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Fabrication and Electrical Properties of Sol–Gel-Derived $0.63Bi(Mg_{1/2}Ti_{1/2})O_3$–$0.37PbTiO_3$ Thin Films

Longdong Liu and Ruzhong Zuo†

Institute of Electro Ceramics & Devices, School of Materials Science and Engineering, Hefei University of Technology, Hefei, 230009, China

High Curie-temperature $0.63Bi(Mg_{1/2}Ti_{1/2})O_3$–$0.37PbTiO_3$ (BMT–PT) ferroelectric thin films with a morphotropic phase boundary composition were successfully fabricated on Pt(111)/$Ti/SiO_2/Si$ substrates by sol–gel spin-coating method. The effect of annealing temperatures on the structure and electrical properties of BMT–PT thin films was explored. The scanning electron microscopy and atomic force microscopy images indicate that the film annealed at 675°C for 30 min has a relatively dense and uniform microstructure and a thickness of about 375 nm, together with optimal dielectric and ferroelectric properties of remnant polarization 17.8 μC/cm², coercive field 75 kV/cm, dielectric permittivity 1477, and loss tangent 0.07 at 1 kHz. The results indicate that the BMT–PT thin film has potential applications in high-temperature ferroelectric devices.

I. Introduction

BISMUTH-BASED perovskite ferroelectric materials with high Curie temperatures (T_c) have received increasing interests in recent years owing to their potential for applications under higher temperature conditions, including $BiMeO_3$–$PbTiO_3$ (where Me = Sc^{3+}, Fe^{3+}, In^{3+}, Yb^{3+}, Ga^{3+}, etc.) and $Bi(Me1,Me2)O_3$–$PbTiO_3$ (where Me1 = Mg^{2+}, Zn^{2+}, Ni^{2+}, etc., and Me2 = Ti^{4+}, Zr^{4+}, Nb^{5+}, etc).[1–7] The $BiScO_3$–$PbTiO_3$ (BS–PT) ceramics with a morphotropic phase boundary (MPB) composition exhibit a high T_c (~450°C) and excellent piezoelectric properties (piezoelectric constant, d_{33} ~460 pC/N and planar electromechanical coupling factor, k_p ~56%),[1] having been considered to be potential high-temperature piezoelectric materials. BS–PT thin films[8,9] were also reported to exhibit good ferroelectric properties. However, the potential application of BS–PT ceramics and thin films was greatly limited by the high cost of scandium sources. Although bismuth-based perovskite-lead titanate solid solutions usually have relatively high T_c, yet most of them have low or inferior piezoelectric properties near their MPB, except for a few compositions such as BS–PT,[1] $Bi(Ni_{1/2}Ti_{1/2})O_3$–$PbTiO_3$ (BNT–PT)[5] and $Bi(Mg_{1/2}Ti_{1/2})O_3$–$PbTiO_3$ (BMT–PT).[4] As for BNT–PT compositions, the conductivity and dielectric loss were relatively high, leading to the difficulty in device applications. By comparison, $(1-x)$BMT–xPT ceramics possess a lower lead content near the MPB and cost much less than BS–PT ceramics. Furthermore, $(1-x)$BMT–xPT ceramics have been reported to have a relatively high T_c (~430°C), good piezoelectric properties (d_{33} ~225 pC/N), and high remnant polarization (P_r ~38 μC/cm²) for MPB compositions (x ~0.37).[4]

As far as the literature review is concerned, processing and electrical properties of BMT–PT bulk ceramics have been extensively investigated.[4,10–13] However, no study has been so far reported on the fabrication and properties of BMT–PT thin films. It should be of value to explore the preparation and electric properties of BMT–PT MPB compositions in the thin film form to meet the miniaturization and performance requirements of microelectronics as operated under high-temperature environments.

