Effects of vanadium doping on structure and electrical properties of SrBi$_4$Ti$_4$O$_{15}$ thin films

Dalhyun Do, Sang Su Kim*, Jin Won Kim

Department of Physics, Changwon National University, Changwon, Kyungsan 641-773, Republic of Korea

**Article Info**

Article history:
Received 22 October 2008
Received in revised form 20 November 2008
Accepted 21 November 2008
Available online 30 November 2008

Keywords:
SrBi$_4$Ti$_4$O$_{15}$ thin film
Chemical solution deposition
Ferroelectric properties
Leakage current
Dielectric properties
Fatigue characteristics

**Abstract**

The effects of vanadium(V) doping into SrBi$_4$Ti$_4$O$_{15}$ (SBTi) thin films on the structure, ferroelectric, leakage current, dielectric, and fatigue properties have been studied. X-ray diffraction result showed that the crystal structure of the SBTi thin films with and without vanadium is the same. Enhanced ferroelectricity was observed in the V-doped SrBi$_4$Ti$_4$O$_{15}$ (SrBi$_{4-x}$Ti$_4$V$_x$O$_{15}$, SBTIV-X (X = 0.03, 0.06, and 0.09)) thin films compared to the pure SrBi$_4$Ti$_4$O$_{15}$ thin film. The values of remnant polarization ($\mathbf{2}\mathbf{P}_r$) and coercive field ($\mathbf{2}\mathbf{E}_c$) of the SBTIV-0.09 thin film capacitor were 40.9 $\mu$C/cm$^2$ and 105.6 kV/cm at an applied electric field of 187.5 kV/cm, respectively. The $\mathbf{2}\mathbf{P}_r$ value is over five times larger than that of the pure SBTi thin film capacitor. At 100 kHz, the values of dielectric constant and dielectric loss were 449 and 0.04, and 214 and 0.06 for the SBTIV-0.09 and the pure SBTi thin film capacitors, respectively. The leakage current density of the SBTIV-0.09 thin film capacitor measured at 100 kV/cm was $6.8 \times 10^{-9}$ A/cm$^2$, which is more than two and a half orders of magnitude lower than that of the pure SBTi thin film capacitor. Furthermore, the SBTIV-0.09 thin film exhibited good fatigue endurance up to $10^{10}$ switching cycles. The improved electrical properties may be related to the reduction of internal defects such as bismuth and oxygen vacancies with changes in the grain size by doping of vanadium into SBTi.

Crown Copyright © 2008 Published by Elsevier B.V. All rights reserved.

1. Introduction

Bismuth layer-structured ferroelectric (BLSF) thin films have been considered as promising materials for the application in non-volatile memory devices in which data is stored even in the absence of an electric field since fatigue-free nature with Pt electrode was found in the BLSF thin films [1]. For such device application, large remnant polarization, low coercive field, and good fatigue endurance are required. BLSFs belong to Aurivillius family with a general formula (Bi$_2$O$_2$)$_2$(A$^+$B$^+$)$_x$O$_{3x}$, where A represents Bi, Ba, Pb, Sr, Ca, K, Na, and rare earth elements, B denotes Ti, Ta, Nb, W, Mo, Fe, etc., and $x$ = 2, 3, 4, refers to the number of BO$_6$ octahedra between neighboring (Bi$_2$O$_2$)$_2^2$ layers.

One of the typical BLSFs is SrBi$_4$Ti$_4$O$_{15}$ (SBTi, for which A = Sr, Bi, B = Ti, and m = 4), which consists of four TiO$_6$ octahedra in the perovskite blocks sandwiched by two neighboring (Bi$_2$O$_2$)$_2^2$ layers along the c-axis in a unit cell. Its relatively high Curie temperature (520 °C) makes it applicable over a wide temperature range [2]. It was reported that the remnant polarization ($\mathbf{2}\mathbf{P}_r$) in SBTi single crystal was $58 \mu$C/cm$^2$ along the a-axis under an applied electric field of 60 kV/cm [3]. In thin film forms, however, although SBTi exhibit no degradation of switchable polarization up to $10^{11}$ switching cycles with metal electrodes, the reported values of remnant polarization ($\mathbf{2}\mathbf{P}_r$), 6–13 $\mu$C/cm$^2$, are very small compared to the single crystal [4,5].

In order to improve the ferroelectric properties of SBTi thin films, intensive research has been performed [2,6–8]. Enhanced ferroelectricity was observed in the thin films by the substitution of higher-valent cation (V$^{5+}$ or W$^{6+}$) for Ti$^{4+}$ ions in the perovskite blocks of SBTi. Our previous study revealed that tungsten-doped SBTi thin films showed remnant polarization ($\mathbf{2}\mathbf{P}_r$) of 20 $\mu$C/cm$^2$ at an applied electric field of 373 kV/cm, which is one and a half larger than that of pure SBTi thin films [6]. The proposed model for the improvement of remnant polarization is the decrease of oxygen vacancies by doping of W$^{6+}$ ions. A similar effect has been reported in V-doped SBTi (with vanadium content of 0.03) thin films, in which the large $\mathbf{2}\mathbf{P}_r$ value, 36 $\mu$C/cm$^2$, was observed under an applied electric field of 317 kV/cm [2].

