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Crystalline and electrical properties of $(Bi,La)Ti_3O_{12}$ thin films coated on Al_2O_3/Si substrates

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Abstract

$Bi_{4-x}La_xTi_{3.0}O_{12}$ (BLT, $x=0.67$–0.70) ferroelectric thin films were prepared on a single crystalline aluminum oxide film onto Si substrate (c-Al_2O_3/Si), and amorphous phase aluminum oxide film onto Si substrates (a-Al_2O_3/Si) by the sol–gel method. In order for crystallization, the as-coated films were annealed at the temperature of 650 and 700 °C for 30 min. The crystalline quality, surface morphologies and electrical properties were affected by the substrate types as well as the annealing temperature. The BLT films annealed at above 650 °C exhibited typical bismuth layered perovskite structures with (00*l*) preferred orientation. From X-ray diffraction analyses, the BLT films coated on c-Al_2O_3/Si substrate were higher in reflection peaks and smaller in full width at half maximum (FWHM) values compared with the ones coated on a-Al_2O_3/Si substrate. The R_{rms} value of the film annealed at 700 °C on c-Al_2O_3/Si substrates was three times smaller than that of the film coated on a-Al_2O_3/Si substrate, showing a rather smooth surface when it was coated on c-Al_2O_3/Si substrate. The memory window voltage of the BLT film coated on c-Al_2O_3/Si substrate was 2.5 V, which is about twice compared with the one coated on a-Al_2O_3/Si substrate. The leakage current of BLT film annealed at 650 °C was approximately 1×10^{-7} A/cm^2 at the applied voltage of 3 V for both samples.

Keywords: Sol–gel processing; $(Bi,La)Ti_3O_{12}$; Aluminum oxide layer; Ferroelectric thin film

1. Introduction

As modern electronic devices such as mobile phones and notebook computers became popular, there has been a considerable focus on ferroelectric devices, particularly, the non-volatile memory devices. Ferroelectric random access memories (FeRAM) have good features such as high speed operation, low power consumption and large scale integration [1,2]. There are two kinds of ferroelectric non-volatile memory devices. One is the memory device with a transistor and ferroelectric storage capacitor and another is the metal–ferroelectric-insulator-semiconductor field effect transistor (MFIS-FET). MFIS-FET has advantages over the ferroelectric storage capacitor types because of non-destructive read-out capability and high memory density.

Until recently, some fabrication methods such as sol–gel method, metal–organic decomposition, RF magnetron sputtering and pulsed laser deposition have been prepared and demonstrated [3–6]. Bismuth-layer-structured ferroelectric materials, such as $SrBi_2Ta_2O_9$, $(Bi,La)Ti_3O_{12}$ (BLT) and $SrBi_2Nb_2O_9$ are known as promising materials [7,8] for the non-volatile FeRAM application due to their good fatigue properties, low leakage current and high remnant polarization [9–13]. In particular, the BLT is one of the most promising candidates for FeRAM. The technologies should be developed to prevent the FeRAM devices from inter-diffusion through the interface between ferroelectric film layer and Si substrate by means of a low temperature process and an optimization of the buffer layer materials.

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For the breakthrough in the FeRAM technologies, it is essential to characterize the various properties of BLT films systematically. In this research, BLT thin films were prepared on two different types of substrates such as a-Al_2O_3/Si (amorphous alumina on Si substrate) and c-Al_2O_3/Si (single crystalline alumina on Si substrate) by using the sol–gel method. The dependences of the crystalline and electrical properties on the annealing temperatures were investigated, and we compared the properties between two types of samples.

2. Experimental procedure

Two types of substrates with different crystalline properties in the insulation buffer layers were used in this experiment. One is a substrate, which has epitaxially grown single crystalline Al_2O_3 film with a thickness of 150 Å on Si substrates, which is used as an insulation buffer layer (herein-after called as 'c-Al_2O_3/Si') for the growth of BLT layer. Epitaxial Al_2O_3 films were grown on Si substrates by the pyrolysis of N_2-bubbled trimethyl aluminum and oxygen in a ultra high vacuum–chemical vapor deposition chamber with a hot wall system [14]. The substrate temperature for the Al_2O_3 growth was 890 °C, whereas the other one is a substrate, which has amorphous Al_2O_3 film structure on Si substrate, used as an insulation buffer layer (herein-after called as 'a-Al_2O_3/Si'). Amorphous Al_2O_3 films were deposited on Si substrates by DC sputtering method at the substrate temperature of 500 °C under the oxygen ambient.

Fig. 1 shows the reflection high energy electron diffraction (RHEED) patterns of the (a) a-Al_2O_3/Si and (b) c-Al_2O_3/Si substrates. The RHEED pattern of c-Al_2O_3 thin film shows a streak pattern, indicating a single crystal structure with a smooth film surface. However, there were no distinct reflection patterns on the a-Al_2O_3/Si substrate showing amorphous phase.

