

Ferroelectric properties of direct-patternable La substituted $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin films formed by photochemical metal-organic deposition

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The surface microstructure and ferroelectric properties of direct-patternable $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ (BLT) films prepared by photochemical metal-organic deposition as a function of La contents were characterized. The surface microstructure showed that La substitution ($x = 0.75$ and 1.00) to $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ films was effective to induce an improved microstructure of the BLT films without the formation of surface holes. The measured remnant polarization values of BLT films with $x = 0, 0.25, 0.50, 0.75$, and 1.00 were $3.7, 7.1, 11.3, 16.0$, and $8.1 \mu\text{C}/\text{cm}^2$, respectively. After 10^9 cycles, the remaining remnant polarizations of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films with $x = 0, 0.25, 0.50, 0.75$, and 1.00 were $64.9, 69.5, 75.9, 94.8$, and 95.0% , respectively. Considering the surface microstructure and ferroelectric properties of the BLT films, the BLT film with $x = 0.75$ showed the best microstructure and ferroelectric properties among all the BLT films. These results suggest the possible application of ferroelectric BLT film, relatively easily and without high cost process such as dry etching.

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Key-words : BLT, Photochemical reaction, Direct-patterning, Photoresist-free

[Received October 30, 2008; Accepted February 19, 2009]

1. Introduction

For the application of film to electronic devices, various thin film deposition techniques such as chemical vapor deposition, sputtering, and sol-gel process etc. have been investigated.¹⁾ After deposition, a patterning process should be carried out. Ion etching and ion milling are presently the most widely applied processes for fine patterning of ferroelectric films.²⁻⁴⁾ However, those processes tend to degrade the properties of the ferroelectric films.⁴⁾ Recently, Kim et al. reported that the Ar ion bombardment and chemical reaction have a degrading effect on ferroelectric properties, the destruction of crystalline structure of BLT films, and nonvolatile etch by-products such as La-chlorides.^{3,5)} Photochemical metal-organic deposition (PMOD) has been researched to minimize an undesirable etching damage because PMOD lithographically produces a patterned structure without using a photoresist or dry etching because of the photosensitive nature of the precursors.^{6,7)} After lithographic exposure, film development can be performed by rinsing in a solvent to remove the unexposed part of the coated film, leaving a patterned structure.

Ferroelectric thin films have attracted much attention in terms of their applicability to ferroelectric random access memory (FeRAM) and microelectromechanical system (MEMS).^{8,9)} Among related materials of interest, lead zirconate titanate (PZT) is probably the most extensively studied. However, PZT films with Pt electrodes suffer serious fatigue with polarization switching.¹⁰⁾ The fatigue problem of PZT film can be solved using metal oxide electrodes, but oxide electrodes generally are difficult to prepare and increase leakage current.¹¹⁾ Recently, it has

been reported that $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT) films with Pt electrodes show good fatigue endurance and greater ferroelectric properties than $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) films.^{12,13)} BLT films were prepared by replacing a part of bismuth ions with lanthanum ions in $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT), which is of a similar structure to SBT with triple TiO_6 octahedron separated by Bi_2O_2 layers.¹²⁾ To apply for our PMOD technique to BLT materials, comparison of the microstructure and ferroelectric properties between BIT and BLT is essential to clarify the effect of La substitution.

Here, we report a direct-patterning method for lithographic deposition of BLT films by PMOD was introduced. Effects of La substitution on the microstructure and ferroelectric properties of direct-patternable BLT films were investigated.

2. Experimental

The precursors used for the photochemical production of BLT films were bismuth 2-ethylhexanoate [$\text{Bi}(\text{C}_7\text{H}_{15}\text{COO})_3$], lanthanum 2-ethylhexanoate [$\text{La}(\text{C}_7\text{H}_{15}\text{COO})_3$], and titanium isopropoxide [$\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$]. The composition of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ precursors was varied with $x = 0$ [$\text{Bi}_4\text{Ti}_3\text{O}_{12}$], 0.25 [$\text{Bi}_{3.75}\text{La}_{0.25}\text{Ti}_3\text{O}_{12}$], 0.50 [$\text{Bi}_{3.50}\text{La}_{0.50}\text{Ti}_3\text{O}_{12}$], 0.75 [$\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$], and 1.00 [$\text{Bi}_{3.00}\text{La}_{1.00}\text{Ti}_3\text{O}_{12}$]. The chosen La^{3+} contents were limited because the Curie temperature (T_c) of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ at $x > 1.25$ decreases below 0°C , which makes these compositions paraelectric at room temperature.¹⁴⁾ A 10% excess of bismuth 2-ethylhexanoate was added to compensate for the loss of Bi during high temperature anneal.¹⁵⁾ The BLT precursors dissolved in hexane were spin-coated at 2000 rpm for 30 s on two different kinds of substrate. One substrate was a chemically cleaned Pt(111)/ TiO_2 /SiO₂/Si(100) substrate for measuring the ferroelectric properties, and the other substrate was p-Si(100) substrate for characterization of direct-patterning process. A 200-nm thick

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direct-patterned BLT film by PMOD was obtained after UV exposure.