Among various deposition methods such as metal–organic chemical vapor deposition, pulsed laser deposition, and chemical solution deposition, the chemical solution deposition method has advantages such as the possibility of working in aqueous solutions with the high stoichiometry control. Moreover, it is a low-temperature process and a cost-effective method.

In this study, we investigated the effects of vanadium doping on the structure and electrical properties of SBTi thin films prepared...
on a Pt(1 1 1)/Ti/SiO₂/Si substrate by a chemical solution deposition method. The partial substitution of V⁵⁺ ions for Ti⁴⁺ by up to 0.09 resulted in improved ferroelectric, dielectric, leakage, and fatigue properties of SBTi thin films. The origin of enhanced properties by vanadium doping was discussed in terms of microstructure and defects such as oxygen vacancies.

2. Experimental details

SrBi₄₋ₓTi₄₋ₓVₓO₁₅ (SBTiV-x, x = 0, 0.03, 0.06, and 0.09) thin films were deposited on a Pt(1 1 1)/Ti/SiO₂/Si substrate by a chemical solution deposition method. Strontium nitrate, bismuth nitrate pentahydrate, titanium isopropoxide, and vanadium oxytripropoxide were used as starting materials for Sr, Bi, Ti, and V, respectively. 2-Methoxyethanol (2-MOE) and acetic acid were used as a solvent and a catalyst, respectively. Strontium nitrate was completely dissolved in 2-MOE at 40 °C and stirred for 30 min. Acetic acid was added to this solution, and then stirred for 30 min. Bismuth nitrate (10 mol% excess) was dissolved into the above strontium solution and stirred for 1 h. Separately, 2-MOE and acetylacetone were mixed at 25 °C in a glove box for 30 min to make a homogeneous solution. Acetylacetone was used as a chelating agent. Titanium isopropoxide and vanadium oxytripropoxide were dissolved in 2-MOE–acetylacetone, and then stirred for 2 h. The titanium–vanadium solution was added to the strontium–bismuth solution with continuous stirring, and the final mixture was stirred for additional 3 h. The concentration of SBTiV-x in the final solution was adjusted to approximately 0.1 M.

For preparing the thin films, the final solution was spin-coated on a Pt(1 1 1)/Ti/SiO₂/Si substrate at a speed of 3500 rpm for 25 s. After drying at room temperature for 3 min, the thin films were preheated on a hot-plate at 200 °C for 5 min and 360 °C for 5 min. The coating and preheating processes were repeated 15 times to obtain desired film thickness. Then, the thin films were heated by a rapid thermal annealing (RTA) at 500 °C for 3 min in oxygen atmosphere. The SBTiV-x thin films were annealed by the RTA process at 650 °C for 3 min in oxygen atmosphere.

The crystal structure and the surface morphology of the SBTiV-x thin films were investigated by X-ray diffractometer (Philips, APD system) and scanning electron microscope (SEM, Hitachi, S-2400), respectively. For the electrical measurements, Au top electrodes were used as a metal–ferroelectric–metal capacitor structure. The electrical properties were investigated by using a precision materials analyzer (Radiant Technologies Inc., Precision LC), an LF impedance analyzer (HP 4192A), and an electrometer (Keithley, 6517A Electrometer/high resistance meter).

3. Results and discussion

The crystal structure of the SBTiV-x (x = 0, 0.03, 0.06, and 0.09) thin films annealed at 650 °C under oxygen atmosphere was investigated by XRD (X-ray diffraction) with Cu Kα radiation. The result from XRD 0–2θ scans is shown in Fig. 1. Diffraction peaks were indexed based on a powder diffraction file of SrBi₂Ti₄O₁₂ with orthorhombic symmetry (PDF # 43-0973). Fig. 1 showed that there is no significant change in the XRD profiles without and with adding vanadium up to 0.09. This indicates that a single SBTi phase was formed regardless of the vanadium contents used in our experiment. We assume that this is due to the low vanadium doping content and the almost equal radii between V⁵⁺ (0.0959 nm) and Ti⁴⁺ (0.0605 nm) ions [9]. A similar result was observed in V-doped Bi₂Ti₄O₁₂ thin films [10]. In addition, all thin films showed a polycrystalline structure without any preferred crystallographic orientation.

Fig. 1 shows the XRD profiles of SBTiV-x thin films with x = 0, 0.03, 0.06, and 0.09. All thin films were deposited on a Pt(1 1 1)-coated Si substrate.

