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$Bi_4Ti_3O_{12}$ Films Grown on SiO_2/Si at Low Temperature by Laser Ablation Method

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Ferroeletric bismuth titanate thin films have been grown on Si and SiO_2/Si substrates by laser ablation method at low temperature. The X-ray diffraction studies show that crystallographic property of the films depend on substrate temperature, O_2 gas pressure, laser repetition frequency and annealing temperature. The c-axis oriented films have been obtained on Si substrate at substrate temperature of 400°C and the annealing at 700°C inproves the crystallinity. The C-V hysteresis loop of bismuth titanate film on SiO_2/Si substrate been have observed corresponding to D-E hysteresis of the film.

1. Introduction

Recently, much attention has been gathered to Bi-based layer-structure ferroelectrics represented by $(Bi_2O_2)^{2+}(A_{m-1}B_mO_{3m+1})^{2-}$(m=1~5), from a viewpoint of application to memory devices. These materials shows useful properties for nonvolatile memory devices[1-4], such as fatigue durability and high structural anisotropy. $Bi_4Ti_3O_{12}$ (BIT) is a typical material of the layer-structure ferroelectric (m=3, A=Bi, B=Ti).[5-7] In recent years, several techniques such as metal-organic chemical vapor deposition (MOCVD),[8-9] rf sputtering,[10-11] sol-gel,[12-13] and laser ablation (pulsed laser deposition) [14-15] have been developed to deposit good-quality BIT thin films. Some researches about preparation of BIT thin films by laser ablation method were reported,[14-15] and generally substrate temperature is so high, for example at 600°C, that the substrate is damaged by atomic diffusion and thermal melting. So, the film should be prepared at low temperature because of reduction of atomic diffusion and thermal damage of Al wiring.

In the present work, BIT films on Si and SiO_2/Si substrates have been prepared at low temperature (450°C) by laser ablation to study basic property for Metal-Ferroelectric-Semiconductor (MFS) FET type memory .

2. Experimental

Schematic diagram of deposition apparatus is shown in Fig. I . Light beam of ArF laser was focused by a quartz lens onto the target rotating in the vacuum chamber. The plume extended from the irradiated point on the target in the direction vertical to the target face. The ablated molecules comprised in the plume pile up on the substrate placed parallel to the target face. Deposition conditions used in the experiment are shown in Table 1. The substrate temperature during the deposition, Ts, was changed from 300 to 500°C and thin SiO_2 layer was formed on Si substrate in the case of heat up in oxygen atmosphere. The chamber was evacuated to a pressure below ~10^{-5} Torr before O_2 gas was introduced up to pressure of 0.01-0.5 Torr.

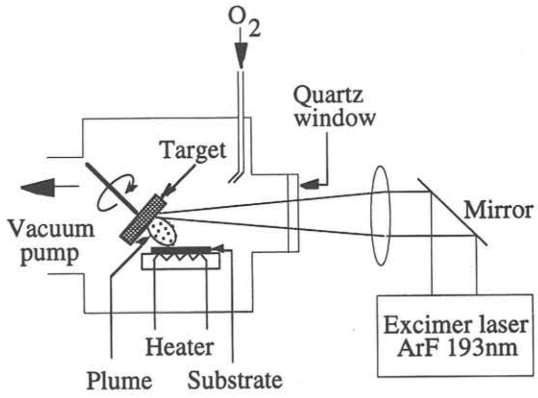

Fig. 1. Schematic diagram of deposition apparatus.

Table I. Deposition condition.

