

Effect of titanium substitution on film structure and ferroelectric properties of Sr-deficient $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ thin films

San-Yuan Chen*, Bang-Chiang Lan, Chang-Sheng Taso

Department of Materials and Science Engineering, National Chiao-Tung University, 300 Hsinchu, Taiwan, ROC

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Abstract

Ferroelectric films of bismuth-containing layered perovskite $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{2-x}\text{Ti}_x)\text{O}_9$ ($x=0-0.8$) have been prepared using a metal-organic decomposition method. The effects of Ti substitution on the microstructure evolution and ferroelectric properties of $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ films were investigated. A maximum remanent polarization of $2P_r=30.7 \mu\text{C}/\text{cm}^2$ was obtained for the $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_{1.8}\text{Ti}_{0.2}\text{O}_9$ film as compared to $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ films ($19.6 \mu\text{C}/\text{cm}^2$) annealed at 800°C in air. The Ti substitution for Ta leads to charge compensation for the self-produced positive Bi_{Sr}^+ due to the occupation of Bi on Sr vacancies and is responsible for the increase in leakage resistance. The leakage current density as low as $2 \times 10^{-8} \text{ A}/\text{cm}^2$ can be obtained at an applied electric field of $100 \text{ kV}/\text{cm}$. Substitution of Ti for Ta shows a positive effect on the fatigue endurance of Sr-deficient $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ film.

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1. Introduction

Layered perovskite ferroelectrics such as $\text{SrBi}_2\text{Nb}_2\text{O}_9$ (SBN) and $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) are being widely used for applications in high-density non-volatile ferroelectric random access memory because of their excellent ferroelectric properties, characterized by limited polarization fatigue and low coercive field [1,2]. They belong to the family of Aurivillius compounds with a general formula of $(\text{Bi}_2\text{O}_2)^{+2}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$, consisting of m -perovskite units sandwiched between bismuth oxide layers. (Here A and B are the two types of cations that enter the perovskite unit. A is Bi^{+3} , Ba^{+2} , Sr^{+2} , Pb^{+2} , or K^{+1} ; B is Ti^{4+} , Ta^{+5} , Nb^{+5} , Mo^{6+} or W^{6+} .) [3,4]. The ferroelectric properties, crystal structure and microstructure are remarkably influenced by the composition fluctuation. Atsuki et al. [5] reported that the remanent polarization (P_r) of $\text{Sr}_x\text{Bi}_{2z}\text{Ta}_2\text{O}_9$ ($0.7 \leq x \leq 1.0$, $2.0 \leq 2z \leq 2.6$) increased

with the decrease of the Sr/Ta mole ratio for films annealed at 800°C . A maximum remanent polarization was also reported for the SBT films with 20 mol.% Sr-deficient and 10 mol.% Bi-excess composition [6,7]. The enhancement in P_r with decreasing Sr content from $x=1.0$ to 0.8 was attributed to the increase in grain growth. On the other hand, Watanabe et al. [8] reported that the dependence of P_r on Sr content in SBN films was entirely due to the sensitivity of grain orientation to Sr content. The randomly oriented Sr-deficient SBN films have larger remanent polarization than c -axis oriented stoichiometric SBN films.

However, although the Sr-deficient SBT films have been reported to exhibit more excellent polarization compared to stoichiometric SBT film, a partial fatigue was also observed due to the substitution of Bi for Sr sites [6,7,9]. From the viewpoint of the general formula of Aurivillius compounds, the substitution of cations for A-sites and B-sites in the $\text{SrBi}_2\text{Ta}_2\text{O}_9$ is possible. Efforts have been made to enhance the ferroelectric properties of layered perovskite ferroelectrics by the substitution of alternative cations. For example, Nb substitution for

*Corresponding author. Tel.: +886-3-5731818; fax: +886-3-5724727.

E-mail address: sychen@cc.nctu.edu.tw (S.-Y. Chen).

