Investigating structural features of Ba and Zr co-substituted strontium bismuth tantalate thin films

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Abstract. Structural (crystal and microstructure), chemical and electronic states, and ferroelectric and electrical features of Ba and Zr co-substituted strontium bismuth tantalate (SBT) were probed in this study. Distinctly, Ba and Zr were substituted for Ta and Sr sites of $\text{Sr}_{0.8}\text{Bi}_{2.2}\text{Ta}_2\text{O}_9$ in the form of $\text{Sr}_{0.8-x}\text{Ba}_x\text{Bi}_{2.2}\text{Ta}_{2-y}\text{Zr}_y\text{O}_9$. To investigate the impact of the co-substitution on the crystal structure, microstructure, ferroelectric and electrical properties, $\text{Sr}_{0.8-x}\text{Ba}_x\text{Bi}_{2.2}\text{Ta}_{2-y}\text{Zr}_y\text{O}_9$ thin films were deposited on Pt/Ti/SiO₂/Si(100) wafers by sol-gel spin by coating method. Crystal structure, microstructure, chemical and electronic states, ferroelectric, capacitance and leakage current characteristics of the films were studied to investigate potential for one transistor type ferroelectric random access memories (1T-type FeRAMs). Successful substitutions up to 10 mol% lead to reduction of double remanent polarization ($2P_r$) to $10.26 \mu\text{C cm}^{-2}$, and dielectric constant (ϵ_r) to 135. These values demonstrate that successful co-substitution of limited Ba and Zr in SBT with stable crystal structure has the ability to decrease P_r and ϵ_r values of the ferroelectric material which can be a candidate gate to be utilized in ferroelectric field-effect transistors (FeFETs) for 1T-type FeRAM applications.

Keywords. Crystal structure; ion substitution; strontium bismuth tantalate; ferroelectric; thin film.

1. Introduction

Owing to superior properties, ferroelectric random access memories (FeRAMs), for instance, those with a metal-ferroelectric-insulator-semiconductor (MFIS) structure have been focussed upon by researchers as a replacement for flash memory and dynamic access memory in recent decades [1–6].

Bismuth (Bi)-layered ferroelectric materials have been considered for use in different applications such as nonvolatile (NV) memories, piezoelectric devices, detectors and optical switches. Strontium bismuth tantalate (SBT) is a Bi-layered Aurivillius compound. It has taken a significant place in NV FeRAMs in recent decades because of reduced operation voltage and leakage current level as well as robust fatigue feature.

There are two types of FeRAMs based on the utilization of ferroelectric material. The capacitor type involves a ferroelectric storage capacitor and a pass-gate nonferroelectric transistor. The other is a field-effect transistor (FeFET), which contains a ferroelectric gate, 1T-type FeRAM. This type of FeRAM includes an MFIS diode structure. In the past decades, FeFET type FeRAMs have been extensively

studied because of their promising properties like nondestructive readout operation, high switching speed, low power consumption and compliance with the scaling rule. However, due to the short retention time, which is the main problem, the commercialization of such memories has not been realized yet. In fact, depolarization field, high leakage current and charge trapping cause a decrease in the retention time [7]. Once the gate dielectric constant in the MFIS structure is much greater than that of the insulator layer, most of the applied voltage drop occurs across the thin buffer layer which results in a gate ferroelectric thin film material having a great depolarization field, but not enough electric field to switch. Besides low permittivity, the gate ferroelectric film requires a relatively low remanent polarization (P_r) of around $1 \mu\text{C cm}^{-2}$ to match the requisite charge for channel conductivity controlling in the memory process [8]. Hence, the key parameters of ferroelectric thin films for 1T-type FeRAMs are quite small dielectric constant (ϵ_r) and remanent polarization (P_r) around $1 \mu\text{C cm}^{-2}$ as discussed by the related researchers [9–11]. These qualities have become the motivation for research devoted to SBT as the most suitable candidate gate ferroelectric for FeFET-type FeRAMs.