The precursor films were lithographically exposed for 15 min using the output of a 1000 W mercury arc lamp that was passed through a chrome mask. The exposed film was rinsed with hexane to develop the latent negative pattern. The resultant film was annealed for 10 min at 400°C. This process was repeated for each layer. The entire structure of multilayer films was annealed at 700°C for 1 h under ambient O₂.

The images of the surface microstructure and direct-patterned film were observed using scanning electron microscopy (SEM) and optical microscopy. The phase formation and crystallinity of the films were studied with an X-ray diffractometer (XRD) using Cu K α radiation. A 150-nm thick Pt top electrode with a 100- μ m radius was sputter deposited for polarization–voltage (P – E) and current–voltage (I – V) characterization of the films.

3. Results and discussion

Surface microstructures of BLT films annealed at 700°C as a function of La contents were observed using SEM, as shown in Fig. 1. The average grain sizes of Bi_{4-x}La_xTi₃O₁₂ films with $x = 0, 0.25, 0.50, 0.75$, and 1.00 were 214, 178, 140, 119, and 54 nm, respectively. An increase in La contents resulted in a decrease in the grain size because the substituted La acts as a grain-growth inhibitor in the BLT films.¹⁶⁾ Additionally, surface holes were observed on the BLT films with $x = 0, 0.25$, and 0.50 while the surface of the BLT films with $x = 0.75$ and 1.00 was closely packed without surface holes. It was observed that La substitution ($x = 0.75$ and 1.00) to BIT film was effective to induce an improved microstructure of the BLT films without the formation of surface holes.

Figure 2(a) represents XRD spectra of 380-nm thick BLT films as a function of La contents on Pt(111)/TiO₂/SiO₂/Si substrate. All the diffraction peaks corresponded to BLT and the Pt substrate. The diffraction intensities showed a distribution similar to BLT ceramics,¹⁷⁾ and Pt(111) was found to not influence the growth orientation of all BLT films.¹⁸⁾ As shown in Fig. 2 (b), XRD intensity proportion of each diffraction orientation in the all BLT films was calculated. The intensity proportion was calculated as the sum of (00 l), (111), (117), and (200) diffraction intensities is the total intensity for each BLT film. According to the increase with La contents, BLT films tended to increase (117) and (200) orientations and decrease (00 l) orientations. This tendency can be explained in terms of the lattice spacing of the (117), (200), and (00 l) planes.¹⁹⁾ As the La contents increase from $x = 0$ to 1.00 , calculated Pt lattice spacing of the (117) and

(200) planes were increased from 2.961 to 2.975 Å and from 2.708 to 2.713 Å, respectively, while that of the (00 l) plane was decreased from 5.438 to 5.405 Å. The observed changes can be attributed to the incorporation of La into the BIT lattice. For higher La contents, the observed diffraction intensities became less intense probably due to a degradation of the crystallinity of BLT films.

P – E hysteresis loops for BLT films annealed at 700°C with an applied voltage of 15 V are given in Fig. 3(a). The measured remnant polarization (P_r) and coercive field (E_c) values of Bi_{4-x}La_xTi₃O₁₂ films with $x = 0, 0.25, 0.50, 0.75$, and 1.00 were 3.7, 7.1, 11.3, 16.0, and 8.1 μ C/cm² and 120, 113, 111, 90, and 73 kV/cm, respectively. As shown in Fig. 3(b), the value of P_r increased gradually with increasing the La contents below the critical level, $x = 0.75$ and decreased thereafter.^{20,21)} Spontaneous polarization of BLT along the a -axis is known to be appreciably higher than BLT along the c -axis.¹³⁾ As shown in the XRD spectra, according to the increase with La contents, BLT films tended to grow toward the non- c -axis orientations. However, BLT film with $x = 1.00$ showed slim hysteresis loop due to the reduced ferroelectric distortion represented by their low T_c .²⁰⁾ The value of E_c decreased gradually with increasing the La contents. Sugita et al. reported that T_c and crystallization temperature of the BLT films decreases with increasing La contents.²²⁾ For higher La contents, since the phase transition temperature reduces with increasing La contents, the residual stress decreases during cooling. As a result, the value of E_c was decreased with increasing La contents.

