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Ferroelectric Properties of Tungsten-Substituted $Bi_4Ti_3O_{12}$ Thin Film Prepared by Sol–Gel Method

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$Bi_4Ti_3O_{12}$ (BIT) and tungsten-substituted $Bi_4Ti_3O_{12}$ (BTW) thin films were prepared on Pt/Ti/SiO_2/Si substrates by a sol–gel method. There are differences in the ferroelectric properties and grain strucure between BIT and BTW thin films. The crystal structure and the surface grain morphology were characterized by scanning electron microscopy and X-ray diffraction. Grains of BIT were grown with *c*-axis preferred orientation, while these of the BTW were randomly distributed. The ferroelectric properties and polarization fatigue characteristics were confirmed by the *P–E* hysteresis loops. The BTW thin film was measured to have remanent polarization ($2P_r$) of 27 μC/cm^2 and a coercive field ($2E_c$) of 130 kV/cm. The dielectric constant and loss tangent at 1 MHz were measured as 210 and 0.05, respectively. On adding a small amount of tungsten in $Bi_4Ti_3O_{12}$, the remanent polarization increased and fatigue resistance improved. [DOI: 10.1143/JJAP.41.6451]

KEYWORDS: tungsten-substituted $Bi_4Ti_3O_{12}$ (BTW) thin film, sol–gel, ferroelectric, *P–E* hysteresis loop, remanent polarization, fatigue

1. Introduction

For application in devices such as optical, electro-optic, and nonvolatile ferroelectric random access memory (NvFRAM), much attention has been paid to ferroelectric thin films.[1,2] Bismuth layer structured ferroelectrics (BLSFs) such as strontium bismuth tantalate (SBT) and bismuth titanate (BIT) have been extensively investigated and have been found to be the most promising candidates for NvFRAM applications. It is important that the materials have a low polarization switching voltage, a low-leakage current, and little fatigue with Pt electrodes. These BLSFs[3–5] and their ferroelectricity were systematically studied by Aurivillius in the 1950s.[6] The structure can be written with a general formula of $(Bi_2O_2)^{2+}(A_{x-1}B_xO_{3x+1})^{2-}$ where A can be mono-, di-, trivalent ions or a mixture of them, B represents Ti^{4+}, Nb^{5+}, Ta^{5+}, and so forth, and x can have values of 2, 3, 4, …. For the BIT structure, A = Bi, B = Ti, and $x = 3$ are given in a general formula. The BIT structure consists of three perovskite-like units $[(Bi_2Ti_3O_{10})^{2-}]$, sandwiched between bismuth oxide $[(Bi_2O_2)^{2+}]$ layers. It is well known that the ferroelectric properties aries in the perovskite block, $(Bi_2Ti_3O_{10})^{2-}$. However, BIT thin films and ceramics have a high leakage current and domain pinning due to defects. These properties prevent their practical application in FRAM. Recently, some researchers have studied the structural characteristics of BIT, and improved the ferroelectric properties with cation doping.[7–10] The consideration of the effects of defects in the perovskite units is important for determining the ferroelecric properties and electrical conduction. However, the physical properties of BIT thin film are yet not fully understood. To realize a practical application of BIT thin film, it is necessary to investigate its ferroelectric properties and electrical conduction by substituting cation at the A or B-site.

In this work, a BTW thin film formed by substituting W^{6+} (ion radius $r = 0.600$ Å) for Ti^{4+} ($r = 0.605$ Å)[9] as well as a BIT thin film were prepared by a sol–gel method. The ferroelectric properties and structural features were also investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), dielectric constant, ferroelectric *P–E* hysteresis loops, leakage current and polarization fatigue analyses.