To avoid the use of toxic materials from the environmental point of view, lead-free Bi-layered perovskites like ferroelectric materials, such as $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) and $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT), were explored for FeRAM applications. Among them, SBT being strontium deficient and Bi excess $\text{Sr}_{0.8}\text{Bi}_{2.2}\text{Ta}_2\text{O}_9$ (SBT) with better ferroelectric properties is considered as potential useful ferroelectric material in above applications because of the outstanding properties as follows: low remanent polarization and switching field, good retention and fatigue-free. As a popular member of Bi-layered Aurivillius compound, SBT contains perovskite-like SrTa_2O_7 units with double TaO_6 octahedral and Bi_2O_2 layers. The octahedra blocked by the Bi_2O_2 layers are sited perpendicular to the c -axis direction. Due to this quite anisotropic crystal structure, the ferroelectric properties depend on the crystal axis. Since the ab plane is the direction of polarization, there is almost no polarization along the c -axis [12]. Although Sr-deficient SBT has higher switchable remanent polarization [12–14] which is a benefit for capacitor-type FeRAM applications, possible formation of a non-ferroelectric pyrochlore secondary phase due to exchange between Sr and Bi [15] causes degradation of ferroelectric and electrical properties in device applications. To overcome such problems and improve ferroelectric and insulation properties, appropriate ion substitutions for constituent elements are effective and common approaches. Specifically, the influence of substitution in SBT was widely reported by researchers who aim to alter ferroelectric and dielectric properties [16,17]. For example, Sm was doped for Bi-inhibited oxygen vacancies which are the main mobile charges to increase the leakage current, thereby deteriorating ferroelectric and dielectric properties [18].

Recently, SBT was modified by larger ions compared to the constituted ions to lower P_r and ϵ_r for 1T-type FeRAM applications [10]. Such doping leads to charged defects, which strongly affect the domain switching process together with grain boundaries. Measuring polarization vs. voltage (P – V) of a ferroelectric thin film capacitor yields a hysteresis loop which allows one to determine coercive field (E_C) and P_r by analysis. In fact, formation of P – V loop is very sensitive to doping elements which are able to change switching characteristics by the formation of defect dipoles, oxygen vacancies and so on.

In the present work, crystal structure, microstructure, electronic binding energy, ferroelectric, capacitance and leakage current of $\text{Sr}_{0.8-x}\text{Ba}_x\text{Bi}_{2.2}\text{Ta}_{2-y}\text{Zr}_y\text{O}_9$ thin films grown by the sol–gel spin-coating method were analysed from the influence of Zr and Ba co-substitution. In fact, X-ray photoelectron spectroscopy (XPS) is a powerful technique to understand the chemical states of the constituent elements [19]. Hence, it can be utilized to study the influence of substitution ions by means of variation of chemical states. The results show that Zr and Ba were successfully substituted for Ta and Sr ions up to 10 mol%, respectively, with decreasing relative dielectric permittivity and switchable polarization

in the Aurivillius phase with a stable perovskite crystal structure.

2. Experimental

A thin film of $\text{Sr}_{0.8-x}\text{Ba}_x\text{Bi}_{2.2}\text{Ta}_{2-y}\text{Zr}_y\text{O}_9$ was grown by the sol–gel spin-coating technique. Sol–gel precursor solutions of $x = y = 0, 5$ and 10 for $\text{Sr}_{0.8-x}\text{Ba}_x\text{Bi}_{2.2}\text{Ta}_{2-y}\text{Zr}_y\text{O}_9$ were spread on a Pt/Ti/SiO₂/Si(100) wafer at 2500 rpm for 30 s, which were labelled as SBT, $5\text{S}_{\text{Ba}}\text{BT}_{\text{Zr}}$ and $10\text{S}_{\text{Ba}}\text{BT}_{\text{Zr}}$ based on the $x = y$ value, respectively. To eliminate the volatile organic complex, wet samples were successively dried on hot plates as follows: 155°C for 2 min, 240°C for 3 min and 400°C for 2 min. Next, gel films were successively heated in a rapid thermal annealing (RTA) furnace at 750°C for 1 min in O₂ atm. This procedure was repeated five times. Finally, the films were heated again in the RTA furnace at 750°C in O₂ atm. for 30 min to enhance crystallinity. Platinum (Pt) top electrodes needed for electrical connection were fabricated by the electron beam deposition technique by forming round-shaped areas of $3.14 \times 10^{-4} \text{ cm}^2$ via a shadow mask. A recovery annealing was additionally performed to improve electrical properties as well as to enhance adhesion between the top electrodes and the film surface. Film crystallinity was probed by the X-ray diffraction technique (XRD). Microstructures of surface and interface cross-section were analysed by scanning electron microscopy (SEM). In addition, atomic force microscopy (AFM) was utilized for morphology examination. XPS with a PHI Quantera scanning X-ray microprobe (SXM) with an Al monochromatic X-ray source, 100 mm slit size, 45° take-off angle, 140 eV pass energy and 0.125 eV energy step measured at Fujitsu Quality Lab, is utilized to understand the influence of chemical substitutions. Ferroelectric properties were measured at a frequency of 10 kHz at room temperature using a ferroelectric test system

