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Electrical Properties of Sol-Gel Derived Ferroelectric $Bi_{3.35}Sm_{0.65}Ti_3O_{12}$ Thin Films

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ABSTRACT

Ferroelectric $Bi_{3.35}Sm_{0.65}Ti_3O_{12}$(BSmT) thin films were synthesized by sol-gel process. In this experiments, $Bi(TMHD)_3$, $Sm_5(O^iPr)_{13}$, $Ti(O^iPr)_4$ were used as precursors, which were dissolved in 2-methoxyethanol. The BSmT thin films were deposited on the $Pt/TiO_x/SiO_2/Si$ substrates by spin-coating. Thereafter, the thin films with the thickness of 240 nm were annealed from 600 to 720°C in oxygen atmosphere for 1 h, and post-annealed in oxygen atmosphere for 1 h after deposition of Pt electrode to enhance the electrical properties. To investigate the effects of Sm-substitution in the BTO thin films, the BTO and BSmT thin films were prepared, respectively. The remanent polarization and coercive voltage of the BSmT thin films annealed at 720°C were 19.48 $\mu C/cm^2$ and 3.40 V, respectively.

Key words : BSmT, BTO, FRAM, Sol-gel, Spin-coating

1. Introduction

In recent years, Ferroelectric Random Access Memory (FRAM) has considerable potential as a new memory due to its properties for ideal memory such as high-density integration, fast read and write operation, long endurance, excellent retention and non-volatility with unlimited usage in practical. Among the materials used as FRAM capacitor, bismuth layer-structured ferroelectrics have received considerable attention as alternative materials to conventional Pb-based ferroelectrics due to the its good fatigue property.[1,2)] Essentially, compared with $SrBi_2Ta_2O_9$ (SBT) and its related materials, $Bi_4Ti_3O_{12}$ (BTO) is known to show high crystallinity at lower temperatures.[3,4)] However, BTO in its structure contains unstable bi ions, which are easily evaporated during the heating process. The volatility of Bi ions affects the ferroelectric and fatigue characteristics of the thin films.[5)] Therefore, Bi^{3+} in the BTO structure can be substituted by trivalent rare-earth ions, such as La^{3+}, Nd^{3+}, and Sm^{3+}, for the improvement of the properties of such layer-structures.[6,7)] Among them, $Bi_{4-x}Sm_xTi_3O_{12}$ (BSmT) has been received much attention due to its large remanant polarization than that of $Bi_{4-x}La_xTi_3O_{12}$ (BLT).[8)] In this study, we substituted Sm ions for Bi ions for improvement of ferroelectric and fatigue characteristics of BTO structure.

The thin films have already been prepared by R.F. sputtering, MOCVD, PLD, MOD, and sol-gel process. Among the various techniques, sol-gel processing has been employed in this study which offers excellent uniformity over large area, easy composition control, short fabrication time, as well as low temperature process at comparatively low cost. In this study, a chelating agent was used for chemical stability of the solution, and the thin films prepared by the spin-coating on the substrates. Ferroelectric properties and microstructures of the BSmT thin films according to the synthetic process and post-annealing temperature were investigated.

2. Experimental Procedure

$Bi_{3.35}Sm_{0.65}Ti_3O_9$ stock solutions were synthesized by sol-gel process. Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth (III) $[Bi((CH_3)_3CCOCHCOC(CH_3)_3)_3]$, Samarium (III) i-propoxide $[Sm_5O(OC_3H_7)_{13}]$ and Titanium (IV) i-propoxide $[Ti[OCH(CH_3)_2]_4]$ were used as precursors. Also, 2-methoxyethanol was used as solvent and ethylacetoacetate [EAcAc], a kind of α-diketonate ligands was used as a chelating agent to improve the solution stability. Thereafter, the mixed solutions were hydrolyzed and condensed. Fig. 1 shows schematic diagram for synthesis of BSmT stock solution. These solutions were spin-coated on the $Pt/TiO_x/SiO_2/Si$ substrates at 3000 rpm for 30 sec and were baked at about 450°C for 5 min. To prepare the thin films with the thickness of 240 nm, these steps were repeated four times. The films were post-annealed at the various temperatures (600 – 720°C) in oxygen atmosphere for 1 h and post-annealed after deposition of Pt top electrode to enhance the electrical properties. Fig. 2 shows the schematic diagram for preparation of the BSmT thin films. And BTO thin films were deposited by same conditions for comparative study with substitution of Sm ions.

