Journal of Alloys and Compounds 489 (2010) 136–139

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Preparation and characterization of $Ca_{0.18}Na_{0.32}Bi_{0.50}TiO_3$ ferroelectric thin films by metalorganic solution deposition

Huizhong Xu[a,b], Liang Zhen[a,*], Yaping Wang[b], Zhuo Wang[b]

[a] School of Material Science and Engineering, Harbin Institute of Technology, Harbin 150001, PR China
[b] School of Environment and Materials Engineering, Yantai University, Yantai 264005, PR China

ARTICLE INFO

Article history:
Received 6 July 2009
Received in revised form 7 September 2009
Accepted 7 September 2009
Available online 15 September 2009

Keywords:
Ferroelectric thin films
Metalorganic solution deposition
NBT films
CNBT films

ABSTRACT

$Ca_{0.18}Na_{0.32}Bi_{0.50}TiO_3$ (CNBT) ferroelectric thin films were prepared by metalorganic solution deposition on silicon substrate and annealed at different temperatures. The morphology and structure of the films were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The crystal structure of Ca-doped $Na_{0.50}Bi_{0.50}TiO_3$ films shows no obvious lattice distortion compared with that of un-doped one. The optimal heat treatment process for CNBT films were determined to be high-temperature drying at 400 °C for no less than 15 min followed by annealing at 600 °C for 5 min, which leads to the formation of compact films with uniform grains of 30–50 nm. Ferroelectric property measurement shows that the remanent polarization of CNBT films is 18 times higher than that of un-doped $Na_{0.50}Bi_{0.50}TiO_3$ (NBT) thin films.

1. Introduction

Non-volatilization lead-free ferroelectric thin films are of great interest due to their wide potential applications in storage devices. Several systems, for example, $SrBi_2Ta_2O_9$ (SBT) [1,2] and $Bi_4Ti_3O_{12}$ (BIT) [3,4] thin films, have been extensively studied during the past several decades. However, the SBT thin films must be synthesized at high-temperature (≥750 °C) and are hard to integrate into semiconductor Si substrate, and the BIT thin films suffer from fatigue problems after 10^9 times polarization switching. In recent years, the research of ferroelectric thin films has been mainly focused on two fields—searching after new composition systems, such as $BaNb_2O_6$ (BNB)[5], $BiFeO_3$(BIF) [6] and so on, and improving BIT's properties by doping certain ions, for example, BLnT(Ln = La, Nd, Sm...) [7–9], BRnT (Rn = Na, K, Sr, Ba, Ca...) [10–14], of which the $Na_{0.5}Bi_{0.50}TiO_3$ (NBT) thin films that can be synthesized at relatively lower temperatures (≤650 °C) have become research focus [15–18]. It was found that NBT thin films on silicon substrates showed good piezoelectric and pyroelectric properties, but relatively poor ferroelectric properties with lower values of remanent polarization and higher coercive fields. Previous research on the NBT ceramics shows that doping using Ba [19], Ca [20], Sr [21] could effectively improve their ferroelectric properties. In this paper, $Ca_{0.18}Na_{0.32}Bi_{0.50}TiO_3$ (CNBT) thin films were prepared on silicon substrates by metalorganic solution deposition (MOSD) method. Its morphology, structure, and ferroelectric properties were investigated. The effect of annealing temperatures on the structure and properties were also studied.

2. Experimental

2.1. Synthesis

Sodium acetate, calcium acetate, bismuth acetate, and tetrabutyl titanate in stoichiometric proportion (Na:Ca:Bi:Ti = 0.32:0.18:0.50:1.00) were dissolved to the solvent of glacial acetic acid. 2-methoxyethanol and acetylacetone were used to adjust the viscosity and stabilize the precursor solution. A 0.2 μm syringe filter was used to remove the dust and other suspended impurities from the solution. Then the precursor solution was deposited on *p*-type Si substrates with low resistance (R < 0.009 Ω) by spin coating at 4000 rpm to make a wet film. Then the wet film was heated at 400 °C for 15 min to remove organic solvent and other volatile materials. The deposition and thermal-treatment procedure were repeated till an expected thickness (about 300 nm) was achieved. The obtained films were annealed at different temperatures for 5 min to prepare polycrystalline films.