Figure 1. XRD patterns of SBT, $5\text{S}_{\text{Ba}}\text{BT}_{\text{Zr}}$ and $10\text{S}_{\text{Ba}}\text{BT}_{\text{Zr}}$ thin films.

(Toyo Corp., FCE-1A/Fop-100V). Leakage current density was measured by using a HP4156C precision semiconductor parameter analyzer (Agilent). Capacitance characteristics were measured using an LCR meter (Toyo Corp.) at a frequency of 1 MHz.

3. Results and discussion

To identify the structure of the crystal and put forth the influence of substitutions, the XRD patterns of SBT and Zr and Ba co-substituted SBT films were comparatively studied as shown in figure 1. It is noted that all characteristic peaks of the layered perovskite phase are observed with diffraction

according to ICDD #01-089-6490 for all films. Owing to the inherent relationship with polarization, the (115) peak is very important in the XRD pattern of SBT. It is apparent that the (115) plane is the most dominant peak, which is slightly broadened by the substitution. The increase in the full-width at half-maximum (FWHM) values of the peaks of $5\text{S}_{\text{Ba}}\text{BT}_{\text{Zr}}$ and $10\text{S}_{\text{Ba}}\text{BT}_{\text{Zr}}$ compared to SBT are associated with relatively weak crystallinity and worse surface microstructures as well as a weak secondary pyrochlore phase. Moreover, different sizes of crystalline grains like fine grains can also contribute to line broadening. Furthermore, the (115) oriented peak is slightly shifted to a lower angle. This is attributed to the comparatively larger ionic radii of Zr and Ba which are dissolved in the strontium tantalate (SrTa_2O_7) perovskite layer. It is revealed that Zr and Ba ions replaced Ta ions in the B-sites and Sr ions in the A-sites of SBT, respectively. Specifically, Zr ions are substituted for Ta in TaO_6 octahedra and Ba ions are substituted for Sr among TaO_6 octahedra. Since the Goldschmidt tolerance factor is useful to evaluate the stability and distortion of perovskite and perovskite-like crystal structures, tolerance values of the samples were calculated according to the formula of $t = [r_{\text{Sr}} + r_{\text{O}}]/1.414[r_{\text{Ta}} + r_{\text{O}}]$,

Table 1. Goldschmidt tolerance factors of SBT, $5\text{S}_{\text{Ba}}\text{BT}_{\text{Zr}}$ and $10\text{S}_{\text{Ba}}\text{BT}_{\text{Zr}}$ thin films.

Sample	Tolerance factor
SBT	0.9846
$5\text{S}_{\text{Ba}}\text{BT}_{\text{Zr}}$	0.9854
$10\text{S}_{\text{Ba}}\text{BT}_{\text{Zr}}$	0.9862

Figure 2. SEM micrographs of (a) SBT, (b) $5\text{S}_{\text{Ba}}\text{BT}_{\text{Zr}}$ and (c) $10\text{S}_{\text{Ba}}\text{BT}_{\text{Zr}}$ thin films.