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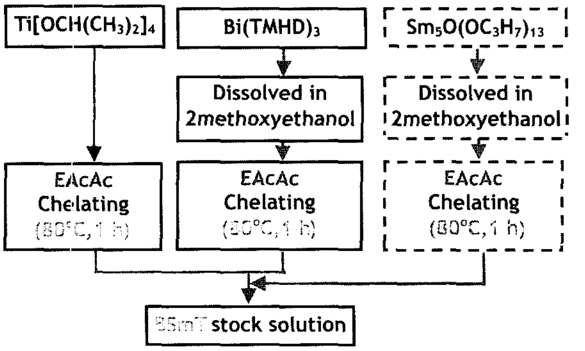

$Bi(TMHD)_3$: Tris(2,2,6,6-tetramethyl-3,5-heptanedionato) bismuth, $Bi[(CH_3)_3CCOCHCOC(CH_3)_3]_3$
EAcAc : Ethylacetoacetate, $CH_3COCH_2COOC_2H_5$

Fig. 1. Experimental procedure for synthesis of the BSmT stock solution.

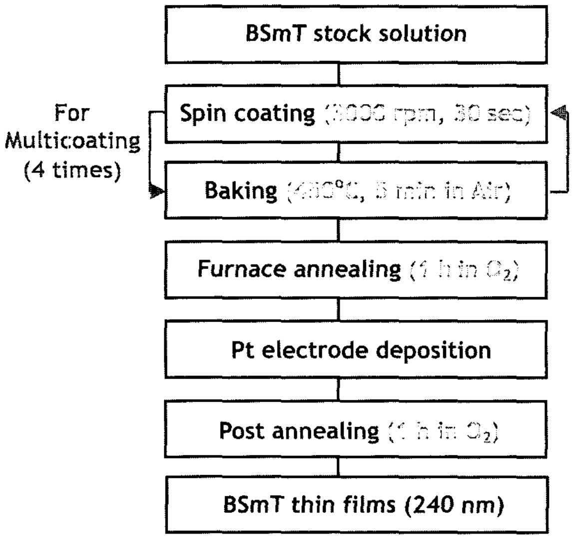

Fig. 2. Experimental procedure for preparation of the BSmT thin films.

In order to observe composition of the BSmT thin films, EPMA (JEOL, JZA-8900A) was investigated. The baking temperature was determined from TG-DSC (Setaram TGA 92 16-18). The crystalline phases after the heat treatment at the various temperatures were identified by XRD (RIGAKU, DXAM 200 X-ray Diffractometer). The surface microstructure was analyzed by FESEM (Hitachi S-4300) and AFM (PSIA, Au toprobe cp). The electrical properties for polarization-electrical field (P-E), leakage currents density (I-V) characteristics and reliability property were performed by the RT66A (Radient Technologies, Inc).

3. Results and Discussion

3.1. Thermal Behavior of the BSmT Gel Powder

In order to decide the baking temperature for decomposing organic material from the BSmT powder, TG-DSC curves were measured. The weight loss of the BSmT gel

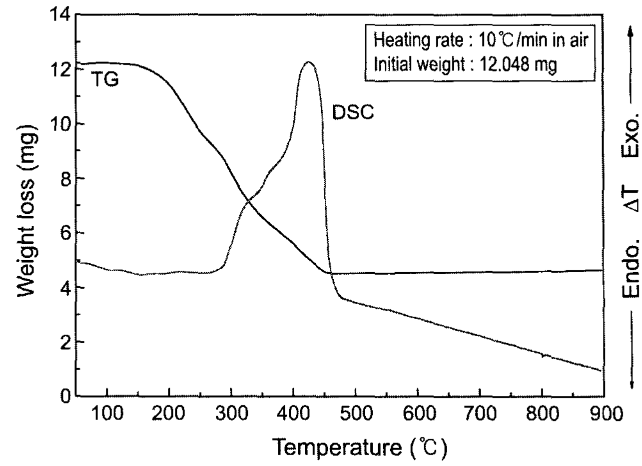

Fig. 3. TG-DSC curves of the BSmT gel powder.