2. Experiment

$Bi_{4-2x/3}Ti_{3-x}W_xO_{12}$ (BTW) thin films ($x = 0$ and 0.03) were prepared by a sol–gel method. A transparent multi-component solution was prepared by mixing bismuth nitrate $[Bi(NO_3)_35H_2O]$ (Aldrich), titanium isopropoxide $[Ti(OC_3H_7)_4]$ (Aldrich), and tungsten isopropoxide $[W(OC_3H_7)_6]$ (Alfa). Bismuth nitrate (20 mol % excess) was dissolved at 40°C in 2-methoxyethanol used as a solvent. The excess bismuth was used for compensation of bismuth evaporation during annealing.[11,12] Separately, titanium isopropoxide and tungsten isopropoxide were dissolved in 2-methoxyethanol and then acetylacetone was treated as a chelating agent in a glove box, and the final solution was stirred for 2 h. To the bismuth solution, titaniun-tungsten solution was added with continuous stirring. The concentration of $Bi_{4-2x/3}Ti_{3-x}W_xO_{12}$ in the final solution was adjusted to 0.1 M. The coating on the Pt/Ti/SiO_2/Si substrates at a speed of 3500 rpm for 20 s and preheating process at 350°C for 10 min was repeated three times. The film was heated at 500°C for 10 min in a furnace. For the complete crystallization of BIT and BTW thin films, these films were finally annealed at 700°C for 30 min in oxygen.

X-ray diffraction studies were carried out to examine the formation of single-phase and crystal structure with Cu Kα radiation. The chemical composition of the BTW thin film was determined as Bi : Ti : W = 54.55 : 43.11 : 2.34 in atomic % by an energy dispersive X-ray spectrometer (EDS). For studying the ferroelectric properties, Au-top electrodes of 7.85×10^{-5} cm^2 area were deposited on the film through a shadow mask by thermal evaporation to form metal–ferroelectric-metal (MFM) capacitors. The grain and film thicknesses were investigated using scanning electron microscopy (SEM). The ferroelectric *P–E* hysteresis loop

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and the fatigue characteristics were investigated by a ferroelectric tester (RT66A). The dielectric constant and loss tangent were investigated over the frequency range of 100 Hz–1 MHz by an impedance analyzer (HP4194A) at room temperature. The leakage currents were measured using an electrometer (Keithley 237).

3. Results and Discussion

BTW thin film with a small amount of tungsten (3 mol%) added was prepared by the sol–gel method. Figure 1 shows the XRD patterns of the BIT and BTW thin films annealed at 700°C for 30 min. The XRD peaks obtained at room temperature were indexed as belonging to the orthorhombic system. From the results of these indexed peaks, lattice constants of BTW thin film were calculated as $a = 5.450$ Å, $b = 5.410$ Å and $c = 32.832$ Å, which are similar to those of BIT given in the previous literature.[9] As seen in the XRD peaks of BIT and BTW thin films, the layered perovskite (117) peak and other perovskite (00*l*) peaks were found. The strong perovskite (00*l*) peaks and weak perovskite (117) peak of BIT suggest that the thin film must be strongly *c*-axis oriented. The degree of *c*-axis orientation is calculated as 97% based on the (006) and (117) peaks, which agrees with the results of previous research.[13] From the strong intensity of the (117) peak of the BTW thin film, the obvious change of the grain orientation was considered. Namely, the layered perovskite (117) peak relative to the (00*l*) peaks is enhanced, and thus the degree of *c*-axis grain orientation was decreased by 67%.

To examine the structure and surface morphologies, SEM was used. Figure 2 shows the SEM micrographs of BIT and BTW thin films. The film thickness of BIT and BTW was estimated as 700 nm from the cross-sectional SEM micrographs. The BIT and BTW thin films were composed of plate-like grains. There are differences in the degree of grain orientation between BIT and BTW thin films. The plate-like grain morphology of BIT grown parallel to the substrate is similar to those of previous reports on BIT prepared by MOD and a sol–gel method. This means that the BIT thin film consisted of a single-phase of BIT with *c*-axis preferred orientation. However, the plate-like grains of BTW were randomly distributed. Thus, the characteristics of grain orientation in SEM agree with those of the degree of *c*-axis orientation in XRD. Compared to the BIT thin film, the surface of the BTW thin film was rough with random grain orientations.

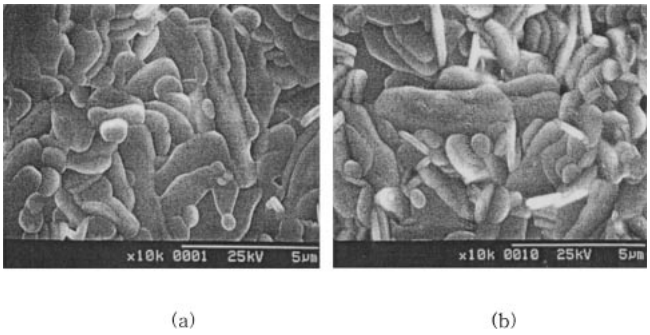

Fig. 2. SEM photographs of BIT and BTW thin films.

