2004년도 대한전기학회 전기물성·응용부문회 추계학술대회 논문집 (2004.11.5-11.6)

$Bi_{3.25}Eu_{0.75}Ti_3O_{12}$ 박막의 구조 및 강유전 특성에 미치는 $LaNiO_3$ 전극의 영향

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Effect of $LaNiO_3$ electrodes on Structural and Ferroelectric Proerties of $Bi_{3.25}Eu_{0.75}Ti_3O_{12}$ Tnin films

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Abstract - $Bi_{3.25}Eu_{0.75}Ti_3O_{12}$ (BET) thin films were deposited on the $LaNiO_3$ (LNO (100))/Si and $Pt/Ti/SiO_2/Si$ substrates by the metal-organic decomposition method. Structural and dielectric properties of BLT thin films for the applications in nonvolatile ferroelectric random access memories were investigated. Both the structure and morphology of the films were analyzed by x-ray diffraction (XRD) and atomic force microscope (AFM). Even at low temperatures 650 °C, the BET thinfilms were successfully deposited on LNO bottom electrode and exhibited (001) and (117) orientation. Compared with the Pt electrode films, the BET thin films on the LNO electrode annealed at 650 °C showed better dielectric constantsand remanent polarization. The BET thin films on the LNO electrode for the annealing temperature of 650 °C, the remanent polarization *Pr* and coercive field were 45.6 C/cm2 and 171 kV/cm, respectively.

1. 서 론

Ferroelectric thin films have been widely investigated due to their potential applications in ferroelectric random access memories (FeRAMs), pyroelectric detectors, and nonlinear optical thin films [1-4]. Lead zirconiumtitanate (PZT) thin films have been the most intensively investigated. The reasons are that PZT has advantagessuch as low processing temperature and large remanent polarization values. However, PZT films on Pt/Ti electrodes have a fatigue problem during electric field cycling, which affords only a limited number of switching cycles to the FRAMs [5]. The layered perovskite compounds containing bismuth (such as $SrBi_2Ta_2O_9$ (SBT) and $Bi_4Ti_3O_{12}$ (BTO)) are important materials associated with the application of FRAMs [6-8].

The SBT thin films have received considerable attention because of their good electric and ferroelectric properties for use in FRAMs, such as low leakage currents and low coercive fields. Moreover, they have fatigue-free properties with simple Pt electrodes during repeated polarization reversals with electric-field cycles. However, for high-density integration of FeRAMs, SBT films have some serious disadvantages, such as high processing temperature (i.e., above 800 °C) and low remanent polarization (*2Pr*: 20 C/cm^2). Park et al. reported on new $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films fabricated by using a pulsed laser deposition method at 650 °C [9]. The BLT thin films showed fatigue-free characteristics and large remanent polarizations. The fatigue-free behavior of SBT and BLT thin films is explained by the charge compensating effect of the Bi_2O_2 layers, resulting in the reduction of space charges, and by the unpinning of domain walls, which occurs as rapidly as domain wall pinning [10]. However, SBT and BLT thin films have a disadvantage for high density integration in NVRAMs in that they have a low remanent polarization (*2Pr* for SBT = 20 C/cm^2, and for BLT = 27C/cm^2) [3]. The ferroelectric properties, the crystal structure, and the microstructure of BIT thin films are influenced by the substitution of different-sized ions in these bismuth layer-structured compounds. Shimakawa *et al.* reported that TiO^6 octahedra in pseudo-perovskite blocks show a shift of the octahedron along the a-axis, which is greatly enhanced when (e.g, La, Pr, Nd, Sm, Eu, etc.) are substituted for Bi in the pseudo-perovskite blocks [11]. Chon *et al.* reported Sm-substituted $Bi_4Ti_3O_{12}$ (BIT) (*2Pr* of BSmT = 49 C/cm^2)to be fatigue free with a large remanent polarization [12]. In addition, our previous reported that the Eu-substituted BIT showed a *2Pr* value (*2Pr* of BET = 60.99 C/cm^2) with fatigue free [13]. However, the annealing temperature of BET thin films was an 800 °C, which was still higher annealing temperature than BLT or PZT thin films. $LaNiO_3$ (LNO) films have attracted attention in few last years using a conducting material for applications in ferroelectric memories [14]. The LNO material hasthe same perovskite-type structure with a lattice constant of 0.38 nm, which matches well ferroelectric and dielectric material such as BST, and PZT perovskite materials. The similarity in crystal structure and lattice constants between the electrode and ferroelectric thin films produces the better lattice matching and favorable structural, and thus ferroelectric properties. Since the BET films for FeRAMs are not widely studied, the main purpose of our work includes to use LNO as the metal oxide bottom electrode and to offerthe benefits of better lattice matching to grow BET thin films with the lower annealing temperatures.

