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Preparation and electrical properties of Sm-doped $Bi_2Ti_2O_7$ thin films prepared on Pt (111) substrates

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Abstract

Crack-free Sm-doped $Bi_2Ti_2O_7$ (Sm:BTO) thin films with strong (111) orientation have been prepared on Pt (111) substrates using a chemical solution deposition (CSD) method. The structural properties and crystallizations were studied by X-ray diffraction. The surface morphology and quality were examined using atomic force microscopy (AFM). The insulating and dielectric properties were also evaluated at room temperature. The results demonstrate that the Sm:BTO films exhibit improved electrical performances as compared to the pure $Bi_2Ti_2O_7$ thin films and suggest a strong potential for utilization in microelectronics devices.

Keywords: A. Films; B. Microstructure; C. Dielectric properties; C. Electrical properties

1. Introduction

Bismuth titanate ($Bi_2Ti_2O_7$) is of increasing interest because it has many applications in the field of microelectronics, electro-optics and dielectrics due to its relatively high dielectric constant and good insulating property [1–4]. Although $Bi_2Ti_2O_7$ exhibits no ferroelectricity or piezoelectricity, it has a relatively high dielectric constant [5,6]. Therefore, $Bi_2Ti_2O_7$ thin films can be used as materials for storage capacitors in dynamic random access memory (DRAM) and as gate insulators to increase the transconductance of MOSFETS [7]. Besides, $Bi_2Ti_2O_7$ films have also been used as buffer layers to improve the electrical properties of ferroelectric $Pb_{0.85}Sm_{0.1}TiO_3$ [8], $Bi_{3.5}Nd_{0.5}Ti_3O_{12}$ [9] and $BiFeO_3$ [10–11] thin films.

Some articles reported that $Bi_2Ti_2O_7$ materials are easily transformed into other phases at high annealing temperatures [15–17]. However, some researchers discovered that the phase stability of the $Bi_2Ti_2O_7$ thin films was improved owing to the doping of lanthanum ions and the phase structure can be stabilized by ionic modification [18–20]. In this paper, we prepared the $Bi_2Ti_2O_7$ thin films doped with Sm ions (Sm:BTO) on Pt (111) substrates by repeated coating/dying cycles. The structure and surface morphology were analyzed and electrical properties were also reported.

2. Experimental procedure

The Sm:BTO thin films were prepared on Pt (111) substrates using a chemical solution deposition (CSD) method. The precursor solution were prepared using bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$), samarium nitrate ($Sm(NO_3)_3$) and tetrabutyl titanate ($C_{16}H_{36}O_4Ti$) materials according to determinate molar. Glacial acetic acid has been used as solvent and the solution was diluted with 2-methoxythanol to adjust the viscosity. Acetylacetone was added to the solution to keep the precursor solution stable. Dust and other suspend impurities were removed by filtering through a 0.2 μm syringe filter. This is the $(Bi_{0.9}Sm_{0.1})_2Ti_2O_7$ precursor solution of 0.1 M.

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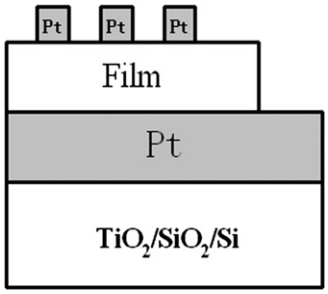

Fig. 1. Schematic diagram of MFM structure.

Then the precursor solution was coated onto Pt (111) substrates by spin coating at 3000 rpm for 30 s. Thickness of the films was controlled through adjusting the viscosity of the solution and the spin speed. The films were heated to 300 °C in air at a rate of 10 °C/min and kept at 300 °C for 20 min to ensure complete removal of solvents, organics and other volatile matters. Then the films were annealed at 600 °C for 5 min in an O_2 atmosphere by rapid thermal processor (RTP). The deposition and heat-treatment procedure were repeated to prepare a desired thickness.