Figure 3. Surface morphologies of (a) SBT, (b) 5S_{Ba}BT_{Zr} and (c) 10S_{Ba}BT_{Zr} thin films analysed by AFM.

where r_{Sr} , r_{O} and r_{Ta} are ionic radii of strontium, oxygen and tantalum, respectively, as summarized in table 1. Also upon substitution of 5 and 10 mol%, the tolerance factor is increased by 0.08 and 0.16%, which demonstrates the stability in the perovskite structure. Owing to the larger ionic radius of substituted elements, the crystal structure expands. This results in the decreasing distortion in the orthorhombic structure. Therefore, the broad diffraction peaks with a higher substitution rate indicated that the crystallization quality of films is slightly decreased.

Surface and interface microstructures are vital for ferroelectric and electrical properties. Therefore, SEM micrographs revealing differences in surface morphology among

SBT, 5S_{Ba}BT_{Zr} and 10S_{Ba}BT_{Zr} thin films are presented in figure 2. It is clearly seen that the microstructure consists of nanograins intervened in between grain boundaries of micrograins with polyhedron shape. Such tiny grains formed among worm-like grains could be attributed to the pyrochlore phase which increases with the substitution ratio. Although a mesoporous microstructure is observed due to the high-temperature crystallization, it also causes Bi evaporation and/or diffusion into the substrate and multi-shaped grains on the surface as well as lack of sinterability and a considerable dense structure was formed. Compared to the SBT film surface, surfaces of 5S_{Ba}BT_{Zr} and 10S_{Ba}BT_{Zr} show various morphologies with very few dissimilar grain shapes

Figure 4. XPS spectra of (a) Bi 4f, (b) Sr 3d, (c) Ta 4d, (d) Ta 4f, (e) Ba 3d, (f) Zr 3d and (g) O 1s.

Figure 5. Ferroelectric polarization measurements (P – E) of (a) SBT, (b) 5SBaBT_{Zr} and (c) 10SBaBT_{Zr} thin films.

and size as well as formation of the secondary pyrochlore phase. Once Zr and Ba are introduced into SBT, such tiny grains become swollen. This is ascribed to the low degree of crystallization as discussed in XRD measurements in which the (115) peaks become broad upon increasing the doping ratios. Hence, by increasing the substitution ratio, the microstructure of the films became non-uniform associated with different grains and porous as well as showed an increase in roughness as presented in AFM study in figure 3. Such morphology yields enhanced surface area and decreased film density. Analysis of the film surface by AFM in tapping mode confirmed that 5SBaBT_{Zr} and 10SBaBT_{Zr} samples had fine and massive grains ranging from 40 to 300 nm in size. With an increase in impurity ratio, it is clearly seen that grains become disordered and are distributed inhomogeneously. Apparently, the microstructure and shapes of grains depend on the substitution ratio as well. Therefore, by increasing the substitution ratio, the microstructure markedly varies. Therefore, introduction of Zr and Ba assisted in growing anisotropic grains. Hence, plate-like grains with relatively larger size are formed among the secondary phase clusters. Also, roughness of the surfaces by means of root mean square (rms) values increased from 5 to 10 nm by co-substitution. Therefore, it is concluded that the morphology of the films and shapes of grains are heavily dependent on the substitution ratio of Zr and Ba ions.

To investigate the variation both in the electronic structures and the chemical state of constituent elements of SBT upon

doping, XPS was utilized. The narrow scan of XPS spectra of Bi 4f, Sr 3d, 4d, Ta 4f, Ba 3d, Zr 3d and O 1s peaks are presented in figure 4.

