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Fabrication of Nd-Substituted $Bi_4Ti_3O_{12}$ Thin Films by Metal Organic Chemical Vapor Deposition and Their Ferroelectrical Characterization

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ABSTRACT

A promising capacitor, which has conformable step coverage and good uniformity of thickness and composition, is needed to manufacture high-density non-volatile FeRAM capacitors with a stacked cell structure. In this study, ferroelectric $Bi_{3.61}Nd_{0.39}Ti_3O_{12}$ (BNdT) thin films were prepared on $Pt(111)/TiO_2/SiO_2/Si$ substrates by the liquid delivery system MOCVD method. In these experiments, $Bi(ph)_3$, $Nd(TMHD)_3$ and $Ti(O^iPr)_2(TMHD)_2$ were used as the precursors and were dissolved in n-butyl acetate. The BNdT thin films were deposited at a substrate temperature and reactor pressure of approximately 600°C and 4.8 Torr, respectively. The microstructure of the layered perovskite phase was observed by XRD and SEM. The remanent polarization value (2Pr) of the BNdT thin film was 31.67 μC/cm² at an applied voltage of 5 V.

***Key words*: BNdT, LDS-MOCVD, FeRAM, Ferroelectrics, Thin film**

1. Introduction

Ferroelectric memory is not only an ideal form of memory with clear advantages such as non-volatility, low power consumption, high endurance and high speed writing, but is also the most suitable device for memory embedded applications.[1)] A number of different methods have been developed for the fabrication of Bi-layered perovskite thin films, such as sputtering,[2)] PLD,[3)] MOD,[4)] Sol-Gel,[5)] and MOCVD.[6)] Among these methods Metal Organic Chemical Vapor Deposition (MOCVD) has the advantage of offering conformable step coverage and good uniformity of thickness and composition.

Many researchers have studied possible candidates for ferroelectric materials that can be used in Non-Volatile Random Access Memories (NVRAMs).[7)] In recent years, some Bi-layered oxide perovskites, such as $SrBi_2Ta_2O_9$ (SBT) and $Bi_{3.75}La_{0.25}Ti_3O_{12}$ (BLT) have been intensively studied, in order to evaluate their possible use in NVRAMs. However, the use of SBT and BLT thin films for high density integration in NVRAMs is disadvantaged by the fact that these films have a low remanent polarization (2Pr for SBT = 20 μC/cm², and for BLT = 27 μC/cm²).[8)] Recently, U. Chon *et al.* reported the fatigue free and large remanent polarization of Nd-substituted $Bi_4Ti_3O_{12}$ (BTO) (2Pr of BNdT = 100 μC/cm²).[9)]

In this paper, the properties of epitaxial BNdT films grown by the Metal Organic Chemical Vapor Deposition (MOCVD) method on a $Pt/TiO_x/SiO_2/Si$ substrate were studied. The crystallinity, microstructure, electrical and ferroelectric properties of the BNdT thin films were investigated and discussed in detail.

2. Experimental Procedure

BNdT films with a thickness of 150 nm were deposited at 600°C by the LDS-MOCVD method. Triphenyl bismuth [$Bi(ph)_3$], tri(2,2,6,6-tetramethyl-3,5-heptanedionate) Neodymium [$Nd(TMHD)_3$] and di(i-propoxide) bis(2,2,6,6-tetramethyl-3,5-heptanedionate) titanium [$Ti(O^iPr)_2(TMHD)_2$] were used as the precursors for Bi, Nd, and Ti, respectively. These precursors were dissolved n-butyl acetate to form a single stock solution. This solution was deposited onto a $Pt/TiO_x/SiO_2/Si$ substrate for 50 min by the liquid delivery system MOCVD (LDS-MOCVD) method. The compositions of the resultant films were characterized by means of an electron probe micro analyzer (JEOL, JXA-8900R). The crystalline structures of the BNdT thin films were studied by X-ray diffraction using a Rigaku DMAX 2500 X-ray diffractometer. The surface microstructure was analyzed by means of a the field emission scanning electron microscope (HITACHI, S-4200). The electric and ferroelectric properties of the deposited films were measured with a standard ferroelectric test system (RADIENT, RT66A) after the formation of Pt top electrodes on the film surface by means of RF-Sputter using a shadow mask. The typical deposition conditions are summarized in Table 1.