The BLT ferroelectric thin films were coated on these a-Al_2O_3/Si and c-Al_2O_3/Si substrates by the sol–gel method. The BLT sol–gel solution was synthesized using a bismuth 2-ethylhexanoate ($Bi[C_4H_9CH(C_2H_5)COO]_3$), titanium tetra-isopropoxide ($Ti[(CH_3)_2CHO]_4$) and lanthanum isopropoxide ($La[(CH_3)_2CHO]_3$) with 2-methoxyethanol ($CH_3OC_2H_4OH$) solution as a dilution. Each BLT reagent was mixed with 2-methoxyethanol in a flask and heated at 160 °C for 1 h under stirring condition. For the preparation of complex alkoxide solutions, Ti precursor solution was added to the lanthanum acetate hydrate and bismuth 2-ethylhexanoate with 60% nitric acid (HNO_3) and 2-methoxyethanol as solvent. Finally, some of the solvents are removed by distillation at 160 °C for 6 h to obtain the desired concentration of 0.1 mol%. A volatile temperature of Bi component is relatively low with a melting temperature of 272 °C under atmospheric pressure. Therefore, it is generally seen that the excessive Bi component is incorporated in the source materials in order to compensate for the loss of this volatile component in the film during sputtering or post-annealing at a high temperature of 650–750 °C [15,16]. In this experiment, the excessive Bi component with 8 mol%, was added in the precursor solution to compensate for its volatility during the annealing process. The sol–gel solution was spin-coated onto the substrates in two steps, with a rotational speed of 400 rev./min for 5 s and then 2500 rev./min for 30 s, to obtain a uniform coating on the film surface. After spin coatings, the films were baked on a hot plate at 330 °C to remove the residual solvent. The coating and drying cycles were repeated five times. For crystallization of BLT films, the annealing was conducted at the temperatures of 650 and 700 °C for 30 min 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 °C in O_2 ambient was carried out for 10 min in the furnace in order to obtain a good contact

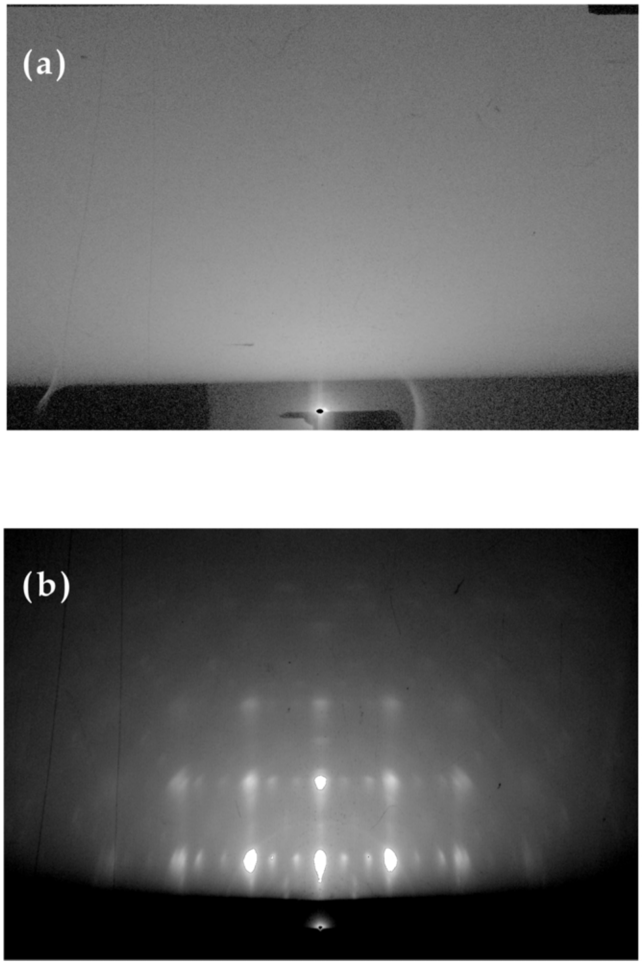


Fig. 1. Reflection high energy electron diffraction patterns of the (a) a-Al_2O_3/Si and (b) c-Al_2O_3/Si substrates.

Table 1
The atomic molar ratios of the BLT films according to the annealing temperatures

Annealing temperature	Atomic molar ratio		
	Bi	La	Ti
As-coated	3.29–3.31	0.67–0.70	3.01–3.02
650 °C	3.14–3.15	0.69–0.72	3.10–3.11
700 °C	3.03–3.07	0.68–0.70	3.20–3.21

between the Pt top electrode and the BLT thin film. The indium was also used as a lower electrode.

The SiO_2 layer on the backside of silicon substrate was removed by the etching solution with distilled hydrogen fluorine (HF) (HF/D.I water = 1;10) prior to the back electrode deposition of indium.

