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Ferroelectric Properties of $Bi_{3.25}Nd_{0.75}Ti_3O_{12}$ Thin Films Prepared by MOD Process

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Abstract. Ferroelectric $Bi_{4-x}Nd_xTi_3O_{12}$(BNdT) thin films with the composition ($x = 0.75$) were prepared on Pt/Ti/SiO_2/Si(100) substrate by metal-organic deposition. The films were annealed by various temperatures from 550 to 650°C and then the electrical and structural characteristics were investigated for the application of FRAM. Electrical properties such as dielectric constant, 2Pr and capacitance were quite dependent on the thermal heat treatment. The measured 2Pr value on the BNdT capacitor annealed at 650°C was 56 μC/cm^2 at an applied voltage of 5 V. No fatigue was observed up to 8×10^{10} read/write switching cycles at a frequency of 1 MHz regardless of annealing temperatures.

Keywords: ferroelectric, $Bi_{4-x}Nd_xTi_3O_{12}$ thin films, MOD method, dielectric constant, fatigue

1. Introduction

During the last decades, ferroelectric thin films have attracted much attention due to potential applications in nonvolative ferroelectric random access memories (FeRAMs) [1–3].

Early works concerning the search of FRAM candidate materials were devoted to the $Pb(Zr_xTi_{1-x})O_3$ (PZT) thin films for their large remanent polarization and low processing temperature [4]. However, PZT suffers severe fatigue failure on metal electrode(Pt) after repeated bipolar reversal [3, 5]. Recently, the two-layer ($n = 2$) ferroelectric Aurivillius phase $SrBi_2Ta_2O_9$ (SBT) [6] and the three-layer ($n = 3$) $Bi_{3.25}La_{0.75}Ti_3O_{12}$(BLT) [7] have been used as substituting materials for PZT due to their fatigue-free characteristics on Pt electrodes. The fatigue-free behavior of SBT and BLT are believed to come from the reduction of space charges due to the charge compensation effect of Bi_2O_2 layers, and from domain wall unpinning that happens at least as rapidly as domain pinning. However, the high processing temperature of SBT above 750°C is an obstacle in integration with silicon devices. BLT shows lower remanent polarization and higher process temperature than PZT while BLT exhibits an excellent ferroelecric characteristics and good fatigue endurance [7].

In this study, we present the results of $Bi_{4-x}Nd_xTi_3O_{12}$(BNdT) ($x = 0.75$) thin films in which La ion in BLT was substituted by trivalent Nd ion, on Pt/Ti/SiO_2/Si(100) substrates by metal organic deposition(MOD) method. And ferroelectric properties were systematically evaluated in terms of different annealing temperature.

2. Experimental

Bi-acetate, Nd-acetate and Ti-ethoxide were used as the starting materials with pyridine [C_5H_5N] and acetic acid [CH_3COOH] as the main solvent. Excess 15 mol% Bi precursor was added to compensate Bi evaporation during annealing. The mixtures were synthesized in pyridine and acetic acid with stirring at about 70°C. The solutions were typically prepared to a concentration

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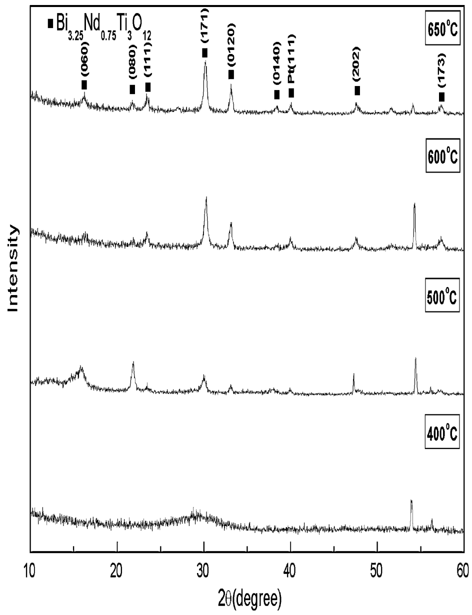

Fig. 1. XRD patterns of $Bi_{3.25}Nd_{0.75}Ti_3O_{12}$ films prepared on $Pt/ti/SiO_2/Si(100)$ substrates annealed for 1 h in oxygen atmosphere.

of 0.05 mol/l. BNdT precursor solutions were spin coated onto $Pt/Ti/SiO_2/Si(100)$ substrates at approximately 2,500 rpm for 30 seconds in air. The measured film thickness on $Pt/Ti/SiO_2/Si(100)$ substrate was about 210 nm. After several spin-dry cycles, the pre-baked films were annealed in an O_2 flow at 550, 600 and 650°C for 1 h respectively. Platinum top electrodes of 200 nm in diameter were deposited with a shadow mask by DC magnetron sputtering.

