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Structure and Reliability Issues of $(Bi,Nd)_4Ti_3O_{12}$ Ferroelectric Thin Films

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Polycrystalline $(Bi,Nd)_4Ti_3O_{12}$ (BNdT) ferroelectric thin films were deposited on platinized Si substrates by chemical solution deposition. Microstructures of BNdT films were characterized by X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy. The Bi-layered perovskite structure was achieved by rapid thermal annealing the spin-on films at 700 ^{0}C for 3 min. Well-saturated hysteresis loops with remanent polarization (Pr) around 10 $\mu C/cm^2$ were obtained on Pt/BNdT/Pt capacitors. Reliability issues of these capacitors, such as fatigue, imprint and resistance to forming gas anneal, were studied. Pt/BNdT/Pt capacitors showed excellent fatigue resistance, even after forming gas anneal at 400 ^{0}C for 10 min when Pr was considerably suppressed. Shifts of hysteresis loops along voltage axis were observed along with the loss of retained polarization after heat treatment of poled Pt/BNdT/Pt capacitors. Possible mechanisms of these issues will be discussed.
Key words: BNdT, fatigue, imprint, retention

1. INTRODUCTION

Recently, lanthanide substituted $Bi_4Ti_3O_{12}$ thin films have attracted much attention for ferroelectric random access memory applications[1-3]. Compared with extensively studied $Pb(Zr_xTi_{1-x})O_3$ and $SrBi_2Ta_2O_9$ thin films, these films show advantages of both large remanent polarization (Pr) and high fatigue resistance. Since Park et al.[1] first introduced $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films, various La, Pr, Sm and Nd-substituted $Bi_4Ti_3O_{12}$ (BiTO) thin films have been reported [2-10]. All these ferroelectric thin films were prepared at 650 ~ 700 ^{0}C, which is favorable to integration with Si devices.

Besides of fatigue behavior, retention and imprint characteristics are also important to future memories based on ferroelectric thin films. Retention is the loss of polarization with time and imprint is the asymmetry of two remanent states. They are two closely related phenomena correlated with inhomogeneous distribution of space charges within the film. In spite of the importance, these electrical properties of lanthanide substituted BiTO thin films have not yet been well studied. In this paper, we present structural and electrical characterizations on $(Bi,Nd)_4Ti_3O_{12}$ thin films. Additionally, the effect of forming gas anneal on fatigue behavior will be reported.

2. EXPERIMENTAL

$(Bi,Nd)_4Ti_3O_{12}$ thin films were deposited by spin-coating and heat treated by rapid thermal annealing. The precursor solutions were prepared as reported, using bismuth nitrate, neodymium sesquioxide, n-butyl titanate, acetic acid, nitric acid and 2-methoxyethanol [4]. The final annealing was performed at 700 ^{0}C for 3 min. Two depositions result in a final film thickness of about 300 nm. Structure analyses were performed using X-ray diffraction (XRD) (Rigaku, D/Max-rA), Raman scattering (Jobin Yvon, HR800) and X-ray photoemission (XPS) (VG ESCALAB MK-II). Electrical properties were tested using a standard ferroelectric tester (Radiant Technology, RT66A) and an impedance analyzer (Agilent 4294A).

3. RESULTS AND DISCUSSION

3.1 Structure analyses

Figure 1 shows the XRD patterns of 700 ^{0}C annealed BiTO, $Bi_{3.54}Nd_{0.46}Ti_3O_{12}$ (BNdT46) and $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ (BNdT85) thin films. The peaks can be indexed according to those of $Bi_4Ti_3O_{12}$, which implies the structure similarity of $(Bi,Nd)_4Ti_3O_{12}$ and BiTO. The films are all polycrystalline with no preferred

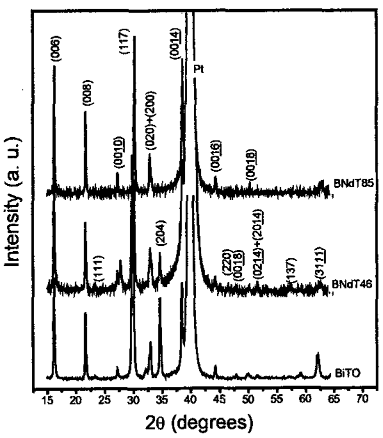

Fig. 1 XRD patterns of 700 ^{0}C annealed BiTO, BNdT46 and BNdT85 thin films.

orientation. It is observed that the lattice shrinks due to the substitution. Assuming a pesudo-tetragonal lattice, the lattice parameters are calculated as a ≈ 5.48 Å and c ≈ 32.89 Å for BiTO, a ≈ 5.40 Å and c ≈ 32.69 Å for

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BNdT46, and a ≈ 5.40 Å and c ≈ 32.64 Å for BNdT85.

