Chapter 7

Electrical Properties of $Bi_{3.25}Nd_{0.75}Ti_3O_{12}$ ferroelectric thin films

7-1. Introduction

Ferroelectric thin films have attracted considerable interest for nonvolatile memory applications. Ferroelectric oxides such as $PbZr_{1-x}Ti_xO_3$ (PZT) and $SrBi_2Ta_2O_9$ (SBT) with perovskite Bi-layered structures are promising materials for film-based devices and have been extensively studied. The PZT and SBT have been extensively investigated as a promising ferroelectric material for nonvolatile random-access memory due to its fatigue-free and low coercive field characteristics. Recently, $Bi_4Ti_3O_{12}$ (BIT), has attracted much attention for potential utilization of thin films for nonvolatile random access memories (NvRAMs), due to its large spontaneous polarization (Ps) and fatigue-free property. Bismuth titanate, BIT, belongs to a class of Aurivillius phases with layer intergrowth structures consisting of alternate stacking of perovskite-like ($Bi_2Ti_3O_{10}$) and fluorite-like (Bi_2O_2) layers. This compound has a high Curie temperature (Tc=675℃) which makes it useful over a wide temperature range either for standard electronic elements or new ones, such as nonvolatile memories. The doping effect is one of the best routes of stabilizing the improved properties superior to those of the parent BIT phase. Some researchers have suggested that ion substitution in BIT crystal may be an effective method for improving the ferroelectric properties, such as La^{+3}, V^{+5} and Nd^{+3} doping or co-doping [130-132]. Watanabe [130] already reported polycrystalline and epitaxially grown films with La-substitution that is effective to obtain superior ferroelectric properties at low deposition temperature, including a low leakage current density. It has been reported for this structure that the rotation of TiO_6 octahedral in the *a*-*b* plane accompanied with a shift of the octahedron along the *a* axis is largely enhanced by the lanthanoid element substitution for Bi in the pseudoperovskite layer.

In this context, an approach for polarization enhancement of polycrystalline $Bi_{3.25}Nd_{0.75}Ti_3O_{12}$ (BNT) film was investigated on SRO/STO/Si substrate fabricated by a metal-organic deposition method. The oxide electrodes with perovskite structure can act as sinks of oxygen vacancies to suppress polarization fatigue and their similarity in lattice parameter and chemical behavior can be expected to enhance the ferroelectric characteristics. The effect of substitution for Bi by Nd [r(Nd^{3+})=1.27Å] with a smaller ionic radius than La [r(La^{3+})=1.36Å] in the pseudoperovskite layer is to improve the ferroelectric properties.

In order to overcome that the remanent polarization of ferroelectric are too large to control the channel conductance of usual metal-oxide -semiconductor (MOS)-FET, a metal-ferroelectric-metal-insulator -semiconductor (MFMIS) structure with a small MFM capacitor on a large MIS capacitor has been investigated in this context.

7-2. Experiment

STO and SRO thin films were deposited on Si(100) substrates by radio-frequency (rf) magnetron sputtering with a ceramic target, respectively. The BNT thin films were prepared by metal-organic decomposition method with the metal-ferroelectric-metal (MFM) structure directly using BNT thin films on SRO/STO/Si substrate. The SBT precursor solution were prepared by using high purity $Bi(OOCCH_3)_3$, $Ti(OCH_2CH_3)_4$, $Nd(OOCCH_3)_3$ as the Bi, Ti, Nd sources and acetic acid and ethylene glycol as solvents. The mole ratios of Bi:Nd:Ti in the MOD solution were 3.25:0.75:3 in order to obtain good electrical characteristics. The BNT thin films were deposited on SRO/STO/Si (in MMN structure), $Pt/Ti/SiO_2/Si$ and $CeO_2/Pt/Ti/SiO_2/Si$ (CeO_2 as a seed) substrates (in MFMIS structure) by spin-coating at 5000 rpm for 30 sec followed by pyrolysis at 150℃ for 10 min to evaporate the solvent, then heated at 450℃ in air for 30 min to eliminate other organic compound. After repeating the process of spin coating and preheating several times, the gel films were crystallized at various temperatures from 550 to 700℃ for 30 min under oxygen atmosphere.