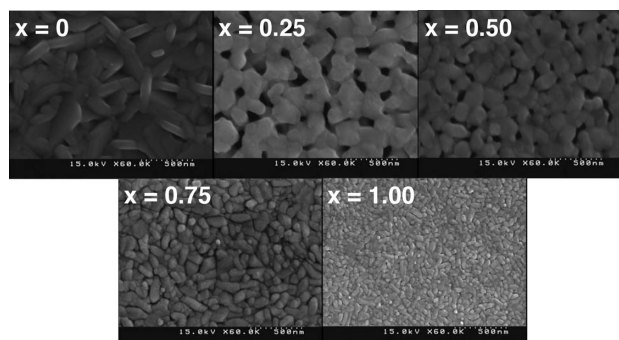


Fig. 1. SEM micrographs of Bi_{4-x}La_xTi₃O₁₂ films annealed at 700°C as a function of La contents.

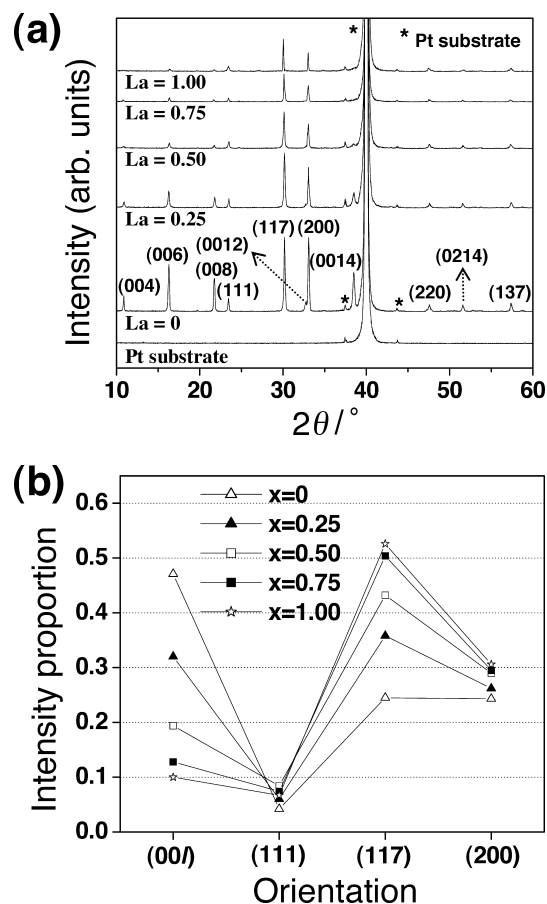


Fig. 2. (a) XRD spectra of BLT films as a function of La contents and (b) proportion of XRD intensities in BLT films with various orientations.

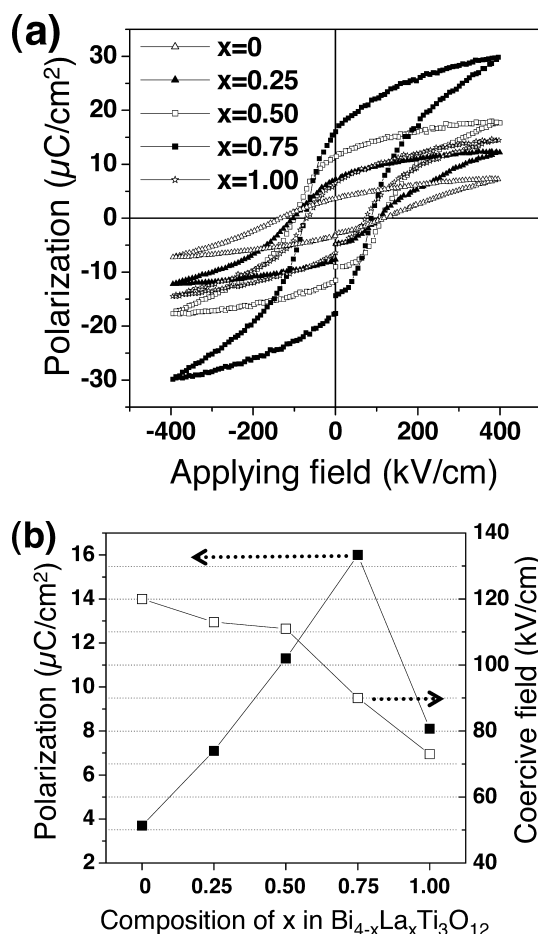


Fig. 3. P - E hysteresis loops of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films annealed at 700°C as a function of La contents.