Ta was reported to enhance the ferroelectric properties [10,11]. The partial substitution of Sr^{2+} by Ba^{3+} can result in the noticeable improvement of the dielectric constant and remanent polarization [12]. An enhanced remanent polarization was also observed in the SBT film with the addition of Pb^{2+} cation [9]. Desu et al. revealed that the thin film with $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9-0.3\text{Bi}_3\text{TiTaO}_9$ compositions and annealed $650-750^\circ\text{C}$ exhibited higher remanent polarization and lower leakage current density [13]. However, to author's knowledge, little work has been done to investigate the role of B-site substitution in Sr-deficient SBT system. Therefore, from the viewpoint of charge compensation, titanium acceptor-doped SBT films were prepared on Pt/Ti/SiO₂/Si substrates. The effect of titanium incorporation on remanent polarization, leakage current and fatigue properties of $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{2-x}\text{Ti}_x)\text{O}_9$ films will be investigated and discussed in this work.

2. Experimental

The starting materials for the metal-organic decomposition process were bismuth 2-ethylhexanoate [$\text{Bi}(\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{COO})_3$], strontium 2-ethylhexanoate [$\text{Sr}(\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{COO})_2$], titanium isopropoxide [$\text{Ti}(\text{OC}_3\text{H}_7)_4$] and tantalum ethoxide [$\text{Ta}(\text{OC}_2\text{H}_5)_5$] with 2-ethylhexanoic acid as the solvent. The metal-organic precursors were mixed to form solutions with compositions of $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{2-x}\text{Ti}_x)\text{O}_9$ (designated as SBTT). Prior to film deposition, the substrate (Pt/Ti/SiO₂/Si) was cleaned in acetone and alcohol ultrasonic baths, and then blown dry with N_2 gas. The solutions were spin-coated onto the substrate at a speed of 3000 rpm. After each coating, the as-deposited film was dried on a hot plate at a temperature approximately 350°C to remove the solvent before application of the next coating. After the process was repeated four times, the as-deposited films were annealed at $500-850^\circ\text{C}$ in air and oxygen atmosphere for 30 min by directly placing the coated substrate into a preheated tube furnace. Most of the data reported here were obtained for films with four layers ($t=0.37-0.42\text{ }\mu\text{m}$).

The crystal structures of the films were analyzed by using Siemens D5000 X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation and a Ni filter. The film thickness was measured by Dektak surface profilometer. Field-emission scanning electron microscopy (FESEM, Hitachi S4000) was performed to investigate the surface morphology of the films. Patterned top Au electrodes through a shadow mask on an area of $8.0 \times 10^{-4}\text{ cm}^2$ area were sputter-deposited onto the SBT layers to define capacitors in order to perform electrical measurements. A ferroelectric testing system (RT-66A, Radiant Technologies Inc.) operating in the virtual-ground mode was used to obtain the remanent polarization (P_r)-coercive field (E_c) hysteresis characteristics and fatigue proper-

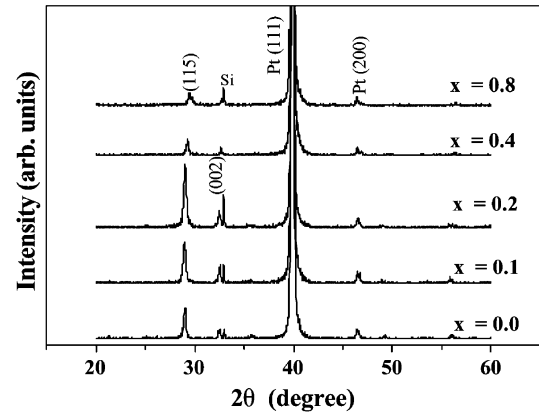


Fig. 1. XRD patterns of $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{2-x}\text{Ti}_x)\text{O}_9$ films annealed at 800°C for 0.5 h.

ties. Fatigue tests of the films were conducted using a bipolar square wave of 6 V at 1 MHz.