Figure 2 is the Raman spectrum of 700 ^{0}C annealed BNdT85 thin films, which is typical for a layered perovskite material. The intense and sharp mode at 60 cm^{-1} appears in Raman spectra of almost all layered

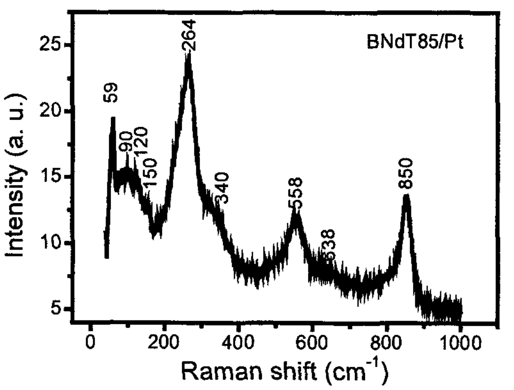

Fig. 2 Raman spectrum of BNdT85 thin films

perovskite ferroelectrics, originating from the rigid vibration between $(Bi_2O_2)^{2+}$ and perovskite slabs [11]. The mode at 90 and 120 cm^{-1} are soft modes associated with vibration of perovskite *A* site atoms. The modes at 264, 340, 558, 638 and 850 cm^{-1} can be assigned to bending and stretching of Ti-O bonds in the TiO_6 octahedron [12].

Figure 3 shows XPS spectra of Bi, Ti and O ions in BNdT85 thin films. Signals from Nd atoms were not detected due to limited instrument sensitivity. The Bi4*f* doublets are located 164.1 and 158.7 eV, with a spin-orbit splitting of 5.4 eV as in BiTO [13]. No contribution from Bi suboxide (at slightly lower binding

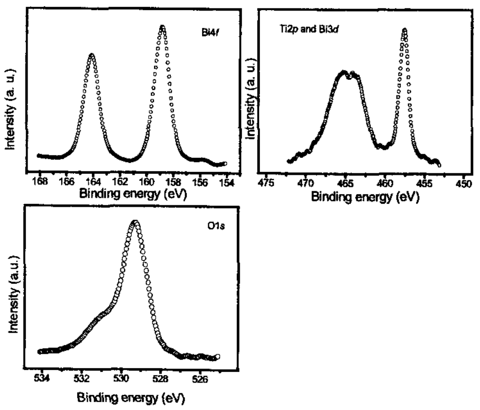

Fig. 3 XPS spectra of BNdT85 thin films

energies) can be deconvoluted. The O1*s* spectrum can be deconvoluted into two components. The peak at 529.3 eV is assigned to oxygen atoms bonded to Bi and Nd, while the peak at 530.1 eV may be originated from chemisorbed oxygens, O-H bonds or carbonates [13]. Ti2*p* spectrum shows a sharp Ti2$p_{3/2}$ peak at 457.6 eV with Ti2$p_{1/2}$ component at around 463.4 eV partially overlapped with Bi4*d* signal. No chemical states other than Ti^{4+} can be assigned.

3.2 Electrical properties

The ferroelectric nature of the Nd-substituted BiTO thin films are demonstrated by hysteresis loops, as shown in Fig. 4. The *Pr* and coercive voltage (*Vc*) values of BNdT85 are 10.5 μC/cm^2 and 1.2 V, respectively. BNdT46 films exhibit a smaller *Pr* of 8.5 μC/cm^2 and a larger *Vc* of 1.4 V. Larger *Pr* makes the sense amplifier

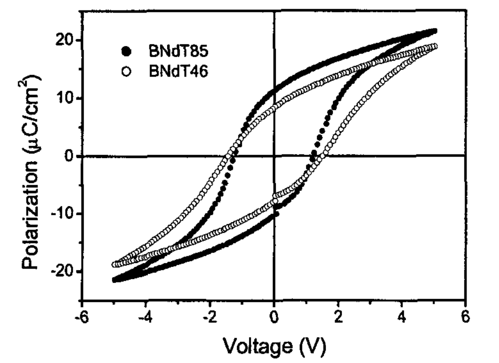

Fig. 4 Hysteresis loops of Pt/BNdT46/Pt and Pt/BNdT85/Pt capacitors.

easier to distinguish digital '1' and '0'. Smaller *Vc* is favorable to low voltage applications for portable or mobile devices. Therefore, BNdT85 may be more suitable for FeRAM applications due to its larger *Pr* and smaller *Vc*.

Imprint properties of Pt/BNdT85/Pt capacitors were observed after heat treatment of the poled capacitors at high temperatures for a period of time. The C-V curves of BNdT85 thin films before and after thermal imprint at 80 ^{0}C for 10 hours are shown in Fig. 5. The capacitance maxima, which correspond to the coercive voltages, shift toward negative voltage. This shift of coercive voltage indicates the existence of an internal voltage formed by trapped space charges [14]. The space charges

