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Electrical properties of $(Bi_{3.5}La_{0.5})Ti_3O_{12}$ thin-films prepared by liquid source misted chemical deposition

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Abstract−The $(Bi_{3.5}La_{0.5})Ti_3O_{12}$ (BLT) thin-films used in this study were fabricated on a $Pt(111)/SiO_2/Si(100)$ substrate by a Liquid Source Misted Chemical Deposition (LSMCD) technique. X-ray diffraction patterns showed that the BLT films were crystallized and no other phases were observed when annealed above 650 °C. Grain size and remnant polarizations increased with increase in the annealing temperature, while leakage current densities decreased. The remnant polarizations (P_r) increased from 2.0 to 4.8 and 19.0 μC/cm^2 with increase in the annealing temperature from 650 to 700 and 750 °C, respectively. The BLT films annealed at 700 °C in O_2 showed a good fatigue resistance of reduced polarization by 10% after 10^9 switching cycles when 9 V of bipolar voltage was applied at a frequency of 40 kHz.

Key words: Liquid Source Misted Chemical Deposition, $(Bi_{3.5}La_{0.5})Ti_3O_{12}$ (BLT) Film, Bismuth Titanate, Ferroelectric Thin-film

INTRODUCTION

Ferroelectric thin-films have been intensively studied for application in ferroelectric random access memory (FRAM), which is used for both nonvolatile operation and high-speed access. Recently, ferroelectric bismuth titanate $Bi_4Ti_3O_{12}$ (BIT) thin-film was introduced as a promising candidate for application in FRAM capacitor and much effort has been made to form ferroelectric BIT thin-films by using several methods [Muhammet et al., 1994; Joshi and Desu, 1996; Neumayer et al., 1997; Park et al., 1998; Sun et al., 1999]. Ferroelectric BIT crystals have a typical perovskite-layered structure and show strong anisotropic properties [Cummins and Cross, 1968; Kim et al., 2003]: coercive field of 3.5 and 50 kV/cm, and spontaneous polarization of 4.0 and 50 μC/cm^2 along the c- and a-axes, respectively. BIT film has potential problems of low spontaneous polarization along c-axis and fatigue failure, which is an essential characteristic for application in FRAM [Joshi and Krupanidhi, 1992]. Therefore, it is important to fabricate BIT thin-film that is highly oriented along the a-axis and fatigue-free. Especially, fatigue failure of BIT film should be removed in order to sustain a memory operation for a long time. It was reported that $(Bi,La)_4Ti_3O_{12}$ (BLT) thin-film prepared by a laser ablation method exhibited fatigue-free behavior [Park et al., 1999]. However, the laser ablation method has limitations of poor uniformity with large substrate and low productivity.

A number of studies on ferroelectric thin-films are available in the literature. Several deposition methods such as dry methods (sputtering [Joo et al., 1997], laser ablation [Cui et al., 1997], and chemical vapor deposition (CVD) [Yamamuka et al., 1997]), wet methods (sol-gel [Seo et al., 2001], metal-organic decomposition (MOD) [de Araujo et al., 1995], and liquid source misted chemical deposition (LSMCD) [Chung et al., 1996; Jeon et al., 2005]) have been studied to prepare ferroelectric thin-films. Among them, LSMCD has the advantages of good reproducibility of composition, high deposition rate and the easy selection of metal precursors [Huffman, 1995].

In this study, we describe our efforts to investigate the effects of annealing temperature on crystalline structure, surface morphology and electrical properties such as polarization, fatigue behavior and leakage current density of $(Bi_{3.5}La_{0.5})Ti_3O_{12}$ thin-films prepared by LSMCD.