In this paper, we carried out an investigation aimed at reducing the annealing temperature of BET thin films on LNO bottom electrode fabricated using metal-organic decomposition (MOD) method.

2. 실 험

The precursor solutions for $Bi_{3.25}Eu_{0.75}Ti_3O_{12}$ were prepared by using the MOD method with bismuth acetate, europium acetate, and titanium iso-propoxide as the starting materials. The solid-state bismuth acetate and europiumacetate were initially dissolved in acetic acid and then mixed together to obtain Bi and Eu stock solutions. Titanium iso-propoxide was dissolved in 2-methoxyethanol under a N2 atmosphere. Finally, both starting solutions were mixed together to prepare the stoichometric, clear, transparent, and stable BETprecursor. An 10% excess amount of bismuth acetate was used to compensate for the Bi loss that occurs during the annealing process. BET precusor solutions were spin-coated on the LNO(100)/Si and Pt(111)/Ti/SiO2/Si substrates, and then pre-baked on a hot plate at 400 °C for 10 min to remove the organic materials. The pre-baked film was annealed at 650 °C for 1 h in the oxygen atmosphere to obtain crystallization. The final thickness of BET thin film was about 200 nm. Measurements of dielectric properties were carried out in the metal-insulator-metal (MIM) capacitor cell. For these purposes, top Pt electrodes with diameter of 300 m were deposited on the BET films by dc sputtering method. The powder precusors were examined using thermogravimetric analysis (TGA) / differential scanning calorimetry (DSC). X-ray diffraction (XRD) profiles were obtained using a CuK radiation source at 30 kV and 60 mA (Rigaku-D/MAX) to determine the crystallinity of the BET thin films. The surface microstructures of the films were examined using a atomic force microscope (AFM Digital Instruments NanoScope IIIa). The plan-view microstructure of the BET thin films was investigated using high resolution transmission electron microscopy (HR-TEM). The dielectric constant and loss were measured using an HP 4192 impedance analyzer. The ferroelectric properties were examined using a precision workstation ferroelectric tester (Radiant Technologies, USA). The fatigue test was measured at room temperature and the data retention test was conducted at both room temperature and high temperature.

3. 본 론

Firstly, we studied the thermal decomposition behaviors of the BET precursor solutions by using TGA / DSC. For this purpose, the precursor solutions were dried at 80 °C for 24 hto produce dry BET powders. Then, the dry BET powders were continuously heated at a rate of 10°C/min up to 800°C in open air. The kinetics for the weight loss is presented in Fig. 1. As determined from the TGA curve, the weight loss of the BET powder was about 31.05% at 800C. In our opinion, several mechanisms are responsible for the weigh loss. Firstly, the weight loss between the temperatures of 103 and 257°C corresponds to an endothermic peak. We assume that this mechanism results from the evaporation of the solvents. Secondly, the weight loss in the temperature range of 257 - 340°C corresponds to exothermic peaks and is caused by the combustion of residual organic compounds. The exothermal shoulder peak at 570°C can probably be attributed to the formation of the BET crystalline structure. Further heating up to 800°C does not lead to additional weight loss.

Figure 2 shows XRD patterns of the BET thin films deposited on the Pt(111)/Ti/SiO2/Si and LNO(100)/Si substrates annealed at 650 °C 1 h. As shown in Fig. 1, all the BET thin films annealed at 650 °C showed the typical XRD patterns of $Bi_4Ti_3O_{12}$. All the films show a well-developed perovskite structure with no evidences of secondary phases formation. We assume that LNO bottom electrodes play an important role of nucleation site for the formation of BET thin films. The positive role of LNO may be caused by the decrease in nucleation activation energy that allows us to obtain better crystallization at lower temperatures. Therefore, the annealing temperature of BET thin films on the LNO electrode is lower than that of BET thin films with Pt electrode. The BET thin film deposited on Pt(111)/Ti/SiO2/Si substrate (Fig. 2(a)) exhibit (117)-oriented structure, while the film was grown on LNO/Si substrate(Fig. 2(b)) showed (001)-oriented structure. The degree of preferred orientation of each film is roughly estimated with the relative intensity ratio $(117) = I(117)/(I(117) + I(001))$ or $(001) = I(001)/(I(117) + I(001))$, where I is peak intensity of the each film [12]. The (001 and 117) values of the BET thin films deposited on LNO substrate and Pt electrode were 0.54 and 0.71, respectively. The values derived from XRD suggest that the BET films deposited on LNO/Si substrate were crystallized with (001) preferred orientation. The results mentioned above indicate that the crystallization and growth of the BET thin films are influenced by the substrate was used. Particularly, (100)-oriented LNO thin film as a substrate provides (001) preferred orientation for BET films due to well matching of the lattice parameter between the LNO and BET film.

