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Effect of vanadium doping on ferroelectric and electrical properties of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin film

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Abstract $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) and V-doped BLT (BLTV) thin films were prepared on Pt/Ti/SiO_2/Si substrates by a pulsed laser deposition method. The effects of V doping on ferroelectric and electrical properties were investigated by polarization-electric field hysteresis loops and leakage current-voltage measurements. BLTV single phases were confirmed by X-ray diffraction. Remnant polarization was increased and the leakage current density was decreased by V doping. The leakage current density of BLT thin films suddenly increased at 100 kV/cm while that of BLTV thin films increased at the higher electric field of 160 kV/cm. The power law relationship $J \alpha E^n$ of current density vs. applied electric field is estimated to be $J \alpha E^{2.0}$ for BLT and $J \alpha E^{1.0}$ for BLTV thin films. The leakage current of the BLT/Pt junction can be explained by space-charge-limited current. However, that of the BLTV/Pt junction was characterized by the Schottky emission behavior.

Keywords Ferroelectric thin film · Leakage current · Vanadium doped BLT · FRAM

1. Introduction

For optical and electro-optic devices, and nonvolatile ferroelectric random access memory (FRAM) applications, much attention has been paid to ferroelectrics [1, 2]. Isotropic perovskite $Pb(Zr_xTi_{1-x})O_3$ (PZT) and Bi-layer structured ferroelectrics (BLSFs), $SrBi_2Ta_2O_9$ (SBT), $Bi_4Ti_3O_{12}$ (BIT) and $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) materials, have been found to be the most promising candidates for FRAM applications [3–10]. It is important that these materials have a low polarization switching voltage, low leakage current, low annealing temperature and little fatigue. PZT has advantages because of its high remnant polarization and low processing temperature; however, PZT suffers severe polarization fatigue at the Pt-electrode after read/write switching cycles. Moreover, SBT has good fatigue resistance; however, high processing temperatures over 750°C are an obstacle to making it in real device.

BIT is a useful material for FRAM applications, and A = Bi, B = Ti and $n = 3$ are given in a general formula for the Bi-layered structure, $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$. BIT materials have high leakage current and fatigue due to defects such as Bi vacancies ($V_{Bi}^{'''}$) accompanied by oxygen vacancies ($V_{\ddot{O}}$). However, fatigue was improved in the La-substituted BIT (BLT) thin films [6]. To improve the ferroelectric and electrical properties [3–6, 8–10], the effects of ion doping on the A- and B-sites have been widely studied [11–23]. In addition, it is necessary to obtain BLT thin film with a high remnant polarization and low leakage current. To investigate the effect of donor doping with a high-valence V^{5+} for Ti^{4+} ion, V-doped BLT thin films were prepared using a PLD method. The effects of V doping on the ferroelectric and electrical properties were investigated.

2. Experimental Work

$Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) and $(Bi_{3.25}La_{0.75})(Ti_{2.97}V_{0.03})O_{12}$ (BLTV) thin films on Pt/Ti/SiO_2/Si substrates were grown by pulsed laser deposition (PLD). Prior to the deposition

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process, the chamber was evacuated to a base pressure of 1.0×10^{-6} Torr and then filled with oxygen to a pressure of 200 mTorr. These thin films were deposited at the substrate temperature of 450°C for 30 min. For complete crystallization, the films were finally annealed at the temperatures of 700°C for 60 min in air atmosphere.

The formation of single-phases or different phases was investigated by XRD with Cu-Kα radiation. The grain morphologies show a spherical shape with a size of ~100 nm. To investigate electrical properties, Pt top electrodes of 2.5×10^{-4} cm^2 were deposited on the film through a shadow mask by dc sputtering to form metal-ferroelectric-metal (MFM) capacitors. Dielectric properties were investigated in the frequency range of 100 Hz ~1 MHz by an impedance analyzer (HP4192A) with a heating rate of 0.5°C/min. The ferroelectric properties and polarization fatigue were investigated by polarization electric field (*P-E*) hysteresis loops (ferroelectric tester, RT66A). The leakage current-voltage (*I-V*) was measured using an electrometer (Keithley 236).

