MOD법으로 제작한 $Bi_{3.25}La_{0.75}Ti_3O_{12}/LaNiO_3$ 박막의 강유전 특성에 관한 연구

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Ferroelectric properties of $Bi_{3.25}La_{0.75}Ti_3O_{12}/LaNiO_3$ thin films prepared by metalorganic decomposition method

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Abstract

$Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) thin films were prepared by using metal organic decomposition method onto the LaNiO3 (LNO) bottom electrode.Both the structure and morphology of the films were analyzed by x-ray diffraction (XRD) and atomic force microscope (AFM). Even at low temperatures ranging from 450 to 650°C, the BLT thinfilms were successfully deposited on LNO bottom electrode and exhibited (117) orientation. The BLT thin films annealed as low as 600°C showed excellent ferroelectricity, higher remanent polarization and no significant degradation of switching charge at least up to 5×10^9 switching cycles at a frequency of 100 kHz and 5 V. For the annealing temperature of 600°C, the remanent polarization P_r and coercive field were 23.5 μC/cm^2 and 120 kV/cm, respectively.

Key Words : BLT; Thin Film; MOD; FeRAM

1. 서 론

Bismuth layered structure ferroelectrics (BLSFs) thin films have been widely investigated aimed at applications in nonvolatile ferroelectric random access memories (FRAMs). The reason is that this family of compounds has superior properties, such as a high fatigue resistance during electric field cycling with a Pt electrode. Among BLSFs, $SrBi_2Ta_2O_9$ (SBT) and BLT have attracted a dominant attention. However, the SBT films have some serious drawbacks, such as high processing temperatures (above 800°C) and low remanent polarization of 4-16 μC/cm^2, which is insufficient for the high-density integration of FRAM [1]. In the case of $Bi_4Ti_3O_{12}$ (BTO) thin films, BTO single crystals have a large spontaneous polarization (Ps) of 45 μC/cm^2 [2], which is three times higher than that of SBT. The BTO is monoclinic structure with the space group $B1a1$ and with the lattice constant of c-axis of about 3.284 nm. Thisvalue is considerably larger than that for the other two axes (a = 0.544 nm, b = 0.541 nm) at room temperature. Because the BTO thin films are

highly *c*-axis oriented, the spontaneous polarization is much lower than that of a-axis oriented BTO film. The reason is that the polarization axis lies on the *a*-*c* plane with closing to the *a*-axis. Many processing techniques have been employed to solve the problem of low polarization [3]. It was found that although the La substitution modifies the structure of BTO thin films, the BLT showed the characteristics similar to BTO films. That is why the growth of non-c-axis oriented films is required to achieve a higher polarization component along the normal to the film plane.

Another problem is that to use the BLT thin films in high-density devices (for example, in FRAMs) a decrease in annealing temperature is needed to reducethe thermal degradation of earlier formed structure. In previous works, the BLT films have been fabricated by various deposition methods suchas sol-gel, laser ablation, and metal-organic chemical vapor deposition. However, several researches reported that the temperature of 650-700 C or higher is required to produce perovskite layered BLT thin films.

In this paper, we carried out an investigation aimed at reducing the annealing temperature of (117)-oriented BLT thin films on LNO bottom electrode fabricated using metal-organic decomposition (MOD) method..

2. 실 험

The BLT films were fabricated on the LNO bottom electrode. First, the LNO thin films were prepared by the MOD method. The precursor materials were lanthanum acetate, and nickel acetate. Acetic acidand de-ionized water were used as the solvents. Initially, the equal moles of lanthanum and nickel acetate were dissolved separately in acetic acid under constant stirring at room temperature. Then, the stock solutions were mixed and stirred at room temperature. The total concentration of the synthesized solution was 0.25M. The final solution became transparent and green colored. The LNO solutions were spun to a Si (100) substrate using the spin-coating method [4000 rpm, 30 s], and then pre-baked on a hot plate at 400°C for 10 min. The pre-baked film was annealed at 650°C for 1 h in the oxygen atmosphere to obtain crystallization. The total thickness of the LNO films was about 130 nm.

The BLT thin films were synthesized according to the formula of $Bi_{4-x}La_xTi_3O_{12}$ (x=0.75). The starting precursor materials were bismuth acetate, lanthanum-acetate hydrate, and titanium iso-propoxide. Solvents for the precursors were acetic acid and 2-methoxyethanol, respectively. A 10% excess of bismuth acetate was used to compensate for the Bi-loss that occurs during annealing process. The BLT films were deposited onto the LNO/Si(001) substrate using the spin-coating method. The spinner operated at 4000 rpm for 30 s. After the spin-coating, the substrate was dried at 400°C for 10 min. For crystallization, the all pre-baked films were annealed at temperatures ranging from 500 C to 650°C, for 1 h in a tube furnace under an oxygen atmosphere. For the electrical measurements, 150-nm-thick Pt top electrodes were fabricated onto BLT thin films with a diameter of 200 m by dc magnetron sputtering using a shadow mask.

The crystalline structures of the BLT thin films were analyzed using X-ray diffraction (XRD) with a Rigaku-D/MAX diffractometer with CuK emission. 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).

3. 결과 및 고찰

Figure 1 shows XRD patterns of the BLT/LNO/Si thin films annealed at temperatures ranging from 500 to 650°C. As the annealing temperature increases to 500°C, the BLT thin

film begins to crystallize. This fact indicates that the beginning of crystallization to a layered perovskite is below 500°C. As shown in Fig. 1, the BLT thin films annealed above 500°C showed the typical XRD patterns of $Bi_4Ti_3O_{12}$. It can be seen also that all the films have a Bi-layered structure with a preferred (117) orientation and no pyrochlore phase. We assume that LNO bottom electrodes play an important role of nucleation site for the formation of BLT 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.

