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Abstract

The ferroelectric behavior in terms of electrical polarization and fatigue and dielectric properties at elevated temperature of the ferroelectric $\text{Bi}_{3.25}\text{Sm}_{0.75}\text{V}_{0.02}\text{T}_{2.98}\text{O}_{12}$ thin film fabricated by the pulsed laser deposition method were studied. Its switchable polarization increased at elevated temperature, and the coercive field decreased at the same time due to the strong domain depinning process at higher temperature. This film shows almost a polarization-fatigue-free character at room temperature, but the aggregation and diffusion of the thermally activated long-range oxygen vacancies caused strong domain pinning, and thus a poor fatigue resistance was observed at elevated temperature.

Keywords

Ferroelectric, properties, $\text{Bi}_{3.25}\text{Sm}_{0.75}\text{V}_{0.02}\text{T}_{2.98}\text{O}_{12}$, thin, film, elevated, temperature

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Ferroelectric properties of $\text{Bi}_{3.25}\text{Sm}_{0.75}\text{V}_{0.02}\text{Ti}_{2.98}\text{O}_{12}$ thin film at elevated temperature

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The ferroelectric behavior in terms of electrical polarization and fatigue and dielectric properties at elevated temperature of the ferroelectric $\text{Bi}_{3.25}\text{Sm}_{0.75}\text{V}_{0.02}\text{Ti}_{2.98}\text{O}_{12}$ thin film fabricated by the pulsed laser deposition method were studied. Its switchable polarization increased at elevated temperature, and the coercive field decreased at the same time due to the strong domain depinning process at higher temperature. This film shows almost a polarization-fatigue-free character at room temperature, but the aggregation and diffusion of the thermally activated long-range oxygen vacancies caused strong domain pinning, and thus a poor fatigue resistance was observed at elevated temperature. © 2007 American Institute of Physics. [DOI: 10.1063/1.2743910]

In recent years, as prospective candidates to replace the lead-based materials $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ for nonvolatile ferroelectric random access memory, bismuth layered ferroelectric oxides have attracted considerable attention. Specifically, trivalent rare earth element doped bismuth titanates (BT) are now the focus of the attention since Park *et al.* showed that their characteristics include fatigue-free and high remanent polarization and a lower deposition temperature for La-doped bismuth titanate films ($\text{Bi}_{4-x}\text{La}_x\text{Ti}_3\text{O}_{12}$) on Pt electrodes, in comparison to other Bi-layered ferroelectrics [e.g., $\text{SrBiTa}_2\text{O}_9$ (SBT)].¹⁻⁸ It also has been shown that samarium substituted bismuth titanate shows quite large ferroelectric polarization with a $2P_r$ up to $54 \mu\text{C}/\text{cm}^2$.⁹ Good fatigue resistance has also been demonstrated by this thin film. It should be noted that all these properties were measured at room temperature. However, in the practical running of ferroelectric memory devices, self-heating effects are a serious problem. In practical application, these memory devices run above room temperature for most of the time. Also, they will sometimes encounter environmental temperatures that are well above normal. So the performance of the devices at elevated temperature is a very important issue, which cannot be neglected in most cases. Heat will affect the performance of the element, leading the element to fail to work, or more seriously, actually destroying the element. To prevent this from happening, action should be taken to release the heat and keep the devices running at normal temperature. Yet it is even more important to make the devices resistant to the heat and able to work normally at elevated temperature. One of the main reasons for the bad performance of ferroelectric thin films at elevated temperature is the activation of dislocations, for example, those due to oxygen vacancies, which will cause serious fatigue due to their accumulation at the electrode interface.¹⁰⁻¹³ So the stability of doped BT thin film at elevated temperature should be evaluated, although its layered structure, where there is alternation with $(\text{Bi}_2\text{O}_2)^{2+}$

slabs, forms a deep potential well to localize the oxygen vacancies, preventing aggregation at the electrode/film interface and resulting in a fatigue-free character at room temperature.¹⁴ In this letter, $\text{Bi}_{3.25}\text{Sm}_{0.75}\text{V}_{0.02}\text{Ti}_{2.98}\text{O}_{12}$ thin film is fabricated and its ferroelectric performance at elevated temperature is evaluated.