EXPERIMENTAL

1. Film Deposition

BLT thin films were prepared by LSMCD method using Bi(III) 2-ethylhexanoate $[Bi(OOCCH(C_2H_5)C_4H_9)_3]$, La nitrate $[La(NO_3)_3]$ and Ti isopropoxide $[Ti(O^iC_3H_7)_4]$ as metallic precursors. These were dissolved in 2-methoxyethanol. An ultrasonic nebulizer (HU-350, Samsung Electronic Co., Ltd. Frequency of sonicator: 1.63 MHz) was used to generate mist of precursor solution. The mist was transported to a deposition chamber by carrier gas (Ar). The Pt-coated Si(100), $Si(100)/SiO_2(500\ nm)/Pt(100\ nm)$, was used as a substrate. The as-deposited films were dried at 230 °C for 2 min followed by a pyrolysis process at 400 °C for 10 min. To increase the thickness of the films, previous processes were repeated twice. After the previous heat treatments, the films were annealed at various temperatures for 1 hr in O_2 atmosphere. The detailed growth conditions of BLT thin-films are listed in Table 1.

2. Film Characterization

The crystalline structure and surface morphology of BLT thin films were characterized by X-ray diffraction [(XRD), Rigaku, D-MAX-RC, Cu target, Ni filter] and scanning electron microscope [(SEM),

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Table 1. The detailed growth conditions of BLT thin films

Metal precursors	La nitrate [$La(NO_3)_3$] Bi(III)2-ethylhexanoate [$Bi(OOCCH(C_2H_5)C_4H_9)_3$] Ti isopropoxide [$Ti(O^iC_3H_7)_4$]
Solvent	2-Methoxyethanol
Substrate temperature	Room temperature
Liquid source Temperature	Room temperature
Pressure during deposition	700 Torr
Baking	230 ºC (2 min), 400 ºC (10 min)
Annealing	650-750 ºC, for 1 hr
Typical deposition rate	25-35 nm/min
Ar flow rate	500 sccm
Wafer	Si(100), Si(100)/SiO_2(500 nm)/ Pt(100 nm)
Top electrode	Pt(100 nm) by sputtering
Rotating speed	3 rpm

Philips 533M], respectively. The elemental ratios of the films were analyzed by wavelength dispersive spectroscopy [(WDS), Micro-spec3-PC]. In order to measure electrical properties, Pt top electrodes of 400 μm diameter were prepared by using shadow mask in an rf-magnetron sputter. Polarization versus electric field (P-E) curves and fatigue tests were measured by using a RT66A tester from Radiant Technology. The leakage current (I-V) properties were measured by a programmable Kethley 617 electrometer with the conditions of 0.2 V of step voltage and 1 second of delay time, respectively.

RESULTS AND DISCUSSION

The BLT films were annealed at 650, 700 and 750 ºC for 1 hr in O_2 atmosphere. The elemental ratios of (Bi : La) were measured by WDS. An excess amount of 20% of Bi was added to the precursor solution to compensate for the loss of Bi during the annealing process. X-ray diffraction patterns of the BLT films annealed at 650, 700 and 750 ºC in O_2 are shown in Fig. 1. The typical XRD patterns of BIT thin-films without other phases, such as Bi_2O_3 or $Bi_2Ti_2O_7$, were obtained. These XRD scan results of BLT films show a polycrystalline structure of BLT(00*l*) (*l*=6, 8, 18) peaks and BLT(117) peak (2θ=30.4º). In addition, BLT thin films were grown preferentially along the a- and b-axes indicated by the difference in the intensity of BLT(00*l*) (*l*=6, 8, 18) peaks and BLT(117) peak. It is easy to grow layered perovskite thin-films such as $SrBi_2Ta_2O_9$ (SBT) and BTO ($Bi_4Ti_3O_{12}$) along the c-axis normal to their substrates. However, using these c-axis oriented films, it is not possible to get good electrical properties, because they are known to have its spontaneous polarization along only the a-axis [Rae et al., 1992; Jeon et al., 2004, 2005]. Therefore, it is highly desirable to grow films preferentially oriented along the a- and b-axes.