A circular Pt top electrode was deposited on the surface of the BNT film using the rf sputtering method for electrical measurement. The crystalline structure of BNT thin films growth on SRO/STO/Si substrates was investigated by standard X-ray diffraction (XRD) analysis with CuKα radiation at 30 kV and 20 mA. The thickness, microstructure and the surface morphology of BNT thin films were examined by field emission scanning electron microscopy (FESEM Hitachi model S4700). The P-E hysteresis loop and the polarization fatigue characteristic of BNT thin films were measured by RT-66A (Radiant Technologies, Inc) test system with MFM structure at 500 kHz. The leakage current density-electric field (J-E) characteristics were measured at the applied field with a step field of 20 kV/cm and a time interval of 10 s with a Agilent 4155C semiconductor parameter analyzer. The C-V characteristic was measured at 100 kHz for the Pt/SBT/CeO_2/p-Si, Pt/SBT/STO/CeO_2/p-Si structure. The capacitance was measured at 100 kHz as a function of voltage from positive to negative bias.

7-3. Results and Discussion

Figure 7-1 shows the XRD patterns of BNT thin films prepared on $SrRuO_3$/$SrTiO_3$ /Si substrates with various annealing temperatures. It was obtained that all of the films consisted of a single phase of a bismuth layered structure with the preferred (117),(008) orientation. The increase in BNT peak intensity with an increase of temperature implies an improved crystalllinity occurred in the films deposited at higher temperature. The sites of Nd^{+3} were ascertained to be the Bi sites in the pseudoperovskite layer by Raman spectroscopy [133]. An obvious change in the orientation due to the substitution was not observed except that the degree of the (117) orientation was dominant for BNT thin films as shown in Fig. 7-1. That is the Nd^{3+} substitution for Bi did not affect the crystal orientation of the BNT film. Kojima et al. reported [131] that the epitaxial BNT film had larger polarization value than that of epitaxial BLT film, which can be explained by a large tilting of TiO_6 octahedra induced by the Nd^{+3} substitutions. The results indicated that the BNT thin films could form the BNT phase when annealed at temperature as low as 550°C.

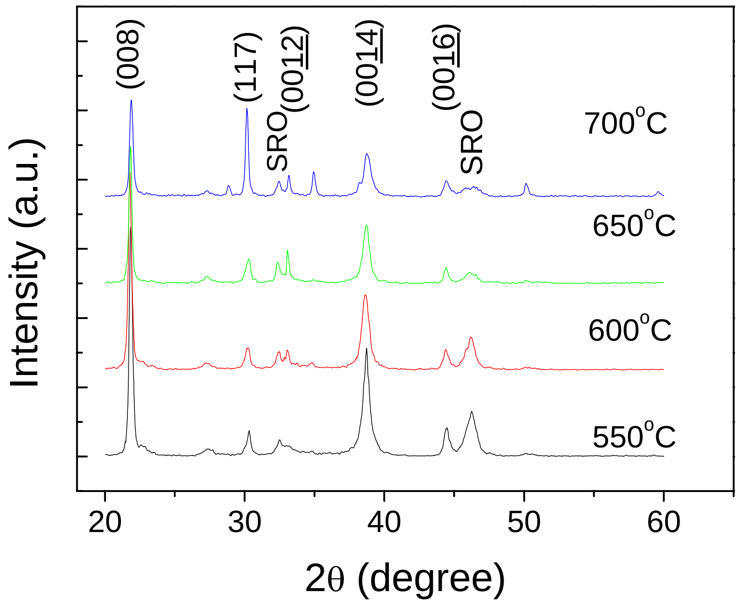
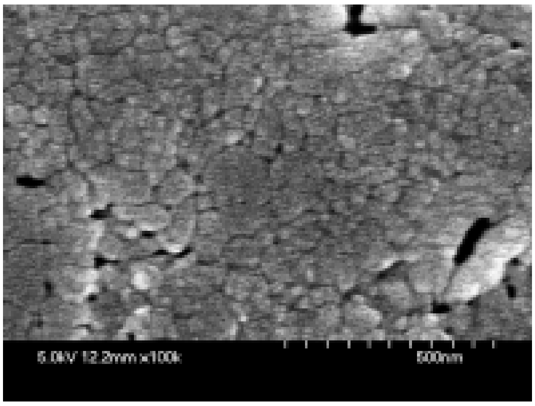
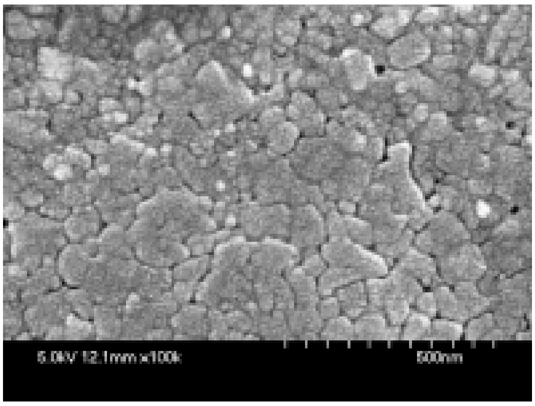


