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Retention characteristics of V-doped $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin film

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Abstract

$Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) and V-doped BLT (BLTV) thin films are prepared on $Pt/Ti/SiO_2/Si$ substrates by a pulsed laser deposition (PLD) method. Ferroelectric and polarization retention characteristics are investigated by leakage current density–electric field (J–E) and P–E hysteresis loops. The single phases with Bi-layered perovskite structure are confirmed by XRD. The increase of leakage current of BLT and BLTV films are produced at 100 kV/cm and 160 kV/cm, respectively. The long-time retention dispalys a stretched exponential decay for BLT film while a logarithmic decay for BLTV film. After a retention time of 1×10^5 s, the retention loss of BLT and BLTV films were about 14 and 7% of the initial value measured at $t = 1$ s, respectively. BLTV thin film exhibits a retention-free characteristics. The effect of vanadium doping on the retention properties of BLT film will be discussed in detail.

Keywords: A. Films; C. Ferroelectric properties; BLT; FRAM; Retention

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1. Introduction

For optical, electro-optic device applications and non-volatile ferroelectric random access memory (FRAM), much attention has been paid to ferroelectrics [1]. Currently, $Pb(Zr_xTi_{1-x})O_3$ (PZT), $SrBi_2Ta_2O_9$ (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 application [2–4]. It was important that these materials have a low polarization switching voltage, low leakage current, low annealing temperature, and little fatigue.

Currently, BIT-based materials were a candidate for FRAM application. For BIT, A = Bi, B = Ti, and $n = 3$ were given in a general formula of Bi-layer structured ferroelectrics (BLSFs), $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$. It was known that BIT materials have a high leakage current and domain pinning due to defects such as Bi vacancies (V_{Bi}''') accompanied by oxygen vacancies ($V_{\ddot{O}}$). The BLT thin film was deposited by substituting a Bi ion with an La ion at A-site, and then fatigue endurance was improved [4]. It has been reported that ferroelectric properties were improved by ion doping on A- or B-site. Recently, effects of ion doping on ferroelectric properties and electrical conduction behavior have been widely studied [5–7]. For practical FRAM application, retention characteristics was important to distinguish between the “1” and “0” states. In other words, the capacitor and the corresponding memory element need to be able to maintain a polarization state. Retention, the ability of maintaining a written logic, was one of the most important topics for ferroelectric random access memory applications [1,2,8]. In this paper, retention loss reduced the difference between switched (P^*) and nonswitched ($P\hat{}$) polarization and led to an inability to distinguish between the two logic states. The retention characteristics of BLT and BLTV thin films were examined at the film temperature of 100 °C. The effect of vanadium doping on the retention properties of BLT film will be discussed.

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) method. Prior to

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

The formation of single-phases or different phases was investigated by XRD with Cu Kα radiation. The grain morphologies showed a spherical shape with ∼100 nm size. To research electrical properties, Pt top electrodes of 2.5×10^{-4} cm^2 area were deposited on the film through a shadow mask by dc sputtering to form metal-ferroelectric-metal (MFM) capacitors. The ferroelectric properties and fatigue were investigated by *P–E* hysteresis loops (Ferroelectric Tester, RT66A). Leakage current were obtained by electrometer (Kiethley 236) and the retention was measured by observing the time dependent changes of P^* and $P^\wedge$ independently. Ferroelectric retention properties were measured at 100 °C using a RT66A ferroelectric test system. At first, a rectangular pulse of −10 V (170 kV/cm) was applied to write a known logic state, then, after a predetermined time, the logic state was sequentially read by applying two rectangular pulses of +10 V (read No.1) and −10 V (read No.2). The pulse width for all rectangular pulses were 0.5 ms. Time decay between the right pulse and the first read pulse was called the retention time.

3. Results and discussion

Fig. 1 shows the XRD patterns of the BLT and BLTV thin films annealed at 700 °C for 60 min. The indexed XRD patterns were agreed with previous results of BIT and BLT. To change the amorphous phase of as-grown film to a BLT single phase, the annealing temperature of 650–700 °C was needed. The as-grown BLT and BLTV thin films exhibited amorphous phases due to the low pre-heating temperature of 450 °C. In this work, crystallized thin films were obtained at an annealing temperature of 700 °C.

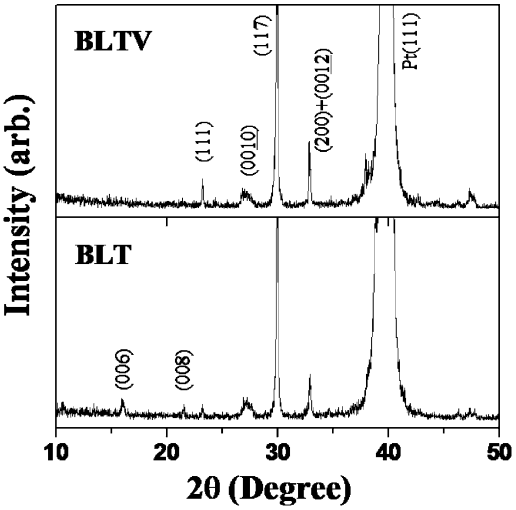

Fig. 1. XRD patterns of BLT and BLTV thin films annealed at 700 °C for 60 min.