For electrical property measurement, Pt circular dots were deposited by dc magnetron sputtering through a shadow mask on the films as top electrodes and one of corners of film was corrode by the mixture of HNO_3 and HF as bottom electrode to form a MFM configuration as shown in Fig. 1.

FT-IR spectra for Sm:BTO samples with different annealing temperatures was under consideration by the FT-IR. The crystallization of the Sm:BTO thin films was studied by X-ray diffraction (XRD) using a Rigaku D/MAX-γA X-ray diffractometer. The surface image of the films was characterized by atomic force microscopy (AFM). The insulating property was conducted using a pA meter/DC voltage source (HP4140B PA) and the dielectric properties were measured using a LF Impedance Analyzer (HP4192A).

3. Results and discussion

3.1. Crystallization behavior of Sm:BTO films

The infrared-absorption spectrum of Sm:BTO samples have been measured for powder samples dispersed in pressed KBr disks. Fig. 2 shows the infrared (IR) spectrum of powders dried at different temperature in air for 10 min. We can see there are a series of absorptions in the range of 600–950 cm^{-1} at 100, indicating non-decomposition of organic substance. The band at 1385 cm^{-1} is attributed to the characteristic peak of NO_3^- and the band at 1624 cm^{-1} is the –COOH rocking modes. At 300 °C, the absorptions at 3422 cm^{-1} is lower due to the losing some water and ether solvent. Meanwhile, because of the not carbonized completely for organic substance, there exists faint absorption at 1624 cm^{-1}. It was noted that the intensity of band at 3422 cm^{-1} is further weak as the

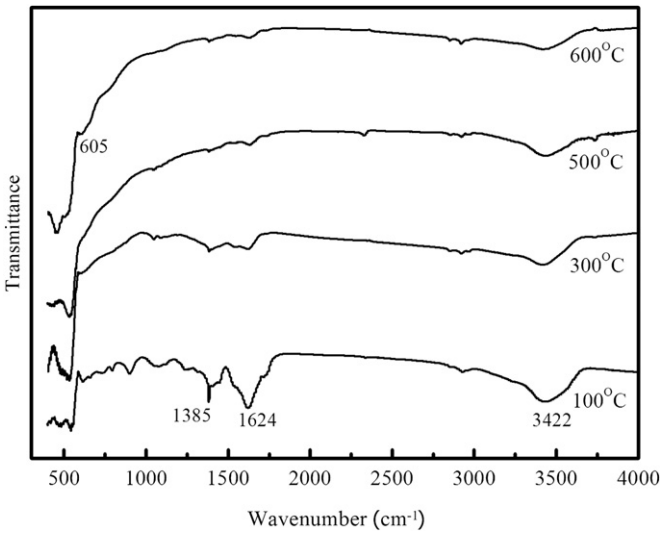

Fig. 2. Infrared spectrum of Sm:BTO precursor powder heated at different annealing temperature for 10 min.

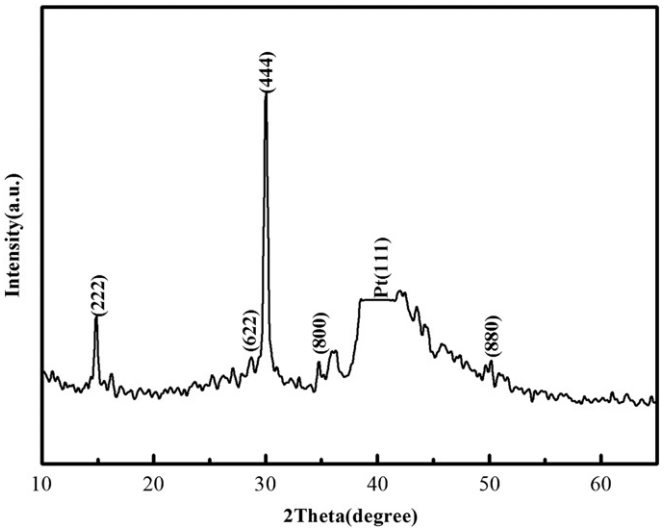

Fig. 3. X-ray diffraction pattern of Sm:BTO films annealed at 600 °C for 10 min.