Among various thin film preparation techniques, the sol–gel method has proved to be effective in fabricating high-quality ferroelectric films as it offers good stoichiometry control, chemical homogeneity, low cost, and ability to make uniform films over a larger area. The purpose of this study was thus to explore sol–gel processing and various electrical properties of BMT–PT thin films (x ~0.37) on Pt(111)/$Ti/SiO_2/Si$ substrates. The influence of annealing temperatures on the crystal structure, film morphology, and dielectric/ferroelectric properties was investigated in detail.

II. Experimental Procedures

According to the stoichiometry of 0.63BMT–0.37PT films, 10 mol% excess Pb and Bi were used to compensate for the volatilization loss. Firstly, $Mg(NO_3)_2{\cdot}6H_2O$ (≥99.0%) and $Bi(NO_3)_3{\cdot}5H_2O$ (≥99.0%) were dissolved in 2-methoxyethanol (2-MOE, ≥99.0%) in sequence. $Ti(OC_4H_9)_4$ (≥98.0%) was dissolved in 2-MOE with acetylacetone as the stabilizer and chelating agents. $Pb(OOCCH_3)_2{\cdot}3H_2O$ (≥99.0%) was dissolved in glacial acetic acid. Then, $Pb(OOCCH_3)_2$ solution was added to $Ti(OC_4H_9)_4$ solution and stirred for 10 min. Subsequently, the above mixed solution was added into $Mg(NO_3)_2$ and $Bi(NO_3)_3$ mixed solution and simultaneously stirred to form a stable sol by adjusting the pH value to be ~5.4. Finally, an appropriate amount of *N-N* Dimethylformamide as drying control chemical additive was added into the above solution to prevent the film from cracking. A little 2-MOE was added to adjust the viscosity and ultimately to form BMT–PT precursor solution with a concentration of 0.2 *M*. After aging for 3–5 days in air, the thin films were deposited onto Pt (111)/$Ti/SiO_2/Si$ substrates by a repeated spin-coating process at 4000 rpm for 30 s. After each spin-coating step, the films were dried at 200°C for 5 min, and pyrolyzed at 500°C for 8 min under ambient atmosphere. Finally, the precursor films were annealed at 650°C–700°C for 30 min.

The phase structures were characterized by an X-ray diffractometer (XRD; D/MAX2500V, Rigaku, Tokyo, Japan) with CuKα radiation. The microstructure on the top surface and fractured cross-section of BMT–PT thin films was observed by an atomic force microscope (AFM; Being Nano-Instruments CSPM-4000, Beijing, China) and a field-emission

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†Author to whom correspondence should be addressed. e-mail: piezolab@hfut.edu.cn

scanning electron microscope (FE-SEM; Sirion200, FEI, Hillsboro, OR), respectively. A ferroelectric testing system (Precision LC; Radiant Technologies Inc., Albuquerque, NM) was used to evaluate the ferroelectric properties of thin films. The dielectric properties (permittivity and loss tangent) as a function of frequency were measured by a precision impedance analyzer (HP 4194A; Hewlett-Packard, Palo Alto, CA).

III. Results and Discussion

The XRD patterns of sol–gel-derived BMT–PT thin films annealed at various temperatures are shown in Fig. 1. It can be seen that major peaks could be indexed as a typical perovskite structure except that the (111) diffraction peak was overlapped by the diffraction lines of the substrate. As the annealing temperature increases, the diffraction peaks become sharper and more intense, indicating better crystallinity. It is obvious that although the peaks of the BMT–PT film annealed at 700°C were a little sharper than those of films annealed at 675°C, the intensity was almost the same, suggesting that the film crystallization was complete as the film was annealed at 675°C. However, the structure of the film looks more like a pseudocubic phase (not MPB between rhombohedral and tetragonal phases), and was different from that of conventionally prepared bulk ceramics,[4] probably because of the grain size effect.[14]

The effect of annealing temperature on the surface morphology of BMT–PT films was examined by AFM, as shown in Fig. 2. It can be seen that the surface morphology of the film is granular and relatively dense and uniform as it was annealed at 650°C and 675°C. Furthermore, the increase of annealing temperature would cause both the grain size and surface roughness to increase. A relatively smooth surface was observed for the films annealed at 675°C with a measured roughness of ~3.4 nm. As the annealing temperature rose to 700°C, the surface roughness of the film distinctly increased owing to the formation of pinholes. This could be ascribed to the volatilization of lead and bismuth components from the grain boundary of large grains. The fractured cross-sectional microstructure of the film annealed at 675°C is shown in Fig. 3. The developed BMT–PT films look homogeneous and dense with an estimated thickness of 375 nm, and stick well to the substrate. No distinct interfaces could be observed between deposited layers formed after each spin-coating step.