A target with the composition of $\text{Bi}_{3.41}\text{Sm}_{0.75}\text{V}_{0.02}\text{Ti}_{2.98}\text{O}_{12}$ for the fabrication of films with the composition of $\text{Bi}_{3.25}\text{Sm}_{0.75}\text{V}_{0.02}\text{Ti}_{2.98}\text{O}_{12}$ (BSVT) plus 5% excess bismuth, which was used to compensate for the loss of bismuth, was prepared by conventional solid state reaction at 1100°C . BSVT thin films with thicknesses of 200–400 nm were deposited on Pt/TiO₂/SiO₂/Si substrates by pulsed laser ablation. The preparation conditions were the same as in the deposition of $\text{Bi}_{3.41}\text{Sm}_{0.75}\text{Ti}_3\text{O}_{12}$ film.⁹ A Pt top electrode with dimensions of 0.0314 mm^2 was coated by magnetron sputtering with a shadow mask to form a metal-ferroelectric-metal structure. The ferroelectric properties of the films were measured by an aixACCT EASY CHECH 300 system. The dielectric properties were measured by an HP 4298A LCR meter. For the measurements at elevated temperatures, the sample was putted in silicone oil with temperature controllable. X-ray diffraction (XRD) measurements were carried out on a JEOL JDX-3500 system with Cu $K\alpha$ radiation. The thickness of the films was measured by the optical reflection

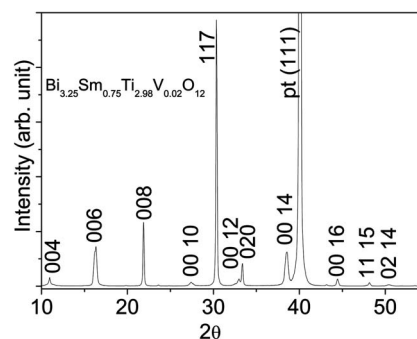


FIG. 1. XRD pattern of the BSVT film on platinumized silicon.

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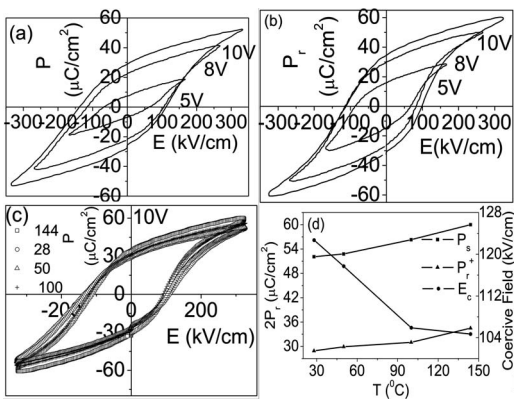


FIG. 2. Polarization–electric field hysteresis loops of BSVT film: (a) measured at 5, 8, and 10 V at room temperature; (b) measured at 5, 8, and 10 V at 144 °C; (c) measured at 10 V at 28, 50, 100, and 144 °C; (d) polarization and coercive field dependence on temperature.

method with a Filmtek™ 4000 from Scientific Computing International, USA.

Figure 1 presents the XRD pattern of a BSVT film deposited on a Pt/Ti/SiO₂/Si substrate at a temperature of 650 °C, revealing a highly (117) oriented growth habit, as well as other relatively weaker peaks, which can be indexed as the (00*n*) diffraction.