temperature increasing to 500 °C and almost disappeared when the temperature further increases to 600 °C. At 600 °C, the band in the low wavenumber (500 cm^{-1}–700 cm^{-1}) is attributed to the M–O bonds [21], which comes from the envelop of the photon bands of a metal–oxygen–metal bond from a solid oxide network, for example, V_{Ti-O} = 653–550 cm^{-1} [22]. In addition, the band at 605 cm^{-1} belongs to the Sm–O bonds, which indicates that a large amount Sm:BTO nano-grains form. Fig. 3 shows the X-ray diffraction patterns of Sm:BTO thin films deposited on the Pt substrates annealed at 600 °C for 10 min. The strong and sharp peaks are indications of good crystallization of the films. The interplanar spacing values (d) of the peaks agree well with those of $Bi_2Ti_2O_7$ given in the standard JCPDS data card (no.32–118). Moreover, the strongest peak at (222) and (444) for the

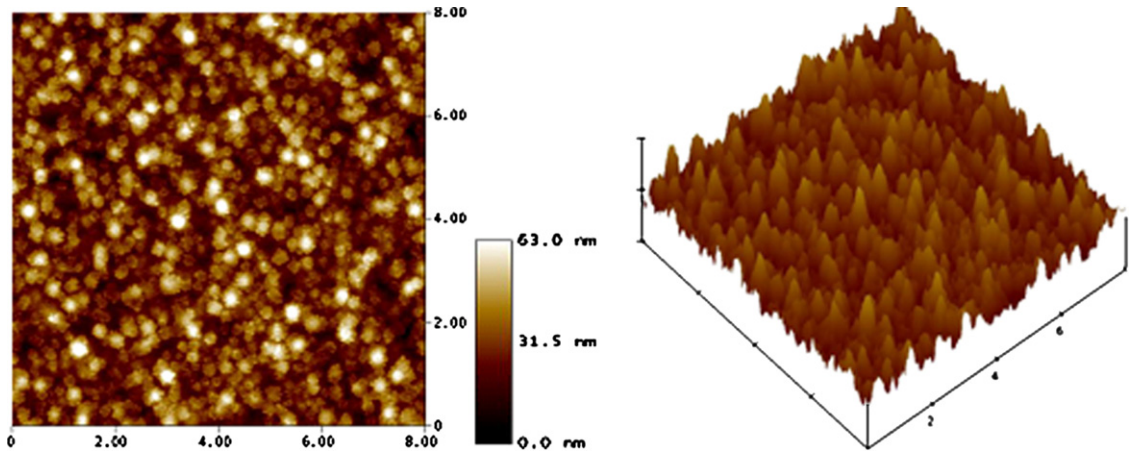

Fig. 4. Two-dimensional and corresponding three-dimensional AFM imagines of Sm:BTO films annealed at 600 °C for 10 min.

Sm:BTO thin films indicate that the Sm:BTO thin films have good (111) orientation [23]. The microscopic surface morphology of the Sm:BTO film was investigated by AFM. Fig. 4 shows the two-dimensional and corresponding three-dimensional AFM images of the films. AFM micrographs indicating that the Sm:BTO thin films are well-crystallized, crack-free and pinhole-free. From the three-dimensional AFM images of the films, the cone-shaped and pointed up grain should be (111) oriented, based on the relative intensities of the diffraction peak of (111) shown in Fig. 3 [24]. It shows that the Sm:BTO thin film consists of homogeneous grain with an average grain-size of about 360 nm estimated from the AFM image. The surface roughness is relatively low with root mean square (RMS) roughness of 8.1 nm, which indicates the films have a relatively smooth surface.