Fig.7-1 XRD patterns of BNT thin films annealed at various temperatures.

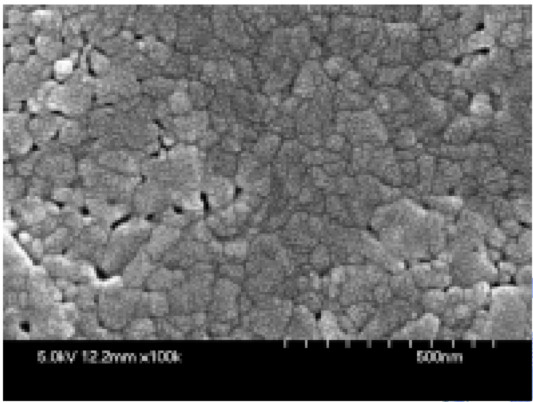
Figure 7-2 shows typical SEM surface and cross section images of BNT thin film annealed at various temperatures. All the films consisted of an isotropic granular structure with diameters of approximately 100 nm, which was considerably different from the platelike or columnar structure. The BNT film formed directly on the SRO/STO/Si substrate exhibits uniform microstructure consisting of large grains. Wang had reported [134] that PZT deposited on SRO could enhance the crystal growth and improve the ferroelectric properties. However, the BNT thin films also show that fine grains tend to become larger due to grain growth during the annealing process. These observations were consistent with previous reports. The thickness of BNT thin film was about 230-250 nm as shown in Fig.7-2(b).