Figure 4 illustrates the change in polarization of 380-nm thick BLT films as a function of the number of switching cycles using a bipolar square wave of ± 10 V at a frequency of 100 kHz. The pulse widths (τ_1), switching period (τ), and duty cycle (τ_1/τ) were $8.6 \mu\text{s}$, $10 \mu\text{s}$, and 0.86, respectively. After 10^9 cycles, the remaining remnant polarizations of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films with $x = 0, 0.25, 0.50, 0.75$, and 1.00 were 64.9, 69.5, 75.9, 94.8, and 95.0%, respectively. According to increasing La contents, fatigue resistance of BLT films was improved. Because of the volatility of Bi and the possible reduction of Ti^{4+} ions to Ti^{3+} , oxygen vacancies may occur in BLT films.²⁰ It is suggested that lanthanum substitution stabilizes the perovskite blocks and hence decreases the concentrations of oxygen vacancies and holes as the conduction carriers. In addition, as shown in the surface microstructure of Fig. 1, surface holes were observed on the BLT films with $x = 0, 0.25$, and 0.50 while the surface of the BLT films with $x = 0.75$ and 1.00 was closely-packed without surface holes. This closely-packed smooth surface microstructure might be one of important factors for the fatigue-free behavior because charged defect accumulation which induces a degradation of mobility of domain boundaries could be minimized.^{23),24)}

The possibility of direct-patterning spin-coated BLT precursor films with $x = 0.75$ was examined and the result is given in **Fig. 5**. To obtain the image, a spin-coated BLT film was exposed to UV for 15 min and then rinsed in hexane. As can be seen in Fig. 5, the dark area corresponds to the direct-patterned BLT film and the bright area corresponds to the Si substrate. Based on the

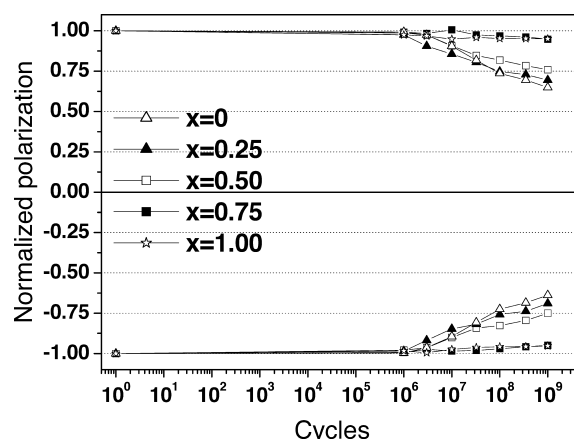


Fig. 4. Fatigue characteristics of $\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$ films annealed at 700°C as a function of La contents.

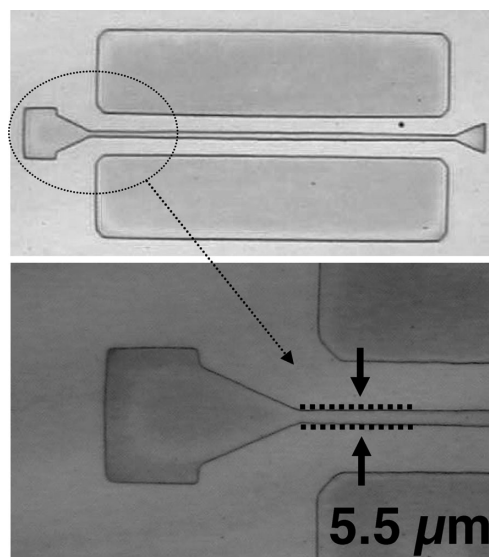


Fig. 5. Optical micrograph of direct-patterned $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ film after rinsing in hexane.

well-defined width in the direct-patterned BLT film, micron-scale patterning was successfully obtained by lithographic patterning using PMOD. From the above results, direct lithographic patterning of BLT film can be accomplished by PMOD for ferroelectric device applications.

4. Conclusions

BLT films as a function of La contents were successfully prepared using photosensitive precursors. Direct-patterning of BLT films by PMOD was accomplished after UV exposure for 15 min and removal of the unexposed area of the film by rinsing with hexane. According to the increase with La contents, BLT films tended to increase (117) and (200) orientations and decrease (00l) orientations. The value of P_r increased gradually with increasing the La contents below $x = 0.75$ due to the growth of BLT films toward non- c -axis orientations and decreased thereafter due to the reduced ferroelectric distortion represented by their low T_c . Also, the value of E_c decreased gradually with increasing the La contents due to the reduced residual stress. The fatigue resistance of BLT films with $x = 0.75$ and 1.00 showed

better than that of BLT films with $x = 0$, 0.25, and 0.50 due to the reduced concentrations of oxygen vacancies and holes and the enhanced surface microstructures. From this work, direct-patterning of BLT films was proven to be effectively adopted for fabrication of micro-patterned systems without dry etching.

Acknowledgment This work was supported by Hynix Semiconductor Inc. of Korea. This work was supported by the second stage of Brain Korea 21 project in 2008. The experiments at the PLS were supported in part by the MOST and the POSTECH.

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