Effect of Mo substitution on ferroelectric properties of Bi$_{3.6}$Ho$_{0.4}$Ti$_3$O$_{12}$ thin films prepared by sol-gel method

Dongyun Guo,¹ Chuabin Wang,¹ Qiang Shen,¹ Lianmeng Zhang,¹,a and Jun Liu²
¹State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, People’s Republic of China
²Department of Physics, Wuhan University, Wuhan 430072, People’s Republic of China

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The series of (Bi$_{0.8}$Ho$_{0.1}$)$_{1-2x/3}$Ti$_{3-x}$Mo$_x$O$_{12}$ (BHTM) ($x = 0$, 0.9%, 1.5%, 3.0%, and 6.0%) thin films on Pt/Ti/SiO$_2$/Si substrates are prepared by sol-gel method, and the effect of Mo content on the microstructure and ferroelectric properties of these films is investigated. When the Mo content is not excessive, the BHTM films consisted of the single phase of Bi-layered Aurivillius phase. The B-site substitution with high-valent cation of Mo$^{6+}$ in Bi$_{3.6}$Ho$_{0.4}$Ti$_3$O$_{12}$ films, enhanced the $2P_r$ (remnant polarization) and reduced the $2E_c$ (coercive field) of these films. The BHTM thin film with $x = 1.5\%$ exhibited the best electrical properties with $2P_r$ of 48.4 $\mu$C/cm$^2$, $2E_c$ of 263.5 kV/cm, dielectric constant of 391 (at 1 MHz), good insulating behavior, as well as the fatigue-free characteristic. © 2008 American Institute of Physics. [DOI: 10.1063/1.3063121]

Ferroelectric thin films have been extensively investigated for applications in ferroelectric random access memory (FeRAM).1–3 Bismuth layer-structured ferroelectrics (BLSF) are recognized as promising film materials for FeRAM applications due to the fatigue-free behavior.4–6 Among these ferroelectrics, Bi$_4$Ti$_3$O$_{12}$ (BTO)-based films are the typical members of the BLSF family. It was reported4–6 that some members of the BLSF family. It was reported that some

The series of (Bi$_{0.8}$Ho$_{0.1}$)$_{1-2x/3}$Ti$_{3-x}$Mo$_x$O$_{12}$ (BHT) films became abnormally large. It was suggested that the A-site or B-site substitution in BTO crystal showed large remanent polarizations ($P_r$).2,7–12 It was also found that the coercive field ($E_c$) in the A-site and B-site substituted BTO films became larger.13–15 Our group reported a remarkable improvement of $2P_r$ in the BTO films by adding Ho$^{3+}$ ions to the A-site.16,17 But the $2E_c$ of the Bi$_3.6$Ho$_{0.4}$Ti$_3$O$_{12}$ (BHT) films became abnormally large. It was suggested that the A-site and B-site cosubstitution in BHTM films could balance the $P_r$ and $E_c$.18–20 In selection of species for substitution, one of the important factors is the ionic radius, which must satisfy a tolerant factor for the formation of perovskite phase. In this case, the ionic radius of Mo$^{6+}$ (0.059 nm) is compatible with that of Ti$^{4+}$ (0.605 nm).21 In this letter, we report the results on the B-site substitution in BHTM films with higher valence cation Mo$^{6+}$ for the purpose of achieving large $P_r$ and small $E_c$. The effect of Mo content on the microstructure and ferroelectric properties is investigated. The series of (Bi$_{0.8}$Ho$_{0.1}$)$_{1-2x/3}$Ti$_{3-x}$Mo$_x$O$_{12}$ ($x = 0$, 0.9%, 1.5%, 3.0%, and 6.0%) samples are abbreviated to BHTM, followed by 0, 0.9, 15, 30, and 60, respectively) thin films were prepared on Pt/Ti/SiO$_2$/Si substrates by sol-gel method. Bi(NO$_3$)$_3$, Ho(NO$_3$)$_3$, (NH$_4$)$_2$MoO$_4$, and titanium butoxide [Ti(OCC$_3$H$_7$)$_4$] were used as the precursors for Bi$^{3+}$, Ho$^{3+}$, Mo$^{6+}$, and Ti$^{4+}$ ions, respectively. All chemical agents used were analytically pure. The desired amounts of Bi(NO$_3$)$_3$ (with 10 mol % excess), Ho(NO$_3$)$_3$, Ti(OCC$_3$H$_7$)$_4$, and (NH$_4$)$_2$MoO$_4$ corresponding to (Bi$_{3.6}$Ho$_{0.4}$)$_{1-2x/3}$Ti$_{3-x}$Mo$_x$O$_{12}$ composition were dissolved in acetic acid and pure water, respectively. After they were fully dissolved, the solutions were put together, and then acetylated was added to the BHTM solutions as a stabilizing agent. The concentration of all the precursors was 0.3 mol/l. The BHTM thin films were coated on Pt/Ti/SiO$_2$/Si substrates using a spin coater, model KW-4A, at 3000 rpm for 30 s. The as-coated films were heated at 350 °C for evaporation of the solvent and decomposition of the residual organic for 15 min. In order to obtain the films with desired thickness, the above process was repeated for several times. The films’ thickness in the present work was measured by scanning electron microscopy (SEM). Finally, the samples were crystallized at 700 °C for 60 min in oxygen atmosphere.