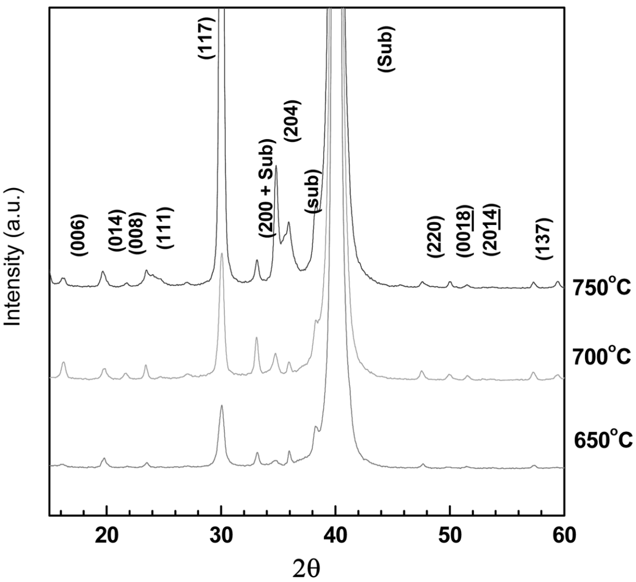

Fig. 1. XRD patterns of $Bi_{3.5}La_{0.5}Ti_3O_{12}$ thin films on Si(100)/SiO_2 (500 nm)/Pt(100 nm) substrate annealed at 650, 700 and 750 ºC.

The surface morphologies of $Bi_{3.5}La_{0.5}Ti_3O_{12}$ thin films recorded by SEM at (a) 650 ºC, (b) 700 ºC and (c) 750 ºC for 1 hr in O_2 atmosphere are shown in Fig. 2. The grains like rod were formed at 650 ºC where the crystallization was observed in Fig. 1. The grain size increased with increased annealing temperature. Notably, the surface morphology at 750 ºC showed that some larger grains like plate were formed and surface roughness increased.

Fig. 3 shows hysteresis loops for 350 nm thick $Bi_{3.5}La_{0.5}Ti_3O_{12}$ films annealed at 650, 700 and 750 ºC for 1 hr in O_2 atmosphere. Remnant polarizations (P_r) were 2.0, 4.8 and 19.0 μC/cm^2, respectively. Coercive fields (E_c) were 78, 95 and 110 (kV/cm), respectively. P_r and E_c values were increased with increase in annealing temperature. These results can be correlated with the grain size change. Small grain size and rod-like shape of the films annealed at 650 and 700 ºC explains the poor ferroelectric properties of the films. The large P_r of the film annealed at 750 ºC shows that large grain size and plate-like shape contributed to enhancement of ferroelectric properties. Especially, the P_r of BLT thin-film annealed at 750 ºC was much larger than those annealed at 650 and 700 ºC. From this result, an annealing temperature of 750 ºC is necessary for good electrical property of BLT films prepared by LSMCD. And the size and shape of the grains are considered to be key factors which determine ferroelectric properties of BLT thin-films.