The electrical polarization hysteresis loops (*P*-*E* loop) of a 240 nm thick BSVT thin film measured at room temperature, 100 Hz, and at maximum voltages of 5, 8, and 10 V are shown in Fig. 2(a). With the maximum voltage of 10 V applied, the sensing margin in terms of the $2P_r=(P_r^+-P_r^-)$ value is $56 \mu\text{C}/\text{cm}^2$ and the coercive field is 112.27 kV/cm. In comparison with the $2P_r$ value of $20 \mu\text{C}/\text{cm}^2$ of the La-doped BT thin film, the polarization of the BSVT film is greatly enhanced through the doping of Sm. With gradual decreasing of the applied voltage, the polarization and coercive fields decrease correspondingly. Figure 2(b) shows a similar measurement to that in Fig. 2(a) at the elevated temperature of 144 °C. A sensing margin of $62 \mu\text{C}/\text{cm}^2$ with a coercive field of 100 kV/cm was obtained. It is obvious that the value of the sensing margin increased and the coercive field decreased. *P*-*E* loops at a maximum applied electrical field of 10 V at different temperatures are shown in Fig. 2(c). A clear trend of enhancement of both the saturated polarization and the remanent polarization and a decreasing trend of the coercive field as the measurement temperature was elevated are shown. Figure 2(d) shows the polarization and coercive field measured at different temperatures. Both the saturated polarization (P_s) and remanent polarization (P_r) values increase with increasing temperature, while at the

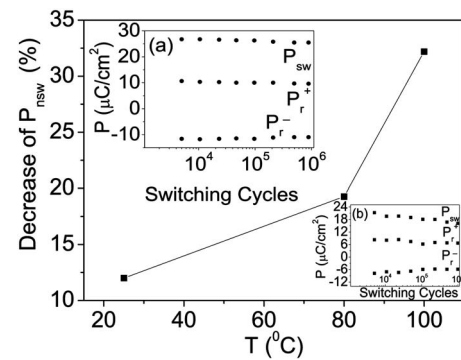


FIG. 3. Fatigue measurements show the decrease of the nonswitchable polarization vs temperature. The insets show the polarization as a function of switching cycles: (a) at room temperature; and (b) at 100 °C. The switching voltage during the fatigue testing is ± 3 V at a frequency of 5 kHz, and the measurement voltage is 5 V.

same time, the coercive field continuously decreases as the temperature rises.

Figure 3 shows the decrease in the nonswitchable polarization P_{ns}^w , the change of polarization from $P_{\text{rrel}+}$ to $P_{\text{max}+}$, $P_{\text{ns}}^w = P_{\text{max}+} - P_{\text{rrel}+}$, where $P_{\text{rrel}+}$ is the positive state of relaxed remanent polarization and $P_{\text{max}+}$ is the state of polarization when the stimulating signal reaches its maximum value of positive saturation. P_{ns}^w after 10^6 read/write cycles at different temperatures is plotted versus temperature. At room temperature, the decrease is 12%, while it goes up to 19% and 32% at 80 and 100 °C, respectively. Inset (a) of Fig. 3 shows fatigue measurements at room temperature at an applied maximum measurement voltage of 5 V, with a fatigue switching voltage of ± 3 V and a switching frequency of 5 kHz. P_{ns}^w remains relatively constant even after 10^6 read/write cycles. In inset (b) of Fig. 3, P_{ns}^w , P_r^+ , and P_r^- in fatigue measurements at 100 °C, under the same conditions as the above measurement at room temperature, decrease continuously as the switching cycles accumulate up to 10^6 times.

Figure 4 shows the frequency dependence of the real part of the relative dielectric permittivity and the dissipation factor [$\epsilon''/\epsilon' = \tan \delta$] of a Pt/BSVT/Pt capacitor at different temperatures. At room temperature and a frequency of 800 kHz, the ϵ' and $\tan \delta$ loss are 361 and 0.034, respectively. For all the measurements at different temperatures, decreases in ϵ' were observed at the low frequency range as the frequency goes up, while ϵ' remains almost constant as the frequency increases in the high frequency range without abrupt changes. At elevated temperature, the value of ϵ' increases. For example, it is 385 at a temperature of 90 °C. It is also observed that ϵ' is obviously decreasing as the fre-