X-ray diffraction (XRD) measurements were performed using a Rigaku D/Max-III A x-ray diffractometer with Cu Kα radiation. The scanning rate was 4 deg/min. The cross-sectional microstructures were characterized by SEM (JSM-5610LV). Top electrode with the area of 1.0 × 10$^{-3}$ cm$^2$ was fabricated by sputtering Pt. The ferroelectric properties, fatigue, and leakage current were measured using a precision workstation ferroelectric tester system (Radiant Technologies). Dielectric properties were measured by an Agilent 4294A precision impedance analyzer. All measurements of electrical properties were carried out at room temperature.

Figure 1 shows the microstructure of BHTM thin films. According to the XRD patterns, although the BHTM60 film shows a little amount of Bi$_2$O$_3$ phase, all the other crystal structures of BHTM thin films consist of the Bi-layered Aurivillius phase, which indicates that the Mo$^{6+}$ ions in the films do not form minority phases or segregate from the interior grain. This implied that Mo$^{6+}$ ions have entered into the pseudoperovskite unit cell and substituted for the Ti$^{4+}$ ions maintaining the Bi-layered Aurivillius structure. MoO$_4$ is so evaporative that the Mo content in these films is likely to be less than the nominal content in the precursors. When the Mo content is higher, more Mo volatilize, which leads to the Bi content exceeding the optimal value. So there is a
little amount of Bi$_2$O$_3$ phase in BHTM60 film. All BHTM thin films show the strong peaks of (00l), (117), and (200), which indicates these films are all randomly oriented. It is found that the Mo content shows little effect on orientation of the grains, but affects the grain size obviously. The relative intensity of peaks is affected by the Mo content. The peaks of BHTM15 film show the strongest relative intensity. With increasing Mo content over 1.5%, the relative intensity of peaks decreases. This implies that the optimal value of Mo content is in favor of grain growth. When Mo content exceeds this value, the integrity of the crystal structure can be undermined. It can be proved by the XRD result of BHTM60 film. The insets in Fig. 1 show the thickness of the BHTM films. The thicknesses are about 741, 794, 767, 728, and 741 nm, respectively. These values are important to calculate the dielectric permittivity and $E_c$ of these films.

Figure 2 shows the dielectric properties of BHTM thin films as a function of frequency from 40 Hz to 1 MHz, and the inset shows the dielectric constant and loss measured at 1 MHz as a function of Mo content. It can be seen that the dielectric constant decreases rather slowly with increasing frequency from 40 Hz to 1 MHz. The dielectric constant of BHTM15 film reaches the maximum value of 391 measured at 1 MHz. The variation in the dielectric loss with Mo content is the similar trend as that of the dielectric constant.