3. Results and discussion

3.1. Microstructure and phase evolution

Fig. 1 shows the XRD patterns of $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{2-x}\text{Ti}_x)\text{O}_9$ film ($0 \leq x \leq 0.8$) annealed at 800°C for 0.5 h. It was noted that the intensity of (1 1 5)-oriented peak slightly increases with increasing Ti content. Above that ($x=0.2$), the peak intensity gradually decreases and becomes broadening, which might be attributed to poor crystallization and smaller grain size. The XRD patterns also reveal that the films are polycrystalline in nature with no evidence of secondary phases. Besides that, with increasing Ti content, the (1 1 5) reflection is slightly shifted to the high diffraction angle, indicating that the Ti ion has been dissolved into TaO_6 octahedral structure and completely substituted for Ta ion. XRD studies of $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.2})\text{O}_9$ films as a function of annealing temperature indicate that the films annealed at 500°C are amorphous. At 600°C , a broad diffraction peak appears approximately $2\theta=28.5^\circ$, indicating that the perovskite SBTT phase starts to develop. At 650°C , as shown in Fig. 2, the (1 1 5) diffraction peak remains broad, which implies that the film is not fully crystallized. With increasing the annealing temperature, at 700°C , the (1 1 5) peak in the XRD patterns becomes sharper and the full width at half-maximum decreases that indicates better crystallinity and an increase in grain size. However, at 850°C , a broad diffraction peak approximately 29.5° (indicated as x-phase in Fig. 2) was found similar to Bi-deficient pyrochlore as reported by Rodriguez et al. [14].

Fig. 3 illustrates typical (FESEM) surface images obtained from SBTT films having various Ti contents and annealed at 800°C . It reveals that the incorporation of Ti into SBT plays an important role in both grain

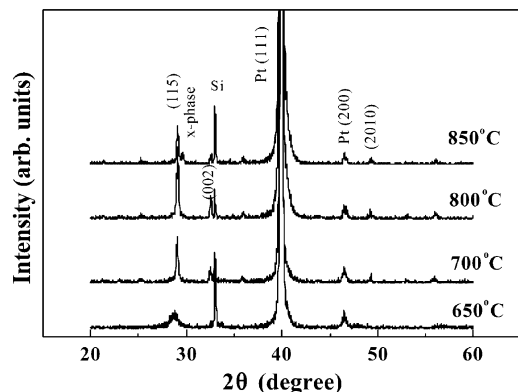


Fig. 2. XRD patterns of $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.2})\text{O}_9$ films annealed at different temperature for 0.5 h.

size and grain morphology of $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ films. The microstructure of undoped SBT ($x=0$) film presents a rod-like grain matrix. In contrast, with the incorporation of Ti into the SBT structure, the grain size of $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.2})\text{O}_9$ film is found larger than that of $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ film. However, further excess Ti (i.e. $x=0.4$) causes the decrease in grain size and forms somewhat porous structure. The enhanced grain size in $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ film with Ti addition up to 0.25 is probably related to chemical structure. The off-stoichiometric composition in the $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.2})\text{O}_9$ film can be approximately considered as a solid solution of 0.75 $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and 0.25 $\text{Bi}_3(\text{Ta,Ti})\text{O}_9$ with approximately 10% excess bismuth content. Ti-based layered perovskite materials are usually expected to exhibit a lower crystallization temperature than SBT or SBN. As

reported by Hu et al. that when the SBT film was deposited on the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ buffered Pt/Ti/ SiO_2 /Si substrates, the SBT film can be crystallized at 650 °C, which is 50 °C lower than that for SBT films without $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ buffer layer because $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ film can be formed at lower temperature compared to SBT film [15]. On the other hand, as excess Ti content (i.e. $x=0.4$) was added, it was observed that the grain size decreased and somewhat porous structure was formed, indicating the densification and grain growth were hampered with further increasing Ti content. In other words, it is impossible to consider the $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.8})\text{O}_9$ composition as a solid solution of $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{Bi}_3(\text{Ta,Ti})\text{O}_9$ and a distorted structure was probably formed.