3. Results and Discussion

3.1. Thermal Properties of BNdT Precursors

Fig. 1 shows the thermal analysis (TG) data of the BNdT

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Table 1. MOCVD Process Conditions Used to Deposit the BNdT Thin Films

Deposition parameters	Range investigated
Substrate temperature	600°C
Total reactor pressure	4.8 Torr
Vaporizer temperature	210 - 220°C
Vaporizer pressure	4.8 Torr
Substrate	Pt(200 nm)/TiO_x(50 nm)/SiO_2/Si
Stock solution concentration [Bi : Nd : Ti]	0.042 : 0.009 : 0.016 (M)
Flow rate of stock solution	0.1 ml/min.
Deposition time	50 min.
Carrier gas (Ar) flow rate	200 sccm
Oxidizing gas (O_2) flow rate	200 sccm

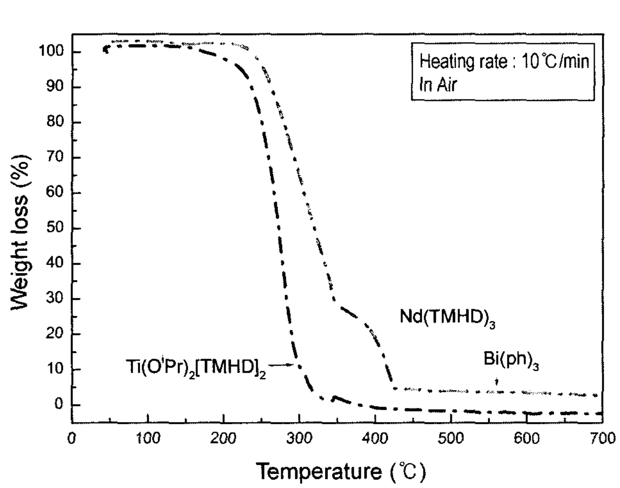

Fig. 1. TG results of $Bi(ph)_3$, $Nd(TMHD)_3$ and $Ti(O^iPr)_2(TMHD)_2$ powders.

precursors. The weight losses of $Bi(ph)_3$ and $Nd(TMHD)_3$ began to decrease at around 240°C. The weight of $Ti(O^iPr)_2$ $(TMHD)_2$ decreased sharply at 230°C. From Fig. 1 it can be seen that the BNdT precursors were decomposed in the temperature range of 230 to 240°C at atmospheric pressure. However, the inner pressure of the actual experimental apparatus was maintained under near vacuum conditions. Therefore, the temperature of the vaporizer and delivery system could be set to around 210~220°C.

3.2. Chemical Composition of BNdT Thin Films

Fig. 2 shows the molar ratio of bismuth and neodymium as a function of the reactor pressure. The molar ratio of titanium was fixed at 3.0. The molar ratio of bismuth increased with increasing reactor pressure, whereas that of neodymium decreased with increasing reactor pressure. From the results shown in Fig. 2, it can be seen that a stabilized film composition is obtained at a pressure of almost 4.8 Torr.

Fig. 3 shows the molar ratio of bismuth and neodymium as a function of the substrate temperature. The molar ratio of titanium was fixed at 3.0. The molar ratio of bismuth at first sharply increased from its initial value of 2.05 up to

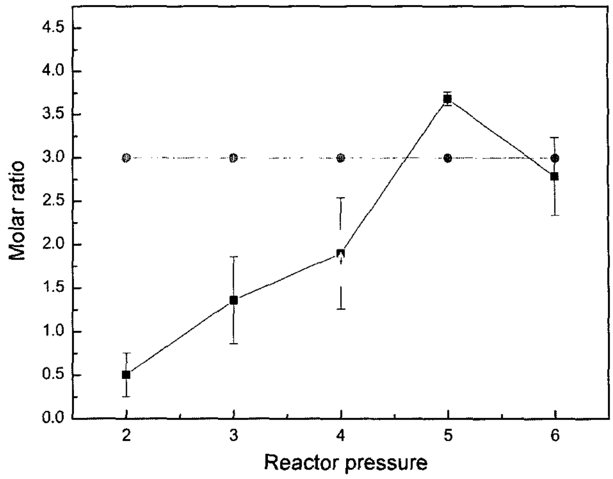

Fig. 2. The reactor pressure dependence of the amount of each element in the as-deposited BNdT thin films.