2.2. Characterization

Thermogravimetry/differential thermal analysis (TG/DTA) of the precursor solution dried at 90 °C for 15 min was conducted using ZRY-2P thermal analyzer. Infrared spectra of annealed powders at different temperatures were obtained with IRPrestige-21 spectrometer. Phase structure was determined using X-ray diffractormeter (XRD, XRD-6100X). The element analyze was achieved by X-ray fluorescence spectrometer (XFS, JSX-3201Z). The surface morphology of CNBT films was observed by scanning electron microscope (SEM, JSM6390). Ferroelectric hysteresis loops of thin films were measured with TF Analyzer 2000 on the configuration as shown in Fig. 1.

* Corresponding author. Tel.: +86 535 6706039; fax: +86 535 6706038.
E-mail address: lzhen@hit.edu.cn (L. Zhen).

0925-8388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2009.09.033

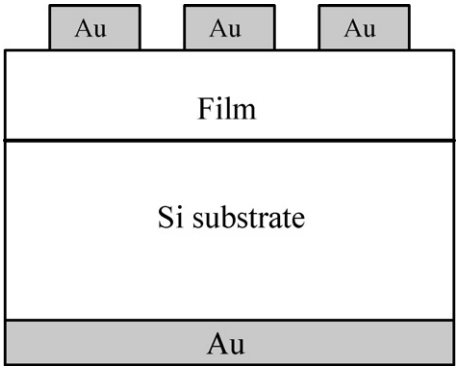

Fig. 1. Configuration for the measurement of hysteresis loops.

3. Results and discussion

3.1. Thermal analysis and infrared spectra

Fig. 2 shows the TG/DTA curves of the dried CNBT solution. When temperature is lower than 400 °C, the thermal gravimetric loss is due to the evaporation of organics. The metalorganic component begins to decompose at around 400 °C, and at the same time, metal oxides start crystallizating, which is finished around 550 °C. However, the thermal gravimetric loss and crystal exothermic reaction is not completed until 680 °C, which is suggested to be the evaporation of some metal elements and the continuous growth of crystal grain.

Infrared spectra of annealed powders at different temperatures are shown in Fig. 3. The band at 1025 cm^{-1} is the bending mode of the C–H group. The bands present around 1421 and 1564 cm^{-1} can be ascribed to ν sym ($-COO^-$) and ν asym (COO^-) of the acetyl group. The broadband around 3426 cm^{-1} is corresponding to the O–H stretching vibration. It can be seen that the contents of organic ingredients are high when the powder are annealed at low-temperature of 100 °C, and decrease significantly when annealed at 300 °C. With the increase of annealing temperature, the contents of organic ingredients further decrease, and when the annealing temperature is higher than 500 °C, most of the organic ingredients have completely decomposed except a few carboxyl. Very few carboxyl can be still found after annealing at up to 700 °C, which might be due to the short time of thermal treating.

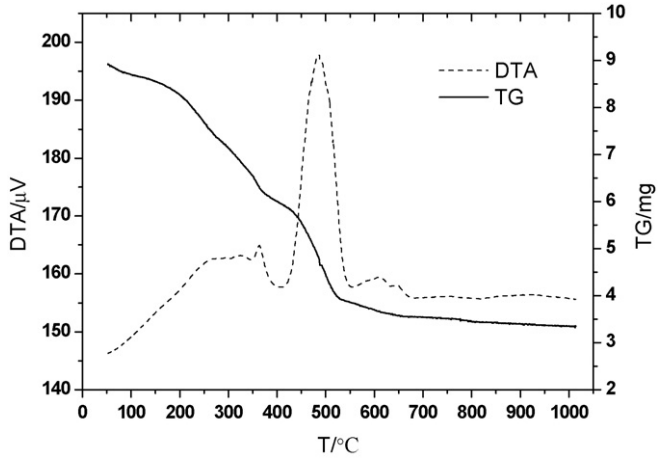

Fig. 2. TG/DTA curves of dried CNBT solutions powder.

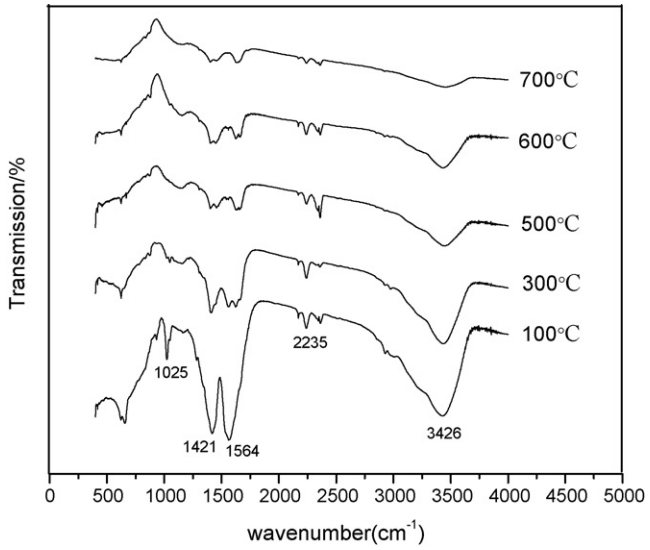

Fig. 3. FTIR spectra for CNBT solutions powder annealed at different temperatures.