The root means square (rms) roughness of the SBT film surfaces calculated from the atomic force microscopy (AFM) morphologies in a $1 \times 1 \mu\text{m}^2$ area is shown in Fig. 4. At $x=0$ –0.3, the films exhibit smooth surface, above that, the surface of the films becomes rough. As it was observed in SEM micrographs (Fig. 3), increasing Ti content makes it relatively easy to merge small grains into large and flat grains.

3.2. Ferroelectric properties

Ferroelectric hysteresis measurements were conducted on $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{2-x}\text{Ti}_x)\text{O}_9$ films in MFM configuration at room temperature using standardized RT 66A ferroelectric test system. Fig. 5 shows typical polarization versus electric field curves of $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.2})\text{O}_9$ films recorded with -6 to $+6$ V excitations. The measured remanent polarization ($2P_r$) and the coercive

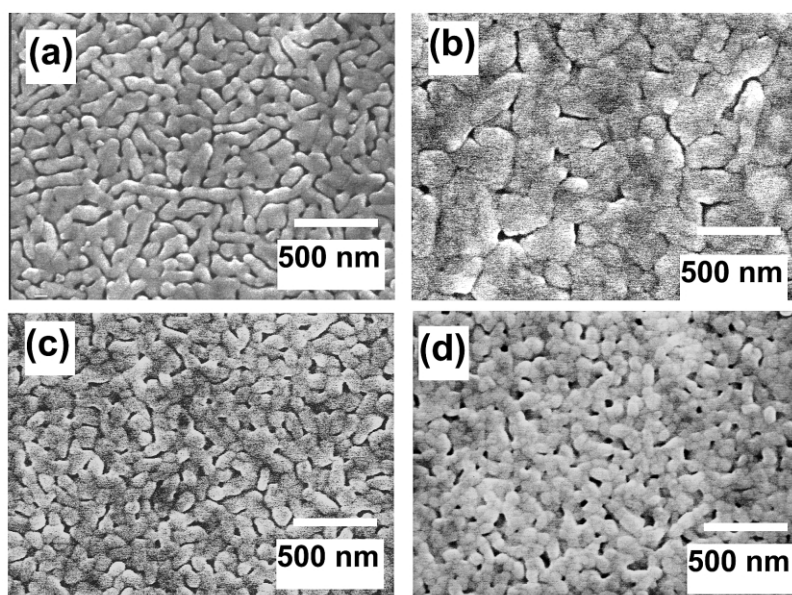


Fig. 3. SEM micrographs of $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{2-x}\text{Ti}_x)\text{O}_9$ films with (a) $x=0$; (b) $x=0.2$; (c) $x=0.4$; and (d) $x=0.8$ compositions annealed at 800 °C for 0.5 h.

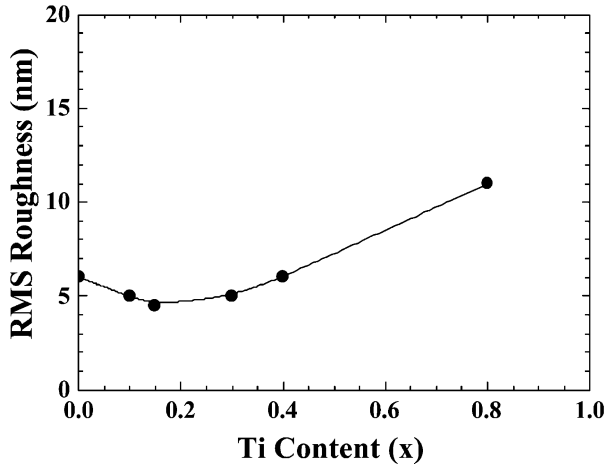


Fig. 4. Rms roughness of various titanium content $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{2-x}\text{Ti}_x)\text{O}_9$ films annealed at 800 °C for 0.5 h.