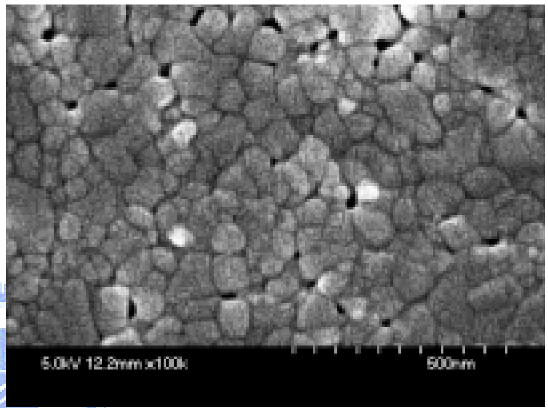
(a) 550°C



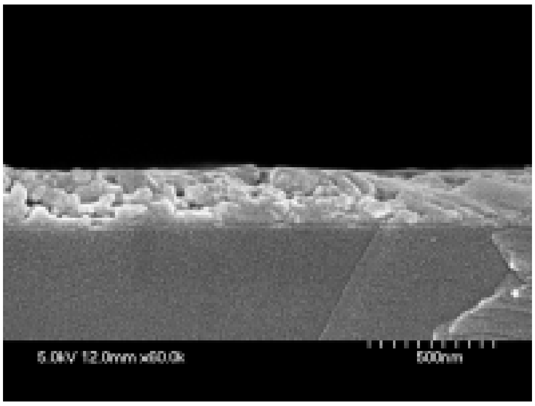
(b) 600°C



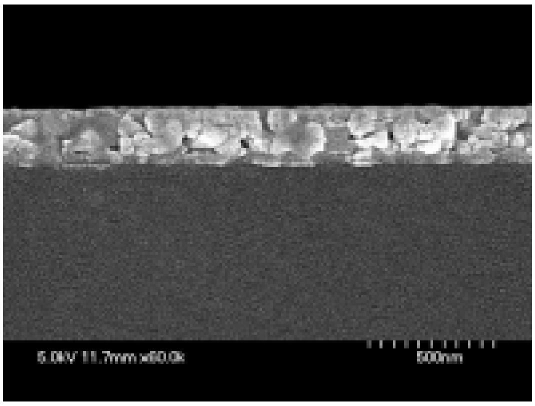
(c) 650°C



(d) 700°C



(e) 550°C



(f) 700°C

Fig.7-2 SEM surface and cross section images of BNT thin film annealed at various temperature.

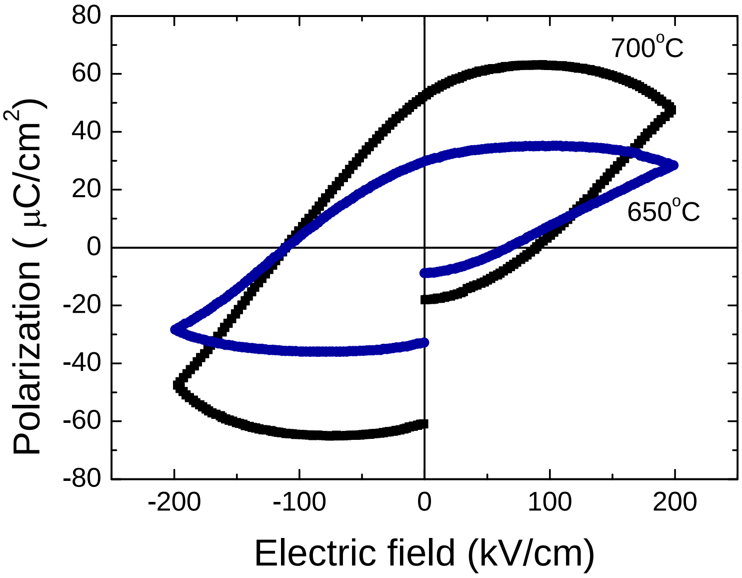


Fig.7-3 Hysteresis loops of the BNT thin film annealed at 650°C and 700°C.

Figure 7-3 shows ferroelectric hysteresis loops measured at maximum applied field (Em) of around 200 kV/cm. The BNT thin film annealed at 700°C has a marked improvement in $2P_r$ than the film annealed at 650°C. The value of P_r and E_c for BNT thin films annealed at 650 and 700°C are 34 (P_r), 58 (E_c), 88 (P_r), 104 (E_c) respectively. The polarization properties were affected by crystallinity of BNT thin film. It shows the higher crystallinity with higher intensity of (117) of BNT annealed at 700°C than annealed at 650°C, which is coincident with XRD pattern of BNT thin film. Another good reason for ferroelectric properties of BNT thin films can be explained by a large tilting of TiO_6 octahedra induced by the substitution of Nd^{+3}, the ionic radius of which is smaller than that of La^{+3}. The enhancement of Pr values of the BNT film over the conventional BLT films would be ascribed to the lattice distortion caused by the Nd-substitution because the lattice strain in these films was larger than that of BLT films.