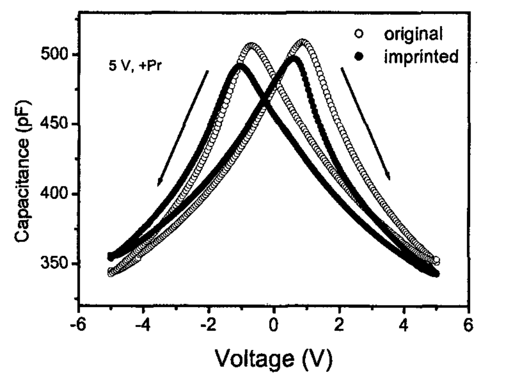

Fig. 5 C-V curves of a Pt/BNdT85/Pt capacitor before and after poling and thermal treatment.

in the films are thermally activated and trapped at each end of polarization to screen the depolarization voltage. The consequence of the existence of internal voltage is that the two *Pr* states are no longer symmetric. Because the internal voltage does not change direction with the applied voltage due to the inertia of space charges, the state at which the capacitor was heat treated would be the preferential state, more stable than the other [15]. The asymmetry of remanences results in an asymmetric retention property of the imprinted thin films. Figure 6 shows a (-*P*^r)/(-*Pr*) versus heat treatment time for a BNdT85 capacitor poled to +*Pr* state, -*P*^r designates the polarization loss within 1 s after writing pulse. With the buildup of internal voltage, the fraction of data loss increases. The details of retention characteristics will be reported elsewhere.

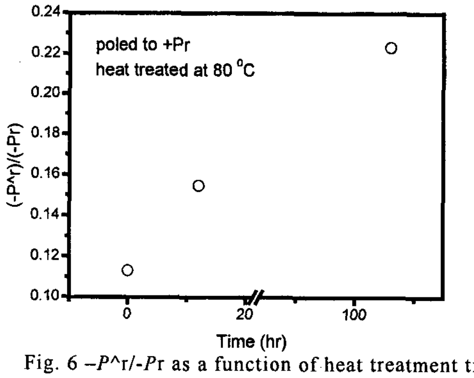

Fig. 6 $-P^r/-Pr$ as a function of heat treatment time.

3.3 Forming gas anneal

One critical step in integration of ferroelectric capacitor with Si devices includes an annealing at 350 ~ 550 °C in a forming gas (FG: H_2-containing atmosphere) to passivate dangling bonds at SiO_2/Si interface [16]. Unfortunately, such a H_2-containing annealing results in a dramatic degradation of the electrical properties of almost all the ferroelectric thin films considered yet. Figure 7 shows non-volatile polarization (*P*nv), the difference between switchable and unswitchable polarization, of Pt/BNdT85/Pt capacitors annealed in FG at various temperatures for 10 min as functions of bipolar switches. *P*nv of 200 °C FG annealed samples is about 17 μC/cm^2, identically the same as that before FG anneal. *P*nv of 300 °C FG annealed samples decreased about 4 μC/cm^2, while that of 400 °C FG annealed sample decreased further to about 8 μC/cm^2, less than half of the original value. However, although *P*nv

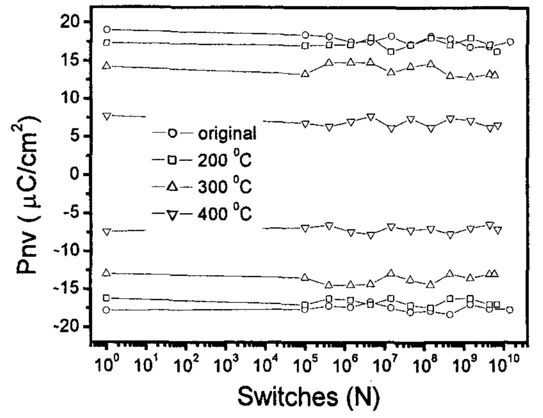

Fig. 7 Fatigue characteristics of Pt/BNdT85/Pt capacitors FG annealed at different temperature.

decreases with increasing FG anneal temperature, it does not change with cycling. That is to say that the fatigue free characteristic of BNdT thin films is preserved after FG annealed. Through X-ray photoemission spectra, it was suggested that the suppressed polarization might be ascribed to polar O-H bonds formed due to H^+ penetration [17]. However, the fatigue characteristics were controlled by mobile space charges, such as oxygen or bismuth vacancies [4]. Therefore, the FG annealed capacitors were still fatigue free, while the polarization was suppressed.

4. CONCLUSIONS

BNdT thin films were prepared by chemical solution deposition at 700 °C. The films of Bi-layered perovskite structure were characterized by XRD, XPS and Raman spectroscopy. The well-saturated hysteresis loops demonstrate the ferroelectric nature of the film, with Pr of 10.5 μC/cm^2. Imprint was observed after heat treatment of poled Pt/BNdT/Pt capacitors. This was attributed to the formation of internal voltage by thermally activated space charges. This internal voltage may increase the data loss of the state opposite to the preferential one. FG anneal results in reduced *P*nv values. *P*nv of 400 °C FG annealed capacitors is less than half of the original value. However, FG annealed BNdT capacitors are still fatigue free. These results show that BNdT is a promising candidate for FeRAM application. But further investigation is necessary to solve reliability and integration issues.

5. ACKOWNLEDGEMENTS

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