It is noted that the related peaks of Sr, Ta and Bi are slightly shifted to a higher energy by introducing Zr and Ba into the crystal. This indicates that the oxidation state of these ions in the 10SBaBT_{Zr} films is higher than those of pure ones. This reveals the formation of stronger bonding. It is interpreted as the stable pyrochlore phase which revealed the formation of different grains rather than only round shape ones as shown in SEM and AFM micrographs. Each of Sr 3d spin–orbit-split pairs constitutes two overlapping peaks. While the pairs of lower binding energy are associated with Sr ions in the perovskite structure, those of higher binding energy are assigned to Sr in oxide or carbonate [20]. Broadening of Sr 3d_{3/2} and 3d_{5/2} evidenced Sr ions in the perovskite structure by Ba substitution. With regard to Ba, two overlapped spin–orbit-splitting peaks of 3d_{3/2} and 3d_{5/2} are separated by 15.3 eV. Similarly, overlapping of lower binding energy is attributed to Ba which is substituted for Sr in the perovskite structure. Bi 4f spectra have spin–orbit splitting of the 4f_{5/2} and 4f_{7/2} states which are ascribed to bonds between Bi and O. The spin–orbit splitting is around 5 eV which is comparable. Metallic Bi (Bi⁰) also appears in the spectrum due to diffusion to the surface and evaporation by sequential annealing. Based on the binding energies of Sr, Ba, Ta and Zr as well as only one spin–orbit splitting for each element, they are considered to be in the chemical states of Sr²⁺, Ba²⁺, Ta⁵⁺

Table 2. Ferroelectric polarization and dielectric constant parameters of SBT, 5S_{Ba}BT_{Zr} and 10S_{Ba}BT_{Zr} thin films.

Sample	Remanent polarization ($2P_r$) ($\mu\text{C cm}^{-2}$)	Average squareness ($\langle P_r/P_s \rangle$)	Coercive field ($2E_C$) (kV cm^{-1})	Dielectric constant ϵ_r
SBT	18.17	0.520	148.3	192
5S _{Ba} BT _{Zr}	14.54	0.513	185.2	158
10S _{Ba} BT _{Zr}	10.26	0.463	203.4	135

Figure 6. Comparative capacitance (C - V) measurements of SBT, 5S_{Ba}BT_{Zr} and 10S_{Ba}BT_{Zr} thin films.

and Zr⁴⁺. The O 1s peak is shifted to higher energy, which is attributed to Zr⁴⁺ substitutions at Ta⁵⁺ sites. On the other hand, the slight broadening of Sr peaks is attributed to the loss of oxygen in perovskite layers. Actually, the introduction of a lower valent Zr⁴⁺ compared to the Ta⁵⁺ site in the SBT structure leads to the formation of oxygen vacancies in accordance with charge neutrality restriction as $\text{Zr}_2\text{O}_4 \leftrightarrow 2\text{Zr}'_{\text{Ta}} + 4\text{O}_\text{O} + \text{V}_{\text{O}}''$, where V_{O}'' is the double positive-charged oxygen vacancy. Therefore, due to the charge neutrality restriction, the oxygen vacancy concentration increases *via* enhancing the substitution ratio. As a matter of fact, oxygen vacancies behave as space charges and lead to pin domains. Moreover, enhancement of defect concentrations causes a decrease in remanent polarization. Hence, such mobile charges have ability to affect ferroelectric and electrical properties seriously [20].

The impact of co-substitution on ferroelectric properties was studied by measuring polarization *vs.* applied voltage (P - V) at 10 kHz. Related P - E saturation behaviour is plotted as shown in figure 5. While good saturation of polarization properties of SBT is observed, those of Zr and Ba co-substituted films show comparatively less polarization saturation properties with decreasing polarization. Corresponding polarization ($2P_r$) values of SBT, 5S_{Ba}BT_{Zr} and 10S_{Ba}BT_{Zr} films are 18.17, 14.54 and 10.26 $\mu\text{C cm}^{-2}$, respectively, that means the reversible capability of domain and

Figure 7. Comparative leakage current density (J - E) measurements of SBT, 5S_{Ba}BT_{Zr} and 10S_{Ba}BT_{Zr} thin films.

switchable component of polarization were decreased by increasing the substitution ratio. In addition to this, average P_r/P_s ratios of SBT, 5S_{Ba}BT_{Zr} and 10S_{Ba}BT_{Zr} films are 0.520, 0.513 and 0.463, respectively, which means squareness of P - E hysteresis loops is decreased. Since, ferroelectric properties arise from the perovskite layer, decrease in polarization properties is associated with less displacement of TaO₆ octahedra by means of a smaller c/a ratio due to larger Zr ion substitution. Therefore, structural distortion decreases with increasing substitution. Moreover, formation of nanograins is another reason for less polarization values. Furthermore, pinning of domain walls by mobile charges like oxygen vacancies also causes weakening of polarization. On the other hand, theoretically high coercive field materials yield a comparatively larger memory window [21]. Coercive fields ($2E_C$) of SBT, 5S_{Ba}BT_{Zr} and 10S_{Ba}BT_{Zr} films increase with the following values of 148.3, 185.2 and 203.4 kV cm^{-1} , respectively, which is evident with weak domain switching. For a practical view, remarkable ferroelectric parameters are summarized in table 2.