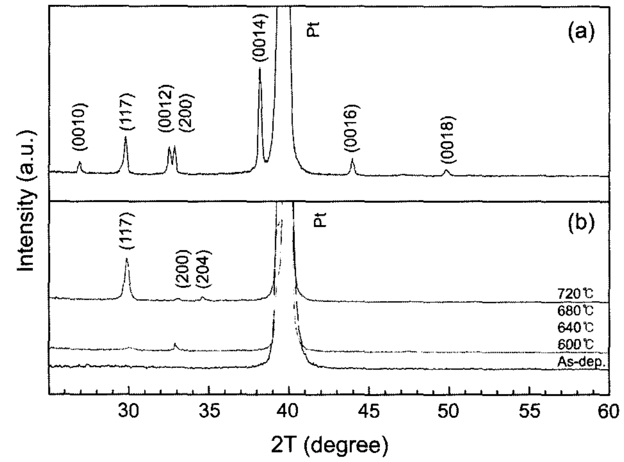

Fig. 4. XRD patterns of the BTO and BSmT thin films (a) the BTO thin films post-annealed at 720°C for 1 h in oxygen atmosphere and (b) BSmT thin films post-annealed at the various temperatures for 1 h in oxygen atmosphere.

powder was started at around 200°C and terminated at around 450°C. These weight loss and exothermic peak show decomposition and phase transformation of materials. From the results of Fig. 3, the BSmT thin films were baked at 450°C and post-annealed at 600~720°C for crystallization with perovskite structure.

3.2. Crystallization Behavior of the BSmT Thin Films

Fig. 4 shows X-ray diffraction patterns of the BTO and BSmT thin films. Cu *Kα* radiation (0.15405 nm) was used for recording X-ray diffraction patterns of the BTO and BSmT thin films. All the XRD patterns are indexed by using the standard XRD data of BTO (JCPDS card, No. 35-0795). The BTO thin films annealed at 720°C for 1 h in oxygen atmosphere randomly exhibited various peaks of a, b-axis and c-axis orientations, as shown in Fig. 4(a). But, substitution of Sm ions tends to obstruct the growth to c-axis of BTO thin films. As the annealing temperature increases, the

(117) peak of BSmT thin films became much stronger and shaper, and (204) peak generated newly at 720°C due to further enhancement in crystallization. Any second phases didn't appear in these films. It indicated that Sm ions could be successfully solid-solved in BTO solutions and the (117) preferred orientation of the thin films becomes dominant with the increase in the annealing temperature. Generally, bismuth-layered structural materials show good ferroelectrics properties in the a, b-axis orientation than c-axis orientation.9) From these results, we supposed that the heat treatment temperature above 600°C was required to prepare BSmT thin films with high crystallinty on $Pt/TiO_x/SiO_2/Si$ substrates and the ferroelectric properties of BSmT thin films would be better than those of BTO thin films.

3.3. Micro-Structures of the BSmT Thin Films

SEM micrographs of the BTO and BSmT thin films with the various annealing temperatures were exhibited in Fig. 5.