3.2. Electrical properties of Sm:BTO thin films

The leakage current density–electric field (J–E) characteristic of the thin films is shown in Fig. 5. The leakage current of $Bi_2Ti_2O_7$ thin films is remarkably reduced upon addition of Sm dopant at each given electric field. A significantly low leakage current has been obtained. J increases very slowly as E increasing below the 100 kV/cm and the order of magnitude is 10^{-9} A/cm**2**. The good insulativity partially depends on the compactness of grains in films. On the basis of above result, we think that leakage current greatly depends on Schottky barrier of FM interface. That is, the J–E curve does not only exhibit ohmic behavior because we cannot ignore interfacial conductance in total conductance. At the moment, $E_{\Phi m}$ of F–M interface is greater than $E_{\Phi f}$ of Sm:BTO films. Meanwhile, the inside films appear obstructed electric field in the opposite direction of the out electric field, that is Schottky barrier. In this condition, there is lower leakage current for large barrier of interface. In summary, the data of Fig. 5 indicates that the Sm:BTO films deposited on the Pt (111) substrates by CSD technique have a good insulating property and resistance to breakdown. For example, at the applied

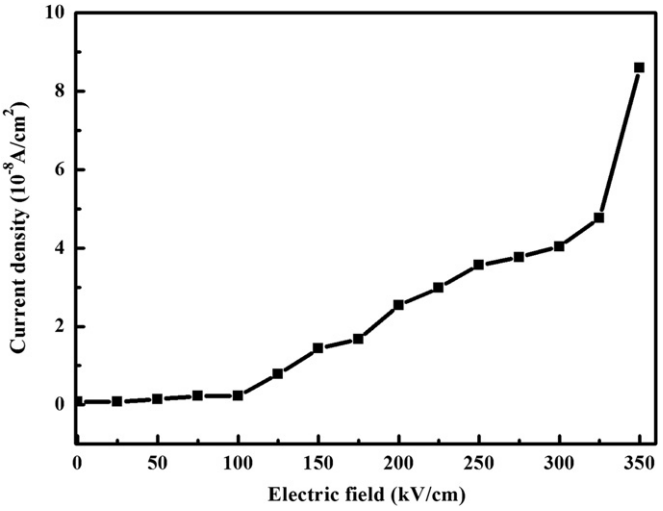

Fig. 5. The *J–E* characteristic of Sm:BTO thin films annealed at 600 °C for 10 min.

electric field of 300 kV/cm, the leakage current of the films is on the order of 10^{-8} A/cm^2, which is much lower than that of the pure $Bi_2Ti_2O_7$ films at the same electric field [25].

The capacitance and dissipation factor (C, tanδ) of the Sm:BTO films were also measured as a function of frequency at room temperature. As is shown in Fig. 6 with the frequency increasing, the capacitance has a relative decrease until about 1000 kHz and belongs to the 10^{-11} F order of magnitude. At about the same frequencies, the dissipation factor has a little increase, whereas much smaller than that on the p-Si (111) substrate [26]. The result indicates that the Sm:BTO films prepared on the Pt (111) substrates have better dielectric properties. At 1 MHz, the dielectric constant of the Sm:BTO films is 160, which is slightly higher than that of pure $Bi_2Ti_2O_7$ films [27]. However, the value of dissipation factor of Sm:BTO films is bigger than that of $Bi_2Ti_2O_7$ films at the same frequency, which may due to the different preparation method of the $Bi_2Ti_2O_7$-based films [27].