Capacitance *vs.* voltage (C - V) behaviour measured at 1 MHz of the films is illustrated in figure 6. Open enough butterfly-type hysteresis loops with two symmetric switching voltages of all the samples once again emphasize

Figure 8. Interface cross-sectional SEM micrographs of (a) SBT, (b) 5S_{Ba}BT_{Zr} and (c) 10S_{Ba}BT_{Zr} thin films grown on Pt/Ti/SiO₂/Si(100) wafers.

the confirmation of ferroelectricity. It is noteworthy that switching voltage increases by increasing the substitution ratio as seen also from P – E measurements by means of coercive field ($2E_C$). It reveals that the orientation of domains is difficult. Since SBT is a member of Bi-layered perovskites which are quite anisotropic, dielectric properties depend on structural properties such as crystal/domain structure as well as domain orientation, chemical composition and grain formation. Therefore, the calculated dielectric constants of SBT, 5S_{Ba}BT_{Zr} and 10S_{Ba}BT_{Zr} films are 192, 158 and 135, respectively. As expected, dielectric constants decrease with increase in the substitution ratio. The formed oxygen vacancies as discussed above enhance the domain pinning which results in decrease in the dielectric constant *via* a weakening polarization mechanism. On the other hand, from the 1T-type FeRAM application point of view, such a decrease in the dielectric constant results in the increase in the voltage of the gate ferroelectric used in the MFIS structure and yields a saturated hysteresis loop. Thus, this would provide a higher memory window as well as longer retention time.

Since leakage current and dielectric constant of a capacitor are related to each other, the leakage current *vs.*

voltage (I – V) is measured and accordingly analysed; leakage current density *vs.* electric field (J – E) characteristic is studied to investigate other electric behaviour of ferroelectric materials. From reliability point of view, successful utilization of such ferroelectric films in realistic device application requires leakage current to be as low as possible. Therefore, J – E characteristics of the films are plotted comparatively in figure 7. Rather symmetric J – E curves explored for positive and negative polarities which indicate the high quality of top and bottom Pt electrodes and interfaces. On the contrary, due to a lower dielectric constant compared to SBT, leakage current densities of 5S_{Ba}BT_{Zr} and 10S_{Ba}BT_{Zr} films are increased by one order of the magnitude compared to that of SBT. The main reason for reducing insulation properties is ascribed to increased oxygen vacancies upon Zr⁴⁺ partial substitution for Ta⁵⁺ in the crystal structure. Moreover, eventual inhomogeneous distribution of Bi in the crystal has potential to enhance leakage current. Furthermore, a film–electrode interface is vital for electrical and ferroelectric properties; therefore, it affects leakage current density. Bottom electrode–film interface cross-sectional SEM images are

shown in figure 8. Cross-sectional view of microstructure indicates comparatively greater granularity and porosity with $5\text{S}_{\text{Ba}}\text{BT}_{\text{Zr}}$ and $10\text{S}_{\text{Ba}}\text{BT}_{\text{Zr}}$ films, which gives rise to a higher electric field in the thinnest region of the film. Regarding the general behaviour of leakage current, at low field quasi-Ohmic conduction takes place due to a linear increase of current density. A slight drop in the field up to 100 kV cm^{-1} for both polarities of SBT indicates the remissible differential negative resistivity due to trap filling [22] and double injection [23] or associated with transit current [24].