3. Results and discussion

Figure 1 shows the XRD patterns of the BLT and BLTV thin films annealed at 700°C for 60 min. The XRD patterns of BLTV thin film agreed with the previous results for BIT and BLT [3–6, 8–10], which indicated that single phases with a Bi-layered perovskite structure were formed. The as-grown BLT and BLTV thin films showed amorphous phases due to the low pre-heating temperature of 450°C. The thin films were crystallized at an annealing temperature of 700°C. At room temperature, the dielectric constant of BLT thin films was 260 at 100 kHz with a $\tan\delta = 0.028$, and these values are comparable to previously reported values [8]. While that of BLTV thin films was 320 with the $\tan\delta = 0.021$. Thus, V doping increased the dielectric constant and decreased the dielectric loss. These results agree with those of higher-valent cation doping in BIT and SBN [14, 15, 17–19] for which a marked decrease in dielectric loss was reported.

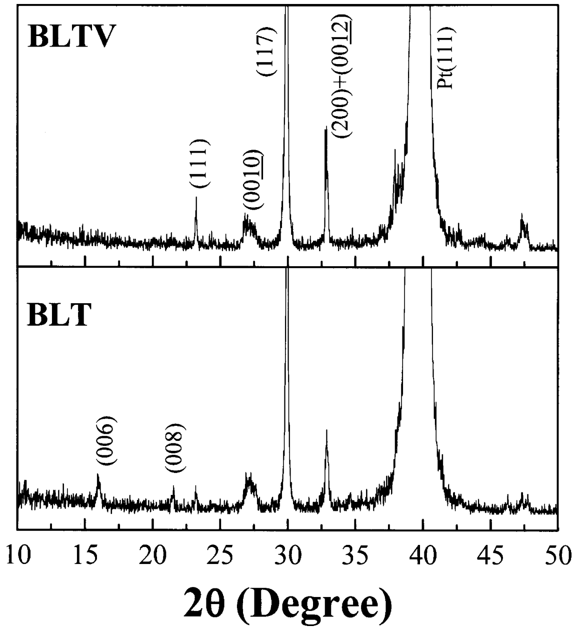

Fig. 1 XRD patterns of BLT and BLTV thin films annealed at 700°C for 60 min

Figure 2 shows the *P-E* hysteresis loops of BLT and BLTV thin films. The corresponding remnant polarization ($2P_r$) and coercive fields ($2E_c$) were obtained from the *P-E* hysteresis loops. The $2P_r$ values rapidly increased and saturated at an applied field of ~250 kV/cm. At an applied field of 250 kV/cm, the $2P_r$ and $2E_c$ of BLT thin films were 22 μC/cm^2 and 148 kV/cm, respectively. While the $2P_r$ and $2E_c$ of BLTV thin films were 30 μC/cm^2 and 153 kV/cm, respectively. The improvement in remnant polarization of BLTV thin films is comparable to that of previous studies of BLT thin films [4–10]. After 10^{10} read/write switching cycles, the polarization of BLT and BLTV thin films was ~85 % of the initial value. Thus BLTV and BLT thin films had good fatigue resistance. These results imply that there is a low accumulation of vacancies and low domain pinning [12, 14].