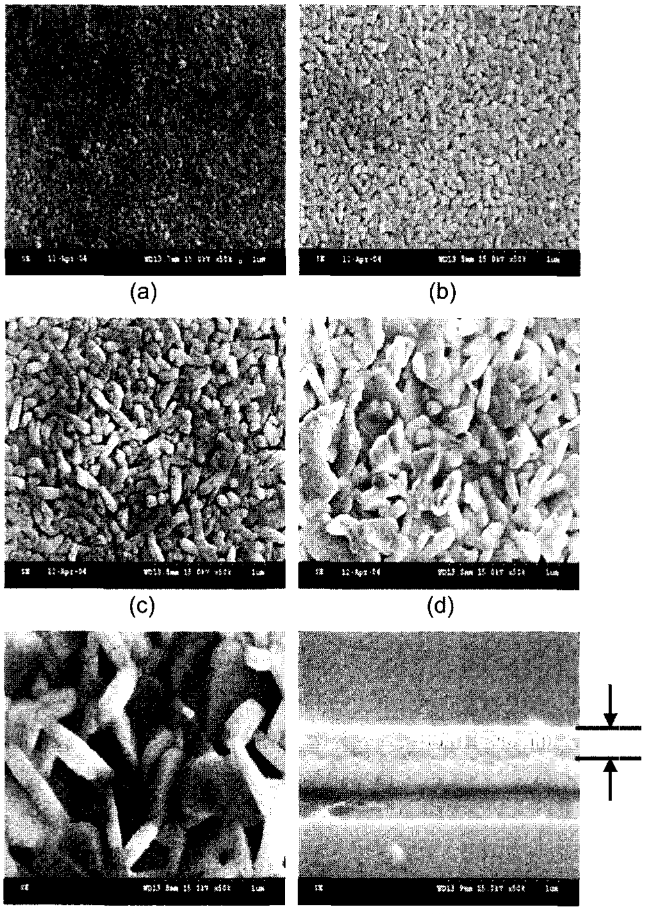

Fig. 5. SEM surface images of the BSmT and BTO thin films post-annealed at the various temperatures for 1 h in oxygen atmosphere (a) BSmT thin film annealed at 600°C, (b) BSmT thin film annealed at 640°C, (c) BSmT thin film annealed at 680°C, (d) BSmT thin film annealed at 720°C, (e) BTO thin film annealed at 720°C, and (f) the cross-sectional image of BSmT thin films annealed at 640°C.

In the case of the BSmT thin films annealed at 600°C, grains of 30 – 50 nm size existed in matrix. With the increase in the annealing temperature to 680°C, grains of 200 – 300 nm size such as rod appeared in matrix. Grains of the BSmT thin films annealed at 720°C turned into rod-like and plate-like ones. Meanwhile, the BTO thin films were easily formed in a plate-like morphology with $(Bi_2O_2)^{2+}$ layers in the ab-plane. Interestingly, grains of the BSmT thin films annealed at 720°C were smaller and the platelets were placed more randomly, compared to those of the BTO thin films prepared under the same process (Fig. 5(e)). It is indicated that substituted Sm ions acted as grain-growth inhibitor and gave rise to the random orientation of grains in the BSmT thin films. Fig. 5(f) shows the cross-sectional image of BSmT thin films annealed at 640°C for 1 h in oxygen atmosphere. The thickness of BSmT thin films were 240 nm.

Fig. 6 shows the surface roughness of the BSmT thin films deposited from 600 to 720°C, which were examined by using the AFM. The root-mean-square of the surface roughness was increased with increase in the annealing temperature. However, the RMS value of the BSmT thin film annealed at 720°C was drastically increased. Consequently, it was considered that the sudden increase of surface roughness affected the electric properties of BSmT thin films.