The crystalline structures of the films were analyzed using X-ray diffractometer (XRD) with Cu–Kα radiation (wave length, $\lambda = 1.54$ Å) at 40 kV bias voltage, and the scan speed was 3° per minute with 10–60° in the scan range. The surface and cross-sectional morphologies were examined using field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM), respectively. In addition, the AFM images were measured by semi-contact method with NTMDT SPM P-47 apparatus. The chemical compositions and impurity contents of the films were examined by Auger electron spectroscopy (AES) and electron probe micro analyzer (EPMA). The AES operating conditions were 5 Å/min in the sputtering rate with beam voltage of 10 keV. The analytical area of the AES sample is 20 μm in square with etching power of 5 mA and 5 keV under Ar ambient with 60° in angle. The electrical properties, such as the leakage current and capacitance–voltage (C–V) characteristics of MFIS capacitors were measured by using 4155B and HP4180A.

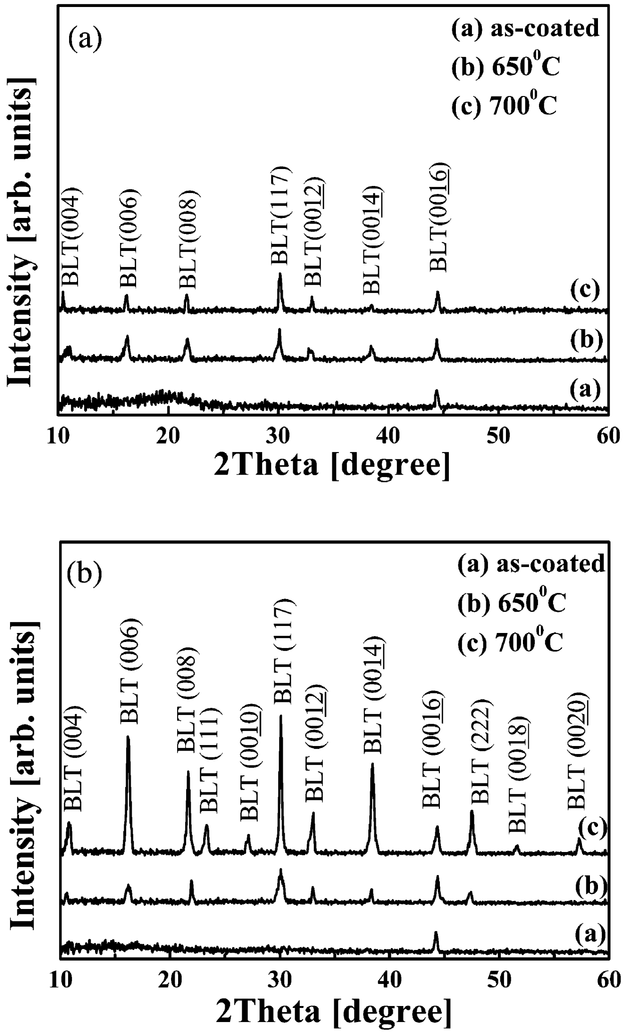


Fig. 2. X-ray diffraction patterns of the BLT thin films annealed at various temperatures on (a) a-Al_2O_3/Si and (b) c-Al_2O_3/Si substrates.

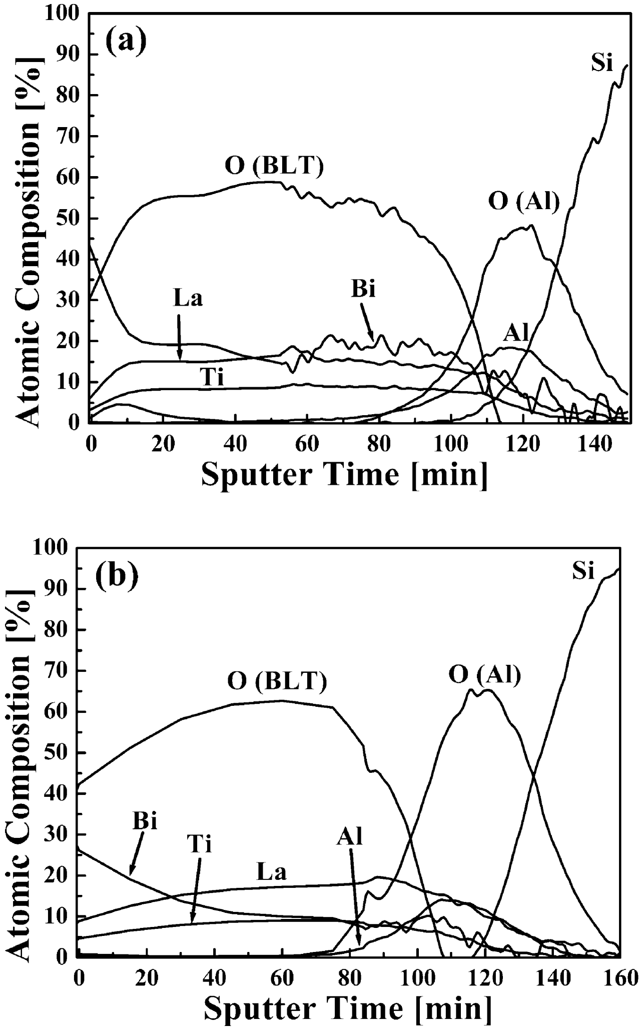


Fig. 3. AES depth profiles of the BLT films annealed at 700 °C on (a) a-Al_2O_3/Si and (b) c-Al_2O_3/Si substrates.