Figures 3 shows the typical AFM micrographs of BET thin films corresponding to Pt electrode and LNO electrode. The surfaces of BET thin films are uniform and crack free. However, the film on the Pt electrode has non-uniform microstructure consisted of small grains and coarse grains but the film on the LNO electrode has larger grains. The coarse grains seem to be a kind of weakly crystalline bismuth layered perovskite phase. Therefore we suggest that the BET films on the Pt electrode cannot be crystallized completely if the annealing temperature is 650 °C. We have found also that, as the using the LNO electrode, theBET films should complete crystallization annealed at 650 °C. Based on this data, it is possible to expect that the BET films on the LNO/Si substrate annealed at 650 °C will improve the ferroelectric properties of BET thin films through the improved crystallization.

For the more detailed investigation on the plan-view microstructure of the BET film on the Pt bottom electrode and LNO electrode were studied by HR-TEM. Figure 4 shows the surface TEM image of the BET on the Pt electrode and LNO electrode specimens annealed at 650 °C (Fig. 4(a)) and (Fig. 4(b)). In these figures, the bright spot at the surface BET/Pt may be identified as the weakly crystalline bismuth layered perovskite phase. The results were obtained may be explained by grain growth rates produced among different grains in oxide thin film. However, the BET thin films deposited on the LNO substrates show the larger grains compared with the BET thin films on the Ptsubstrates. These results correspond to AFM images. The dielectric constant and dielectric loss at 1 kHz of BET thin films on the Pt electrode and LNO electrode were 313, 352, and 0.067, 0.043, respectively. In this experiment, we have found higher dielectric constant using LNO electrode that may be related to the grain size. Accordingly, the lower value of dielectric constant with Pt electrode was obtained for the films annealed at 650 °C. In our opinion, the reasons are poor crystallinity as well as coarse grain size. Also, the dielectric loss showed higher value for the films with Pt electrode than that of films with LNO electrode. It is well known that the dielectric loss in ferroelectric and dielectric materials is affected by various factors such as space charge polarization, crystallinity, domain wall pinning, secondary phase, and interfacial diffusion. Therefore, highest dielectric loss obtained for the films with Pt electrode annealed at 650 °C may be explained by poor crystallinity.

Figure 5 show the polarizationelectric field (P-E) hysteresis curves of the BET thin film with Pt electrode and LNO electrode annealed at 650 °C. These ferroelectric properties are relatedto content stoicheometry, grain size and crystallinity of the film. As the using the LNO electrode films showed higher remanent polarization than that of BET film with Pt electrode. Additionally, it can be seen that the polarizations for the BET thin films on the Pt electrode annealed at 650 °C are significantlysuppressed compared with the films on the LNO electrode. A noticeable improvement of ferroelectric properties mentioned abovemay be attributed to better crystallization and larger grain size. The BET thin films with LNO electrode annealed at 650 °C show remanent (2*Pr*) value of about 45.6 C/cm2, which is quite comparablewith the result of for BET films on the Pt electrode ($2P r$ = 60.9 C/cm^2) annealed at 800 °C.

Figure 6 shows the results of polarization fatigue experiment for the Pt/BET/Pt and Pt/BET/LNO thin films. The test was performed at room temperature using 5 V, 100 kHz bipolar square pulses. In this figure, normalization *Pnv*is the difference between switchable (P*) and non-switchable (P^) polarizationvalues. It can be seen that, Pt/BET/LNO capacitors showed fatigue-free behavior after 5 × 10^9 switching cycles. However, the BET thin films with Pt electrode show a noticeably worse fatigue behavior under the same conditions. The probable reason of this result is the pinned domain walls, which inhibits switching of the domains. Fatigue has been related primarily to electronic and pining and unpinning of domain walls during polarization reversals. The pinning of domain may be caused by generation of space charges due to lower crystallization temperature [11]. BET thin films annealed at 650 C on LNO bottom electrode exhibited no significant degradation of switching charge at least up to 5 × 10^9 switching cycles at a frequency of 100 kHz and 5 V.