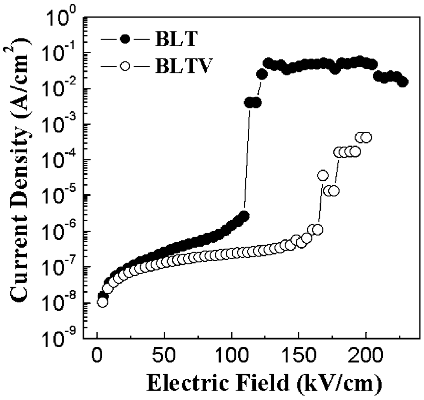

Fig. 2. The leakage current density–electric field (*J–E*) characteristics of BLT and BLTV films.

Fig. 2 shows the leakage current density–electric field (*J–E*) characteristics of BLT and BLTV films. The leakage currents of two samples exhibited the similar value of 10^{-7} A/cm^2 at room temperature. The leakage current of BLT film was abruptly enhanced at the electric field of 100 kV/cm while that of BLTV was increased at 150 kV/cm. The abruptly increase of current density in the BLTV film was about 50 kV/cm higher than that of BLT, which could be attributed to the reduced concentration of oxygen vacancies after V addition. The improvement of ferroelectric and piezoelectric properties of the BLTV film could be attributed to the decrease in space charge density due to the recombination between holes and electrons as was reported in the donor-doped material system. It was most likely that the defect such as oxygen vacancies act as space charges, which cause strong domain pinning.

Retention characteristic is the time-dependent change of the polarization state in the ferroelectric film. After a long-time, polarization loss can be caused in the ferroelectric memory device. Fig. 3a exhibits the long-time retention characteristics of BLT and BLTV films and Fig. 3b and c, corresponding *P–E* hysteresis loop before and after retention test with applied field of 170 kV/cm. As can be seen, the polarization values of BLTV capacitors almost remained constant, but those of BLT capacitor displayed a little reduction. The corresponding *P–E* hysteresis loops obtained after the retention test was also nearly identical to that observed before the retention test. The switchable polarization has almost no loss and the structures have a little tendency to imprint after 3×10^5 s. After a retention time of 1×10^5 s, the polarization loss of BLT and BLTV films were about 14 and 7% of the initial value measured at $t = 1$ s, respectively. Addition of V^{5+} enhanced the retention properties compared to that of the BLT thin film. Thermally accelerated retention failure tests, performed at 100 °C for 1×10^5 s, showed that the BLTV films had quite good retention characteristics, retaining 92% of the

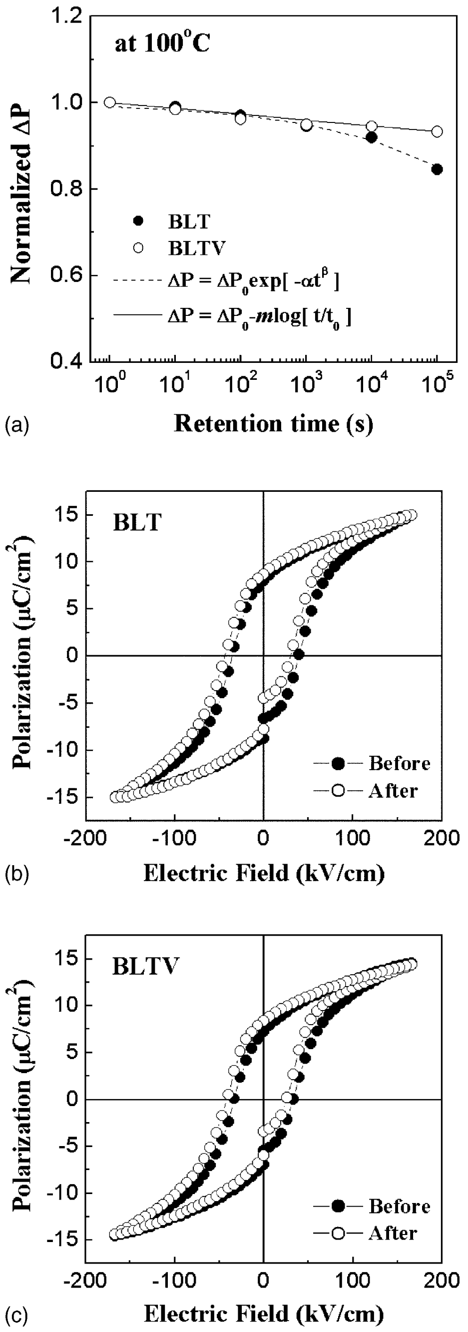

Fig. 3. Retention properties of Pt/BLT/Pt and Pt/BLTV/Pt films and corresponding hysteresis loop before and after retention test with applied field of 170 kV/cm.

value measured at $t = 1$ s. After long-time retention, the nonvolatile polarization of BLT film exhibited the stretched exponential decay behavior. However, logarithmic decay was seen in BLTV films.