3.2. Crystal structure

Fig. 4 shows the XRD patterns of NBT and CNBT thin films. Compared with that of NBT films, the XRD pattern of CNBT film displays lower diffraction intensity, and the peak positions of CNBT are almost the same as that of NBT. This indicates that the crystal lattice of CNBT films shows no noticeable distortion from that of NBT films though Ca doping reduces integrity and uniformity of crystallization. In addition, with the increase of annealing temperature, the diffraction intensity of characteristic crystal planes shows no apparent enhancement, indicating that the crystallinity of CNBT films is not sensitive to the annealing temperature in the range of 550–700 °C. The minor phase (marked with "■") is thought to be with cubic symmetry and results from the amorphous phase during the crystallization procedure [15]. Kim figured out that it can be eliminated by annealing at temperatures higher than 1050 °C [22].

3.3. Elements analysis

Fig. 5 shows the XFS analysis of CNBT film annealed at 600 °C. Compared with the designed proportion, the statistical relative

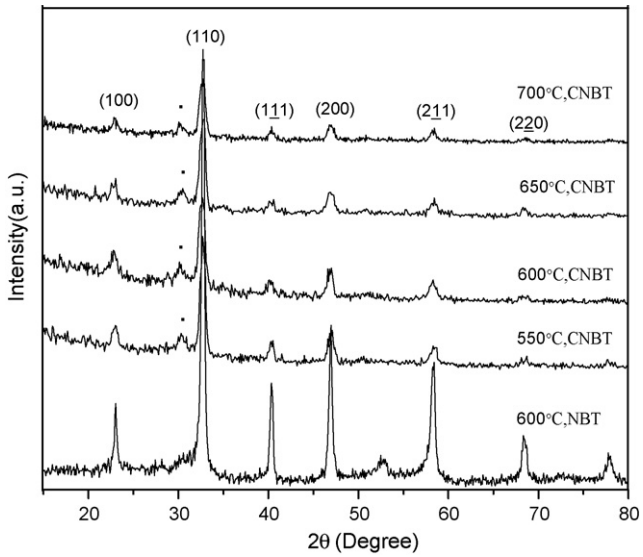

Fig. 4. XRD patterns of CNBT films annealed at different temperatures and NBT annealed at 600 °C.

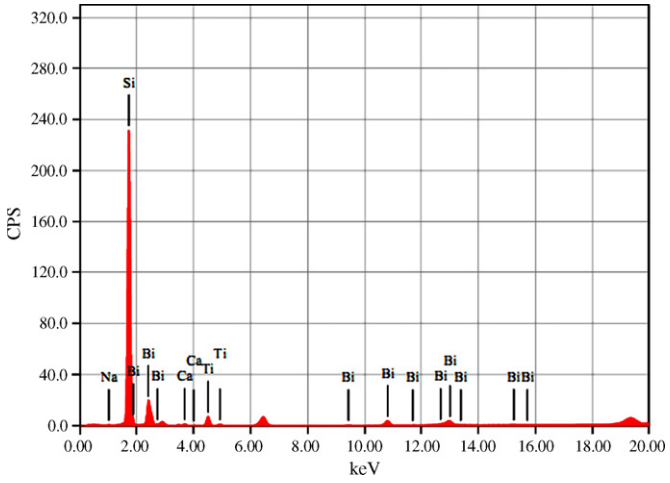

Fig. 5. XFS pattern of CNBT films annealed at 600 °C.