4. 결 론

In this work, we have shown that BET films with high remanent polarization, low losses and fatigue free can be prepared onto the LNO/Si substrate annealed at 650 °C by metal organic decomposition method. AFM analysis showed uniform surface. The BET films directly grown on the Pt/Ti/SiO2/Si substrates showed (117) orientation. The BET thin films are crystallized preferably with (001)-oriented grains on LNO bottom electrode annealed at 650 C for 1h. We assume that LNO bottom electrodesplay an important role of nucleation site for the formation of BET thin films. This may be caused by the decrease of nucleation activation energy. A Pt/BET/LNO capacitor annealed at 650 °C showed excellent ferroelectricty, remanent polarization *Pr* and coercive voltage *Ec* are 45.6 C/cm2 and 171 kV/cm, respectively. Additionally, the BET thin films deposited on LNO substrate exhibited no significant degradation of switching charge at least up to 5 × 10^9 switching cycles at a frequency of 100 kHz below cycling fields of 5 V.

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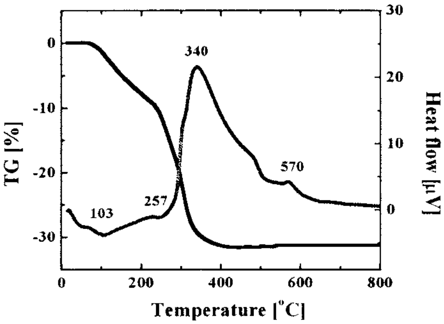

Figure1.DSC/TGAcurvesofthedriedBET powders.

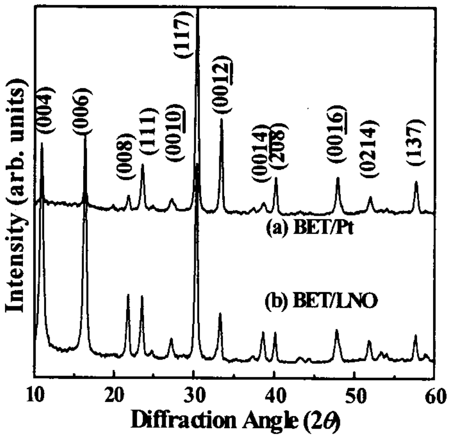

Figure2.XRDpatternsof(a)BET/Pt(111)/Ti/SiO2/Si and(b)BET/LNO/Si

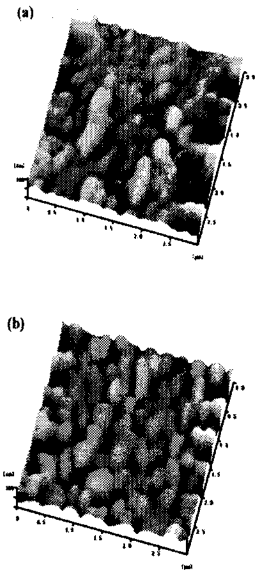

Figure3.AFMimagesoftheBETthinfilmsdepositedon:(a)Ptbottomelectrode,and(b)LNObottomelectrodeannealedat650°C.

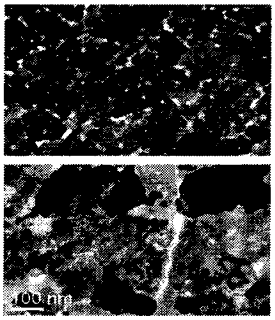

Figure4.Plan-viewTEMmicrographsoftheBETthinfilmsdepositedon:(a)Ptbottomelectrode,and(b)LNObottomelectrodeannealedat650°C.

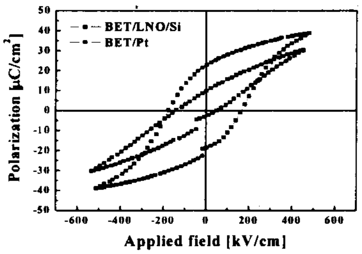

Figure5.P-EhysteresiscurvesoftheBETthinfilmsdepositedon:(a)Ptbottomelectrode,and(b)LNObottomelectrodeannealedat650°C.

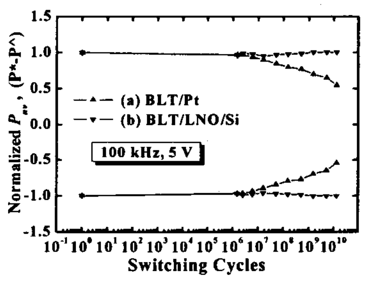

Figure6.ThefatiguebehavioroftheBETthinfilmsdepositedon:(a)Ptbottomelectrode,and(b)LNObottomelectrodeannealedat650°C.