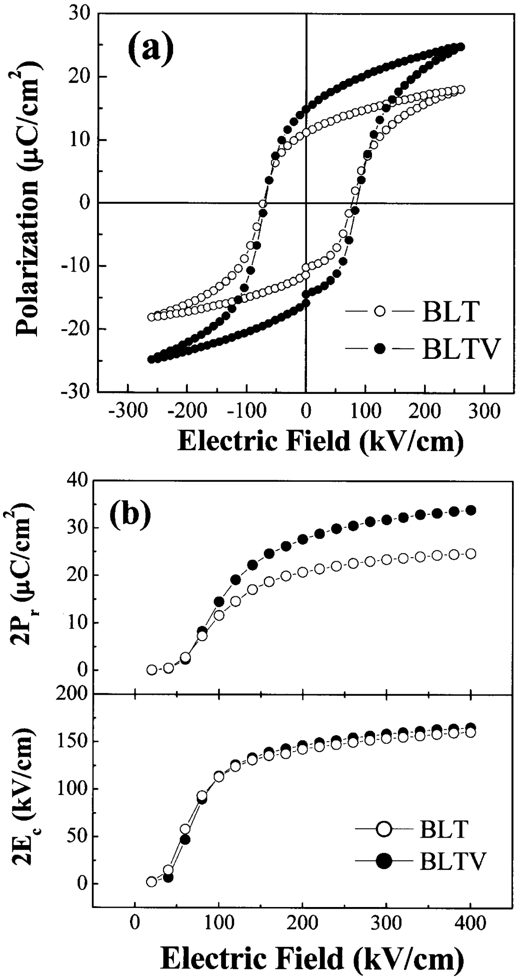

Fig. 2 (a) *P-E* hysteresis loops of BLT and BLTV thin films and (b) remnant polarization ($2P_r$) and coercive field ($2E_c$)

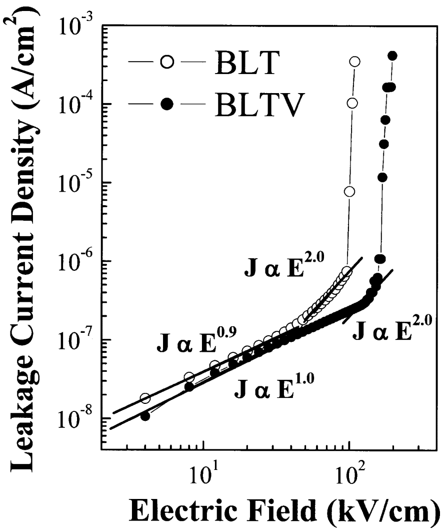

Fig. 3 Leakage current density *J* vs. electric field *E* of BLT and BLTV thin films

Figure 3 shows the leakage current density (*J*) vs. applied electric field (*E*) at room temperature. The leakage current was measured with a time delay of 0.5 s as the voltage increased 0.1 V. The leakage current density increased as electric field increased, and it increased rapid at 100 kV/cm for BLT thin films and 160 kV/cm for BLTV thin films. The leakage current density of BLTV thin films decreased and increased at the higher electric field. Then the leakage current density of BLT thin films was 6.2 × 10^{-7} A/cm^2 at 90 kV/cm [9, 14] while that of BLTV thin films was 2.2 × 10^{-7} A/cm^2. The leakage current abruptly increased above 100 kV/cm (BLT) or 200 kV/cm (BLTV) and then the dielectrics breakdown at the higher dc electric field. However, the P-E hysteresis loops of both films did not show any signal of degradation all the way to saturation field strength (around 250 kV/cm). As applied electric field increased, defects interacted strongly with domain boundaries and had significant influence on the conducting process. It seems that mobile vacancies, such as Bi and O vacancies, can assemble in extended structures near the domain boundaries and may contribute to an increase of leakage current. For the dc electric field on leakage current measurement, the ferroelectrics breakdown occurred at high field, which was caused by the accumulation of the charge carrier. However, the ac response of the P-E hysteresis loops was remained at the higher field above 250 kV/cm, it was possible due to the the low accumulation of charge carriers, such as O and Bi vacancies.

The log(*J*) vs. log(*E*) plot shows the slopes of leakage current in a power law relationship *J α E^n* [2, 13, 15]. As can be seen there are some regions that depend on the applied electric field. The *J-E* relationship is *J α E*$^{1.0}$ for the low applied field and *J α E*$^{2.0}$ for the high applied field. When the applied field is greater than 40 kV/cm, the exponent *n* of BLT thin films is ∼ 2.0, which indicates that the leakage current is a space-charge-limited current with deep traps. However, when the applied field is less than 110 kV/cm, the exponent *n* of BLTV thin films is ∼1.0, which indicates that the current is an ohmic-like conduction process. Since the abrupt increase indicates the existence of a trap-filled limit V_{TFL}, which is equivalent to 100 kV/cm for BLT and 160 kV/cm for BLTV thin films, then the traps are filled and further charges are injected directly into the conduction band. Some of the physical properties are summarized in Table 1.

