# Preparation of $(Bi,La)Ti_3O_{12}$ Thin Films on $Al_2O_3/Si$ Substrates by the Sol-Gel Method

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$(Bi,La)Ti_3O_{12}$(BLT) ferroelectric thin films were prepared on $Al_2O_3/Si$ substrates by the sol-gel method. The as-coated films were post-annealed at the temperature of 650℃ and 700℃ for 30 min. The crystallinty, surface morphologies and electrical properties were affected by the annealing temperatures. The BLT films annealed at above 650℃ exhibited typical bismuth layered perovskite structures with (00*l*) preferred orientation. The granular shaped grains with a size of approximately 90nm was formed in the film sample annealed at 700℃. The memory window volatge of the BLT film was 2.5 V. The leakage current of BLT films annealed at 650℃ was about $1\times10^{-7}$ A/cm$^2$ at 3 V .

## 1. Introduction

As modern electronic devices such as mobile phones and notebook computers become to be popular, there has been considerable focused to ferroelectric non-volatile memory devices. Ferroelectric random access memories (FRAM) have good features such as high speed operation, low power consumption and large scale integration. FRAM is a RAM-based device that use the ferroelectric effect for a charge storage mechanism. The ferroelectric effect is the ability of a material to store an electric polarization in the absence of an applied electric field (Pr). Nowadays, Bismuth-layer-structured ferroelectric materials, such as $SrBi_2Ta_2O_9$ (SBT), $(Bi,La)Ti_3O_{12}$ (BLT) and $SrBi_2Nb_2O_9$ (SBN) are known as promising materials for the non-volatile FRAM application due to their good fatigue properties, low leakage current and high remanent polarization.[1-6] BLT is one of the most promising candidates for FRAM. The technologies should be developed to prevent the FRAM devices from inter-diffusion between deposited film layers during the annealing process by means of a low temperature process and optimization of the buffer layer materials. In this work, BLT thin films were prepared on $Al_2O_3/Si$ substrates by using the sol-gel method. The dependences of the crystallinity and the electrical properties were investigated.

## 2. Experimental Procedure

The BLT ferroelectric thin films were coated on $Al_2O_3/Si$ substrates by the sol-gel method. The BLT sol-gel solution was spin-coated onto the substrates with a rotational speed of 2500 rpm for 30 seconds. The spin-coated films were baked in a hot plate at 330℃ to remove residual solvent. The coating and drying cycles were repeated 5 times. For the crystallization of as-coated BLT films, the annealing process was conducted at temperatures of 650 ℃ and 700 ℃ for 30 minutes under an air ambient. For the electrical measurements, Pt top electrode was deposited onto the BLT film layer by using DC sputtering through a metal shadow mask to form ferroelectric capacitors. Annealing at 470 ℃ in $O_2$ ambient was carried out for 10 minutes in the furnace in order to obtain good ohmic contact between the Pt top electrode and the BLT thin film. The crystalline structures of the films were analyzed using X-ray diffractometer (XRD). The surface and cross-sectional morphologies were examined using field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM), respectively. The chemical compositions and impurity contents of the films were examined by auger electron spectroscopy (AES). The capacitance-voltage (C-V) characteristics was also measured by using HP4155B and HP4180A.

## 3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of the BLT films coated on the $Al_2O_3$/Si substrate as a function of annealing temperatures. The as-coated BLT films showed the amorphous structures. However, the films annealed at above 650℃ exhibited typical bismuth layered perovskite structures with (00*l*) preferred orientation. The peak intensities of the films increased as the annealing temperature increased from 650℃ to 700℃.

Figure 2 shows the AES depth profiles of the films coated on $Al_2O_3$/Si substrates which were annealed at 700℃. The AES results show that no significant interdiffusion was found at the interface between the BLT film and $Al_2O_3$ insulator layer.