3.4. Ferroelectric Property of the BSmT Thin Films

Fig. 7 shows the P-V hysteresis loops of the BTO and

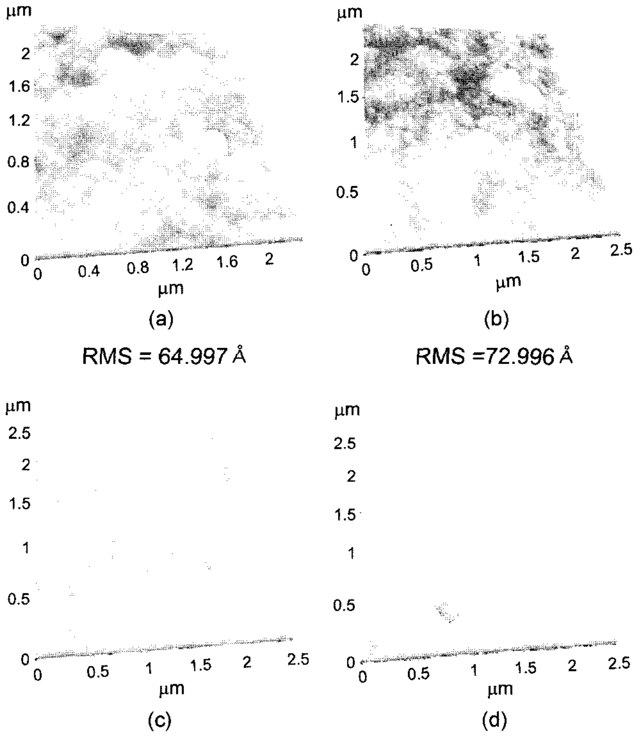

Fig. 6. AFM images of the BSmT thin films post-annealed at the various temperatures for 1 h in oxygen atmosphere (a) 600°C, (b) 640°C, (c) 680°C, and (d) 720°C.

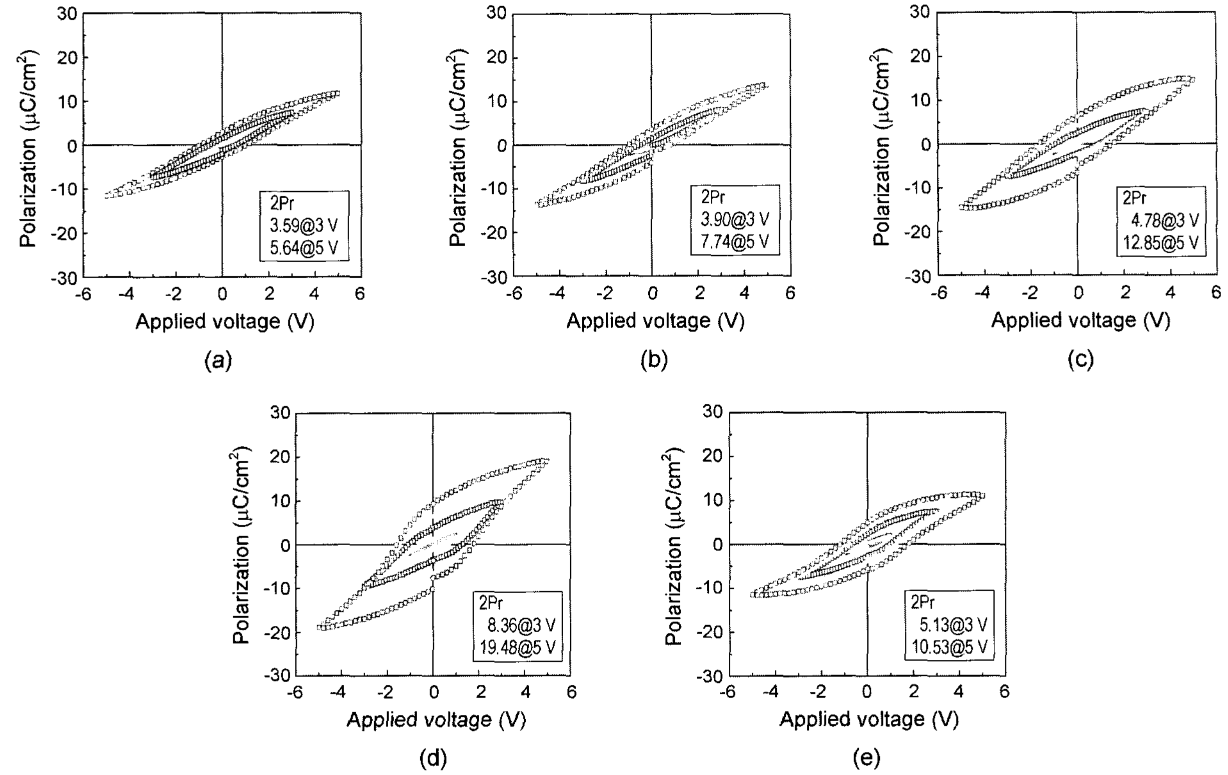

Fig. 7. Hysteresis loops of the BTO and BSmT thin films post-annealed at the various temperatures for 1 h in oxygen atmosphere (a) BSmT thin film annealed at 600°C, (b) BSmT thin film annealed at 640°C, (c) BSmT thin film annealed at 680°C, (d) BSmT thin film annealed at 720°C, and (e) BTO thin film annealed at 720°C.