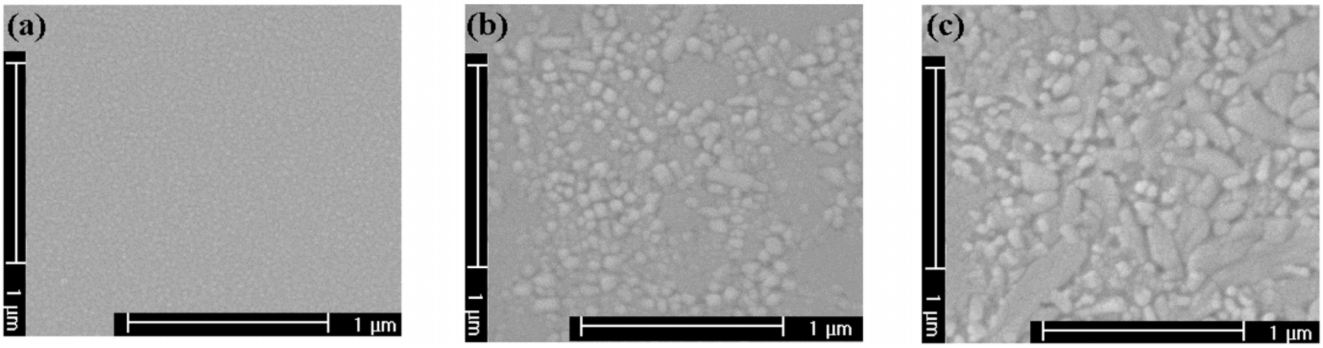


Fig. 4. FE-SEM surface micrographs of the (a) as-coated BLT film and the films annealed at (b) 650 °C and (c) 700 °C on a-Al_2O_3/Si substrates.

3. Results and discussion

To investigate the atomic molar ratios of BLT thin films, we used EPMA to analyze the films. The atomic ratio of the as-coated film was found to be non-stoichiometry with the average molar formula of $Bi_{3.3}La_{0.7}Ti_{3.0}O_{12}$. The Bi content decreased by approximately 8 mol% when the annealing temperature was increased to 700 °C, resulted in the volatility of the Bi component during the annealing. Table 1 shows the atomic molar ratios of the as-coated BLT film and the ones annealed at 650 and 700 °C.

Fig. 2 shows the XRD patterns of the BLT films coated on the (a) a-Al_2O_3/Si and (b) c-Al_2O_3/Si substrates as a function of annealing temperature. The as-coated BLT films showed almost amorphous structures with the weak BLT (0016) peak at approximately $2\theta = 44°$ (degree). From the XRD measurement, the appearance of BLT peak for the as-coated film may be caused by the partial crystallization with preferred direction when the as-coated films were baked at 330 °C on the hot plate. It is also reported that the crystallization at lower temperature of 350 °C in the $Sr_{0.7}Bi_2Ta_2O_9$ (SBT) films is believed to be related to the existence of excessive Bi components [17]. In contrast, the BLT films post-annealed at above 650 °C were crystallized completely and exhibited typical bismuth layered perovskite structures with (00*l*) preferred orientation. This result indicates that the grains of BLT films coated on Al_2O_3/Si substrates may be grown preferentially along *c*-axis orientation during the high temperature annealing at 650 and 700 °C. The BLT films coated on c-Al_2O_3/Si substrate at an annealing temperature of 700 °C showed higher peak intensities and larger *c*-axis orientation than those of the film samples coated on a-Al_2O_3/Si substrates. In addition, the peak intensities increased as the annealing temperature increased from 650 to 700 °C. To investigate the crystallization of the BLT films, the full width at half maximum (FWHM) values were also observed between the film samples. The FWHM value of (117) reflection peak of the BLT films annealed at 700 °C coated on a-Al_2O_3/Si substrate was approximately 0.26°, and decreased to 0.20° when the film was coated on c-Al_2O_3/Si substrate. As a result of the XRD measurement, we found that the films coated on c-Al_2O_3/Si substrate showed better crystallization compared with the ones coated on a-Al_2O_3/Si substrate. From the Scherrer formula [18], the crystal size of the BLT film annealed at 700 °C on c-Al_2O_3/Si substrate was calculated to be approximately 14 nm.

The depth profiles of the films were measured to confirm the interfacial reactions and the compositional variations across the film interfaces.