Polarization–electric field (P–E) hysteresis loops of BMT–PT films annealed at different temperatures are shown in Fig. 4. It can be seen that the P_r value of the film first increases as the annealing temperature increases from 650°C to 675°C and then decreases with further increasing the temperature to 700°C. The possible reason could be ascribed to the increase of the grain size with annealing temperature, as can be seen from AFM images. Potential wells are usually

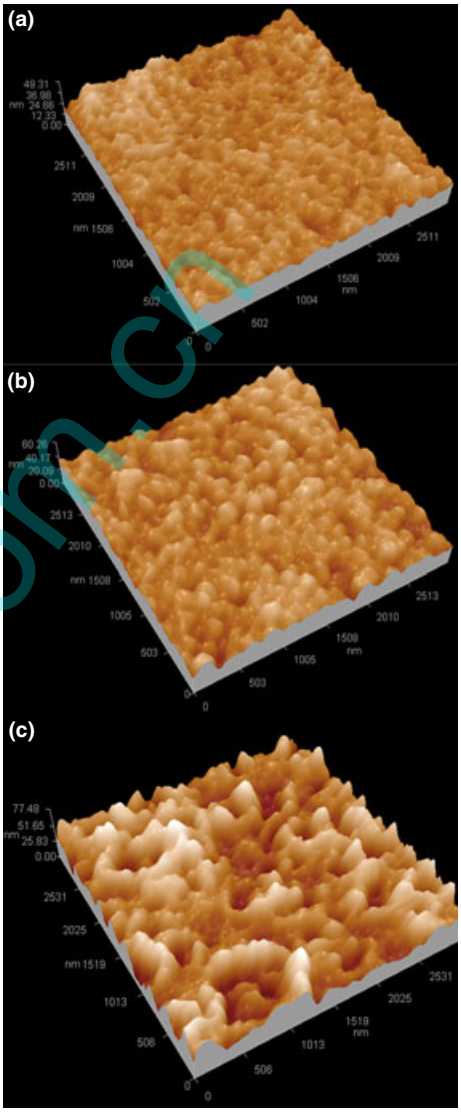

Fig. 2. AFM micrographs of the BMT–PT thin films annealed at (a) 650°C, (b) 675°C and (c) 700°C.

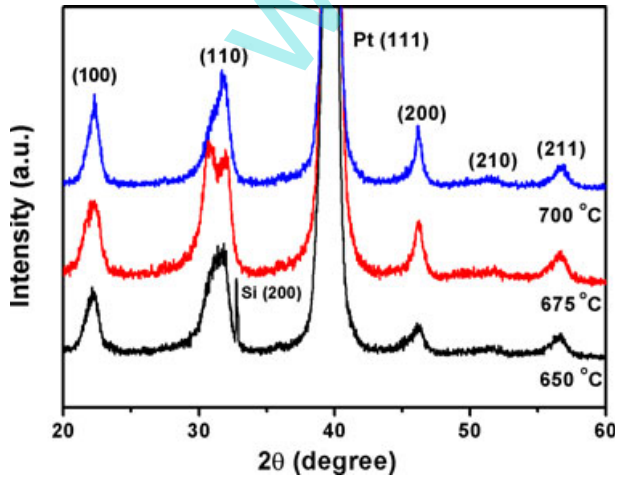

Fig. 1. XRD patterns of the BMT–PT thin films annealed at different temperatures.