For BLT thin film, the nonvolatile polarization, ΔP was explained by the stretched exponential decay

$$\Delta P(t) = \Delta P(0) \exp\left[-\frac{t}{\tau}^{\beta}\right] \tag{1}$$

were β is a exponent of a stretched exponential decay. In this work, the exponent β and the characteristic-time τ were 0.248 and 108.7 s, respectively.

For BLTV thin film, the polarization ΔP was explained by the logarithmic decay

$$\Delta P(t) = \Delta P_0 - m \log\left[\frac{t}{t_0}\right] \tag{2}$$

Here, t is the retention time, t_0 is the characteristic time at which the linear behavior of $P(t)$ begins with respect to $\log t$, P_0 is the polarization at $t = t_0$, and m is the decay rate of 0.01331 which is found by the slope of Fig. 3.

The logarithmic time dependence for BLTV film suggested that the polarization decay process had a distribution over orders of magnitude in relaxation time. Power law behavior has been used to describe polarization behaviors of some kinds of ferroelectric materials. In this work, retention loss of BLT thin film explained by the power law behavior. However, the retention characteristics of the BLTV thin film was changed into logarithmic decay. Previously, retention property was explained by power law behavior and the long-time retention loss was attributed to the effects of redistribution of defect charges. The redistribution of charge may cause imprint failure and a decrease in the polarization. From our long-time retention data, polarization loss of ferroelectric memory device can be calculated after 10 years by using Eqs. (1) and (2). The retained polarization of BLTV film was maintained to 86% of the initial value measured at $t = 1$ s, but in BLT films a rapid reduction to 49% of the initial value measured at 1 s was seen.

Why is such a result obtained? The large currents through the ferroelectric film during anti-parallel biases less than coercive voltages were caused by depolarization. The retention loss of BLT film originated mainly from depolarization of ferroelectric polarization during memory retention time. In the case of long retention time more than 1000 s, since the lattice defect existed in the film, then the space charges due to leakage current was not eliminated if the bias was retained during this retention period of time. Retention loss in ferroelectric capacitors was generally attributed to the presence of the internal electric field due to the bias effect originated from the incomplete screening of the depolarizing field. Mehta et al. [9] explained that the polarization charges were not completely compensated by the electrode charges due to the distribution between polarization charge and electrode charges are separate from each other. The origin of charge separation may be the existence of a spatial variation of polarization near the electrode. The residual depolarization field was polarization dependent and quickly changes its polarization reversal. At the same time, the field produced space charge, the screen field retains its polarity long after switching, since its decay rate was determined by the RC time constant. Thus, space charge was created at the boundaries/interfaces, and retention occurs in the films but V-doped BLT film with bismuth layer structure oxide get a relatively decreased space charge by V-doping. The retention-free nature of BLTV film were attributed to the fact that the oxygen vacancies can be easily moved. Once the electric field was switched on, the defects easily go back into the film from the trap sites. There was no accumulation of vacancies at interfaces with electrodes, space charge buildup and domain pinning.

From the result of our experiments, V-doping cause the improved retention behavior. The high valence cation which is substitute B-site reduced defect such as oxygen vacancy and anti-site defects. The role of the B-site substitution was known mainly to compensate defects which cause fatigue and domain pinning. The distribution in trap depth for the space charge redistribution leading to the irreversible change in resultant hysteresis loops.

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. The crystallized single phase with Bi-layer perovskite structure is confirmed by XRD analysis. The abrupt increase of current density in the BLTV film is about 50 kV/cm higher than that of BLT, which could be attributed to the decrease of oxygen vacancies after V addition. It is indicates that the small V-doping increased the remnant polarization. The V^{5+} substitution for Ti^{4+} site is effective for the decrease of Bi vacancies accompanied by oxygen vacancies. Retention loss in ferroelectric capacitors is generally attributed to the presence of the internal electric field such as oxygen vacancy and anti-site defects. The long-time retention show a stretched exponential decay for BLT thin film while show a logarithmic decay for V-doped BLT thin film. After a retention time of 10 years, the retained polarization of BLTV film is maintain about 86% of the initial value measured at 1 s, but that of BLT film was rapid reduction about 49% of the initial value measured at 1 s.

Acknowledgements

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