Target	$Bi_4Ti_3O_{12}$ ceramic disk
Substrate	SiO_2/Si,Si
Substrate temperature	300~500°C
Gas pressure	0.01~0.5 Torr
Laser	ArF excimer (193 nm)
Repetition frequency	5 Hz
Beam size	0.3 cm^2
Fluence	2.0~5.0 J/cm^2 shot
Target-substrate distance	2.0cm
Deposition time	30~45 min

The target was a BIT ceramic plate. Bi_2O_3 and TiO_2 powders were mixed with a cation molar ratio of Bi:Ti= 4:3 . The mixture was pressed into a disk shape of 2.5 cm in diameter and 5 mm in thickness and then was sintered for 5 hours at 1100°C. Crystal structures of the deposited films were analyzed by X-ray diffraction (XRD) (RINT 2000) and surface morphology was observed by atomic force microscope (AFM) (Nano Scope II). X-ray photoelectron spectra (XPS) were measured by ESCA-850M(Simadzu Co.).

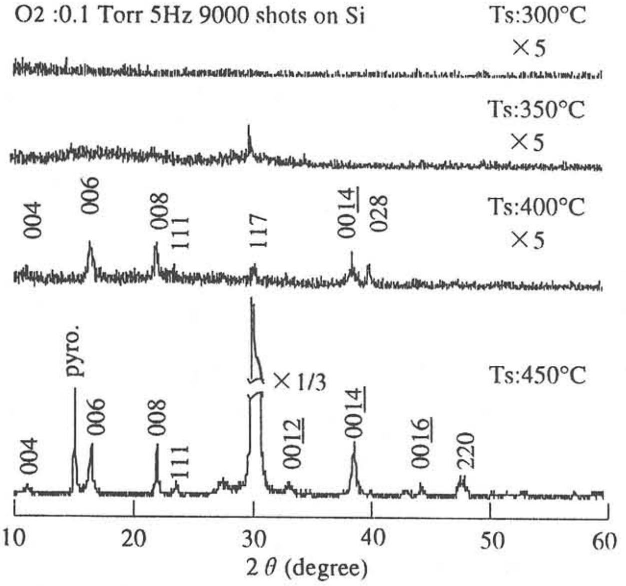

Fig.2. XRD patterns of BIT films as a parameter of substrate temperature. pyro.:pyrochlore structure.

3. Results and discussion

X-ray diffraction (XRD) patterns of the BIT films deposited on Si at different substrate temperatures are shown in Fig. 2. O_2 gas pressure was 0.1 Torr, repetition frequency of laser shot was 5Hz and the total shot number was 9,000. BIT film is amorphous at 300°C, pyrochlore phase appears at 350°C, and perovskite phase is observed at 400°C, but the peaks intensities in XRD pattern are still small. When substrate temperature increases to 450°C, the peaks in XRD pattern become sharp and large, but unexpected pyrochlore phase appears again.

Figure 3 shows the XRD patterns of the films grown on Si at 400°C and various O_2 gas pressures. The repetition frequency is 5Hz and the total shot number was 9000. The peaks of (117) and pyrochlore phase appear for O_2 gas pressure of 0.01 Torr. As O_2 gas pressure was increased to 0.05 Torr, the c-axis-orientation BIT film was the highest. The pyrochlore disappears at 0.1 Torr, but at 0.5 Torr, the pyrochlore is observed with (117) peaks.

Figure 4 is sputtering time dependence of Bi4f and Ti2p XPS spectra of BIT films deposited on Si. Besides Bi2O3 and TiO2, Bi signals are observed and oxidation of Bi is insufficient in deep position of the film. Bi signals are the intensities around 159 eV (oxidized bismuth) and 156.6eV (metallic Bi). Ti signal is that 459 eV and shows oxidized titanium. Intensity of Bi_2O_3 decrease with depth, but TiO_2 and Bi increase. This behavior is similar to the depth profile reported in Pb-based perovskite film.