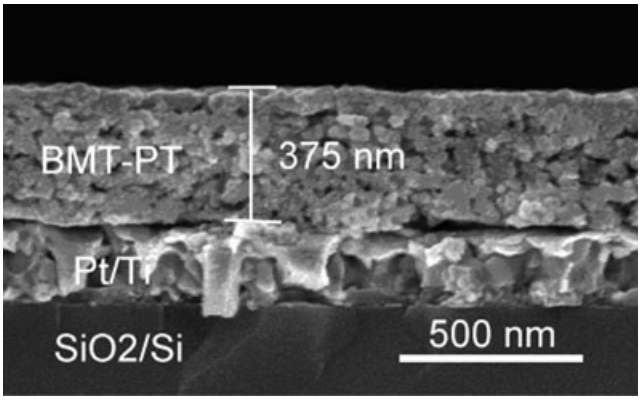

Fig. 3. Cross-sectional microstructure of the sol–gel-derived BMT–PT thin film annealed at 675°C.

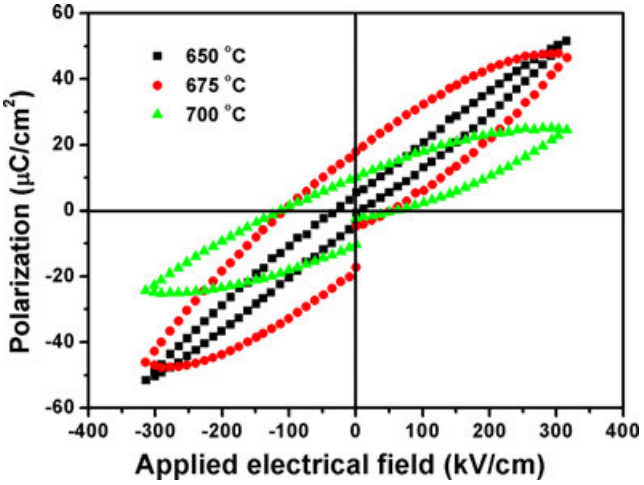

Fig. 4. P–E hysteresis loops (1 kHz) of the BMT–PT thin films on $Pt/Ti/SiO_2/Si$ substrates annealed at various temperatures for 30 min.

formed at grain boundary where charged carriers are easily trapped and then pin the domains nearby.[15] This will make it difficult for pinned domains to be depinned, thus leading to reduced amount of switchable domains. As the grain size increases, the volume fraction of grain boundaries will be reduced and the contribution of switchable domains to the polarization should be then increased.[16] In addition, the domain size usually increases with increasing grain size, such that the reorientation of the domains becomes easier.[17] As a result, the contribution of the domain wall motion to the polarization would increase accordingly. However, because of relatively serious evaporation loss of lead and bismuth component as the annealing temperature increases to 700°C, the presence of pinholes and relatively low density as observed by AFM result in the degradation of the P_r value. The BMT–PT thin film annealed at 675°C with a P_r value and a coercive field E_c of 17.8 μC/cm^2 and 75 kV/cm, respectively. The P_r value is almost as same as that of the bulk ceramics (P_r = 18 μC/cm^2) prepared by introducing polyethylene glycol into the conventional solid state reaction process to aid the formation of the perovskite phase,[10] and higher than that of bulk ceramics (P_r = 7.9 μC/cm^2) fabricated by conventional solid-state reaction method.[13] However, it is lower than that of bulk ceramics (P_r = 38 μC/cm^2) prepared by a high-pressure technique.[4] It can be seen that the shape of the hysteresis loop of the film was not saturated owing to the leakage current. Higher conductivity of BMT–PT materials has been reported even for bulk ceramics.[10,13] It is anticipated that this drawback will get modified by adding a few dopants such as Mn^{2+} in future, considering the multivalence characteristic of Mn ions.[10]

Frequency dependence of the dielectric permittivity and dissipation factor for the film annealed at various temperatures is shown in Fig. 5. It can be found that the dielectric permittivity and loss tangent against frequency decrease with increasing measurement frequency, which is a typical characteristic of a normal dielectric. The dielectric permittivity of the film annealed at 675°C is relatively high. The increase of grain size would decrease the grain boundary proportion and thus result in higher volume fraction of switchable domains, leading to an increase of dielectric permittivity.[18,19] The dielectric loss is also a little higher than that of the film annealed at 650°C, owing to a slight reduction of the density as the grain size increases. The inferior dielectric properties for the film annealed at 700°C can be attributed to the bad topography as observed by AFM.