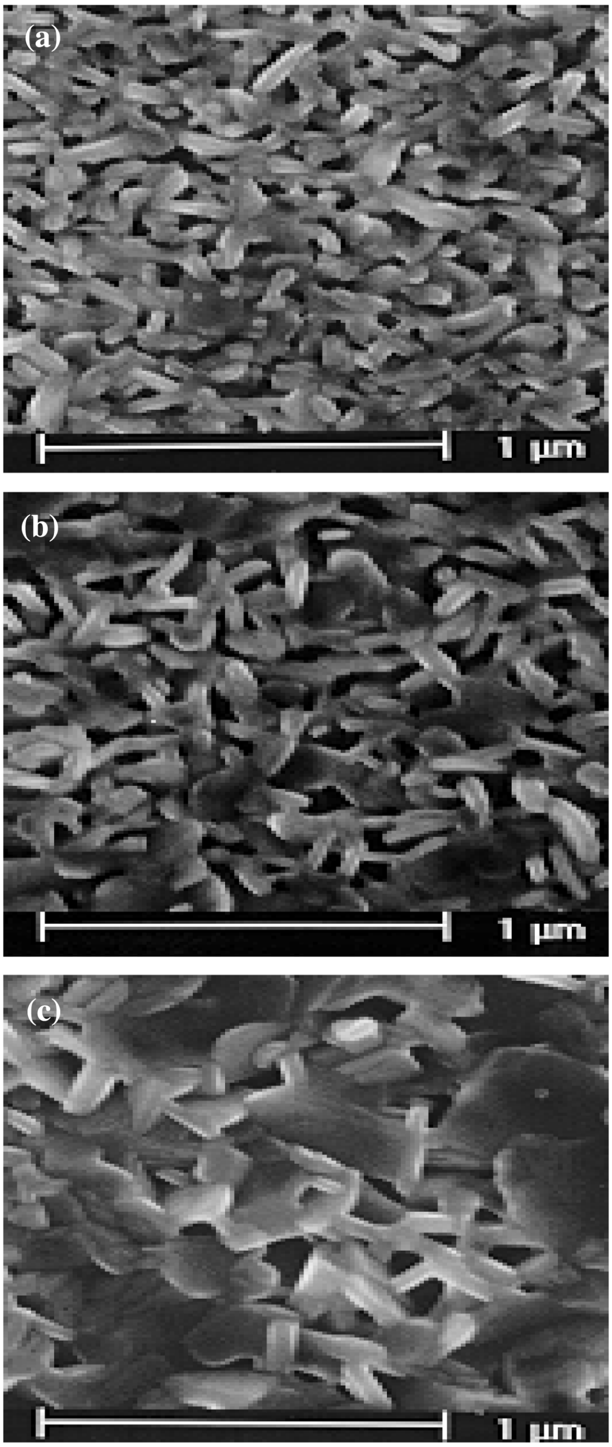

Fig. 2. The surface morphologies of $Bi_{3.5}La_{0.5}Ti_3O_{12}$ thin films recorded by SEM at (a) 650 °C, (b) 700 °C and (c) 750 °C for 1 hr in O_2 atmosphere.

Fig. 4 shows the leakage current density variation as a function of the applied voltage of 350 nm thick BLT (Bi/La=3.5/0.5) films annealed at 650 °C, 700 °C and 750 °C for 1 hr in O_2 atmosphere when positive bias voltage is applied to the top electrode. The leakage current density values of the films annealed at 650 and 700 °C were about 5×10^{-6} A/cm^2 at 5 V of applied voltage. However, as the annealing temperature increased to 750 °C, the leakage current density

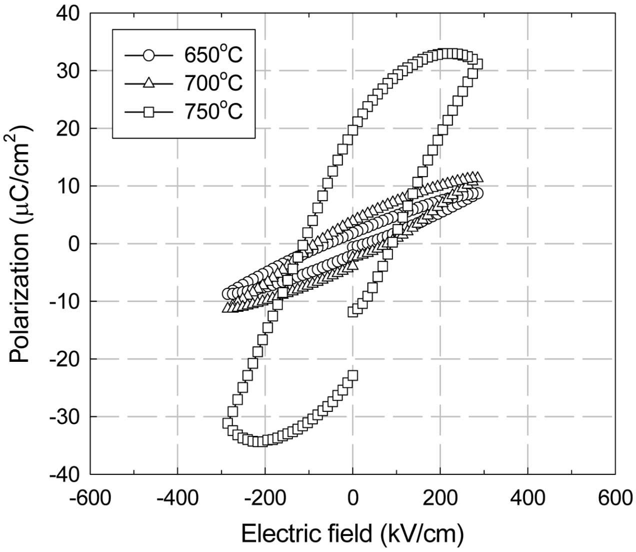

Fig. 3. Hysteresis loops for 350 nm thick $Bi_{3.5}La_{0.5}Ti_3O_{12}$ thin films annealed at 650 °C, 700 °C and 750 °C for 1 hr in O_2 atmosphere.