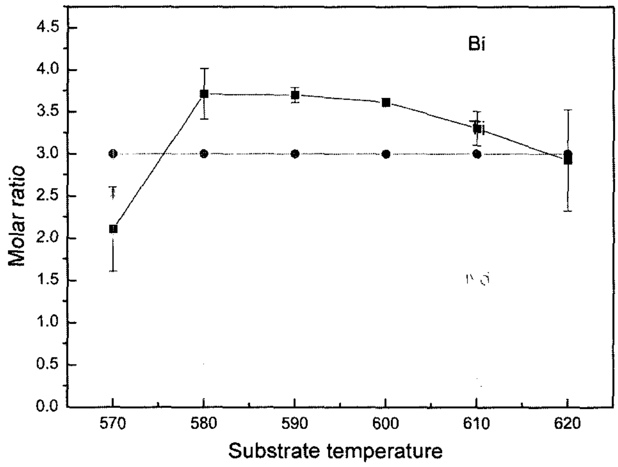

Fig. 3. The substrate temperature dependence of the amount of each element in the as-deposited BNdT thin films.

580°C, and then gradually decreased with increasing substrate temperature thereafter. The molar ratio of neodymium sharply decreased from its initial value of 2.51 up to 580°C, and remained constant thereafter. As a result, the optimum substrate temperature and reactor pressure for this study were determined to be 600°C and 4.8 Torr, respectively.

3.3. Crystalline Phases and Preferred Orientations of BNdT Thin Films

Fig. 4 shows the X-ray diffraction patterns of the BNdT thin films deposited on the Pt/TiO_x/SiO_2/Si substrate. Following their deposition, these thin films were annealed at various temperatures for 1 h in an O_2 atmosphere. All of the films exhibited a Bi-layered perovskite structure, which could be well indexed by the JCPDS card (No. 12-0213) of $Bi_4Ti_3O_{12}$. The most notable characteristics were the predominant (117)-oriented growth on the Pt bottom layers, and the fact that the (117), (200) random orientation of the

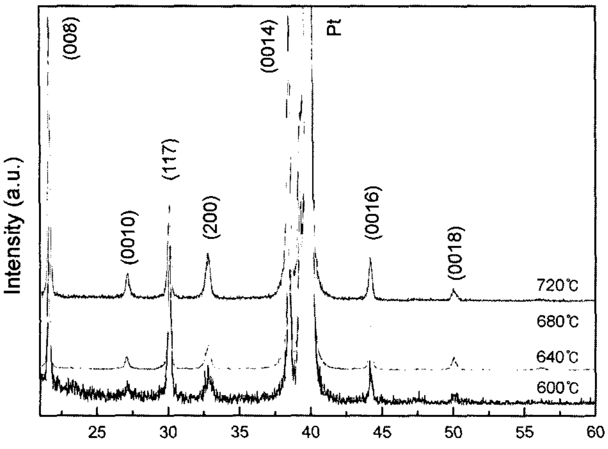

Fig. 4. X-ray diffraction patterns of $Bi_{3.61}Nd_{0.39}Ti_3O_{12}$ thin films crystallized at various annealing temperatures.

films became dominant with increasing annealing temperatures and the BNdT films annealed at higher temperatures exhibited stronger and sharper diffraction peaks. It can thus be assumed that the grain size increased with increasing annealing temperature. The correlation of the diffraction peaks of the BNdT thin films with those of BTO implies that the Nd substitution does not affect the layered-perovskite structure of $Bi_4Ti_3O_{12}$. This implies that the Nd^{3+} ions in the BNdT films do not form a pyrochlore phase, but dissolve into the pseudo-perovskite structure.[10] Based on the XRD patterns, it is suggested that the resultant properties can be attributed to the combination of the a, b and c-axis orientation. This combination of a, b and c-axis orientation leads to an improvement in the remanent polarization.