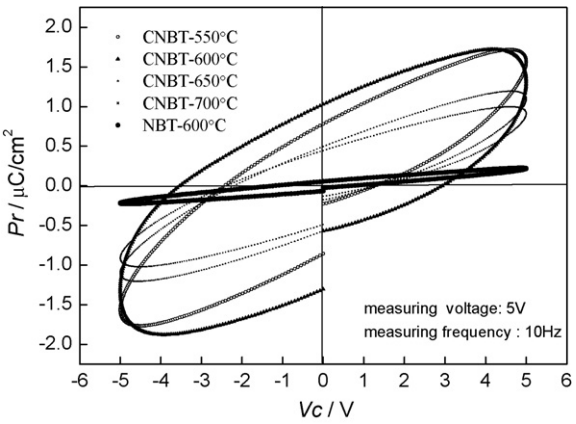

Fig. 7. *P–E* hysteresis loops of CNBT thin films annealed at different temperatures and NBT films annealed at 600 °C.

contents of Na and Bi decreased about 15% and 10%, respectively. It indicated that there was notable evaporation of Na and Bi during the thermal-treatment process.

3.4. Morphology characterization

Fig. 6 shows the surface morphologies of CNBT films annealed at different temperatures as observed by SEM. When the films are annealed at 550 °C, the round-shaped metal-oxide grains are formed and a wealth of microvoids can be also found between the grains, indicating the films are not compact enough. When the annealing temperature increases to 600 °C, the film grows more compact than that annealed at 550 °C, and the grains are rather uniform with diameters of around 30–50 nm. With annealing temperature further increasing, some of the grains grow bigger up to 100 nm. Meanwhile, the porosity increases and compactness reduces, and larger microvoids can be easily found in the surface of CNBT films annealed at 650 °C and 700 °C.

3.5. Ferroelectric property

Fig. 7 shows the hysteresis loops of CNBT thin films annealed at different temperatures. The figure reveals that ferroelectric thin films on Si substrates hardly display a closed *P–E* loop due to ferroelectric relaxation. Alemany et al. have explained the current leakage and incompleteness of ferroelectric thin films in an asymmetric capacitor by the fully deplete asymmetric double-schottky barrier model [23]. In addition, the CNBT films' ferroelectric property is better at suitable annealing temperatures. When annealed at 600 °C, the film is most compact and has highest Pr^{+} of 1.032 μC/cm^2, which is 18 times higher than that of NBT thin film prepared with the same parameters.

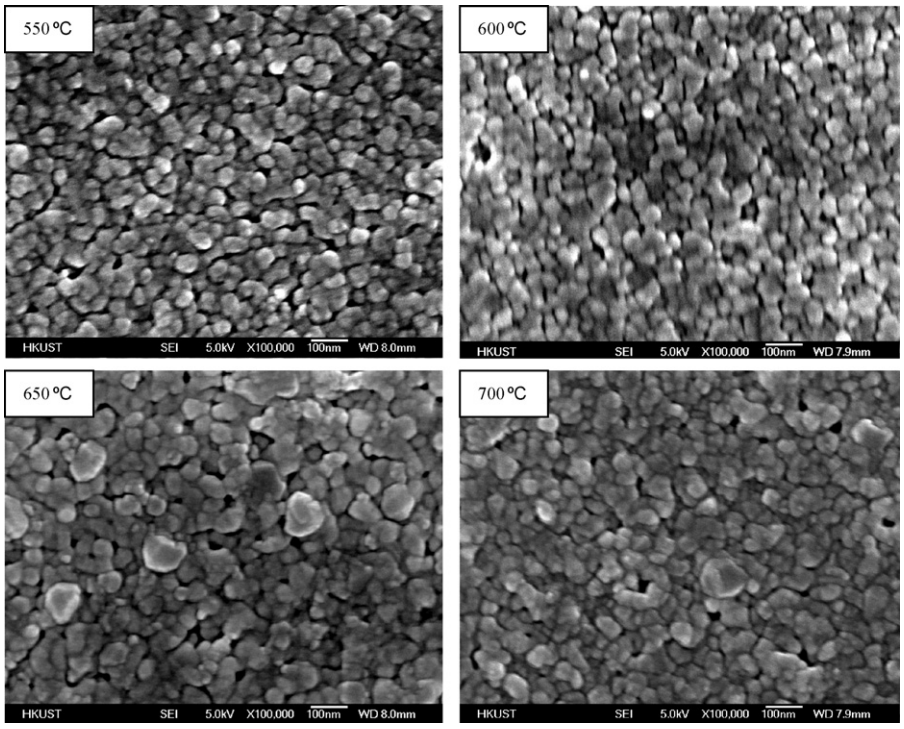

Fig. 6. SEM micrographs of CNBT thin films annealed at different temperatures.