field ($2E_c$) at an applied electric field of 150 kV/cm are 30.7 $\mu\text{C}/\text{cm}^2$ and 75 kV/cm, respectively, for the films annealed at 800 °C. The effect of Ti addition on the remanent polarization ($2P_r$) of SBT films is further illustrated in Fig. 6. It was found that the SBT films with Ti substitution show much improved ferroelectric characteristics compared to $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ films. A maximum remanent polarization was obtained with the SBT film at $x=0.2$ – 0.25 depending on annealing atmosphere. The enhanced ferroelectric properties in the $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.2})\text{O}_9$ films prepared from precursor solution with Ti addition can be elucidated by the aforementioned solid solution of 0.75 $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and 0.25 $\text{Bi}_3(\text{Ta,Ti})\text{O}_9$. The $\text{Bi}_3(\text{Ta,Ti})\text{O}_9$ ceramic was reported to have a Curie temperature approximately ~ 880 °C [16], much higher than that (~ 310 °C) of $\text{SrBi}_2\text{Ta}_2\text{O}_9$, so that the $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.2})\text{O}_9$ film is expected to show good ferroelectric properties. Another possibility is the larger grain size (Fig. 3) in $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.2})\text{O}_9$ film as compared to $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ film. On the other hand, as the titanium addition was more than that ($x=0.2$), the $2P_r$ value that was reduced can be attributed to poor crystallinity and decreased grain size as observed from XRD patterns and SEM microstructure. A maximum value of $2P_r$ ($2P_r=30.7 \mu\text{C}/\text{cm}^2$) was obtained at the SBT film with $x=0.2$ under air atmosphere. For comparison, the effect of oxygen atmosphere on the $2P_r$ value of the $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{2-x}\text{Ti}_x)\text{O}_9$ films was also shown in Fig. 5. According to this figure, after the SBT films was annealed in an atmosphere of O_2 , the $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.75}\text{Ti}_{0.25})\text{O}_9$ film exhibits a maximum remanent polarization ($2P_r$) of 34.9 $\mu\text{C}/\text{cm}^2$ which is larger than that of the film annealed in air atmosphere. The higher remanent polarization in oxygen-annealed films reveals that the polarization is possibly related to defect concentration. The oxygen vacancy can be produced as the

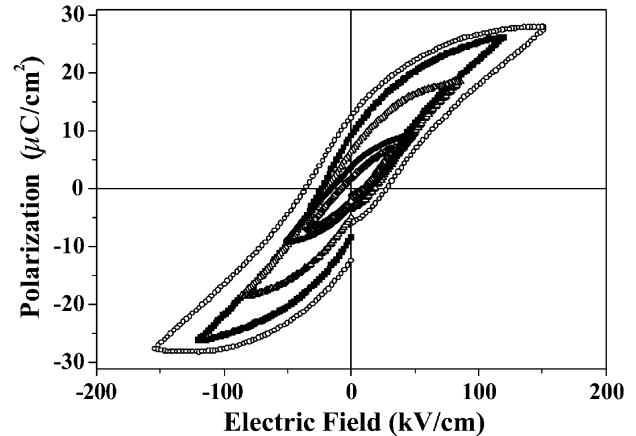


Fig. 5. P – E hysteresis loops of $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.2})\text{O}_9$ films with 800 °C heat treatment at applied voltages of 1.5, 2, 3.5, 5 and 6 V.

tantalum is substituted by Ti acceptor but will be reduced later in the oxygen atmosphere. Therefore, a larger remanent polarization can be obtained in oxygen atmosphere.