XRD patterns of BIT films on Si as a parameter annealing temperature are shown in Fig.5. The deposited films were annealed in order to improve the crystalinity. As annealing temperature increases, intensity of the peak (006) increases and c-axis lattice constant decreases, because grain grows and film is densified. After annealing at 800°C, FWHM decreased very much. FWHM at 600°C, 700°C and 800°C are 0.78°, 0.87°,and 0.42°,respectively. When annealing temperature increases, c-axis lattice constant decreases,because

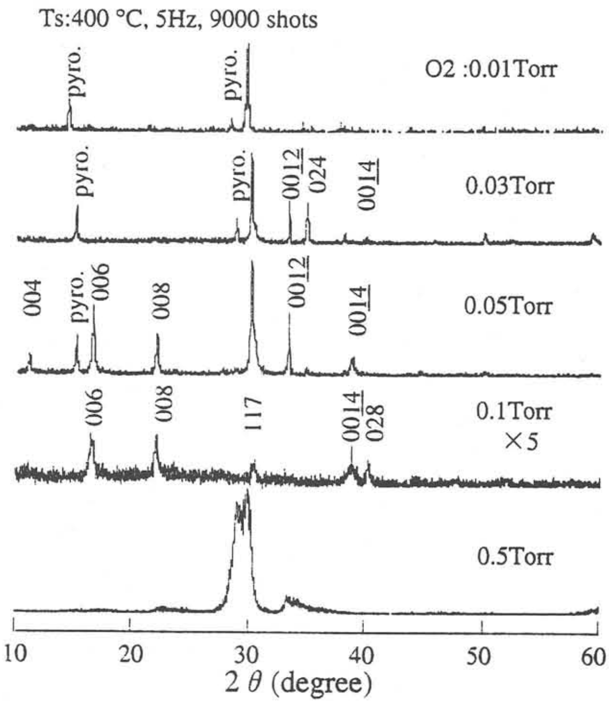

Fig.3. XRD patterns of BIT films as a parameter of O_2 gas pressure. pyro.:pyrochlore structure.

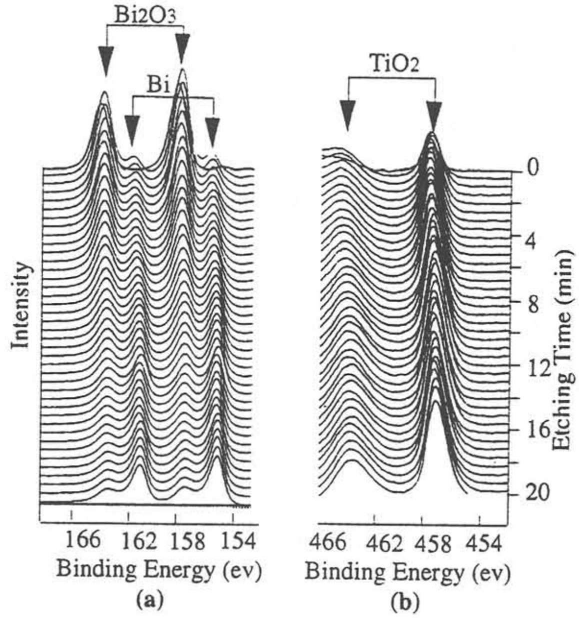

Fig.4. Sputtering time dependence of (a) Bi4f and (b) Ti2p XPS spectra of BIT film deposited on Si substrate.

grain grows and film is densified at high temperature. Thermal expansion coefficients of Si and a-axis of BIT are 0.42 $\times 10^{-5}$/deg.(25°C) and 1.2$\times 10^{-5}$/deg.(300°C), respectively. The thermal expansion coefficient of Si is smaller than that of axis of BIT. Then, BIT film receive expansion stress, when the film deposited at high temperature is cooled. Therefore, lattice constant of c-axis expands and so, that of a-axis shrinks. The c-axis lattice of annealed BIT films are 33.69Å, 32.93Å, and 32.7Å at 600°C, 700°C and 800°C, respectively.The c-axis lattice of BIT ceramic is 32.84Å.