3. Results and Discussion

Figure 1 shows X-ray diffraction patterns of the BNdT ($x = 0.75$) films on $Pt/Ti/SiO_2/Si(100)$ annealed at different temperatures (400–700°C) for 1 h in oxygen atmosphere. As can be seen in Fig. 1, initially the film annealed at 400°C was amorphous and then film became crystallize as the annealing temperature increase from 400 to 500°C. Above 600°C, well crystallized BNdT thin films with bismuth layered perovskite structure were achieved and revealed a random orientation

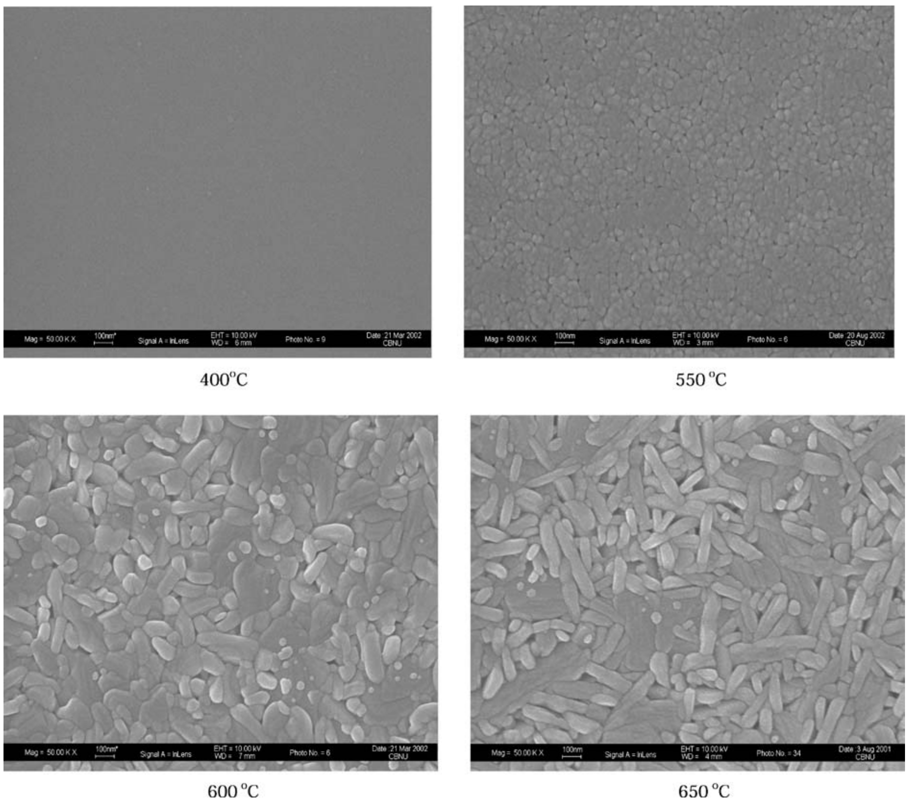

Fig. 2. SEM images of $Bi_{3.25}Nd_{0.75}Ti_3O_{12}$ films prepared on $Pt/ti/SiO_2/Si(100)$ substrates as a function of annealing temperature for 1 h.

with weak (00l) diffraction patterns. On the other hand, the (171) preferred orientation became dominant with increasing annealing temperature. It was found that the peaks of BNdT films with Nd were quite similar to those of BLT films without any pyrochlore phase. The substitution of small ionic radius in the Bi site is expected to increment of polarization with tilting the TiO_6 octahedra from *c*-axis to *a-b* plane [9, 10]. The coincidence of diffraction patterns of BNdT with those of BLT implies that the the Nd substitution does not affect the layered perovskite structure.

The surface morphology of thin films was observed by SEM in Fig. 2. Microstructures of the films heat treated above 600°C was found to be rod-like structure and the grains with the layered-perovskite phase were oriented randomly at the surface of the films. The films are uniform and composed of closely packed spherical grains of around 90 nm in size.

The dielectric properties of BNdT thin films were evaluated in terms of dielectric constant and dissipation factor. The dissipation factor (tanδ) of BNdT ($x = 0.75$) thin films on Pt/Ti/SiO_2/Si(100) substrates was measured in terms of different annealing temperatures (Fig. 3(a)). The typical dissipation factors (tanδ) at 100 kHz linearly increased with increasing temperature, that is, 0.01, 0.018 and 0.095 at 550, 600 and 650°C respectively. Systematic increment of dissipation factor as a function of temperature would be explained by the increase of interface roughness between electrode and film with increasing annealing temperature.