Although the produced oxygen vacancies probably lead to the domain pinning as one can see in PZT films [17,18], in this work, the polarization enhancement instead of reduction is obtained for the films with titanium doping. The unique phenomenon reveals that it is possibly related to the occupation of Bi on Sr site in the Sr-deficient SBT compositions because the substitution of Bi for Sr will lead to charge unbalance and produce electrons or cation vacancies. Therefore, as the Ti ions are incorporated into SBT structure, the produced oxygen vacancies, $V_{\text{O}}^{\bullet\bullet}$, can be primarily used to react with electrons or $V_{\text{Sr}}^{\bullet\bullet}$ to decrease the defect concentration. Consequently, the enhanced $2P_r$ value in SBT films with $x=0$ – 0.2 can be attributed to the contribution from the increased grain size and the reduced defect concentration.

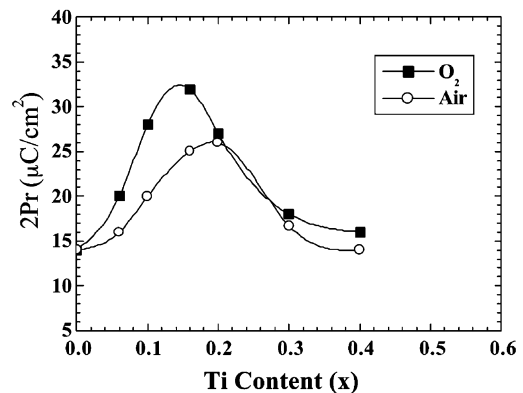


Fig. 6. Dependence of remanent polarization on the Ti content in case of $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{2-x}\text{Ti}_x)\text{O}_9$ films annealed at 800 °C for 0.5 h in air and O_2 atmospheres at an electrical field of 150 kV/cm.

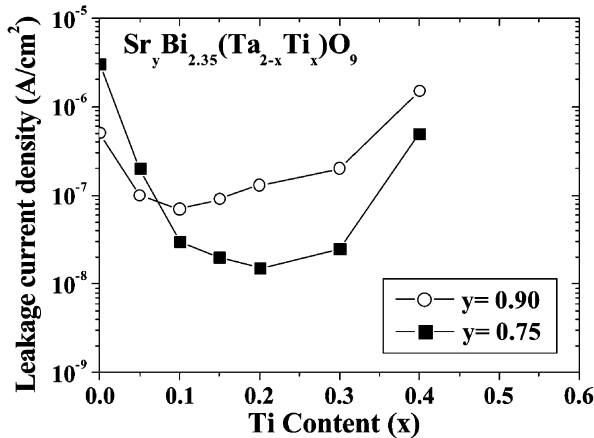


Fig. 7. Leakage current density of various titanium content $\text{Sr}_y\text{Bi}_{2.35}(\text{Ta}_{2-x}\text{Ti}_x)\text{O}_9$ films at an electric field of 100 kV/cm.

3.3. Leakage current

In general, nominally undoped SBT film exhibits p-type conductivity due to Bi_2O_3 volatilization during high-temperature processing [19]. Furthermore, the occupation of Bi on Sr site often occurs in the Sr-deficient SBT compositions since both radii of Sr^{2+} and Bi^{3+} are very close [20], where some fraction of the positive charged $\text{Bi}_{\text{Sr}}^{\bullet}$ ions might be compensated by electrons [21]. By considering only the most probable defects, the charge neutrality can be given as follows:

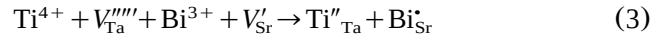
$$2[V_{\text{O}}^{\bullet}] + [h^{\bullet}] + [\text{Bi}_{\text{Sr}}^{\bullet}] = 2[V_{\text{Sr}}^{\prime\prime}] + e^{-} \quad (1)$$

The charge neutrality condition can be modified through the addition of acceptor impurities to be

$$2[V_{\text{O}}^{\bullet}] + [h^{\bullet}] + [\text{Bi}_{\text{Sr}}^{\bullet}] = 2[V_{\text{Sr}}^{\prime\prime}] + [A'_{\text{Ta}}] + e^{-} \quad (2)$$