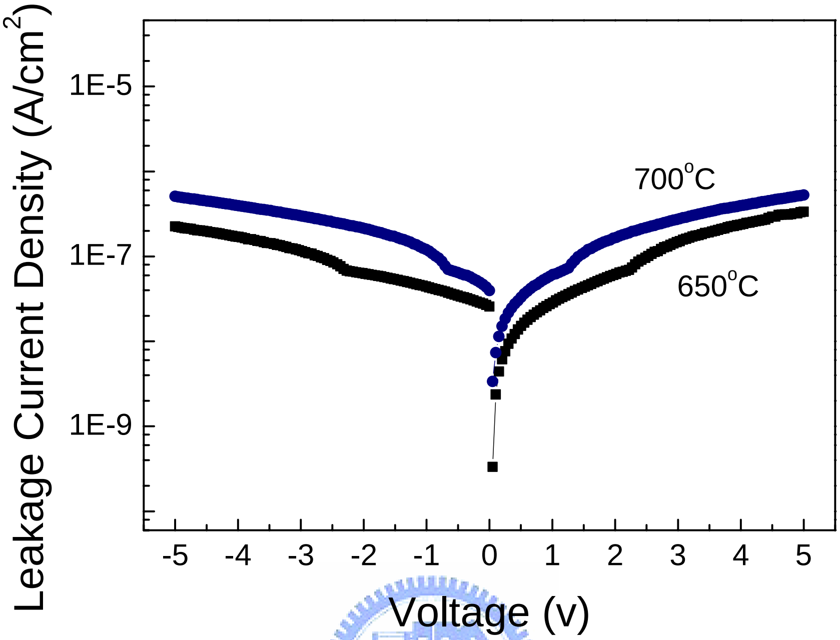


Fig.7-4 The leakage current density of the BNT thin films annealed at 650℃ and 700℃.

Figure 7-4 shows the leakage current density for the Pt/BNT/SRO/STO/Si structure as a function of the applied electric field. The leakage current density of the BNT thin films annealed at high temperature is higher than that annealed at lower temperature. The best leakage character was obtained for the BNT film annealed at 650℃ with a leakage current density on the order of 10^{-9} A/cm^2 for fields up to 200 kV/cm. As shown in Fig. 7-3, the Pr and Ec values of the BNT film annealed at lower temperature did not become saturated and were found to be small value.

Figure 7-5 shows the switching polarization as a function of switching cycles for BNT films annealed at 700℃ using a 1 MHz bipolar square wave at a sufficient applied electric field. A good fatigue resistance of BNT thin film was confirmed up to 10^{10} switching cycles. In the case of polycrystalline BIT films deposited on Pt bottom substrates degradation of the polarization below 10^{10} switching cycles with the same frequency as the present study. This suggests that the substance of the bottom electrode and the quality of the film affect the fatigue character of BNT films.

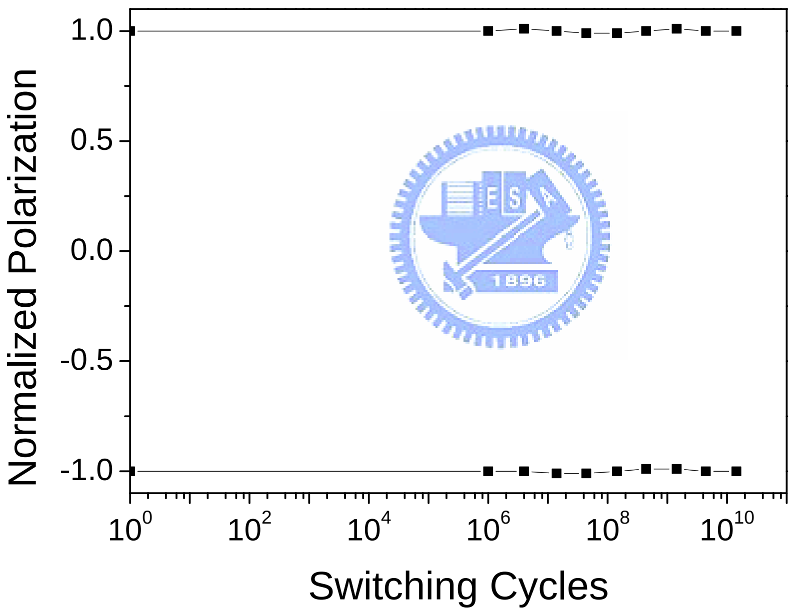


Fig.7-5 Switching cycles of the BNT thin films annealed at 700 ℃ for using a 1 MHz bipolar square wave.