Figure 3 shows the *P–E* hysteresis loops and the related properties, i.e., the remanent polarization ($2P_r$) and the coercive field ($2E_c$). The $2P_r$ values rapidly increase and saturate at an applied electric field of ~280 kV/cm. At an applied electric field of 230 kV/cm, the remanent polarization ($2P_r$) and the coercive field ($2E_c$) of the BTW thin film were 27 μC/cm^2 and 130 kV/cm, respectively. For the BIT thin film prepared under the same growth conditions, the remanent polarization ($2P_r$) and the coercive field ($2E_c$) were 12 μC/cm^2 and 110 kV/cm, respectively, which were similar to those of previous results.[13] The remanent polarization of the BTW was approximately 2 times higher than that of BIT thin film and was comparable to that of La-doped BIT (BLT) thin film.[7] The ferroelectric property improved with the addition of tungsten in BIT thin film.

Figure 4 shows the frequency dependence of the dielectric constant (ε) and loss tangent ($\tan\delta$) of the BIT and BTW thin

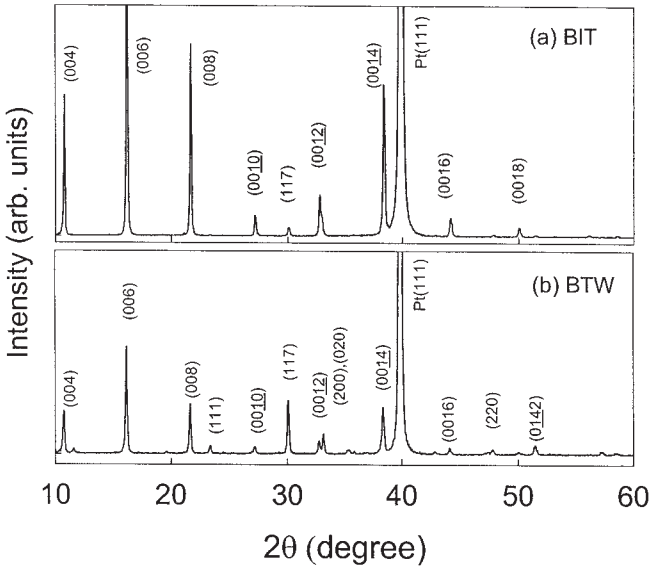

Fig. 1. X-ray diffraction patterns of (a) BIT and (b) BTW thin films.

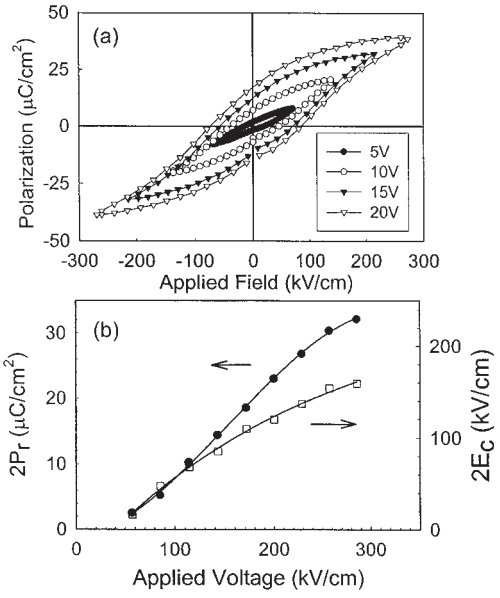

Fig. 3. (a) *P–E* hysteresis loops of BTW thin film and (b) remanent polarization and coercive field.

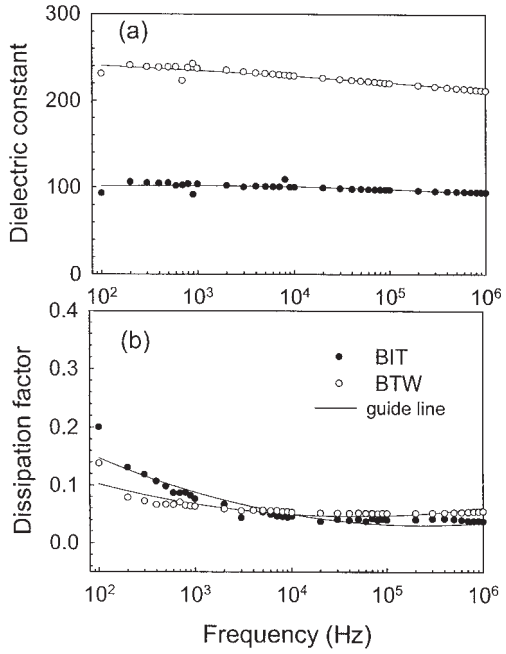

Fig. 4. (a) Dielectric constants and (b) loss tangent as a function of frequency of BIT and BTW thin film.