Figure 3 shows the FE-SEM surfacial morphologies of the (a) as-coated BLT thin film and the films annealed at (b) 650℃ and (c) 700℃ on $Al_2O_3$/Si substrates. The surfacial morphology of the as-coated films was found to be relatively smooth and the grain growth was occurred at the annealimg temperature of above 650℃. The granular shaped grains with a size of approximately 90nm was formed in the BLT film annealed at 700℃.

Figure 4 shows the capacitance versus voltage characteristics of the annealed BLT films at 700℃ coated on $Al_2O_3$/Si substrates. The film samples showed typical ferroelectric hysteresis property which is originated from remanent polarization caused by the electric field effect in the BLT films. The window volatges were calcualted from these C-V hysteresis loops. The window volatge of the film was found to be 2.5 V at the applied bias volatege of 5V.

The current densities of the BLT films as a function of the annealing temperatures of 650℃ and 700℃ are shown in figure 5. The current density of the as-coated film was about $6.1\times10^{-9}$ A/cm$^2$ and increased to $1.4\times10^{-7}$ A/cm$^2$ at 3 V when the BLT films were annealed at 650℃. That result can be explained by the grain growth and volatility of Bi component caused by the increased annealing temperature as seen in the FE-SEM morphologies.

## 4. Conclusions

$(Bi,La)Ti_3O_{12}$(BLT) ferroelectric thin films were coated on $Al_2O_3$/Si substrates by the sol-gel method and then post-annealed at 650℃ and 700℃ for 30 minutes. The annealed BLT films were exhibited c-axis oriented perovskite crystalline structures. The BLT film showed a dense microstructure with a granular grain shapes. The window volatge of the BLT film annealed at 700℃ on $Al_2O_3$/Si substrate was found to be 2.5 V at the bias volatege of 5V. The leakage current of the annealed film was about $1.4\times10^{-7}$ A/cm$^2$ at 3 V.

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## References

[1] S. H. Hwang and H. J. Chang, J. Korean Phys. Soc. 41, 139 (2002).
[2] M. Noda, H. Sugiyama and M. Okuyama, Jpn. J. Appl. Phys. 38, 5432 (1999).
[3] J. K. Yim and H. J. Chang, J. Korean Phys. Soc. 39, 232s (2001).
[4] H. J. Chang, K. J. Suh, M. Y. Kim and G. K. Chang, J. Korean Phys. Soc. 32, 1679s (1998).
[5] B. H. Park , B. S. Kang, S. D. Bu, T. W. Noh, J. Lee and W. Jo, Nature, 401, 682 (1999).
[6] T. Nakamura, Y. Nakao, A. Kamisawa and H. Takasu, Jpn. J. Appl. Phys. 33, 5307 (1994).
[7] D. Akai. M. Ishida, Annual Report No.15, Electron Device Group, Toyohashi Univ. of Technology. (2001) p.46.

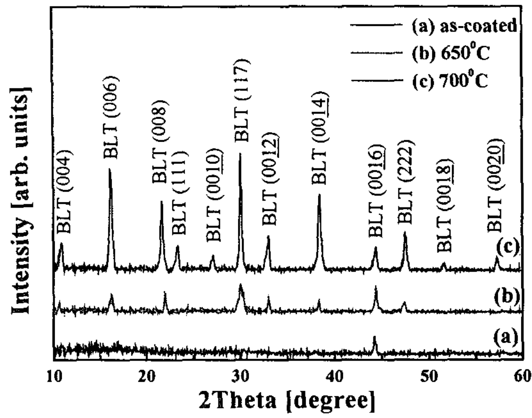


Fig.1 XRD patterns of the as-coated BLT thin films and annealed at 650℃ and 700℃ on $Al_2O_3$/Si substrate.