3.4. Surface Morphology of BNdT Thin Films

Fig. 5 shows the dependence of the annealing temperature on the surface morphology of the BNdT thin films. The surface morphology was very sensitive to the annealing temperature. It is clearly seen that each film has a rod-like and plate-like morphology. Rod-like grains of about 3 – 4 μm appear on the 600°C annealed films, and the grain size increased with increasing annealing temperature. In addition, the grains of the layered-perovskite phase are randomly oriented at the surface of the films. Therefore, the increased grain size observed for the BNdT films annealed at high temperature can be attributed to the polarization. A cross-sectional view of the annealed BNdT thin film annealed at 720°C, presented in Fig. 6, revealed the presence of a clear boundary between the film and the Pt electrode, and good uniformity of thickness. The thickness of the BNdT thin film was about 150 nm.

3.5. Eletrical Properties of BNdT Thin Films

Fig. 7. shows the Polarization-Electric field (P-E) hysteresis loops of the BNdT thin films annealed in the temperature range of 600 to 720°C. From Fig. 6(a) and (b), it can be seen that the BNdT thin films annealed at 600 and 640°C exhibited 2Pr values of 12.13 and 16.97 μC/cm² and 2Vc val-

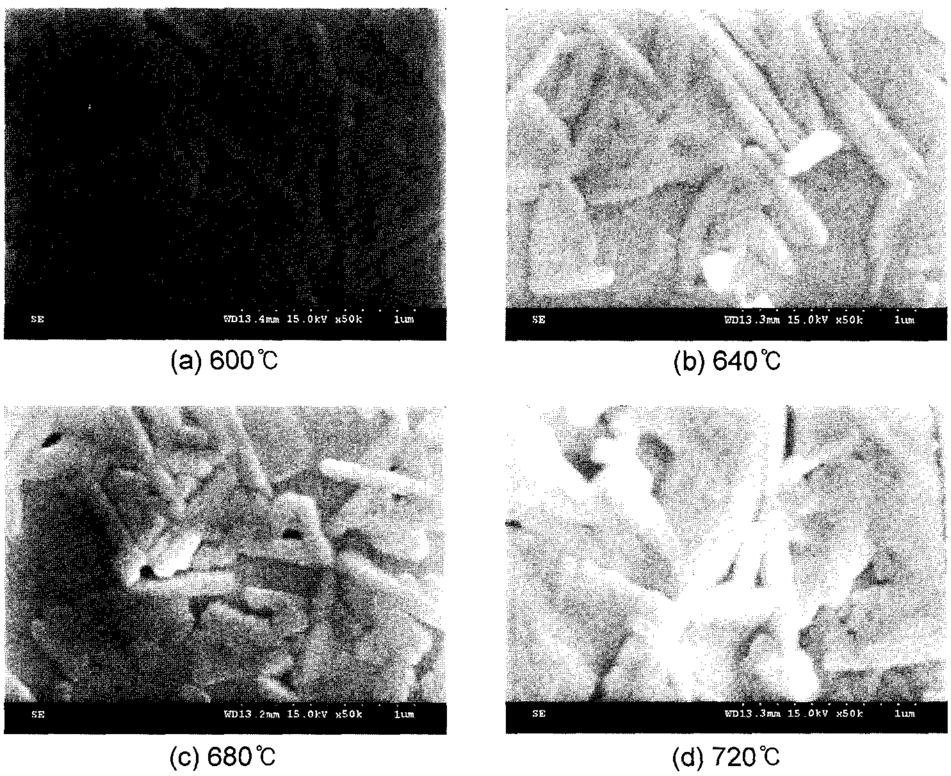

Fig. 5. SEM surface images of BNdT thin films furnace-annealed at various temperatures for 1 h in O_2.

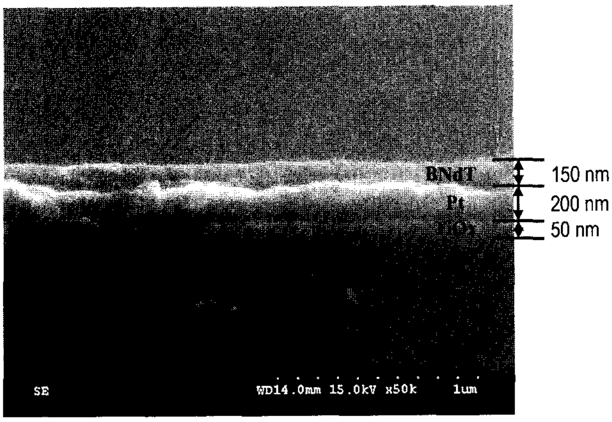

Fig. 6. SEM micrograph of cross section of BNdT thin film furnace annealed at 720°C for 1 h in an oxygen flow.