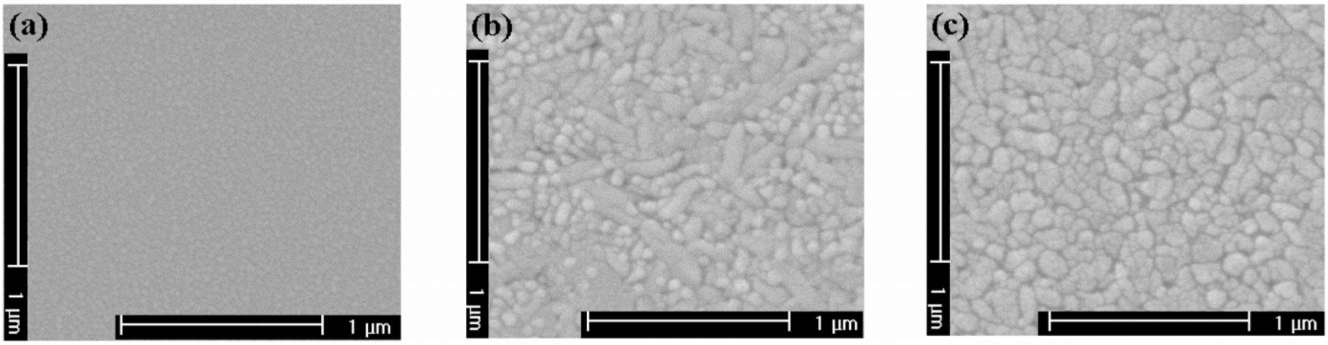
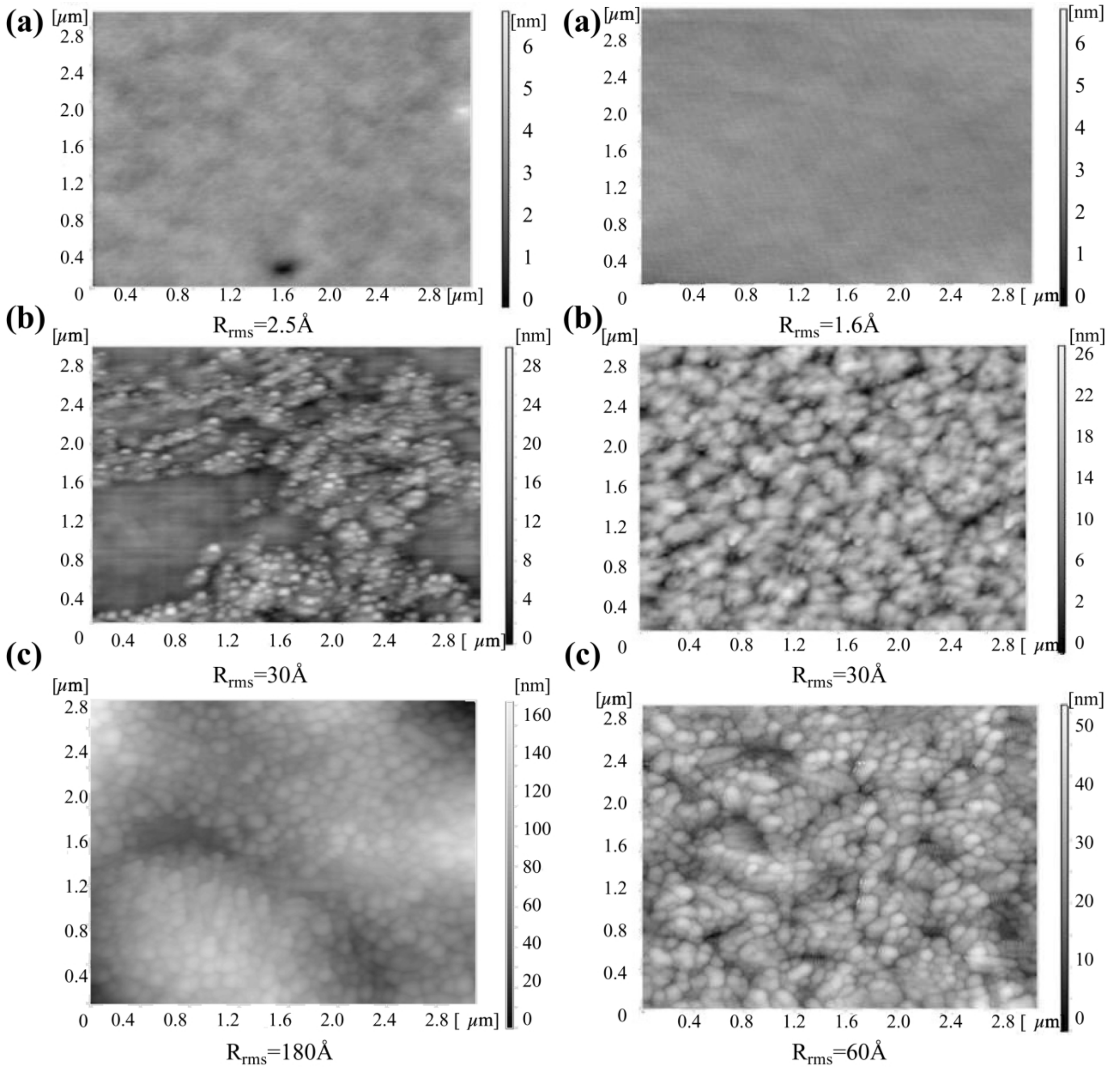


