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Ceramics International 40 (2014) 2489–2493

CERAMICS INTERNATIONAL

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Short communication

High stable dielectric permittivity and low dielectric loss in sol–gel derived $BiFeO_3$ thin films

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Received 15 May 2013; received in revised form 27 June 2013; accepted 10 July 2013
Available online 17 July 2013

Abstract

$BiFeO_3$ (BFO) thin films were prepared on (111)Pt/Ti/SiO_2/Si substrates via a sol–gel spin-coating method, and the influence of the annealing temperatures on the phase formation, the microstructure and the electrical properties was systematically studied by X-ray diffraction (XRD), scanning electron microscopy (SEM) and an HP 4294A precision impedance analyser and a ferroelectric material test system, respectively. The XRD analysis revealed the films to be well-crystallised, and those annealed at approximately 700 °C were well-formed in the perovskite phase. The SEM images confirmed that the BFO films had a uniform and dense microstructure with an average thickness of 300 nm. As the frequency increased to 1 MHz, the dielectric constant of the BFO films remained stable and exhibited only a slight decrease. The film annealed at 715 °C exhibited the best dielectric properties with a high dielectric permittivity (ε_r=194 at 100 kHz) and a low dielectric loss (tanδ=0.02 at 100 kHz). The leakage current density of the BFO thin films was also notably low, i.e., 10^{-6} A/cm^2, under an applied electric field of 200 kV/cm for the film annealed at 715 °C. The excellent electrical properties obtained in the sol–gel-derived BFO films are attributed to the improved phase purity and microstructure.

Keywords: A. Sol–gel; C. Dielectric properties; $BiFeO_3$; Microstructure; Thin films

1. Introduction

Perovskite-type $BiFeO_3$ (BFO) is a typical single-phase multiferroic material [1]. Because of its high Curie temperature (T_C=850 °C) and Néel temperature (T_N=370 °C), BFO exhibits the coexistence of magnetic and ferroelectric orderings at room temperature [2,3]. The so-called ferroelectromagnetism, which can be anticipated in $BiFeO_3$, has attracted increasing interest from researchers in materials science and physics due to the intriguing physics and potential applications of BFO in information storage, sensors and magneto-electric devices [4]. Ferroelectric and dielectric materials with a high dielectric permittivity (ε_r) and a low dielectric loss tangent (tanδ) may be used in various capacitors and microwave dielectric elements, such as multi-layer capacitors, resonators, filters and oscillators [5,6]. More interestingly, multiferroic BFO may provide more degrees of freedom for device tuning, including both electric and magnetic methods for device tuning; therefore, a systematic investigation of the process–structure–property relationships in BFO thin films and the acquisition of high-performance BFO film samples has become crucial for further pushing BFO into practical applications. However, previous studies have illustrated that the drawback of serious leakage current problem aroused by impurity phases, boundaries and non-stoichiometry in BFO has hindered its applications [7]. To date, researchers have made attempts to dope and/or add a buffer layer to improve the electrical properties of $BiFeO_3$ thin films [8].

Many fabrication methods for epitaxial and polycrystalline $BiFeO_3$ thin films have been reported, such as pulsed laser deposition, magnetron sputtering, sol–gel processing and chemical solution deposition. Among these methods, the sol–gel method is an effective, simple way to synthesise BFO films because it can lead to large area films with chemical homogeneity and good control of the stoichiometry [9,10]. However, there are few reports on the sol–gel process than on

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http://dx.doi.org/10.1016/j.ceramint.2013.07.051

magnetron sputtering and pulsed laser deposition techniques for $BiFeO_3$ thin film preparation, mainly due to the appearance of impure phases and low resistivity in sol–gel-derived $BiFeO_3$ thin films [11]. For better compatibility with silicon microelectronics, (111)Pt/Ti/SiO_2/Si substrates were selected for our BFO film depositions. In this study, we attempted to widen the range of annealing temperatures to obtain phase pure $BiFeO_3$ thin films with better electrical properties. We prepared $BiFeO_3$ thin films with a wide annealing temperature range of 685–745 °C on (111)Pt/Ti/SiO_2/Si substrates and systematically analysed their crystallisation, morphology and electrical properties. Finally, a frequency-independent high dielectric permittivity of 200 and a low dielectric loss of 0.02 were realised in the 715 °C annealed $BiFeO_3$ thin film.

2. Experimental

The $BiFeO_3$ films presented in this study were synthesised with bismuth nitrate [$Bi(NO_3)_3 \cdot 5H_2O$] and iron nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] by a sol–gel process. Due to the volatilisation of Bi element during annealing, we weighed $Bi(NO_3)_3 \cdot 5H_2O$ with 5% mol excess to compensate for the Bi loss. Bismuth nitrate and iron nitrate with a mole ratio of 1.05:1 were firstly dissolved in the 2-methoxyethanol, and then a small amount of acetic acid was added to the solution to promote the dissolution of the raw materials. After stirring for 12 h, we obtained the stock solution with a concentration of 0.3 M. All of the steps above were performed in an ambient atmosphere at room temperature.