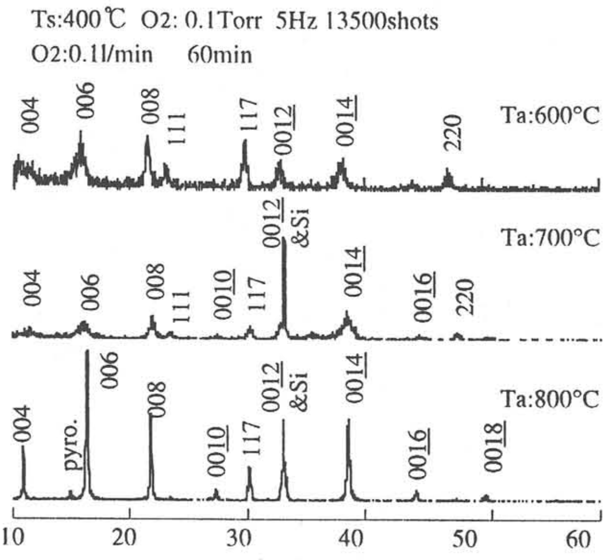

Fig.5. XRD patterns of BIT films on Si as a parameter annealing temperature.

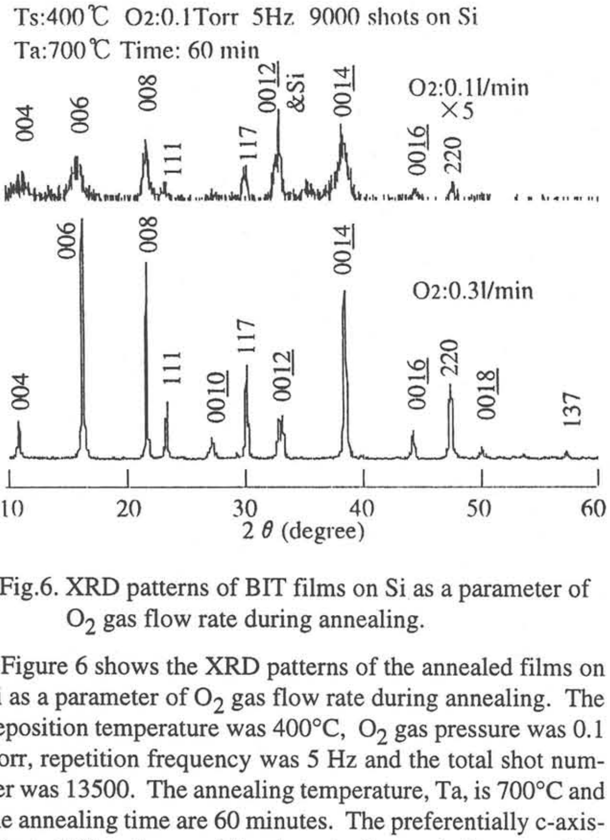

Fig.6. XRD patterns of BIT films on Si as a parameter of O_2 gas flow rate during annealing.

Figure 6 shows the XRD patterns of the annealed films on Si as a parameter of O_2 gas flow rate during annealing. The deposition temperature was 400°C, O_2 gas pressure was 0.1 Torr, repetition frequency was 5 Hz and the total shot number was 13500. The annealing temperature, Ta, is 700°C and the annealing time are 60 minutes. The preferentially c-axis-oriented film of perovskite phase is observed after annealing at O_2 gas flow rate of 0.1l/min. As the O_2 gas flow rate increases to 0.3l/min, the peak intensities increase and FWHM are narrowed. It is considered that grain grows and its size becomes large as O_2 gas flow during the annealing increases.