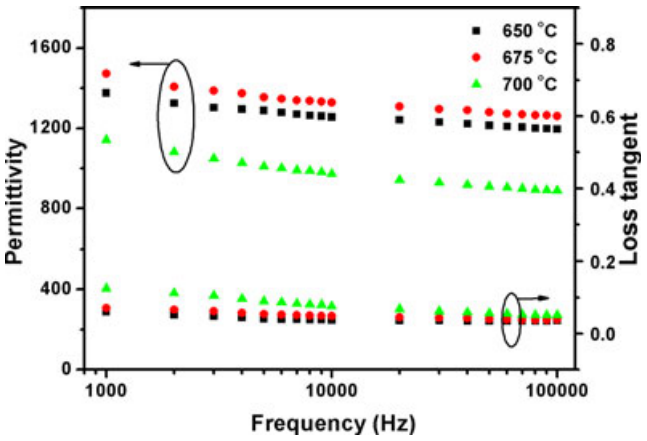

Fig. 5. Dielectric permittivity and loss tangent as a function of frequency for BMT–PT thin films annealed at various temperatures.

IV. Conclusions

The BMT–PT thin films with an MPB composition were successfully prepared on $Pt/Ti/SiO_2/Si$ substrate via sol–gel spin-coating technology. AFM and SEM results indicated that a relatively dense and uniform microstructure and a film thickness of about 375 nm could be obtained as the annealing temperature was optimized. The BMT–PT film annealed at 675°C exhibited good dielectric and ferroelectric properties of P_r ~17.8 μC/cm^2, dielectric permittivity ~1477, and loss tangent ~0.07 at 1 kHz. The good electrical characteristics suggest that the BMT–PT thin films have potential applications in high temperature ferroelectric devices.

Acknowledgments

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References

[1]R. E. Eitel, C. A. Randall, T. R. Shrout, and S. E. Park, "Preparation and Characterization of High Temperature Perovskite Ferroelectrics in the Solid Solution (1−x) $BiScO_3$-$XPbTiO_3$," *Jpn. J. Appl. Phys.*, **41** [4A] 2099–104 (2002).

[2]J. R. Cheng, W. Y. Zhu, N. Li, and L. E. Cross, "Fabrication and Characterization of $XBiGaO_3$-(1−x)$PbTiO_3$: A High Temperature Reduced Pb-Content Piezoelectric Ceramic," *Mater. Lett.*, **57**, 2090–4 (2003).

[3]T. P. Comyn, S. P. McBirde, and A. J. Bell, "Processing and Electrical Properties of $BiFeO_3$-$PbTiO_3$ Ceramics," *Mater. Lett.*, **58**, 3844–6 (2004).

[4]C. A. Randall, R. Eitel, B. Jones, and T. R. Shrout, "Investigation of a High T_c Piezoelectric System: (1−x)$Bi(Mg_{1/2}Ti_{1/2})O_3$-$XPbTiO_3$," *J. Appl. Phys.*, **95**, 3633–8 (2004).

[5]S. M. Choi, C. J. Stringer, T. R. Shrout, and C. A. Randall, "Structure and Property Investigation of a Bi-Based Perovskite Solid Solution: (1−x)Bi$(Ni_{1/2}Ti_{1/2})O_3$-$XPbTiO_3$," *J. Appl. Phys.*, **98** [3] 034108, 4pp (2005).

[6]M. R. Suchomel and P. K. Davies, "Enhanced Tetragonality in (x)$PbTiO_3$-(1−x)$Bi(Zn_{1/2}Ti_{1/2})O_3$ and Related Solid Solution Systems," *Appl. Phys. Lett.*, **86**, 262905, 3pp (2005).