Table 1 Dielectric properties at 100 kHz and electrical conduction of BLT and BLTV thin films

Film	ε (25°C)	tanδ (25°C)	$2P_r$ (μC/cm^2)	$2E_c$ (kV/cm)	Leakage current (A/cm^2) at 90 kV/cm
BLT	260	0.028	22	148	6.2×10^{-7}
BLTV	320	0.021	30	153	2.2×10^{-7}

The electric field and temperature dependences of the leakage current are explained by the space-charge-limited current, Schottky and Frenkel-Poole emission [13, 15, 16, 21]. The Schottky emissions are presented as;

$$J \sim T^2 \exp\left[-q\left(\Phi_B - (qE/4\pi\varepsilon_i)^{0.5}\right)/kT\right]$$

where Φ_B = barrier height, E = electric field, and ε_i = dielectric dynamic permittivity. Schottky emission is based on the interface between a semiconductor (metal) and an insulating film as a result of lowering the barrier due to the applied field and the image force [16]. If straight lines are obtained for log (*J*/*T*^{2}) vs. 1/*T*, then the leakage current can be explained by the Schottky emission behavior.

Figure 4 shows the leakage current density (*J*) vs. square root (*E*$^{0.5}$) plot of BLTV thin films at several temperatures. The log (*J*/*T*^{2}) increases linearly with *E*$^{0.5}$ at the applied electric field range. The inset shows the variations of the extrapolated log (*J*/*T*^{2}) vs. 1/*T* plot for the applied electric field *E* = 0. The fitting line of log (*J*/*T*^{2}) vs. 1/*T* plot of BLTV thin films increased as temperature increased. Thus, the Schottky emission behavior [15] would result in positive values for the height of the barrier $\Phi_B = 0.2$ eV in the researched temperature region. Compared with previous results, it is reported the Schottky barrier height of SBT/SBN thin films in the range of about 1 eV [15, 21]. The barrier height [24–26] of $Ba_{0.4}Sr_{0.6}TiO_3$, Ta_2O_5 and PZT thin films is 0.46 eV, 0.36 eV and about 0.6 eV, respectively. The Schottky barrier height of $\Phi_B = 0.2$ eV for BLTV thin films is lower than that of other results. The oxygen and it's related vacancies were formed at the surface of the thin films during the annealing process. The source of barrier height is related to the possible defects such as oxygen and bismuth vacancies. To obtain the better result, further study is needed.

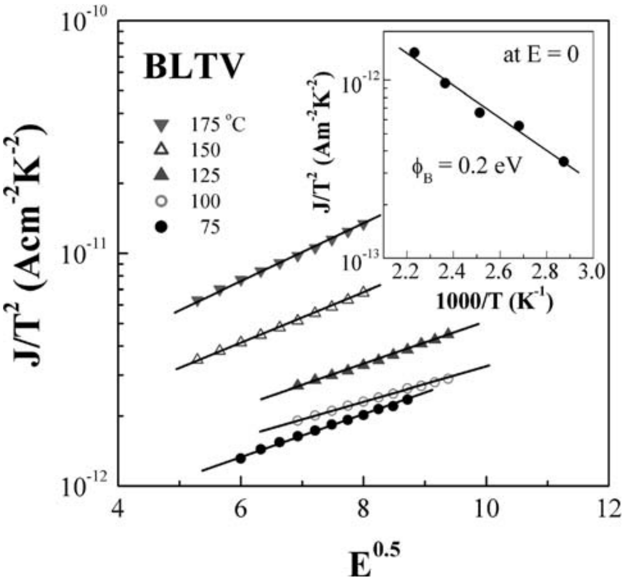

Fig. 4 Leakage current density J/T^2 vs. square root $E^{0.5}$ of BLTV thin film. The inset shows the extrapolated current density vs. $1/T$ plot at $E = 0$