A typical 1 MHz C-V characteristic for a Pt/BIT/SiO_2/n-Si structure is shown in Fig. 7. BIT film was deposited at 450°C on Si (100) substrate having thin SiO_2 layer of 28 nm grown thermally in dry O_2, and was annealed at 700°C. The C-V plot has a clockwise hysteresis loop which means that ferro-

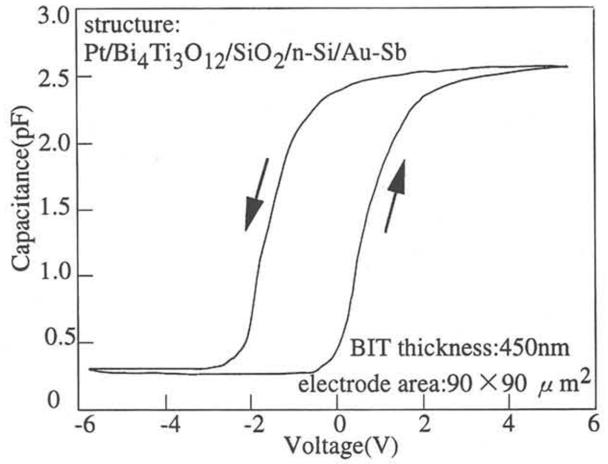

Fig.7 C-V plot of Pt/BIT/SiO_2/n-Si structure.

electric hysteresis controls Si surface potential, although the hysteresis window is small.

4. Conclusions

BIT perovskite thin films have been prepared by laser ablation on Si substrate at low temperature 400°C and 450°C. Annealing at 700°C promotes grain growth and c-axis-oriented growth because intensity of peak increases and FWHM of peak is narrowed. Preferentially c-axis-oriented BIT thin films were obtained on Si at deposition temperature of 400°C with assistance of annealing at 700°C. BIT/SiO2/ n-Si structure shows C-V hysteresis corresponding to ferroeletric hysteresis.

5.Acknowledgmets

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1) H. Buhay, S. Sinharoy, W. H. kasner, M. H. Francombe, D. R. Lampe and E. Stepke: Appl. Phts. Lett. **58** (1991) 1470.
2) R. Ramesh, A. Inam, B. Wilkens, W. K. Can, T. Sands, J. M. Tarascon, D. K. Fork, T. H. Geballe, J. Evans and J. Bullington: Appl. Phys. Lett. **59** (1991) 1782.
3) N. Maffei and S. B. Krupanidn: Appl. Phys. Lett. **60** (1992) 781.
4) W. Jo, G-C. Yi, T. W. Noh, D-K. Ko, Y. S. Cho and S-I. Kwun: Appl. Phys. Lett. **61** (1992) 1526.
5) B. Aurivillius: Ariv Kemi **1** (1949) 463.
6) B. Aurivillius: Ariv Kemi **1** (1949) 499.
7) B. Aurivillius: Ariv Kemi **2** (1950) 519.
8) T. Nakamuwa, R. Muhammet, M. Shimizu and T. Shiosaki: Jpn. J. Appl. Phys. **32** (1993) 4086.
9) K. Yoshimura, S. Okamura and T. Tsukamoto: J.Ceram. Soc. Jpn. **102** (1994) 512.
10) T. S. Kalkur, J. Kulkurni, Y. C. Lu, M. Rowe, W. Han and L. Kammerdiner: Ferroelectrics **116** (1991) 135.
11)Y. Masuda, A. Baba, H. Masumoto, T. Goto, M. Minakata and T. Hirai: Jpn. J. Appl. Phys. **30** (1991) 2212.
12)M. Toyoda, Y. Hamaji, K. Tomono, and D. A. Payne: Jpn. J. Appl.Phys. **32** (1993) 4158.
13)M. Toyoda, Y. Hamaji, K. Tomono, and D. A. Payne: Jpn. J. Appl.Phys. **33** (1994) 5548.
14)H. Buhay, S. Sinharroy, W. H. Kasner and M. H. Francombe: Appl.Phys.Lett. **58** (1991) 1470.
15)R. Ramesh, K. Luther, B. Wilkens, D. L. Hart, E. Wang, J. M. Tarascon, A. Inam, X. D. Wu and T. Venkatesan: Appl. Phys. Lett. **57** (1990) 1505.