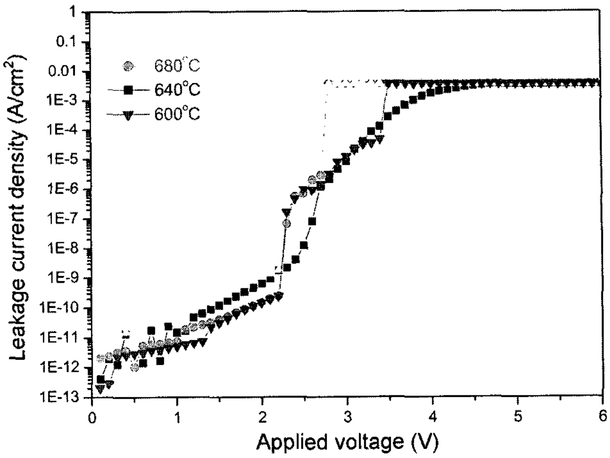

Fig. 8. Leakage current density-voltage characteristics of the Pt/BNdT/Pt/TiO_x/SiO_2/Si capacitor furnace-annealed at various temperatures.

ues of 3.35 and 3.18 V, respected, even when the applied voltage was as low as 5 V. Furthermore, well-saturated P-E hysteresis curves were obtained for the BNdT thin films annealed at 680 and 720°C, which showed 2Pr values of 21.78 and 31.91 μC/cm^2 and 2Vc values of 2.61 and 3.58 V, as shown in Fig. 7(c) and (d), respectively. The substitution of Nd for bismuth titanate in the $Bi_4Ti_3O_{12}$(BTO) thin films was found to be effective for improving the ferroelectric properties of the thin films. Therefore, the poor ferroelectric and fatigue characteristics if the BTO thin films can be attributed to the volatility of the Bi ions.[11] The Bi^{3+} ions in the BTO structure can be substituted by Nd^{3+} in order to improve the properties of such layer-structures.

The leakage current of the Pt/BNdT/Pt thin films was measured by applying a staircase DC voltage to the top and bottom electrodes. Fig. 8 shows a plot of the leakage current density of the BNdT thin films versus the applied DC electric voltage. The leakage current density is typically less than 10^{-6} A/cm^2 under an applied voltage of up to about 2.5 V, which demonstrates the relatively good insulating properties of the thin films. The breakdown voltage of the 150 nm BNdT thin films was about 2.6 V.