Figure 7-6 was the C-V characteristic of the BNT thin film with various capacitor area ratios in MFMIS (Pt/BNT/Pt/Ti/SiO_2/Si) structure. A gate bias voltage was increased from -5 V to +5 V continuously and decreased from +5 V to -5 V. The amplitude of probing voltage for the capacitance measurements was 0.1 V, and the frequency was 100 kHz. When the gate voltage is increased, the capacitance of the MFMIS capacitor suddenly decreases. While the gate voltage is decreased, the capacitance suddenly goes up. It shows a clockwise hysteresis loop which is due to the ferroelectric characteristics of gate insulator. It is also found that the capacitance changes rapidly, which indicates good interface properties.

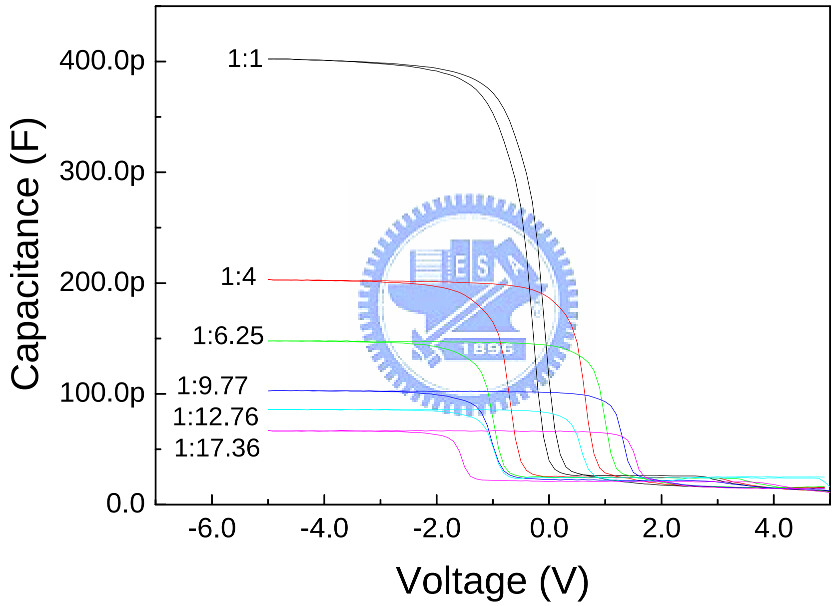


Fig.7-6 C-V characteristics of BNT thin film for Pt/BNT/Pt/Ti/SiO_2/Si (MFMIS) structure.

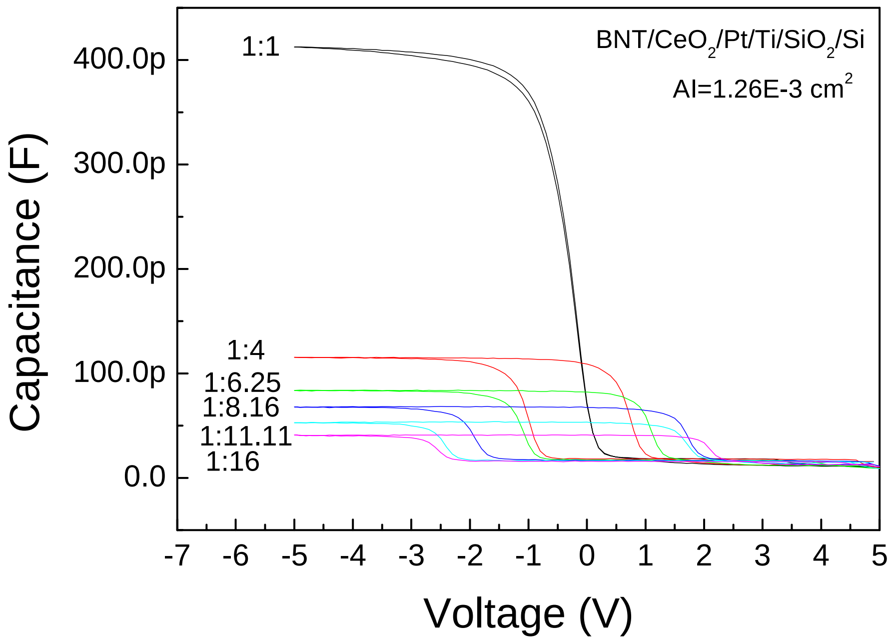


Fig.7-7 C-V characteristics of BNT thin film for $Pt/BNT/CeO_2/Pt/Ti/SiO_2/Si$ (MFMIS) structure.