Fig. 2 shows SEM images of the surface morphology of the thin films. It is clear that adding vanadium modifies the microstructure of the pure thin films. The pure SBTi thin film exhibited the rounded grains, which are approximately 150 nm in diameter. The similar surface morphology was observed in the SBTiV-0.03 thin films. However, adding vanadium more than 0.06 into SBTi caused the change in the grain shape and size. The increased grain size, larger than 200 nm in diameter, was observed in the SBTiV-x thin films with x = 0.06 and 0.09. The thickness of all the thin films was approximately 400 nm.

In order to investigate ferroelectric properties, the values of remnant polarization (2P_r) and coercive field (2E_c) at a series of applied electric fields (125, 187.5, 250, 312.5, and 375 kV/cm) were calculated from the polarization–electric field (P-E) hysteresis loops. All loops were measured at a frequency of 1.25 kHz with each of the given electric fields. Fig. 3(a) and (b) shows 2P_r and 2E_c as a function of the applied electric fields, respectively. From Fig. 3(a), it was found that larger 2P_r was observed with increasing vanadium content. Also, the 2P_r value increased gradually with the electric field for all thin films. The SBTiV-0.09 thin film capacitor shows the largest 2P_r compared to others. The values of 2P_r and 2E_c were 51.3 μC/cm² and 120 kV/cm at an applied electric field of 312.5 kV/cm, respectively. The 2P_r value we observed is similar to that of V-doped SrBi₂Ti₄O₁₂ ceramics, which is over 50 μC/cm² [11]. In the ceramic sample, the 2E_c value of around 200 kV/cm was reported, which is much larger than our thin film. The capacitor was broken down when an electric field of 375 kV/cm was applied. On the other hand, the SBTiV-0.03 thin film capacitor showed almost the same 2P_r value compared to the pure SBTi thin film capacitor.

Fig. 4 shows the P-E hysteresis loops of the SBTiV-x thin film capacitors. All loops were measured at an applied electric field of 187.5 kV/cm, which is below the breakdown electric field of the pure SBTi film. The rounded and unsaturated P(E) loop was obtained in the SBTiV-x thin film capacitors with x = 0 and 0.03, implying weak ferroelectricity. The estimated values of remnant polarization (2P_r) were 7.4 and 8.6 μC/cm², respectively. On the other hand, the SBTiV-x thin film capacitors with x = 0.06 and 0.09 showed almost saturated P(E) loop. The measured 2P_r values of the SBTiV-x thin films with x = 0.06 and 0.09 were 25.0 and 40.9 μC/cm², respectively. The 2P_r value obtained from the SBTiV-0.09 thin film capacitor is over five times larger than that from the pure SBTi thin film capacitor.
The plot of leakage current density vs. dc electric field of the SBTiV-x thin film capacitors is shown in Fig. 5. The leakage current density of the pure SBTi thin film at an electric field of 100 kV/cm was $2.4 \times 10^{-6}$ A/cm$^2$, which is comparable with other SBTi thin films [2]. After applying an electric field of 125 kV/cm to the pure SBTi film capacitor, abrupt increase of the leakage current density was observed, leading the possibility of dielectric breakdown. The same phenomenon was observed in the SBTiV-0.03 thin film capacitor at a higher electric field. However, it was not observed in the SBTiV-0.09 thin film at the electric field range up to 187.5 kV/cm. The leakage current density of the SBTiV-0.09 thin film at 100 kV/cm was $6.8 \times 10^{-6}$ A/cm$^2$, which is more than two orders of magnitude lower than that of the pure SBTi thin film.

Dielectric properties of the SBTiV-x thin films were investigated at room temperature. Fig. 6 shows the plot of capacitance as a function of an applied electric field. All loops were measured at 100 kHz with an oscillating level of 0.05 Vrms. The butterfly shape of the loops clearly indicates that all samples exhibit ferroelectricity as confirmed by the $P(E)$ hysteresis loop study.

The frequency dependence of dielectric constant and dielectric loss were measured and shown in Fig. 7. The measurement was performed at the frequencies ranging from 100 Hz to 10 MHz. The result shows that the V-doped SBTi thin films show better dielectric properties than the pure SBTi thin film. Also, thin films with higher vanadium concentration exhibit larger dielectric constant. At 100 kHz, the values of dielectric constant of the SBTiV-x thin film capacitors with $x = 0, 0.03, 0.06,$ and 0.09 were 214, 264, 320, and 449, respectively. The dielectric constant of the SBTi-x thin film capacitor with $x = 0.09$ is two times larger than that of the
pure SBTi thin film. The values of dielectric loss of the SBTiV-\(x\)-thin film capacitors with \(x = 0, 0.03, 0.06,\) and 0.09 were 0.06, 0.027, 0.035, and 0.04, respectively.