Figure 3(b) shows the dielectric constant (ε_r) of BNdT ($x = 0.75$) films with different temperatures for 1 hr. The variation in dielectric constant measured between 100 Hz and 10^5 Hz was almost constant regardless of annealing temperatures. The measured dielectric constants (ε_r) at 100 kHz were 117, 285 and 347 at 550, 600 and 650°C respectively.

In Fig. 4(a) the C-V curve of BNdT ($x = 0.75$) thin films was evaluated as different annealing temperatures (550, 600 and 650°C) for 1 hr at 5 V. Preliminary result suggests that the capacitance values of BNdT thin films systematically increased with the amount of crystallization in BNdT films. The capacitance at 650°C reached to the highest as compared with any other film. On the other hand, it is considered that asymmetry of C-V curve at 0 volt is attributed to the difference of properties between top/bottom electrode and BNdT interface, that is, Pt/BNdT or BNdT/Pt.

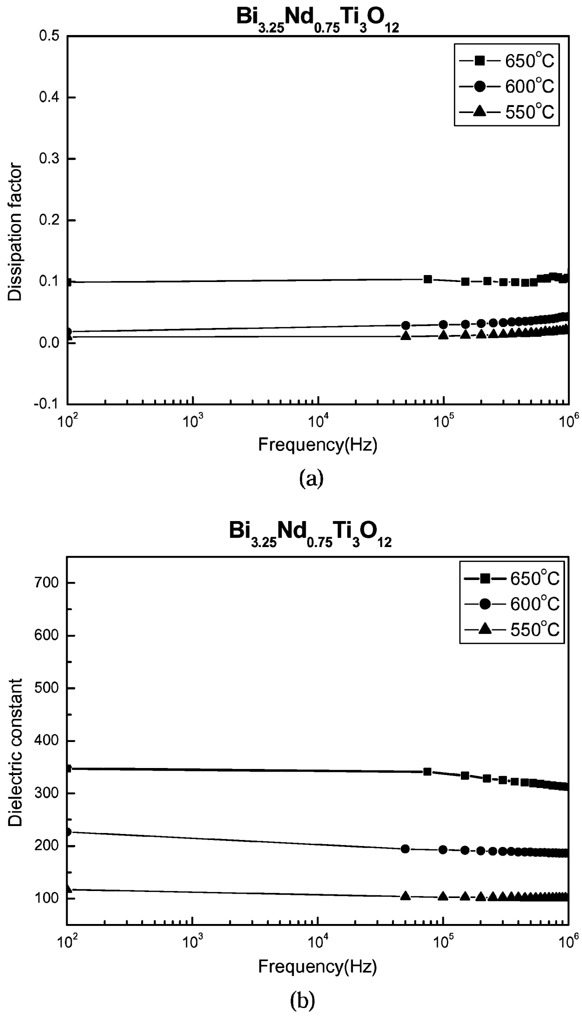

Fig. 3. Dissipation factor (a) and dielectric constant (b) of $Bi_{3.25}Nd_{0.75}Ti_3O_{12}$ films prepared on Pt/Ti/SiO_2/Si(100) substrates with increasing annealing temperatures.

Figure 4(b) shows the hysteresis loop (P-E curve) of Pt/210 nm-thickness BNdT ($x = 0.75$)/Pt capacitor was measured at an applied voltage 5 V. Well saturated P-E hysteresis pattern at 650°C was observed as compared with other films annealed at 550 and 600°C. The remanent polarizations (2Pr) were 11, 32 and 56 $\mu C/cm^2$ at 550, 600 and 650°C respectively. Especially the BNdT film annealed at 650°C exhibited the remanent polarization (2Pr) of 56 $\mu C/cm^2$ and coercive field (2Ec) of 232 kV/cm. It could be understood that high Pr value of BNdT film annealed at 650°C was attributed to both XRD pattern with perovskite structure and rodlike grains with dense microstructure. It was known that Nd