4. Conclusions

Metalorganic solution deposition was utilized to fabricate $Ca_{0.18}Na_{0.32}Bi_{0.50}TiO_3$ ferroelectric thin films on silicon substrate. The optimal heat-treatment temperature is 600 °C, 150 °C lower than that of SBT and BTO films. There is notable evaporation of Na and Bi during thermal-treatment, and thus excess Na and Bi should be considered for composition design. CNBT films have the similar structure with that of $Na_{0.50}Bi_{0.50}TiO_3$ and lower diffraction intensity upon Ca doping. The ferroelectric properties of CNBT films depend mainly on its compactness as well as annealing temperature, but not crystallinity or grain size. When annealed at 600 °C for 5 min, the prepared nano-scale polycrystalline films are compact with uniform grains and have higher Pr^+, which is 18 times higher than that of NBT thin film prepared with the same parameters.

References

[1] Z.G. Zhang, Y.N. Wang, J.S. Zhu, F. Yan, X.M. Lu, H.M. Shen, J.S. Liu, Appl. Phys. Lett. 73 (1998) 3674–3676.
[2] K. Amanuma, T. Hase, Y. Miyasaka, Appl. Phys. Lett. 66 (1995) 221–223.
[3] B.H. Park, S.J. Hyun, C.R. Moon, B.-D. Choe, J. Lee, C.Y. Kim, W. Jo, T.W. Noh, J. Appl. Phys. 84 (1998) 4428–4435.
[4] B.H. Park, T.W. Noh, J. Lee, C.Y. Kim, W. Jo, Appl. Phys. Lett. 70 (1997) 1101–1103.
[5] W. Sakamoto, M. Mizuno, T. Yamaguchi, K. Kikuta, S. Hirano, J. Alloys Compd. 408–412 (2006) 538–542.
[6] A.Z. Simões, R.F. Pianno, E.C. Aguiar, E. Longo, J.A. Varela, J. Alloys Compd. 479 (2009) 274–279.
[7] B.H. Park, B.S. Kang, S.D. Bu, T.W. Noh, J. Lee, W. Jo, Nature 401 (1999) 682–684.
[8] T. Kojima, T. Sakai, T. Watanabe, H. Funakuboa, K. Saito, M. Osada, Appl. Phys. Lett. 80 (2002) 2746–2748.
[9] C.H. Yang, S.D. Wang, D.M. Yang, J. Alloys Compd. 467 (2009) 434–437.
[10] Z.H. Zhou, J.M. Xue, W.Z. Li, J. Wang, H. Zhu, J.M. Miao, Appl. Phys. Lett. 85 (2004) 804–806.
[11] C.H. Yang, J.R. Han, X.F. Cheng, X. Yin, Z. Wang, M.L. Zhao, C.L. Wang, Appl. Phys. Lett. 87 (2005), pp. 192901-1-1192901-3.
[12] A.Z. Simões, M.A. Ramírez, C.S. Riccardi, E. Longo, J.A. Varela, J. Alloys Compd. 455 (2008) 407–412.
[13] W.H. Tao, Y. Wang, X.H. Fu, Q.H. Wei, Bull. Mater. Sci. 29 (2006) 523–527.
[14] W.X. Xianyu, T.-Y. Won, W.I. Lee, Integr. Ferroelectrics 65 (2004) 57–67.
[15] J.P. Mercuric, P. Marchet, Integr. Ferroelectrics 61 (2004) 163–165.
[16] F. Rémondière, B. Malič, M. Kosec, J.-P. Mercurio, J. Euro. Ceram. Soc. 27 (2007) 4363–4366.
[17] N. Scarisoreanu, M. Dinescu, F. Craciun, P. Verardi, A. Moldovan, A. Purice, C. Galassi, Appl. Surf. Sci. 252 (2006) 4553–4557.
[18] X.G. Tang, J. Wang, X.X. Wang, H.L.-W. Chan, Chem. Mater. 16 (2004) 5293–5296.
[19] Q. Xu, D.P. Huang, M. Chen, W. Chen, H.X. Liu, B.H. Kim, J. Alloys Compd. 471 (2009) 310–316.
[20] B.V. Bahuguna Saradhi, K. Srinivas, T. Bhimasankaram, Int. J. Modern Phys. B 16 (2002) 4755–4766.
[21] E. Venkata Ramana, V. Vijay Kiran, T. Bhima Sankaram, J. Alloys Compd. 456 (2008) 271–276.
[22] C.-Y. Kim, T. Sekino, Y. Yamamoto, K. Niihara, J. Sol–Gel. Sci. Technol. 33 (2005) 307–314.
[23] C. Alemany, R. Jiménez, J. Revilla, J. Mendiola, M.L. Calzada, J. Phys. D 32 (1999) 79–82.