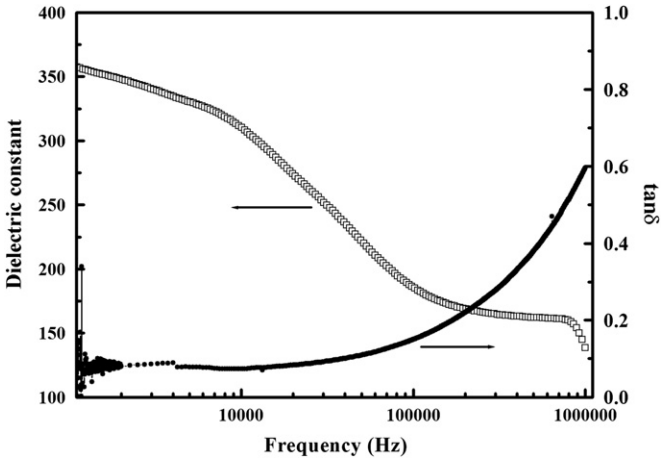

Fig. 6. Dielectric constant and dissipation factor of Sm:BTO thin films annealed at 600 °C for 10 min as a function of frequency.

4. Conclusions

In summary, Sm-doped $Bi_2Ti_2O_7$ thin films have been prepared successfully on Pt (111) substrates using CSD method. The samples crystallized very well at an annealing temperature of 600 °C for 10 min. The J–E characteristic showed that the films have good insulating properties and resistance to breakdown. The dielectric constant of the Sm:BTO films is higher than the pure $Bi_2Ti_2O_7$ thin films.