Acceptor doping can result in a decrease in the concentration of “mobile” defects (e^{-}) through the various mass action relations in the system. Complete compensation by acceptor ions occurs when the acceptor concentration equals the concentration of produced extra $\text{Bi}_{\text{Sr}}^{\bullet}$ species. As shown in Fig. 7, when the $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{2-x}\text{Ti}_x)\text{O}_9$ thin films were annealed at 800 °C in air, the leakage current density was found to decrease with increasing Ti content to $x=0.2$, above that the leakage current density becomes larger due to the produce of anion vacancies. Additionally, it was found that for the SBTT films of $x>0.3$, the grain size becomes smaller and the film surface becomes rough according to AFM analysis (Fig. 4). The rough surface measurement suggests that the films have a larger leakage current density. Therefore, a minimum leakage current density of approximately 2×10^{-8} A/cm² can be obtained for $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.2})\text{O}_9$ film at an electric field of 100 kV/cm that is much lower than that (1×10^{-6}) of undoped SBT film by the two orders of magnitude. The lowered leakage current was also report-

ed by Desu et al. for the films with $0.7\text{SrBi}_2\text{Ta}_2\text{O}_9 - 0.3\text{Bi}_3\text{Ti}(\text{Ta}_{1-y}\text{Nb}_y)\text{O}_9$ composition [13]. The decreased leakage current might be attributed to the addition of Ti acceptor ions for reducing the charge unbalance due to the occupation of Bi on the Sr sites. When the acceptor concentration is close to the concentration of the produced extra $\text{Bi}_{\text{Sr}}^{\bullet}$ species, the complete charge compensation occurs as follows:



Furthermore, for the less Sr-deficient SBTT films, i.e. $\text{Sr}=0.9$, Fig. 7 illustrates that the addition of acceptor (Ti) only leads to a slight improvement in the leakage resistance in comparison with more Sr-deficient SBT films ($\text{Sr}=0.75$). The minimum leakage current density shows up at $x=0.1$ for the less Sr-deficient $\text{Sr}_{0.9}\text{Bi}_{2.35}(\text{Ta}_{2-x}\text{Ti}_x)\text{O}_9$ film. This result suggests that the concentration of the produced $\text{Bi}_{\text{Sr}}^{\bullet}$ species is reduced in the less Sr-deficient SBT films. This finding again indicates that an enhanced insulating characteristic was obtained by substituting Ti for Ta to reduce electron concentration in the Sr-deficient SBT films. Such a decrease is reasonable for charge compensation of $\text{Bi}_{\text{Sr}}^{\bullet}$ species. In order to mark the role of Ti acceptor in the leakage current of SBT films, another work was performed. Tungsten (W) donor was added into the SBT films to substitute for Ta. On the contrary, it was observed that for the same doping amount as Ti, the addition of W donor leads to the increase of leakage current (not shown here). This phenomenon confirms that this is an acceptor effect for the reduced leakage current in the Sr-deficient SBT films.

3.4. Fatigue behavior

Fatigue endurance was tested with 1 MHz bipolar pulses at 6 V. Fig. 8 shows the fatigue behavior of SBT films annealed at 800 °C for 0.5 h. It was observed that

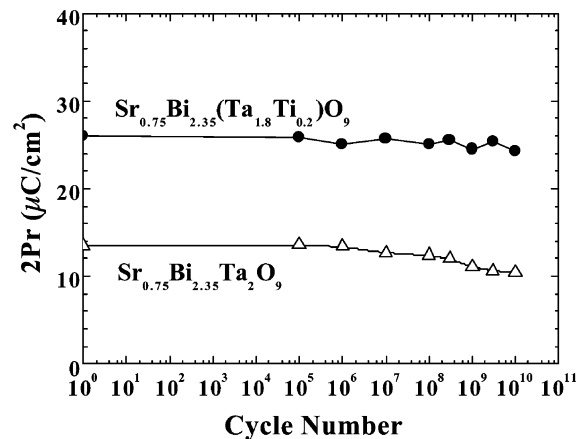


Fig. 8. Fatigue behavior of $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.2})\text{O}_9$ and $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ films under an applied voltage of 6 V at 1 MHz.

