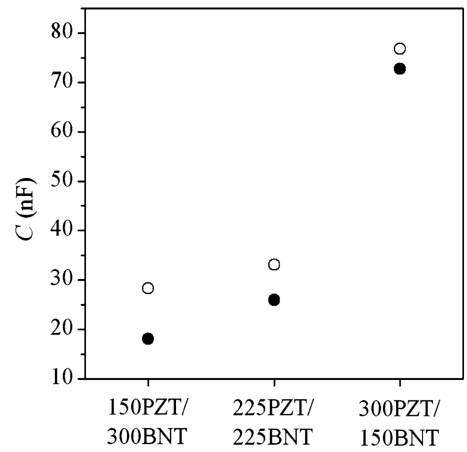

Fig. 5 Capacitance of the bilayered thin films at 10 kHz. Solid circles correspond to experimental data and hollow circles are calcualted from Eq. (1)

where d_t is the total thickness of bilayered film, d_{PZT} and d_{BNT} are the respective thicknesses of PZT and BNT layers contained in the bilayered thin film; $\varepsilon_{PZT/BNT}$, ε_{PZT} and ε_{BNT} are the dielectric permittivity of the bilayered film, constituting PZT and BNT layers respectively. ε_{PZT} and ε_{BNT} can be obtained from the single layered PZT and BNT films of various thicknesses as described by Lee et al. [8]. The measured values and the theoretically expected values from the series connection model of $C_{PZT/BNT}$ are shown in Fig. 5, where the measured values are generally lower than those of theoretically expected values. This suggests that there exists a layer of lower dielectric permittivity connecting in series with the bilayers.

As mentioned above, fatigue endurance is one of the important parameters for ferroelectric thin films. Figure 6 shows the change of switchable polarization ($P_{switching}$–$P_{non\text{-}switching}$) as a function of switching number of *300PZT/150PZT*, under 300 kV/cm and 200 kHz. The switchable polarization shows an initial increase, with the

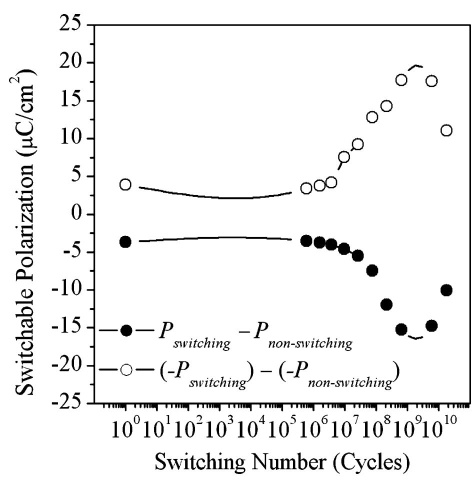

Fig. 6 Fatigue behavior of *300PZT/150BNT* bilayered thin film

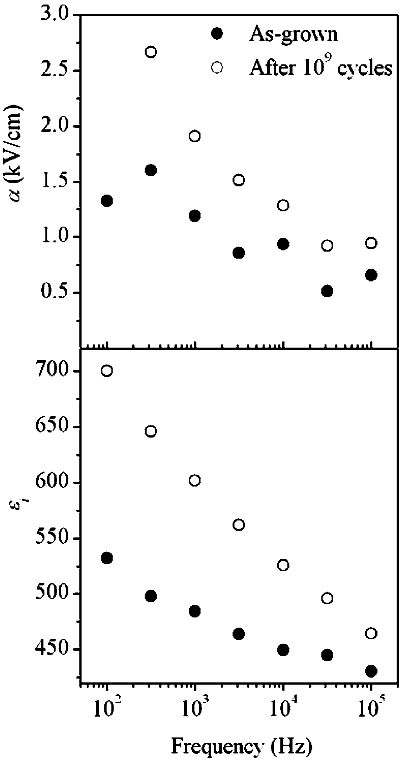

Fig. 7 Frequency dependence of the reversible and irreversible parameters of *300PZT/150BNT* thin films before and after 10^9 switching cycles

switching number, up to about 10^9 cycles; after which the P_r starts to degrade. The other two bilayered thin films of different layer thickness ratios exhibit similar behaviors in fatigue behaviors too. Such abnormal fatigue endurance was also reported by Du et al. in SiO_2-overcoat PZT films where the improved fatigue endurance was attributed to the breakdown of the dielectric layer [9]. The dielectric permittivity is found to increase by 11 to 35%, upon application of 10^9 cycles of polarization switching. In addition, the increment in the dielectric permittivity increases with decreasing frequency. The dielectric permittivity can be described by Rayleigh law [10],

$$\varepsilon = \varepsilon_{\text{init}} + \alpha E_o \tag{5}$$

where $\varepsilon_{\text{init}}$ and $\alpha E_\circ$ is the intrinsic and extrinsic contribution to permittivity respectively. The latter denotes the extrinsic contribution due to the irreversible domain wall displacement, where a higher α denotes weaker domain pinning effect. Both $\varepsilon_{\text{init}}$ and α were obtained by the subswitching measurement as described in the study of Taylor and Damjanovic [10]. $\varepsilon_{\text{init}}(f)$ and $\alpha(f)$ thus determined shows that both these two parameters increase upon application of 10^9 cycles of polarization switching, as shown in Fig. 7. The observed increase in $\varepsilon_{\text{init}}(f)$ can be attributed to an increase in the effective electric field after the breakdown of the dielectric layer [9]. The increase in $\alpha(f)$ however implies the pinning of domains becomes weaker after cycling.

4 Conclusions

Bilayered thin films consisting of PZT and BNT layers of different thicknesses were successfully deposited on Si(100)/SiO_2/Ti/Pt by a combination of sol-gel and magnetron sputtering. The constituent PZT and BNT layers were well preserved as confirmed by studies using both XRD and SEM. Investigations into their electrical behaviors revealed the occurrence of a dielectric layer of low dielectric permittivity in the bilayered films, which lowers the measured ε. On the other hand, it can give rise to an improvement in fatigue resistance up to 10^{10} switching cycles. The domain pinning effect in the bilayered thin film upon 6×10^9 cycles of polarization switching, however, was reduced greatly.

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