Acknowledgments

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References

[1] J.F. Scott, Applications of Modern Ferroelectrics, Science 315 (2007) 954–959.
[2] Y. Hou, T. Lin, Z.M. Huang, G.S. Wang, Z.G. Hu, J.H. Chu, X.H. Xu, M. Wang, Electrical and optical properties of $Bi_2Ti_2O_7$ thin films prepared by metalorganic decomposition method, Applied Physics Letters 85 (2004) 1214.
[3] J. Cagnon, D.S. Boesch, N.H. Finstrom, S.Z. Nergiz, S.P. Keane, S. Stemmer, Microstructure and dielectric properties of pyrochlore $Bi_2Ti_2O_7$ thin films, Journal of Applied Physics 102 (2007) 044102–044105.
[4] J.Z. Zhang, X.G. Chen, K. Jiang, Y.D. Shen, Y.W. Li, Z.G. Hu, J.H. Chu, Evolution of orientation degree, lattice dynamics and electronic band structure properties in nanocrystalline lanthanum-doped bismuth titanate ferroelectric films by chemical solution deposition, Dalton Transactions 40 (2011) 7967–7975.
[5] S. Shimada, K. Kodaira, T. Matsushita, Crystal growth of bismuth titanates and titanium oxide from melts in the system Bi_2O_3-V_2O_5-TiO_2, Journal of Crystal Growth 41 (1977) 317–320.
[6] L.W. Fu, H. Wang, S.X. Shang, X.L. Wang, P.M. Xu, Preparation and characterization of $Bi_2Ti_2O_7$ thin films grown by metalorganic chemical vapor deposition, The Journal of Crystal Growth 139 (1994) 319–322.
[7] X.M. Wu, S.W. Wang, H. Wang, Z. Wang, S.X. Shang, M. Wang, Preparation and characterization of $Bi_2Ti_2O_7$ thin films by chemical solution deposition technique, Thin Solid Films 370 (2000) 30–32.
[8] F.Y. Jiang, R.C. Liu, Main characteristics of $Pb_{0.85}Sm_{0.1}TiO_3$ ferroelectric thin films with $Bi_2Ti_2O_7$ buffer layer, The Journal of Crystal Growth 263 (2004) 385–388.
[9] C.H. Yang, H.T. Wu, D.M. Yang, Effects of a $Bi_2Ti_2O_7$ seeding layer on properties of $Bi_{3.5}Nd_{0.5}Ti_3O_{12}$ thin film, Materials Letters 61 (2007) 4166–4168.
[10] C.H. Yang, G.D. Hu, Z. Wen, H.L. Yang, Effects of $Bi_2Ti_2O_7$ buffer layer on memory properties of $BiFe_{0.95}Mn_{0.05}O_3$ thin film, Applied Physics Letters 93 (2008) 172906.
[11] S.H. Han, C.I. Cheon, H.G. Lee, H.W. Kang, H.I. Hwang, Low temperature hydrothermal epitaxy of heteroepitaxial $BiFeO_3$ film, Ceramics International 38S (2012) S391–S395.
[15] H. Wang, L.W. Fu, S.X. Shang, X.L. Wang, M.H. Jiang, The influence of substrate temperature and annealing on phase formation and crystalline properties of bismuth titanate film by APMOCVD, Journal of Physics D: Applied Physics 27 (1994) 393.
[16] N. Tkashi, M. Rusul, S. Masaru, S. Tadashi, Preparation of *c*-axis-oriented $Bi_4Ti_3O_{12}$ thin films by metalorganic chemical vapor deposition, Japanese Journal of Applied Physics 32 (1993) 4086–4088.
[17] W.F. Su, Y.T. Lu, Synthesis, phase transformation and dielectric properties of sol–gel derived $Bi_2Ti_2O_7$ ceramics, Materials Chemistry and Physics 80 (2003) 632.
[18] X.N. Yang, B.B. Huang, H.B. Wang, S.X. Shang, W.F. Yao, J.Y. Wei, Effect of La doping on structural and electrical properties of $Bi_2Ti_2O_7$thin films, Journal of Crystal Growth 270 (2004) 98–101.
[19] X.Y. Jing, Y.B. Hou, X.Y. Zhang, X.Y. Qin, Study of the Structure and properties of $(Bi_{1-x}Ce_x)_2Ti_2O_2$ thin films prepared by chemical solution decomposition method, Surface Review amd Letters 18 (2011) 17–21.
[20] X.L. Fang, B. Shen, J.W. Zhai, X. Yao, Preparation and ferroelectric properties of $(Na_{0.5}Bi_{0.5})_{0.94}Ba_{0.06}TiO_3$ thin films deposited on Pt electrodes using $LaNiO_3$ as buffer layer, Ceramics International 38S (2012) S83–S86.
[21] D.H. Bao, X.Q. Wu, L.Y. Zhang, X. Yao, Preparation, electric and optical properties of (Pb,Ca)TiO_3 thin films using a modified sol-gel technique, Thin Solid Films 350 (1999) 30–37.
[22] S. Music, M. Gotic, M. Ivanda, S. Popovic, A. Turkovic, R. Trojko, A. Sekulic, K. Furic, Chemical and micro structural properties of TiO_2 synthesized by sol–gel procedure, Materials Science and Engineering B-Solid 47 (1) (1997) 33–40.
[23] Z.G. Hu, Y.W. Li, M. Zhu, F.Y. Yue, Z.Q. Zhu, J.H. Chu., Growth and ellipsometric characterizations of highly (111)-oriented $Bi_2Ti_2O_7$ films on platinized silicon by metal organic decomposition method, Journal of Vacuum Science and Technology A 26 (2008) 1287.
[24] G.D. Hu, S.H. Fan, C.H. Yang, W.B. Wu, Low leakage current and enhanced ferroelectric properties of Ti and Zn codoped $BiFeO_3$ thin film, Applied Physics Letters 92 (2008) 192905.
[25] S.W. Wang, W. Lu, N. Li, Z.F. Li, H. Wang, M. Wang, X.C. Shen, Insulating properties of rapid thermally processed $Bi_2Ti_2O_7$ thin films by a chemical solution decomposition technique, Materials Research Bulletin 37 (2002) 1691–1697.
[26] D.M. Yang, C.H. Yang, C.X. Yuan, X. Yin, J.R. Han, Preparation and characteristics of Sm-doped $Bi_2Ti_2Q_7$ thin films, Surface Review Letters 14 (2007) 147–150.