a partial loss of $2P_r$ after fatigue was observed for the Sr-deficient $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ film without Ti doping. The percentage of the remanent polarization after 10^{10} cycles was approximately 87% of the initial value, which is consistent with the literature results [6,7]. On the other hand, as Ti was added to substitute for Ta in the SBT films, i.e. $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.2})\text{O}_9$, the film shows no decay in the polarization change up to approximately 10^8 switching cycles but the decay in P_r was observed to be approximately 9% of the initial value after 10^{10} cycles. This indicates that the incorporation of limited titanium into the layered perovskite structure does not cause appreciable fatigue degradation. Kang et al. revealed that $\text{SrBi}_2\text{Ta}_2\text{O}_9$ and $\text{Bi}_3\text{TiTaO}_9$ films grown at the similar deposition conditions showed different fatigue behaviors. The difference should come from the oxygen stability in the perovskite layer [22]. However, Desu et al. reported that thin films of $0.8\text{SrBi}_2\text{Ta}_2\text{O}_9-0.2\text{Bi}_3\text{TiTaO}_9$ solid solution exhibit good fatigue characteristics and the decay in remanent polarization was observed to be less than 5% of initial value after 10^{10} switching cycles [23]. If attention was paid to the atomic ratio of $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.2})\text{O}_9$, it was found that both films of $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.2})\text{O}_9$ (this work) and $0.8\text{SrBi}_2\text{Ta}_2\text{O}_9-0.2\text{Bi}_3\text{TiTaO}_9$ (Desu et al.) have similar compositions. Although the oxygen vacancy will be produced as the Ta was substituted by Ti, it does not cause further degradation in fatigue behavior of $\text{Sr}_{0.75}\text{Bi}_{2.35}(\text{Ta}_{1.8}\text{Ti}_{0.2})\text{O}_9$ film.

There are several proposals that attempt to explain the fatigue behavior of ferroelectric thin films especially for PZT [24–26]. These proposals are all related to defects, which may be trapped at domain boundaries to lower their mobility. However, there have been different views of the species of the defects and the location of the trapping sites. Oxygen vacancy and electron/hole injection have been suggested as possible mechanisms for the fatigue of PZT films [25,26]. In our case, for Sr-deficient $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ film, it was considered that the electron could be produced by substituting Bi for Sr vacancy since both radii of Sr (1.16 Å) and Bi (1.02 Å) are very close. The electron can be produced by substituting Bi for Sr vacancy. According to the fatigue model proposed by Warren et al. [26], the released electronic charge trapped at domain walls can inhibit the domain motion and lead to the partial suppression of the switchable polarization in $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ film that is in agreement with our fatigue data shown in Fig. 8. However, the released electron is possibly compensated from the oxygen vacancies produced from the substitution of Ti for Ta. Consequently, the addition of Ti into SBT structure shows a positive effect on fatigue behavior of $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ film.

4. Conclusions

1. With the incorporation of Ti into $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ films, the grain growth can be further enhanced. However, excess Ti content causes the poor crystallization and reduces the grain size.
2. Ferroelectric properties of $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ films have been significantly enhanced with titanium doping up to $x=0.2-0.25$ (i.e., $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_{1.8}\text{Ti}_{0.2}\text{O}_9$). The measured remanent polarization ($2P_r$) values increases from 19.6 to 30.7 $\mu\text{C}/\text{cm}^2$ at an electrical field of 150 kV/cm.
3. The substitution of Ti ions for Ta can lead to an increase in leakage resistance and the leakage current density is as lower as 2×10^{-8} A/cm² at an applied electric field of 100 kV/cm.
4. Substitution of Ti for Ta shows a positive effect on the fatigue endurance of $\text{Sr}_{0.75}\text{Bi}_{2.35}\text{Ta}_2\text{O}_9$ film.

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