Fig. 5. FE-SEM surface micrographs of the (a) as-coated BLT film and the films annealed at (b) 650 °C and (c) 700 °C on c-Al_2O_3/Si substrates.



(A) a-Al_2O_3/Si substrate (B) c-Al_2O_3/Si substrate

Fig. 6. AFM images of (a) the as-coated BLT film and the films annealed at (b) 650 °C and (c) 700 °C on (A) a-Al_2O_3/Si and (B) c-Al_2O_3/Si substrates.

Fig. 3 represents the AES depth profiles of the films coated on (a) a-Al_2O_3/Si and (b) c-Al_2O_3/Si substrates, which were annealed at 700 °C. The AES results show that no significant inter-diffusion was found at the interface between the BLT film and c-Al_2O_3 insulation layers. However, the atomic diffusion occurred at interface between Al_2O_3 buffer layer and Si substrate for the BLT film sample coated on a-Al_2O_3/Si substrate.

Fig. 4 shows the FE-SEM surface micrographs of (a) the as-coated BLT thin film coated on a-Al_2O_3/Si substrates and the films annealed at (b) 650 °C and (c) 700 °C. The surface morphology of the as-coated BLT film was found to be smooth and the grain growth occurred at the annealing temperature of above 650 °C, showing the island-like grain shapes.

Fig. 5 shows the FE-SEM surface micrographs of (a) the as-coated BLT thin film on c-Al_2O_3/Si substrates and the films annealed at (b) 650 °C and (c) 700 °C. The surface morphology of the as-coated BLT film was found to be similar to the sample coated on a-Al_2O_3/Si substrates and the grain growth was occurred with the mixture of the island-like and granular grain shapes at the annealing temperature of 650 °C. Moreover, it has been found that the granular shaped grains with a size of approximately 52 nm was formed in the BLT films annealed at 700 °C on c-Al_2O_3/Si substrate. From the surface morphologies of the films, the BLT film coated on c-Al_2O_3/Si substrate showed denser microstructure than the film sample coated on a-Al_2O_3/Si substrate.

From the cross-sectional views of FE-SEM micrographs, we found that the thickness of the BLT films was approximately 1500 Å.

In order to investigate the surface roughness of the BLT films, the values of root mean square in roughness (R_{rms}) were measured by using AFM images. R_{rms} can be obtained by surface scanning mode where feedback is provided for keeping constant the repulsion between the cantilever and the sample during surface scanning.

Fig. 6 shows the AFM images of (a) the as-coated BLT films on (A) a-Al_2O_3/Si and (B) c-Al_2O_3/Si substrates and the films annealed at (b) 650 °C and (c) 700 °C. AFM images indicated that the surface roughness was affected by the annealing temperature as well as the substrate type. The R_{rms} value of the as-coated BLT film on c-Al_2O_3/Si substrate was approximately 1.6 Å, showing a relatively smooth surface. In contrast, the R_{rms} values increased from 30 to 60 Å by increasing the annealing temperature from 650 to 700 °C. The increment of roughness at higher temperature is preferably resulted from the grain growth, and also these results are consistent with the FE-SEM surface micrographs as shown in Figs. 4 and 5. The R_{rms} value of the film annealed at 700 °C on a-Al_2O_3/Si substrates was three times compared with the BLT film coated on c-Al_2O_3/Si substrate, showing a rather rough film surface in the film coated on a-Al_2O_3/Si substrate. This result suggests that the film surface may be improved by the good crystallization and the increment of the degree of *c*-axis orientation as shown in the XRD analyses.