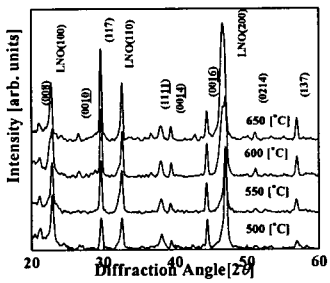

Figure 1. X-ray diffraction patterns of BLT films as a function of annealing temperature.

Figures 2 shows the typical AFM micrographs of BLT thin films corresponding to annealing temperatures of 550 ~ 650°C. The surfaces of BLT thin films are uniform and crack free. However, the films annealed at 500°C have non-uniform microstructure consistedof small grains and coarse grains. The coarse grains seem to be a kind of weakly crystalline bismuth layered perovskite phase. Therefore we suggest that the BLT films cannot be crystallized completely if the annealing temperature is lower than 500°C. We have found also that, as the annealing temperature increases, the grain size of the BLT films increases too. Based on this data, it is possible to expect that the increase in annealing temperature will improve the ferroelectric properties of BLT thin films through the improved crystallization.

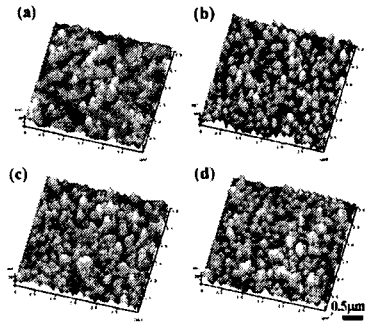

Figure 2. AFM images of surface roughness of the BLT thin films annealed at (a) 500°C, (b) 550°C, (c) 600°C, and (d) 650°C.

Figure 3 shows the dielectric constant and the dielectric loss at 1 kHz of BLT thin films annealed at different temperatures. In this experiments, we have found increasing dielectric constant with increasing annealing temperatures that may be related to variations in the grain size. Accordingly, the lower value of dielectric constant was obtained for the films annealed at 500°C. In our opinion, the reasons are poor crystallinity as well ascoarse grain size. Figure 3 shows also that the dielectric loss decreaseswith increasing annealing temperatures. 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 annealed at 500°C may be explained by poor crystallinity. The BLT thin films annealed at 600°C have a dielectric constant of 271 and a dielectric loss of 1.73 %. These values are comparable with those obtained for BLT thin films annealed at 650°C using pulse laser deposition.

Figure 4 shows the polarization electric field (P-E) hysteresis curves of the BLT thin film annealed 550°C as well as the remanent polarization and coercive field of the BLT thin film annealed in the range of 550 - 600°C. These

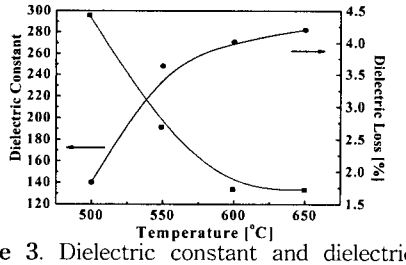

Figure 3. Dielectric constant and dielectric loss of BLT thin films as a function of the annealing temperature

ferroelectric properties are related to content stoicheometry, grain size and crystallinity of the film. As the annealing temperature increases, the remanent polarization also increases while the coercive field decreases. Additionally, it can be seen that the polarizations for the BLT thin film annealed at 500°C [Fig. 4(a)] are significantly suppressed compared with the films annealed at temperatures above 550°C. A noticeable improvement of ferroelectric properties mentioned above may be attributed to better crystallization and larger grain size. The BLT thin films annealed at 600°C show remanent ($2Pr$) value of about 23.5 μC/cm^2 which is quite comparable withthe result of [8] for BLT films annealed at 650°C using the pulse laser deposition ($2Pr$ = 24 μC/cm^2).

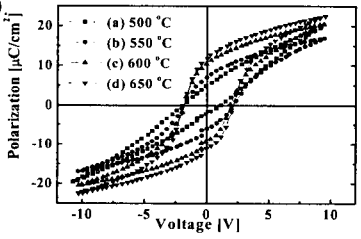

Figure 4. P-E hysteresis curves of the BLT thin films annealed at (a) 550°C, (b) 600°C, (c) 650°C and (d) 700°C..

Figure 5 shows the results of polarization fatigue experiment for Pt/BLT/LNO thin films. It can be seen that, Pt/BLT/LNO capacitors showed fatigue-free behavior after 5×10^9 switching cycles. However, the BLT thin films annealed at 500 and 550°C 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. The pinning of domain may be caused by generation of space charges due to lower crystallization temperature.

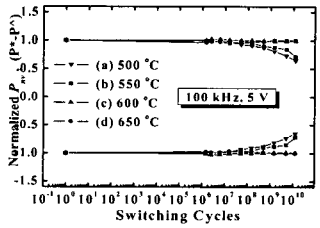

Figure 5. The fatigue behavior of BLT thin films as a function of the annealing temperature.

4. 결 론

BLT thin filmswere prepared by using metal organic decomposition method. AFM analysis showed uniform surface. The BLT thin films are crystallized preferably with (117)-oriented grains on LNO bottom electrode annealed at 550 C for 1h. We assume that LNO bottom electrodes play an important role of nucleation site for the formation of BLT thin films. This may be caused by the decrease of nucleation activation energy.

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