[7]S. J. Zhang, C. Stringer, R. Xia, S. M. Choi, C. A. Randall, and T. R. Shrout, "Investigation of Bismuth-Based Perovskite System: (1−x)$Bi(Ni_{2/3}Nb_{1/3})O_3$-$XPbTiO_3$," *J. Appl. Phys.*, **98**, 034103, 5pp (2005).

[8]T. Yoshimura and S. T. Mckinstry, "Growth and Properties of (001) $BiScO_3$-$PbTiO_3$ Epitaxial Films," *Appl. Phys. Lett.*, **81** [11] 2065–6 (2002).

[9]H. Wen, X. H. Wang, C. F. Zhong, L. K. Shu, and L. T. Li, "Epitaxial Growth of Sol-Gel Derived $BiScO_3$-$PbTiO_3$ Thin Film on Nb-Doped $SrTiO_3$ Single Crystal Substrate," *Appl. Phys. Lett.*, **90** [20] 202902, 3pp (2007).

[10]S. H. Yu, Y. Ye, H. T. Huang, L. M. Zhou, and Z. Q. Wang, "Preparation, Structure and Properties of $Bi(Mg_{1/2}Ti_{1/2})$-$PbTiO_3$ Ceramics and Mn-Doping Effect," *Proc. SPIE*, **6423**, 6423H, 6pp (2007).

[11]Q. Zhang, Z. R. Li, F. Li, Z. Xu, and X. Yao, "Temperature Dependence of Dielectric/Piezoelectric Properties of (1−x)$Bi(Mg_{1/2}Ti_{1/2})O_3$-$XPbTiO_3$ Ceramics with an MPB Composition," *J. Am. Ceram. Soc.*, **93** [10] 3330–4 (2010).

[12]J. Chen, X. L. Tan, W. Jo, and J. Rödel, "Temperature Dependence of Piezoelectric Properties of High T_c $Bi(Mg_{1/2}Ti_{1/2})O_3$-$PbTiO_3$," *J. Appl. Phys.*, **106**, 034109, 7pp (2009).

[13]R. Rai, A. Sinha, S. Sharmac, and N. K. P. Sinham, "Investigation of Structural and Electrical Properties of (1−x)Bi($Mg_{0.5}Ti_{0.5}$)O_3-X$PbTiO_3$ Ceramic System," *J. Alloys Compd.*, **486**, 273–7 (2009).
[14]M. H. Frey and D. A. Payne, "Grain-Size Effect on Structure and Phase Transformation for Barium Titanate," *Phys. Rev. B*, **54** [4] 3158–68 (1996).
[15]Z. H. Zhou, J. M. Xue, W. Z. Li, J. Wang, H. Zhu, and J. M. Miao, "Leakage Current and Charge Carriers in ($Na_{0.5}Bi_{0.5}$)TiO_3 Thin Film," *J. Phys. D: Appl. Phys.*, **38**, 642–8 (2005).
[16]Y. Y. Wu, X. H. Wang, C. F. Zhong, and L. T. Li, "Effect of Anneal Conditions on Electrical Properties of Mn-Doped ($Na_{0.85}K_{0.15}$)$_{0.5}Bi_{0.5}TiO_3$ Thin Films Prepared by Sol-Gel Method," *J. Am. Ceram. Soc.*, **94** [6] 1843–9 (2011).
[17]T. M. Shaw, S. T. Mckinstry, and P. C. Mcintyre, "The Properties of Ferroelectric Films at Small Dimensions," *Annu. Rev. Mater. Sci.*, **30**, 263–98 (2000).
[18]D. V. Taylor and D. Damjanovic, "Evidence of Domain Wall Contribution to the Dielectric Permittivity in PZT Thin Films at Sub-Switching Fields," *J. Appl. Phys.*, **82**, 1973–5 (1997).
[19]C. Ang and Z. Yu, "DC Electric-Field Dependence of the Dielectric Constant in Polar Dielectrics: Multipolarization Mechanism Model," *Phys. Rev. B*, **69**, 174109, 8pp (2004). □