Figures 3(a)–3(e) show the polarization-electric ($P$-$E$) field hysteresis loops of the BHTM films, and the inset in Fig. 3(c) shows the fatigue behavior of BHTM15 film. It is obviously observed that the Mo content results in a remarkable change in ferroelectric properties. The BHTM60 film shows a distorted loop at high electric field. It can be attributed to the large leakage current. With increasing the Mo concentration, the $2P_r$ increases first and then decreases, and the $2E_c$ shows the opposite trend. The BHTM15 thin film shows the maximum value of $2P_r$, 48.4 \( \mu \)C/cm$^2$, and the minimum values of $2E_c$, 263.5 kV/cm. The widely accepted explanations are listed below. First, the ionic radius of Mo$^{6+}$ is smaller than that of Ti$^{4+}$, thus the displacement of the polar ions in BHTM becomes easier. Second, since the valency of the substituted cation (Mo$^{6+}$) is higher than the parent cation (Ti$^{4+}$), the substitution can be effective to decrease oxygen vacancy by considering the charge neutrality, and the contribution of the high-valence cation substitution to the large $P_r$ is explained by a decrease in defect concentration (mainly oxygen vacancy) that considerably pins the domain motion. These factors lead to the increase in $P_r$ and the decrease in $E_c$. Furthermore, ferroelectric properties are dependent on both grain orientation and grain size. Since all the films in this work show random orientation, the variation in ferroelectric properties can be explained in terms of grain size. The number of domain variants will increase with increasing grain size. This is because increasing grain size reduces the volume fraction of grain boundaries. The coupling between the grain boundaries and the domain wall, which makes domain reorientation more difficult and severely constrains the domain wall motion, will decrease. This then translates to an increase in the achievable domain alignment corresponding to an increase in the values of $P_r$ and a decrease in the values of $E_c$. It can be proved by the XRD results (Fig. 1) that the grain size is affected by Mo content. So when Mo content exceeds 1.5%, the ferroelectric properties become worse. The polarization fatigue test is carried out by applying bipolar pulses of 1 MHz on the BHTM15 thin film at 300 kV/cm. The $P_r$ values are normalized by their initial values. After the switching of 4.46 \( \times \) 10$^9$ cycles, the BHTM15 thin film shows good fatigue-free characteristic.

Figure 4 displays the leakage current density-electric ($J$-$E$) field characteristics of the BHTM thin films. When Mo content increases from 0% to 1.5%, the values of $J$ decrease, and the curves are symmetric. This phenomenon can also be explained by oxygen vacancy, which is regarded as charge carrier in the ferroelectric films. It is well known that the BTO-based thin films are not perfectly stoichiometric but contain a certain amount of inherent defects (e.g., oxygen vacancies) resulting from the volatilization of Bi$_2$O$_3$ at high temperatures. As mentioned above, the appropriate Mo content can decrease the concentration of oxygen vacancy by...
considering the charge neutrality. When Mo content exceeds 1.5%, the curves are not symmetric and show an abrupt increase in the leakage current at high electric field region (approximately above 200 kV/cm). When Mo content exceeds the optimum value, the second phase will appear, and the integrity of crystal structure can be undermined due to the volatilization of MoO3 during heat treatment. This result can also explain why the BHTM60 film shows distorted hysteresis loop.

In summary, the B-site substitution in BHT films with Mo6+ can effectively decrease oxygen vacancy by considering the charge neutrality, which is important to enhance the Pr and reduce the Ec. Also, there is an optimal value of the Mo doping. The BHTM15 thin film exhibits the best electrical properties with 2Pr of 48.4 μC/cm2, 2Ec of 263.5 kV/cm, dielectric constant of 391 (at 1 MHz), good insulating behavior, as well as the fatigue-free characteristic. It is suggested that Mo-substituted BHT could be an alternative material for FeRAM applications.

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