Fig. 8 shows polarization fatigue properties of the thin films measured with \(-4 V, 1 MHz\) square wave pulses. The switchable remnant polarization was normalized to the initial value. The improved fatigue endurance was observed V-doped SBTi thin films. The pure SBTi thin film capacitor showed a 25% decrease in the remnant polarization after \(10^{10}\) switching cycles. For the SBTiV-0.09 thin film capacitors, however, the remnant polarization dropped to 10% of its initial value.

From our experimental results, it was found that the doping of a small amount of vanadium into SBTi thin films causes the change in the grain size and enhanced ferroelectric, leakage current, dielectric, and fatigue properties. The properties of ferroelectric materials can be related to the microstructure of ferroelectric thin films, such as film thickness and grain size. As increasing the grain size, improved dielectric properties [12], remnant polarization [13,14], and leakage properties [15] were observed. However, the effect of the grain size on the properties of ferroelectric materials is not just simple but usually accompanied by other factors such as the nature of material itself, the domain configuration, the motion of domain walls, etc. Therefore, although the grain size is closely linked to the properties, it is difficult to interpret our experimental observation in terms of the grain size effect.

It is well known that ferroelectric properties are strongly affected by a domain wall motion. If domain boundaries are trapped by defects such as oxygen vacancies, the domains trapped by the defects do not contribute to polarization switching [16]. As a result, the reduced switchable polarization can be observed. It is often reported that bismuth layer-structured ferroelectric thin films exhibit small remnant polarization and increased leakage property due to the existence of defects such as bismuth vacancies accompanied by oxygen vacancies. Oxygen vacancies are easily generated due to the volatility of bismuth during annealing process. Bi\(_4\)Ti\(_3\)O\(_{12}\) [17] and SrBi\(_4\)Ti\(_4\)O\(_{15}\) [9] suffer from oxygen vacancies, causing small remnant polarization and large leakage current density. We observed the similar phenomena in the pure SBTi thin film in that small remnant polarization and higher leakage current density were obtained, indicating that the serious
degradation is affected by the defects such as bismuth vacancies accompanied by oxygen vacancies. On the other hand, doping of a small amount of vanadium into SBTi thin films improved ferroelectric, leakage current, dielectric, and fatigue properties compared to the pure SBTi thin film. X-ray photoemission scattering experiments revealed that the chemical valence of vanadium in V-doped SBTi ceramics is +5, which is higher than Ti $^{4+}$ [9]. The same result was also confirmed in V-doped Bi$_4$Ti$_3$O$_{12}$ thin films [18]. The substitution of V$^{5+}$ for Ti$^{4+}$ leads to the reduction of oxygen vacancies due to the charge neutrality. Thus, it is easily expected that reduced oxygen vacancies provide the weakening of domain wall pinning and the increasing of the mobility of domain wall motion. As a result, better ferroelectric and leakage properties can be achieved. The large values of remnant polarization and dielectric constant, good fatigue endurance, and low leakage current density of the SBTiV-$x$ thin films with $x=0.06$ and 0.09 observed in our experiment are probably because of the reduction of the defects. It should be noted that the SBTiV-0.03 thin films exhibited almost similar values of remnant polarization, dielectric constant, and leakage current density compared to the pure SBTi thin films. The effect of vanadium doping is somewhat different in this case and it would be worth to further investigation. We, thus, conclude that the origin of the improved properties of V-doped SBTi thin films is related to the reduction of defects such as bismuth and oxygen vacancies by substitution of V$^{5+}$ for Ti$^{4+}$ as well as effect of modification of microstructure such as the grain size.

4. Conclusions

The effects of vanadium doping into SBTi thin films on the structure, ferroelectric, dielectric, leakage current, and fatigue properties were investigated. The crystal structure of the SrBi$_{4-x}$Ti$_3$V$_{0.25}$O$_{15}$ (SBTiV-$x$, $x=0.03$, 0.06, and 0.09) thin films was not affected by adding a small amount of vanadium up to $x=0.09$ but the modified microstructure was observed depending on vanadium contents. Vanadium doping leads to the significant improvement of the electrical properties. The values of remnant polarization and dielectric constant of the SBTiV-0.09 thin film were over five and two times larger than those of the pure SBTi thin film, respectively. Also leakage current was improved by two and a half orders of magnitude. Polarization fatigue test of the SBTiV-0.09 thin film showed good endurance up to $10^{10}$ switching cycles. The improvement of the electrical properties with vanadium doping into SBTi could be attributed to the reduction of defects such as bismuth and oxygen vacancies, associated with the grain size effect.

Acknowledgment

This work was supported by the Korea Research Foundation Grant funded by the Korean Government (MOEHRD) (KRF-2007-412-J00901).

References