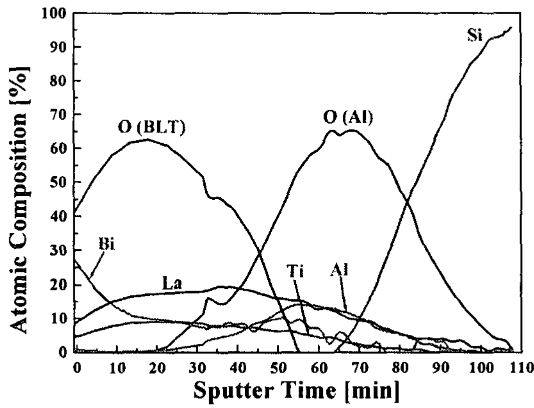


Fig.2 AES depth profile of the BLT film annealed at 700℃ on $Al_2O_3$/Si substrate.

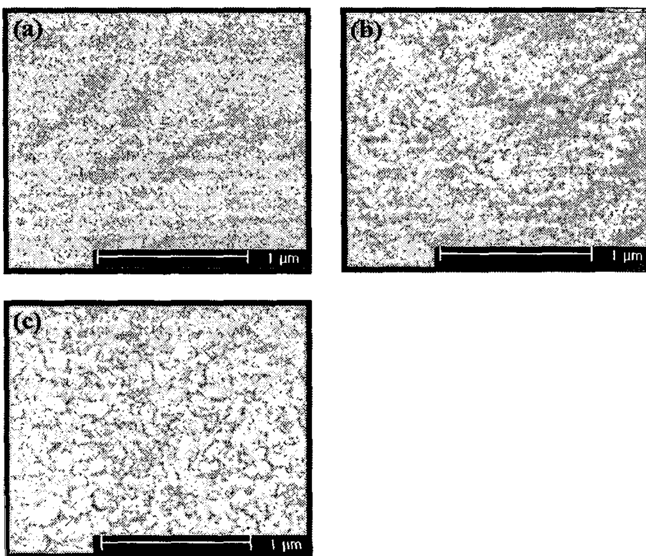


Fig.3 FE-SEM surfacial morphologies of the (a) as-coated BLT films and the ones annealed at (b) 650℃ and (c) 700℃ on $Al_2O_3$/Si substrate.

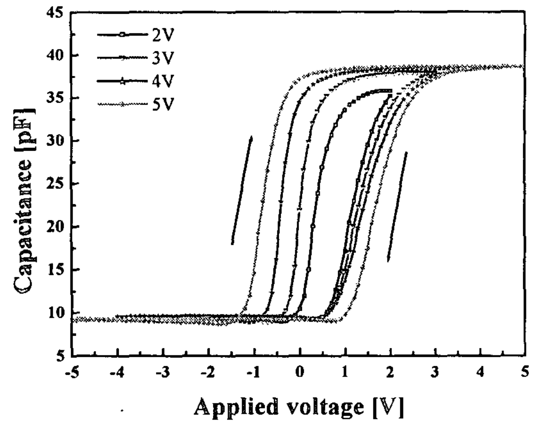


Fig. 4 Capacitance-Voltage characteristics of BLT thin film annealed at 700℃ on $Al_2O_3$/Si substrate.

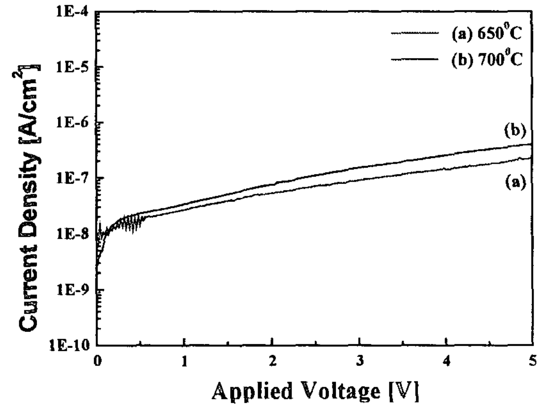


Fig.5 Current-Voltage curves of BLT thin films annealed at (a) 650℃ and (b) 700℃ on $Al_2O_3$/Si substrates.