The large memory window is desirable for the stable and reliable memory operation of the MFMIS structure. To obtain the large memory window, it is effective to use a large coercive field material because the large hysteresis loop of the ferroelectric layer is generated by the larger coercive field. It is also important to apply large enough voltage to the ferroelectric layer to reverse the polarization. If the ferroelectric material in the MFMIS structure has the large relative dielectric constant, the voltage fraction applying to the ferroelectric layer becomes small and the hysteresis loop cannot be observed. So the dielectric constant of the ferroelectric film should be small. By reducing the ferroelectric MFM capacitor area size, it can reduce the polarization of the ferroelectric film and match the induced charge of the MIS capacitor. If the area ratio between the MIS and ferroelectric MFM capacitors is correctly adjusted, it can utilize the saturated loop and large memory window.

In the MFMIS structures, the ferroelectric capacitor area and the MIS capacitor area can be independently designed. When the area ratios become large, the remanent polarization and the dielectric constant of the ferroelectric layer can be equivalently reduced. Hence, the MFMIS structure with a large area ratio, a sufficiently low voltage can be easily applied to the ferroelectric layer and obtain the saturated P-E hysteresis loop, which results in a large memory window. The area ratios between ferroelectric (MFM) and MIS capacitors are varied from 1 to 17.36. The memory window is increased with increasing the capacitor area ratios. The C-V characteristics of BNT films on MFMIS structure with a CeO_2 seeding layer have larger memory window than without ones which is shown in Fig.7-7. The result also showed the clockwise hysteresis loop and the memory window increased with capacitor area ratio increasing from 1 to 16. (as shown in Fig.7-8)

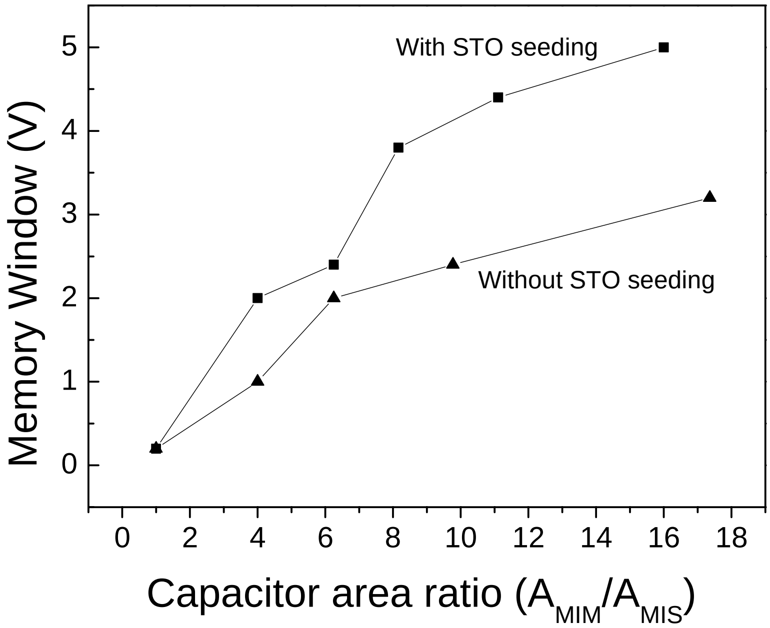


Fig.7-8 Relationship between MFM area-to-MIS area ratio and memory window.