The current densities of the BLT films coated on (A) a-Al_2O_3/Si and (B) c-Al_2O_3/Si substrates annealed at

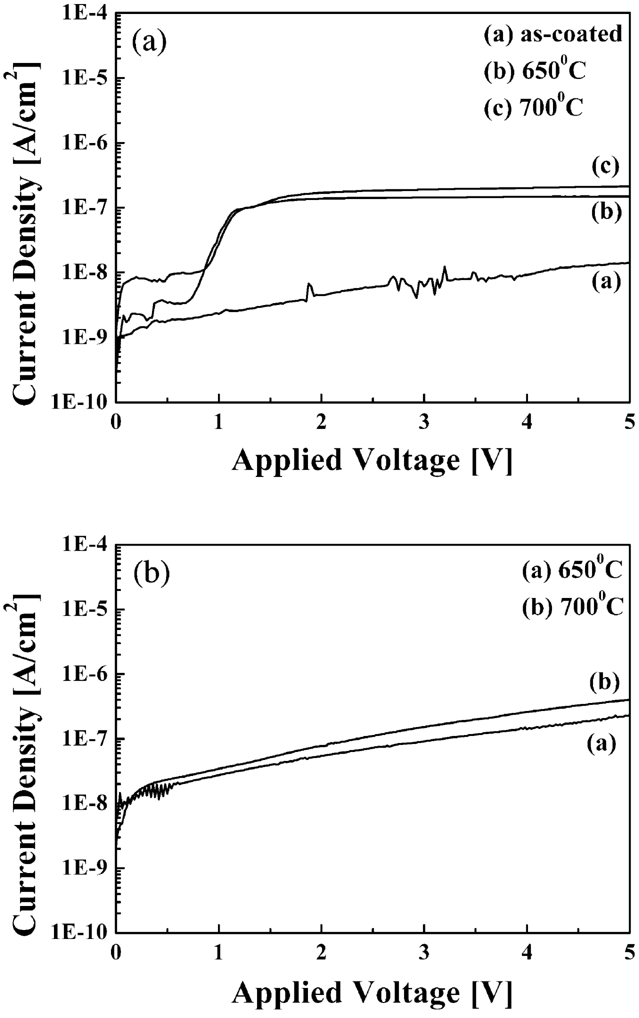


Fig. 7. Current–Voltage curves of BLT thin films annealed at various temperatures on (a) a-Al_2O_3/Si and (b) c-Al_2O_3/Si substrates.

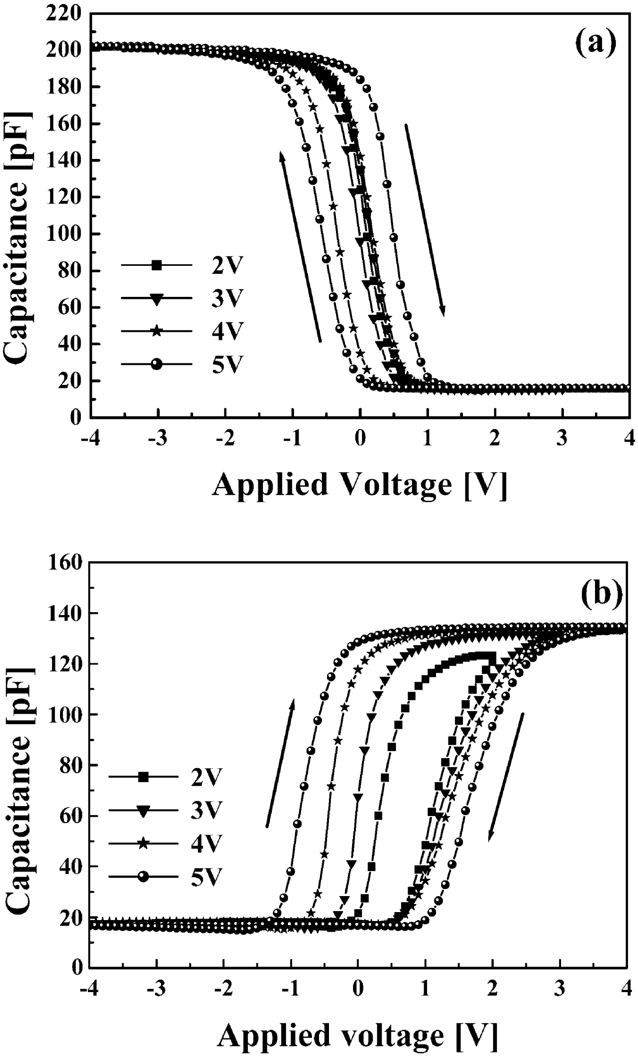


Fig. 8. Capacitance–Voltage characteristics of BLT thin films annealed at 700 °C on (a) a-Al_2O_3/Si and (b) c-Al_2O_3/Si substrates.

the temperature of 650 and 700 °C are shown in Fig. 7. There was no remarkable difference in the current densities between the two samples. However, the current density of the as-coated film on a-Al_2O_3/Si substrate was approximately 6.1×10^{-9} A/cm^2 and increased to 1.4×10^{-7} A/cm^2 at the applied voltage of 3 V when the BLT films were annealed at 650 °C. It is generally accepted that grain boundaries and void defects in the film act as a leakage current path. Therefore, the increase of the grain boundary proportion may result in a higher leakage current density [19]. As a result, the increase of leakage current density in case of the film annealed at higher temperature can be explained by the increase of the grain boundary proportion and/or the existence of the surface defects like voids in the film as shown in the FE-SEM morphologies.