BSmT thin films with the various post-annealing temperatures. In case of BTO thin films annealed at 720°C, it has relatively low remanent polarization value. And the BSmT thin films annealed at the relative low temperatures (600, 640°C) also exhibited poor ferroelectric properties. However, as the annealing temperature increases, the BSmT thin films exhibit better ferroelectric property. As the annealing temperature of the BSmT thin film from 600 to 720°C increases, the remanent polarization (2Pr) values of the BSmT thin films are 5.64, 7.74, 12.85, and 19.48 μC/cm² at the applied voltage of 5 V, respectively. And coercive voltage (2Vc) values are 2.00, 1.80, 3.20, and 3.40 V at the applied voltage of 5 V, respectively.

Fig. 8 shows the leakage current densities of the BTO and BSmT thin films annealed at various temperatures as a function of the applied field. Generally, in the application of

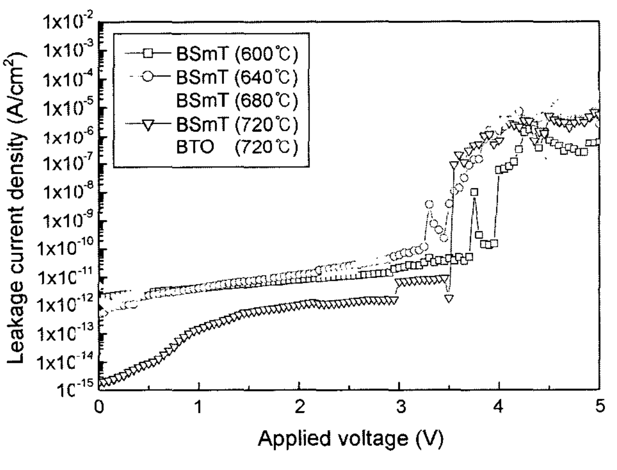

Fig. 8. Leakage current density of the BTO and BSmT thin films at the various temperatures for 1 h in oxygen atmosphere.

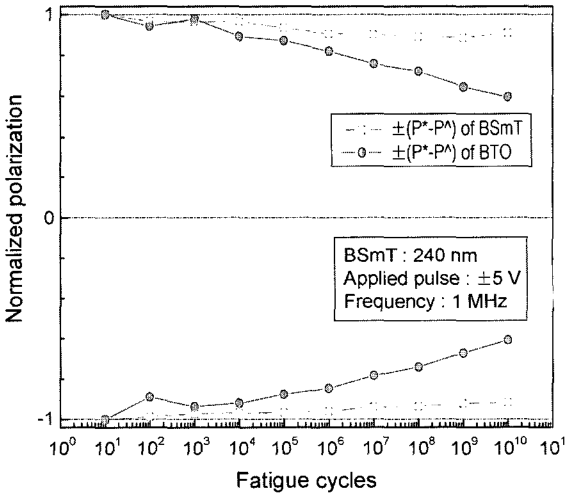

Fig. 9. Results of the fatigue test of the BTO and BSmT thin film at 1 MHz bipolar square pulse wave.

FRAM capacitor, it is required leakage current density under 10^{-6} A/cm^2. The BTO and BSmT thin films exhibit a resistivity below 10^{-6} A/cm^2 when the D.C. bias of 0 – 3 V is applied to the capacitor. As the annealing temperature of the BSmT thin films from 600 to 720°C increases, the leakage current densities of the BSmT thin films had a tendency of decrease. It is assumed that lower leakage current may be caused by the higher crystallinity of the BSmT thin films.