It has been reported that the data retention time of SBT/Si (MFISFET) is only 1-2 h [135] and improving the data retention characteristic is one of the major issues of ferroelectric-gate FET development. Capacitance retention characteristics of the Pt/BNT/CeO_2/Pt/Ti/SiO_2/Si have been evaluated, as shown in Fig.7-9. The Off state is obtained after a positive pulse bias is applied to the gate electrode. The On state is obtained just after a negative pulse bias is applied. The On and OFF state are memorized by applying -5 and +5 V for 0.1 sec, respectively. The memorized MFMIS structure was held at constant voltage to obtain the retention characteristics. Here, retention time is defined as time when the difference between capacitances of the

ON and OFF stated becomes half its initial value. It was found that the retention time of Pt/BNT/CeO_2/Pt/Ti/SiO_2/Si was bout 3200 s at capacitor ratio 16. It is clearly observed that the capacitances of “On” and “OFF” states monotonically decrease and increase, respectively, from the beginning of the hold states. But this behavior of the retention characteristic significantly differs from that predicted by Migita [136] and Kijima [137]. It is assumed that the retention loss is caused by factors other than the leakage through BNT film, such as polarization relaxation of BNT film and carrier trapping induced the depolarization, and very slow ion drift in the BNT film.

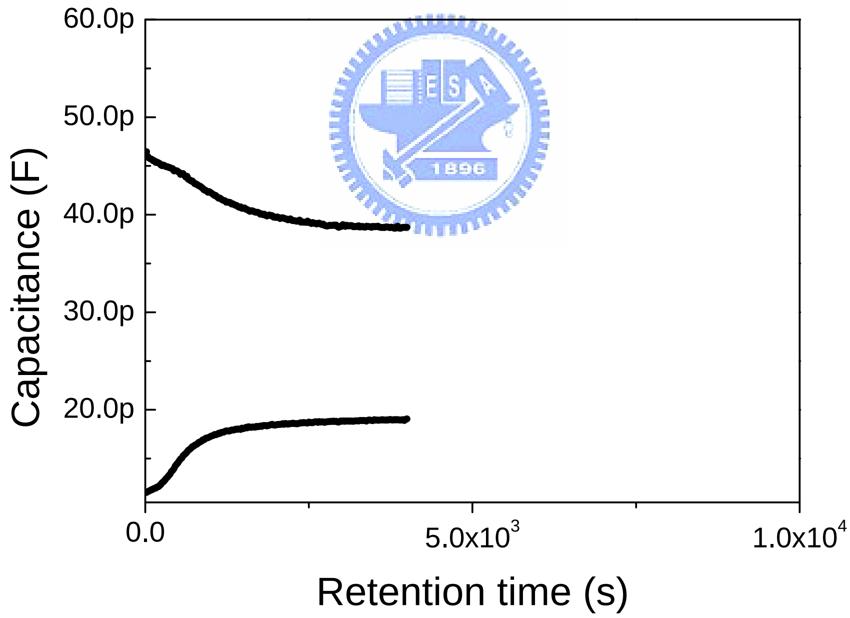


Fig.7-9 Retention characteristics of BNT thin film in the MFMIS structure.

7-4. Summary

Nd-substituted $Bi_4Ti_3O_{12}$ films were successfully grown on

$SrRuO_3/SrTiO_3/Si$ substrates at 550 ℃ by metalorganic deposition method. The films all showed strong (117),(008) preferred orientations. The values of the remanent polarization (Pr) and coercive field (Ec) of the BNT ($Bi_{3.25}Nd_{0.75}Ti_3O_{12}$) thin film annealed at 700℃ were 58 $\mu C/cm^2$ and 104 kV/cm, respectively. The remanent polarization (Pr) values of the Nd-substituted $Bi_4Ti_3O_{12}$ films were found to be larger than those of the BIT, BLT films and were also compatible to those of the commercially used PZT films for Fe-RAM application. A memory window of BNT film with write voltage 5 V was obtained in the MFMIS structures. The memory window of BNT film was increased with increasing capacitor area ratios. The retention time of BNT thin film in $Pt/BNT/CeO_2/Pt/Ti/SiO_2/Si$ (MFMIS) structure with capacitor area ratio 16 is about 3200s.