films at room temperature. The dielectric constant and loss tangent show a small variation in the frequency range of 100 Hz–1 MHz. The dielectric constant of BIT thin film was measured as 95 at 1 MHz with the $\tan\delta$ of about 0.04, and these values are comparable to the previously reported values.[7] While the dielectric constant of BTW thin film was measured as 211 at 1 MHz with the $\tan\delta$ of about 0.05. The dielectric constant of BTW thin film was 2 times higher than that of BIT thin film. However, the dielectric loss of BTW thin film was a little higher than that of BIT thin film. The results of dielectric loss tangent in BTW thin film did not agree with those of higher-valent cation doped ceramics[9] for which a marked decrease in dielectric loss was reported.

Figure 5 shows the leakage current density as a function of applied electric field for BIT and BTW thin films. It is well known that BIT ceramics and thin films prepared from stoichimetric composition suffer from high leakage current due to defects such as Bi vacancies accompanied by oxygen vacancies. To improve the leakage current properties in this experiments, the BIT and BTW thin films were prepared using a Bi-excess composition. The leakage current density of BIT thin film decreased, which agreed with the previous results. Compared to the leakage current density of BIT thin film, however, the leakage current density of BTW thin film was not improved. Defects such as oxygen vacancies interact strongly with domain boundaries and have significant influences on the polarization properties and conduction process. When the electric fields were increased for BTW thin film with randomly distributed grains, the increase of leakage current may be considered to be because mobile vacancies can assemble in extended structures near the domain boundaries.

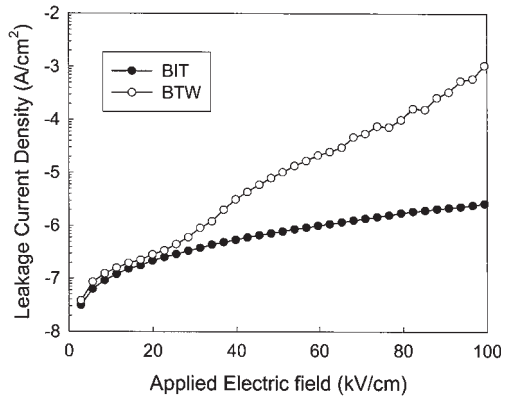

Fig. 5. Leakage current density of BIT and BTW thin films.

Figure 6 shows the fatigue characteristics of the normalized polarization as a function of switching cycle at 1 MHz and the comparison of *P–E* hysteresis loops before and after the fatigue test at an applied voltage of 12 V. After 4.5×10^{10} read/write cycles, the polarization of the BIT is 73% of the intial value. While the polarization of the BTW is 83% of the initial value and fatigue resistance was improved by about 10%. It is well known that both $PbBi_2Nb_2O_9$ (PBN) and $SrBi_2Nb_2O_9$ (SBN) have good fatigue resistance regardless of stoichiometry, whereas BIT does not.

To solve the fatigue problem and improve the ferroelectric properties, the ferroelectric properties for the substitution effect on A or B-site ion have been widely reported.[7–10] It was reported that the fatigue of La-doped BIT was improved by substituting Bi ion with La ion at A-site. The effect of substitution of another lanthanoid element such as La, Nd and Sm elements has been studied for the purpose of applications in FRAM. On the other hand, ferroelectric properties were also changed by the high-valent cation substitution in B-site. It is known that the role of A-site substitution is to displace the volatile Bi with La to suppress