From the results of the P-E hysteresis loops and leakage current measurements, V doping on BLT thin films influenced the ferroelectric and electrical properties. The electric field dependence of the leakage current density of BLT thin films is quadratic as shown in Fig. 3, then the electrical conduction on BLT/Pt junction can be characterized by the space-charge-limited current. Bi ions easily evaporate during the sintering process. To achieve charge neutrality in BLT, oxygen vacancies would need to be created by a generation of the inevitable Bi vacancies, V_{Bi}'''. Thus, defects, such as the bismuth V_{Bi}''' and oxygen vacancies $V_{\ddot{\mathrm{O}}}$, are assumed to be the most mobile charges and play an important role in polarization and electrical properties. Below T_c, defects get trapped at sites like grain boundaries and grain-electrode interfaces and the conduction process might be a trap-controlled space-charge current. Pentavalent V ion doping in B-site reduces the $V_{\ddot{\mathrm{O}}}$ concentration that results from Bi volatilization. The substitution of V^{5+} was accomplished by the incorporation of oxygen into the oxygen vacancies, $V_{\ddot{\mathrm{O}}}$. Thus, this results in the elimination of oxygen vacancies and oxygen vacancy complexes, $V_{\mathrm{Bi}}''' - V_{\ddot{\mathrm{O}}}$. Thus electrical conduction decreased. The results of BLT system are similar to that of SBN system. One explanation [17, 18] for the incorporationof V doping that V^{5+} cations are stable after oxygen annealing and thus no appreciable oxygen vacancies are created and no hopping conduction is introduced to the system.

The BLSFs' ferroelectric properties were originated by TiO_6 oxygen octahedron and were influenced by ion substitution [11, 12, 17–19, 21, 22]. The A-site substitution of the lanthanide ion for the volatile Bi or the B-site substitution by high-valent cation was effective for eliminating defects, such as oxygen vacancies and vacancy complexes. This means that a decrease in the number of defects lowered the fatigue and domain pinning. In this work, the V^{5+} substitution for Ti^{4+} ion improved the remnant polarization and reduced the leakage current density. Regardless of small V-doping, BLTV thin films have good ferroelectric properties. V doping is an effective method for decreasing the oxygen vacancies, which cause the space charge. Then, the BLTV/Pt junction showed ohmic-like conduction at the high electric field and the conduction mechanisms of BLTV thin film were explained by Schottky emission.

4. Conclusions

$Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) and $(Bi_{3.25}La_{0.75})(Ti_{2.97}V_{0.03})O_{12}$ (BLTV) thin films were prepared by the PLD method. BLT and BLTV single phases with the Bi-layered perovskite structures were crystallized at the annealing temperatures of 700°C and corresponding structures were confirmed by XRD analysis. V doping on BLT thin films increased the dielectric constant and decreased the dielectric loss. The remnant polarization ($2P_r$) of BLT and BLTV thin films was 22 μC/cm^2 and 30 μC/cm^2 respectively. The leakage current density of BLT and the BLTV thin films was 6.2×10^{-7} A/cm^2 and 2.2×10^{-7} A/cm^2 at 90 kV/cm, respectively. The remnant polarization improved for the BLTV thin films and the leakage current density decreased. The V^{5+} substitution for Ti^{4+} effectively decreased the Bi and oxygen vacancies which contribute to conduction process. Because of the electric field dependence of the leakage current, the space-charge-limited currents can dominate the BLT/Pt junction. However, the Schottky emission behavior can characterize the BLTV/Pt junction with a barrier height of $\Phi_B = 0.2$ eV. High-valent cation doping decreased the concentration of oxygen vacancies, which caused the low domain pinning and high fatigue resistance. These results indicate that small V-doping reduced the leakage current density and improved the ferroelectric properties.

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