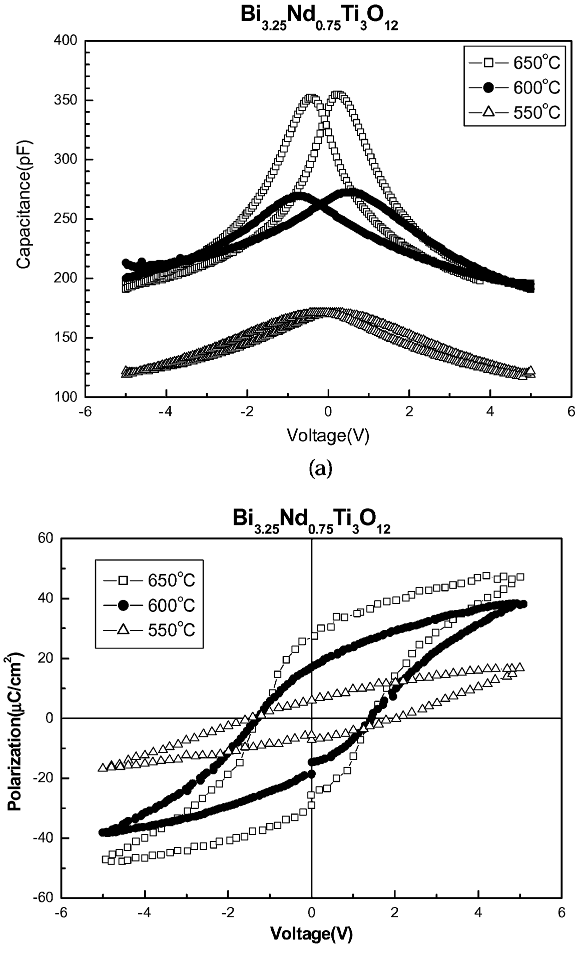

Fig. 4. C-V curves (a) and P-E hysteresis loops (b) of $Bi_{3.25}Nd_{0.75}Ti_3O_{12}$ films prepared on $Pt/Ti/SiO_2/Si(100)$ substrates as a function of annealing temperature for 1 h.

substitution in BLT leads the large ferroelectricity as compared with BLT film and high Pr and low Ec maybe attributable to the change of crystal orientation from the (00l) preferred orientation to the random orientation with (171) preferred orientation [9, 10]. However these films have relatively large coercive field (Ec) for switching.

The change of switable polarization and coercive voltage were displayed as a function of annealing temperature in Fig. 5(a). The measurements were performed using the pulse with 1 MHz bipolar square wave at 5 V. Based on the fatigue test, no significant fatigue behavior was observed up to 8×10^{10} switching cycles regardless of annealing temperatures.

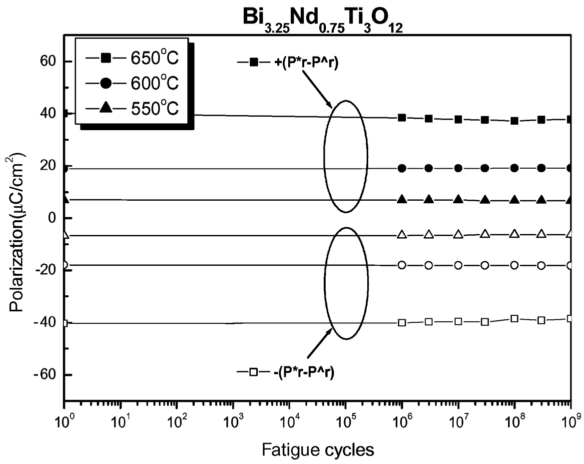

Fig. 5. Fatigue characteristics of $Bi_{3.25}Nd_{0.75}Ti_3O_{12}$ films prepared on $Pt/ti/SiO_2/Si(100)$ substrates in terms of annealing temperature.

4. Conclusion

We prepared BNdT ($x = 0.75$) thin films on $Pt/Ti/SiO_2/Si(100)$ substrate by MOD method. In terms of XRD results the coincidence of diffraction patterns of BNdT with those of BLT implies that the Nd substitution does not affect the layered perovskite structure. All the MOD-derived BNdT films were fully crystallized to polycrystalline with almost random orientation above 600°C. With increasing the grain size of the BNdT films in terms of annealing temperatures, the dielectric constant (ε_r) and dissipation factor ($\tan\delta$), remnant polarization (2Pr), coercive field (2Ec), and the saturation characteristic also simultaneously increased. For the BNdT film annealed at 650°C, dielectric constant (ε_r) and dissipation factor ($\tan\delta$) were 346.7, 0.095 and the remnant polarization (2Pr), and the coercive field (2Ec) at an applied voltage of 5 V were 56 $\mu C/cm^2$ and 232 kV/cm respectively.

BNdT ($x = 0.75$) thin films did not show the polarization fatigue up to 8×10^{10} switching cycles at 5 V regardless of annealing temperatures.

Acknowledgments

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