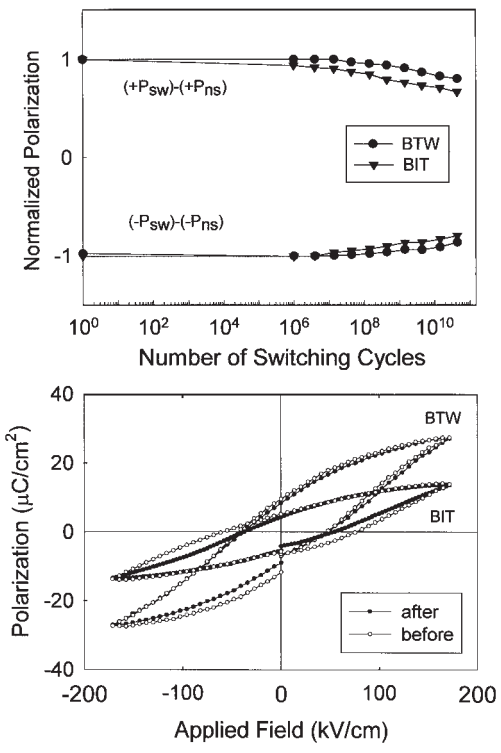

Fig. 6. Fatigue characteristics of BIT and BTW thin films are shown before and after 4.5×10^{10} switching cycles at 1 MHz.

the A-site vacancies which are accompanied with oxygen vacancies which act as space charges. The role of B-site substitution by a high-valent cation is, however, mainly that of compensation of defects which cause a fatigue phenomenon and strong domain pinning.[14)]

The results of XRD, SEM, *P–E* hysteresis loops and dielectric properties are in good agreement with each other. For the BTW thin film, the reduction of *c*-axis preferred orientation was found in the XRD and SEM experiments. This means that the value of remanent polarization and dielectric constant increased due to the anisotropic nature. Due to the structural characteristics, BIT single crystal is strongly anisotropic in terms of the ferroelectric properties such as polarization and coercive field.[15)] The polarization direction of BIT is 4.5° off the base plane of its cell structure, thus giving rise to a much larger *a*-axis polarization ($P_s = 45$–$50\,\mu C/cm^2$) than *c*-axis polarization ($P_s = 4.5\,\mu C/cm^2$). If BIT thin film with *c*-axis oriented grain is grown, then the thin film shows a smaller polarization. The BIT thin film in this work shows a small degree of polarization, which agrees with that of *c*-axis oriented grains. While, the BTW thin film with randomly distributed grains shows increased polarization. Therefore, it is considered that the reason for the improvements might be related to the decrease of the degree of *c*-axis preferred orientation.

Defects such as oxygen vacancies are considered to be the most mobile charges in perovskite ferroelectrics and play an important role in determining the polarization fatigue and the conduction process. For PZT thin film, oxygen vacancies move and reach the interface/electrodes, and are trapped at trap sites. Thus, space charges are created at the boundaries/interfaces, and fatigue occurs in the PZT materials. It is known that BIT with Bi layered oxide are relatively fatigue-free, but BIT thin films suffer from high leakage electric current and domain pinning due to defects, leading to a small remanent polarization after read/write cycles. For the BTW thin film, fatigue was improved by 10%. By the reduction of the defect-caused domain pinning, it is considered that the BTW thin film shows a good fatigue resistance. The results imply that there is a low accumulation of vacancies at interfaces with electrodes, space charge buildup and domain pinning. For Bi-excess BIT thin film, the decrease of leakage current was explained by the reduction of Bi vacancies accompanied by oxygen vacancies. However, the leakage current of BTW thin film was not improved, and it is suggested that the leakage current properties are attributed not only to Bi vacancies but also to oxygen vacancies related to the substitution of W for Ti. When the dc electric field was increased in BTW thin film, mobile vacancies such as Bi and O vacancies can assemble into extended structures near the domain boundaries and may contribute to the increase of leakage current.

4. Conclusion

Ferroelectric tungsten-substituted $Bi_4Ti_3O_{12}$ (BTW) thin films were prepared by a sol–gel method, and its ferroelectric and polarization fatigue characteristics were investigated. The lattice constants of BTW thin film were caculated as $a = 5.450$ Å, $b = 5.410$ Å and $c = 32.832$ Å which were similar to those of BIT. Since the intensity of the layered perovskite (117) XRD peak increased in the BTW thin film, the degree of the *c*-axis preferred orientation of grains was decreased. The remanent polarization ($2P_r$) was $27\,\mu C/cm^2$ and the coercive field was 130 kV/cm. The dielectric constant and loss tangent of BTW thin film were estimated to be 211 and 0.05 at 1 MHz, respectively. On the addition of tungsten to $Bi_4Ti_3O_{12}$, the ferroelectric properties and polarization fatigue were improved.

Acknowledgements

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