Fig. 8 shows the capacitance vs. voltage (C–V) characteristics of the BLT films coated on (a) a-Al_2O_3/Si (b) c-Al_2O_3/Si substrates and the films were annealed at 700 °C. The C–V measurement was carried out in the voltage ranges from ±1 to ±5 V.

All the film samples showed typical ferroelectric hysteresis property, which originated from remnant polarization caused by the suppressed charge injection in the BLT films [20]. The C–V memory window increased gradually with the sweep voltage up to 5 V. The memory window voltages were calculated from these C–V hysteresis loops.

Fig. 9 shows the memory window voltages of the BLT films coated on (a) a-Al_2O_3/Si and (b) c-Al_2O_3/Si substrates, which were annealed at 650 and 700 °C. The window voltage of the BLT film annealed at 700 °C on c-Al_2O_3/Si substrate was 2.5 V, which is about twice that compared with the one coated on a-Al_2O_3/Si substrate at the applied bias voltage of 5 V. This increase of memory windows may be attributed to the suppression of charge injection due to the improved crystalline quality and dense microstructures in the BLT film coated on c-Al_2O_3/Si substrate.

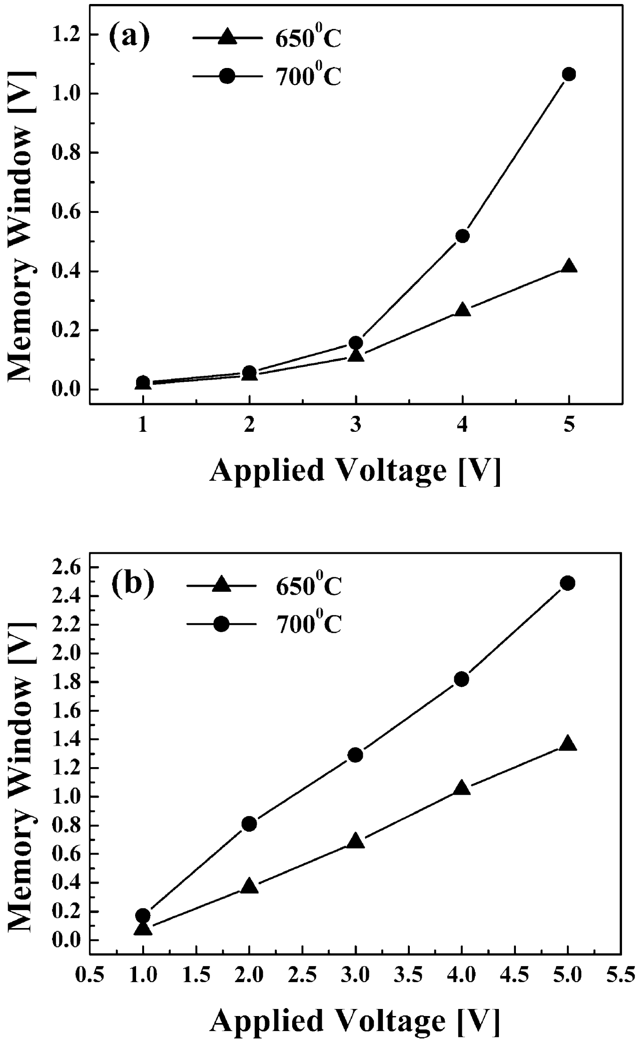


Fig. 9. Memory window vs. applied voltage of BLT thin films annealed at 650 and 700 °C on (a) a-Al_2O_3/Si and (b) c-Al_2O_3/Si substrates.

4. Conclusions

$Bi_{4-x}La_xTi_{3.0}O_{12}$ (BLT, $x=0.67$–0.70) ferroelectric thin films were coated on c-Al_2O_3/Si and a-Al_2O_3/Si substrates by the sol–gel method and annealed at 650 and 700 °C for 30 min under an air ambient. The annealed BLT films were exhibited on *c*-axis oriented perovskite crystalline structures. The BLT film coated on c-Al_2O_3/Si substrate showed better crystallization and electrical properties compared with the one coated on a-Al_2O_3/Si substrate under the same process conditions. The BLT film coated on c-Al_2O_3/Si substrate showed denser microstructure with a granular grain shapes rather than the film sample coated on a-Al_2O_3/Si substrate, which exhibited island-like grain shapes. The R_{rms} value of the film annealed at 700 °C on a-Al_2O_3/Si substrates was three times those of the BLT film coated on c-Al_2O_3/Si substrate, showing a rather rough surface in the BLT film coated on a-Al_2O_3/Si substrate.

The window voltage of the BLT film annealed at 700 °C on c-Al_2O_3/Si substrate was twice (with 2.5 V) that of the sample coated on a-Al_2O_3/Si substrate at the bias voltage of 5 V. There were no remarkable differences in the current densities between the two samples with a value of approximately 1×10^{-7} A/cm^2 at 3 V.

Acknowledgments

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