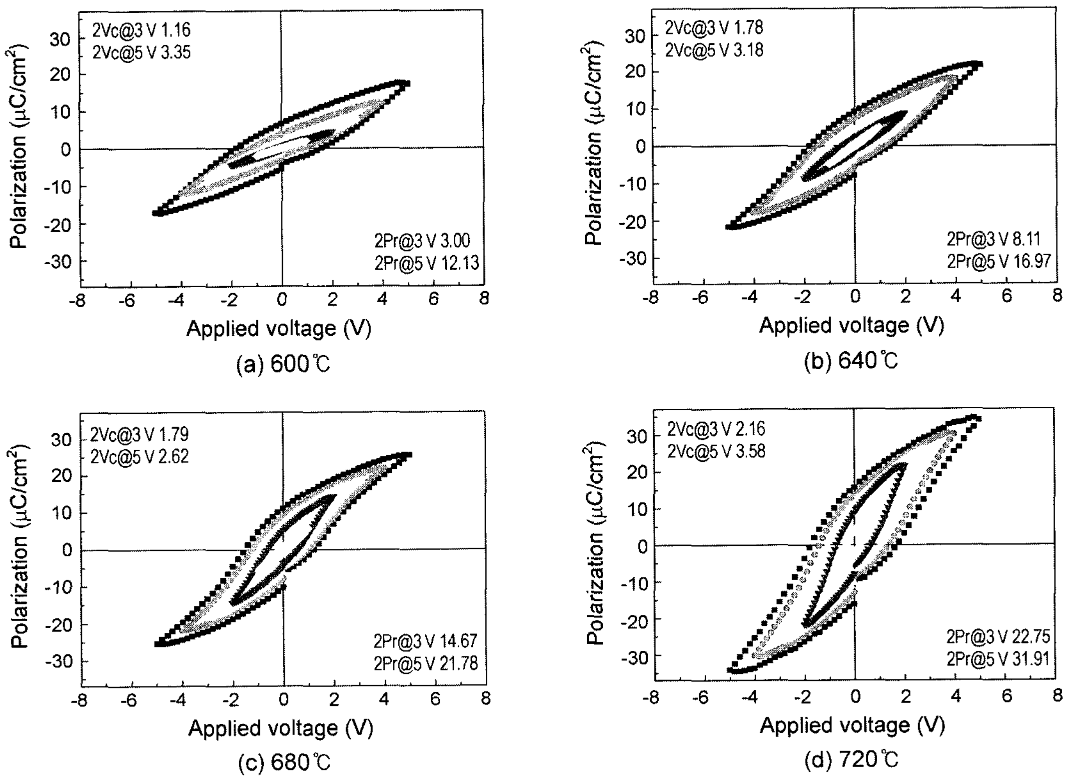

Fig. 7. Hysteresis loops of $Bi_{3.61}Nd_{0.39}Ti_3O_{12}$ thin films furnace-annealed at various temperatures.

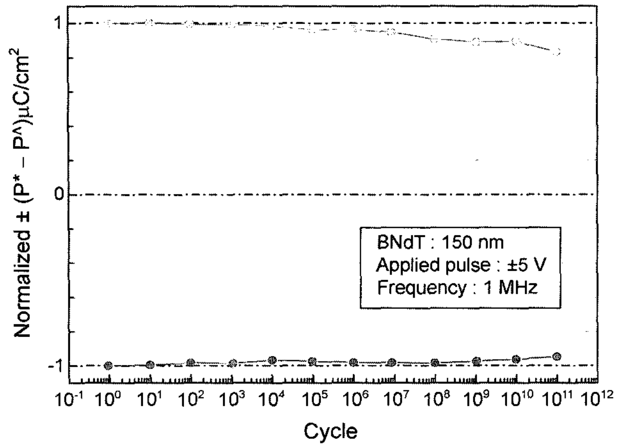

Fig. 9. Results of the fatigue test of BNdT thin film furnace-annealed at 720°C for 1 h in O_2.

The switched polarization was determined as a function of the number of switching cycles using bipolar pulses of ±5 V at 1 MHz, and the results are plotted in Fig. 9. The degradation of the switching charge after 1×10^{11} switching cycles was within 10%. As seen in this figure, the hysteresis loops obtained during the fatigue periods indicate that the BNdT thin film has a strong resistance against fatigue.

4. Conclusion

Ferroelectric BNdT thin films were successfully fabricated on $Pt(111)/TiO_2/SiO_2/Si$ substrates by LDS-MOCVD techniques. The BNdT thin films showed good ferroelectric properties and a low annealing temperature that should satisfy the requirements for high-density and non-volatile memory device applications. The ferroelectric characteristic of the $Bi_{3.61}Nd_{0.39}Ti_3O_{12}$ thin films was optimized at a substrate temperature of 600°C and a reactor pressure of 4.8 Torr. All of the deposited BNdT thin films were fully crystallized to almost randomly oriented polycrystalline structures at annealing temperatures of over 640°C. As a result, well-saturated hysteresis loops are obtained for the BNdT films at a maximum applied voltage of 5 V. The saturated 2Pr and 2Vc values are 31.91 μC/cm² and 3.58 V, respectively. The leakage current density is typically less than 10^{-7} A/cm² at an applied voltage of up to about 3 V. The degradation of the switching charge after 1×10^{11} switching cycles was within 10%. Thus, it is anticipated that ferroelectric BNdT could be used to fabricate high-density FeRAMs.

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