The fatigue-free characteristics of the BTO and BSmT capacitor films are summarized in Fig. 9. The BSmT capacitors show little change both (P* – P^) and (–P*) – (–P^) value at the switching voltage of ± 5 V. The degradation of the switching charge after 1×10^{10} switching cycles was within 10%. However, in case of the BTO thin films, the degradation of the switching charge after 1×10^{10} switching cycles was about 40%. These improved fatigue characteristics of the Sm-substituted BTO thin films may be attributed to lesser oxygen vacancies in the perovskite layers than the BTO thin films annealed at 720°C.[10)]

4. Conclusions

Ferroelectric BSmT thin films were prepared by the spin-coating method using sol-gel solution. Electric properties of the BSmT thin films were investigated. The results can be summarized as following;

The BSmT thin films showed better ferroelectric properties than the BTO thin films, and its 2Pr and 2Vc values at 720°C were 19.48 μC/cm^2, 3.40 V at the applied voltage of 5 V, sol-gel derived the BSmT thin films showed better fatigue property than that of the BTO thin films. The degradation of switching charge of the BSmT thin films after 1×10^{10} switching cycles was within 10%.

REFERENCES

1. C. A-Paz de Arujo, J. D. Cuchiaro, L. D. McMillan, M. C. Scott, and J. F. Scott, "Fatigue-Free Ferroelectric Capacitors with Platinum Electrode," *Nature*, **374** 627-29 (1995).
2. B. H. Park, B. S. Kang, S. B. Bu, T. W. Noh, J. Lee, and W. Jo, "Lanthanum-Substituted Bismuth Titanate for Use in Non-Volatile Memories," *Nature*, **401** [14] 682-84 (1999).
3. T. Watanabe, T. Sakai, K. Sakai, K. Saito, and H. Funakubo, "Film Thickness Dependence of Ferroelectric Properties of *c*-Axis-Oriented Epitaxial $Bi_4Ti_3O_{12}$ Thin Films Prepared by Metalorganic Chemical Vapor Deposition," *J. of Appl. Phys.*, **89** [7] 3934-38 (2001).
4. D. Wu, A. Li, T. Zhu, Z. Li, Z. Liu, and N. Ming, "Processing and Composition-Dependent Characteristics of Chemical Solution Deposited $Bi_{4-x}La_xTi_3O_{12}$ Thin Films," *J. of Mater. Res.*, **16** 1325-32 (2001).
5. Y. Ding, J. S. Liu, H. X. Qin, J. S. Zhu, and T. N. Wang, "Why Lanthanum-Substituted Bismuth Titanate Becomes Fatigue Free in a Ferroelectric Capacitor with Platinum Electrodes," *Appl. Phys. Lett.*, **78** [26] 4175-77 (2001).
6. U. Chon and J. S. Shim, "Ferroelectric Properties and Crystal Structure of Praseodymium-Modified Bismuth Titanate," *J. of Appl. Phys.*, **93** [8] 4769-75 (2003).
7. H. Uchida, I. Okada, H. Matsuda, T. Iijima, T. Watanabe, and H. Funakubo, "Fabrication of Ion-Cosubstituted Bismuth Titanate Thin Films by Chemical Solution Deposition Method," *Integrated Ferroelectrics*, **52** 41-54 (2003).
8. U. Chon, K. B. Kim, H. M. Jung, and G. C. Yi, "Fatigue-Free Samarium-Modified Bismuth Titanate $Bi_{4-x}Sm_xTi_3O_{12}$ Film Capacitors having Large Spontaneous Polarizations," *Appl. Phys. Lett.*, **79** [19] 3137-39 (2001).
9. T. Watanabe, H. Funakubo, K. Saito, R. Suzuki, M. Fujimoto, M. Osada, Y. Noguchi, and M. Miyayama, "Preparation and Characterization of *a*- and *b*-Axis-Oriented Epitaxially Grown $Bi_4Ti_3O_{12}$-Based Thin Films with Long-Range Lattice Matching," *Appl. Phys. Lett.*, **81** [9] 1660-62 (2002).
10. Y. W. So, B. S. Kang, S. A. Seo, D. J. Kim, T. W. Noh, and J. G. Yoon, "Effects of Lanthanide Dopants on the Ferroelectric Property of $Bi_4Ti_3O_{12}$ Thin Films," *Ferroelectrics*, **271** 347-52 (2002).