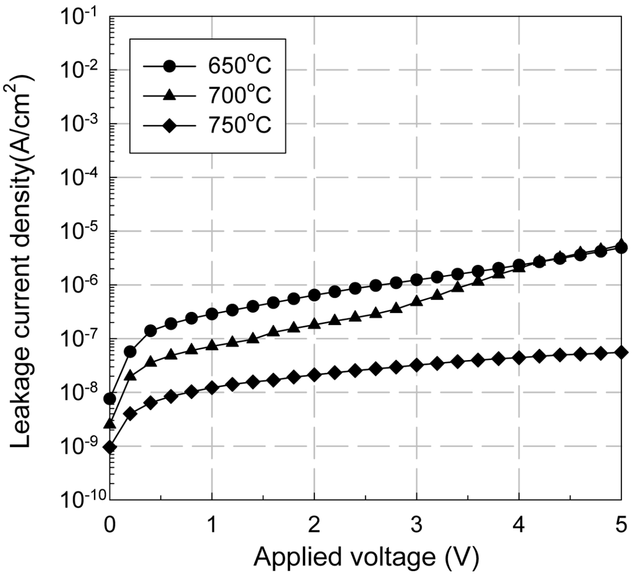

Fig. 4. Leakage current density variation as a function of the applied bias voltage of 350 nm thick BLT $Bi_{3.5}La_{0.5}Ti_3O_{12}$ thin films annealed at 650 °C, 700 °C and 750 °C for 1 hr in O_2 atmosphere when positive bias voltage is applied to the top electrode.

was dramatically decreased to 5×10^{-8} A/cm^2. This result shows a similar trend to the results of a hysteresis test, indicating that the increase of grain size also contributed to the decrease of leakage current density by reducing density of grain boundaries which can act as leakage paths. Fig. 5 shows fatigue characteristics of a 350 nm thick BLT (3.5 : 0.5) thin-film annealed at 700 °C for 1 hr in O_2 atmosphere. 40 kHz bipolar square wave of 9 V was used for the fatigue test of the film. Excellent fatigue endurance was observed, as observed by other researchers [Park et al., 1999; Watanabe et al., 2001]. The decrease in polarization after 10^9 switching cycles was less than 10% of the initial value.

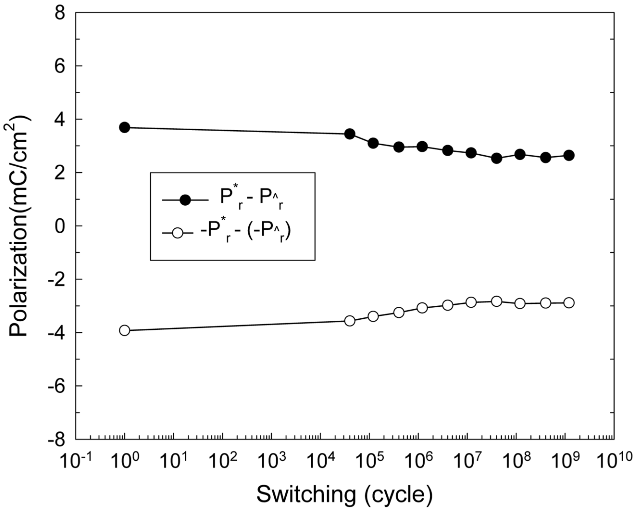

Fig. 5. Fatigue characteristics of a 350 nm thick $Bi_{3.5}La_{0.5}Ti_3O_{12}$ thin films annealed at 700 °C for 1 hr in O_2 atmosphere. 40 kHz bipolar square wave of 9 V was used to fatigue the film (P*r and P^r are switching remnant polarization and nonswitching polarization when the positive read voltage is biased, respectively. –P*r and –P^r are switching remnant polarization and nonswitching polarization when the negative read voltage is biased, respectively).

CONCLUSIONS

$Bi_{3.5}La_{0.5}Ti_3O_{12}$ (BLT) thin-films were fabricated by a Liquid Source Misted Chemical Deposition (LSMCD) technique without any other secondary phases when annealed above 650 °C in O_2. The BLT films annealed at 750 °C showed excellent electrical properties. The P_r and E_c values of the film were 19.0 μC/cm^2 and 110 kV/cm, respectively, and the leakage current density value of the film was 5×10^{-8} A/cm^2. The BLT film annealed at 700 °C showed good fatigue resistance, showing only 10% decrease in polarization after 10^9 switching cycles. From these results, it can be concluded that LSMCD technique is a promising method for the fabrication of BLT thin-films that are considered as a good candidate for FRAM capacitor materials.

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