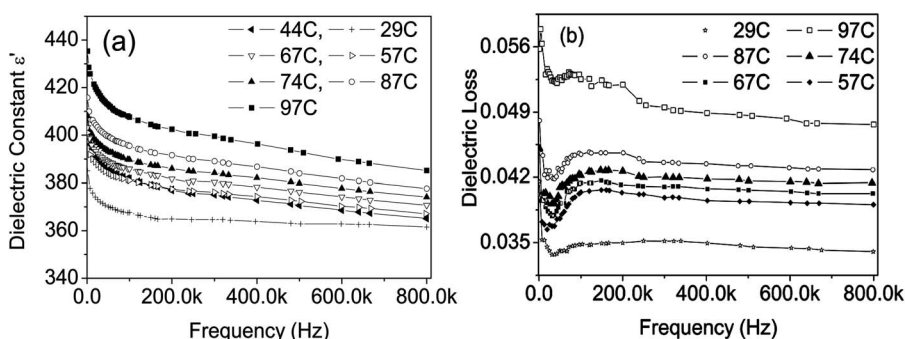


FIG. 4. Frequency dependence of the dielectric constant (a) and the loss (b) measured at different temperatures.

quency goes up, over the full range of measured frequency. The dielectric loss also increases at elevated measuring temperatures. The value of the dielectric loss at 90 °C is 0.047.

The domain switching in ferroelectric materials is modulated by the competition between domain pinning and depinning processes. The domain pinning usually is mainly contributed by the domain wall pinning, which is favored by the long-range diffusion of oxygen vacancies and consequent aggregation.¹⁴ Also, a high density of domain walls has benefits for the domain pinning. The domain depinning is driven by the electric field E and favored at high temperature. In our measurements, an enhancement of P_s and a decrease in E_c at higher temperature were observed. At higher temperature, a lower density of domain walls is expected, which leads to weaker domain pinning. Moreover, the domain depinning is kinetically easier due to the reduction of the domain wall density at high temperature, resulting in larger P_s and small E_c .

There are several physical origins responsible for the polarization fatigue effect, including domain wall pinning, formation of interfacial layers, and internal stress derived from 90° domains.¹⁵ However, for those thin films with layered-perovskite structure, such as SBT and BT, no significant fatigue was observed at room temperature due to the deep potential well formed by the $(\text{Bi}_2\text{O}_2)^{2+}$ slabs, which trap oxygen vacancies locally, preventing them from aggregating at the electrode/film interface. Similarly, samarium and vanadium codoped BT film in this experiment at room temperature is almost fatigue-free. However, at elevated temperature, the thermal activation of the trapped oxygen vacancies for diffusion through the $(\text{Bi}_2\text{O}_2)^{2+}$ slabs and aggregation at the domain walls and electrode/film interface will more likely happen. So the observed fatigue at high temperature demonstrates that the domain pinning process due to long-range diffusion and aggregation of the oxygen vacancies is dominant in competition with the depinning process, resulting from the decrease in the domain wall density and other thermal effects. So, for the layered BSVT film, the thermal energy could help the oxygen vacancies overcome the energy barrier due to the natural layers and reach low energy trapped positions. It is also proven that the effect of variations in the domain wall density and of depinning kinetics on the fatigue is very weak in comparison with that of the long-range diffusion and aggregation of oxygen vacancies at elevated temperature.

The larger dielectric constant at higher temperature at the same frequency is due to the ferroelectric phase transition

happened above 600 °C. However, the more serious loss at high temperature means that there is higher conductivity caused by the thermally activated charge carriers, revealing that the charge carriers, mainly oxygen vacancies, have a larger mobility at higher temperature than at room temperature. This also indicates that the thermally activated charge carriers can overcome the energy barrier formed by the $(\text{Bi}_2\text{O}_2)^{2+}$ layers in the BSVT structure at higher temperature.

In summary, the ferroelectric properties of the BSVT thin films at elevated temperatures have been studied. Higher temperature causes the depinning of the electrical domains, resulting in an enhancement of the switchable polarization and a decrease in the coercive field. At the same time, thermally activated oxygen vacancies can penetrate the energy barrier formed by the $(\text{Bi}_2\text{O}_2)^{2+}$ slabs to cause serious polarization fatigue. These strongly affect the reliability of the performance of the BSVT ferroelectric random memory elements at elevated temperature.

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