4. Conclusions

In summary, Zr and Ba co-substituted SBT respectively for Ta and Sr thin films were successfully grown on Pt/Ti/SiO₂/Si wafers by a sol-gel spin coating system up to 10 mol%. Structure of crystal, surface and cross-sectional microstructure, ferroelectric, electric and capacitance properties were analysed to investigate potential of Zr and Ba co-substituted SBT for a candidate gate ferroelectric to be utilized in FeFET MFIS structure for 1T-type FeRAM application by means of required ferroelectric and electrical properties. Stable perovskite crystal structure with calculated Goldschmidt tolerance factor deviated only 0.16% and binding energies related to chemical states of Sr^{2+} , Ba^{2+} , Ta^{5+} and Zr^{4+} evidenced the successful substitutions of Zr and Ba for Ta and Sr sites, respectively. Comparatively larger Zr substitution yields contraction of rattling distance of Ta_{Zr} ions of octahedra in the middle of perovskite units and results in decrease of ionic polarizability, so polarization. Hence, dielectric constants decrease with increasing substitution ratio. Hence, the enhancement of voltage in the ferroelectric layer in the MFIS structure would yield saturated hysteresis loop which could be enough for FeRAM operation and provide a higher memory window and possible longer retention time.

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References

- [1] Mikolajick T, Slesazeck S, Park M H and Schroeder U 2018 *MRS Bull.* **43** 340
- [2] Medwal R, Gupta S, Pavunny S P, Katiyar R K, Thomas R and Katiyar R S 2018 *J. Mater. Sci.* **53** 4274
- [3] Fengler F P G, Nigon R, Murali P, Grimley E D, Sang X H, Sessi V et al 2018 *Adv. Electron. Mater. Lett.* **4** 1700547
- [4] Shin H W and Son Y J 2018 *Electron. Mater. Lett.* **14** 59
- [5] Sugandha and Jha A K 2013 *Ceram. Int.* **39** 9397
- [6] Sugandha and Jha A K 2013 *Ferroelectrics* **447** 136
- [7] Ma T P and Han J P 2002 *IEEE Electron. Device Lett.* **23** 386
- [8] Bozgeyik M S, Cross J S, Ishiwara H and Shinozaki K 2012 *J. Electroceram.* **28** 158
- [9] Yan K, Takahashi M and Sakai S 2012 *Appl. Phys. A: Mater.* **108** 835
- [10] Bozgeyik M S, Cross J S, Ishiwara H and Shinozaki K 2009 *Mater. Sci. Eng. B* **161** 130
- [11] Bozgeyik M S, Cross J S, Ishiwara H and Shinozaki K 2010 *Microelectron. Eng.* **87** 2173
- [12] Shimakawa Y, Kubo Y, Nakagawa Y, Kamiyama T, Asano H and Izumi F 1999 *Appl. Phys. Lett.* **74** 1904
- [13] Atsuki T, Soyama N, Yonezawa T and Ogi K 1995 *Jpn. J. Appl. Phys. I* **34** 5096
- [14] Noguchi T, Hase T and Miyasaka Y 1996 *Jpn. J. Appl. Phys. I* **35** 4900
- [15] Li Y B, Zhang S, Fei W D, Gan Z H and Mhaisalkar S 2007 *Adv. Appl. Ceram.* **106** 180
- [16] Kannan B R and Venkataraman B H 2014 *J. Mater. Sci.: Mater. Electron.* **25** 4943
- [17] Golosov D A, Zavadski S M, Kolos V V and Turtsevich A S 2016 *Phys. Solid State* **58** 50
- [18] Kannan B R and Venkataraman B H 2016 *Ferroelectrics* **493** 110
- [19] Akazawa H and Ando H 2010 *J. Appl. Phys.* **108** 083704
- [20] Bozgeyik M S, Cross J S, Ishiwara H and Shinozaki K 2009 *Jpn. J. Appl. Phys.* **48** 061403
- [21] Miller S L and McWhorter P J 1992 *J. Appl. Phys.* **72** 5999
- [22] Chen H D, Udayakumar K R, Gaskey C J and Cross L E 1997 *Integr. Ferroelectr.* **15** 89
- [23] Scott J F, Melnick B M, McMillan L D, de Araujo C A P and Azuma M 1993 *Ferroelectrics* **150** 209
- [24] Kang S K and Ishiwara H 2002 *Jpn. J. Appl. Phys. I* **41** 6899