The deposition processes were performed in a clean room by spin coating at 3000 rpm for 20 s. After spin-coating, the wet films were dried at 80 °C for 5 min and 180 °C for 5 min immediately to remove volatile materials. The as-deposited films were further crystallised at different temperatures of 685, 700, 715, 730 and 745 °C in air for 90 s with a heating rate of 5 °C/s by a rapid thermal process. The spin-coating and annealing procedures were repeated several times to obtain the desired film thickness. Top Pt electrodes of 0.00126 cm^2 were deposited through a shadow mask on the surface of BFO films by sputtering. The films with top electrodes were annealed at 300 °C for 10 min for the electrode and the film to achieve full contact.

The phase of the BFO films was characterised by X-ray diffraction (XRD, DX-2700, Dandong, China) with Cu Kα radiation and a scan step of 0.03°. The surface and cross-section morphologies were analysed by a field-emission scanning electron microscope (FESEM, JSM-7500F, JEOL, Japan). An HP 4294A impedance analyser was utilised to measure the dielectric constant (ε_r) and the loss tangent (tanδ) of the BFO films. The ferroelectric property was measured using a Radiant ferroelectric test system.

3. Results and discussion

The XRD patterns of the BFO films annealed at various temperatures are shown in Fig. 1. The diffraction peaks were indexed by using PDF card no. 72-2112. No other phases were observed in the limit of the sensitivity of the diffractometer for the BFO films annealed at approximately 700 °C, whereas the other temperature annealed films had more or less of the impurity phase of $Bi_2Fe_4O_9$ indicated by "*" in Fig. 1. All XRD patterns indicate that the films possessed the perovskite structure with rhombohedral symmetry and are well crystallised, especially the thin films annealed at approximately 700 °C. The (110) and (1 − 10) peaks are more intense compared with the other peaks, and the (1 − 10) peak is split from (110) peak because of the distortion of cubic perovskite cell along the [111] direction [12]. With the increase in the annealing temperature, the impurity phase of $Bi_2Fe_4O_9$ gradually increased when the temperature was above 715 °C, which we attribute to the easier volatilisation of Bi and the greater reduction of Fe^{3+} species to Fe^{2+} at higher temperatures [13].

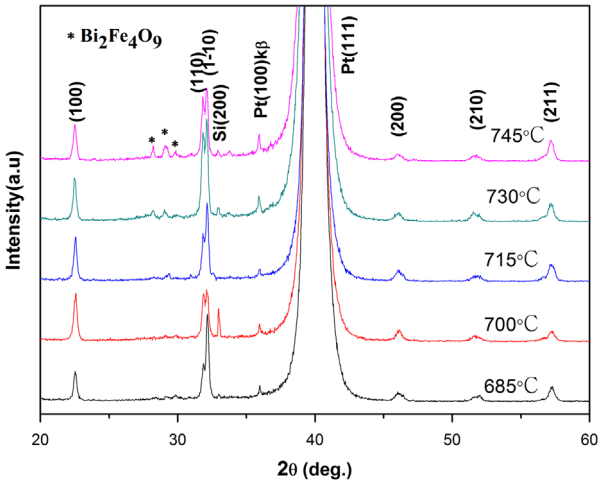

Fig. 1. XRD patterns of the $BiFeO_3$ thin films deposited on (111)Pt/Ti/SiO_2/Si substrates with different annealing temperatures ranging from 685 to745 °C.

Fig. 2(a) shows the cross-section SEM image of the $BiFeO_3$ thin film annealed at 700 °C, and Fig. 2(b)–(f) the surface morphology SEM photographs of the BFO films annealed at different temperatures corresponding to Fig. 1. As shown in Fig. 2(a), the interface is clear without apparent diffusion between the $BiFeO_3$ film and the Pt bottom electrode. The $BiFeO_3$ layer has a homogenous thickness of approximately 300 nm, which is approximately identical for the other temperature annealed films. It is easy to see that the film annealed at 715 °C exhibits a denser microstructure, and its grains pack more uniformly, while the other films have more large or small pores and more apparent grain boundaries. Thus, we conclude that 715 °C is an optimal temperature for BFO thin films to nucleate and grow on (111)Pt/Ti/SiO_2/Si substrates by rapid thermal processing.

The relative dielectric constant (ε_r) and dielectric loss tangent (tanδ) of the BFO films annealed at various temperatures are plotted in Fig. 3. According to Fig. 3(a), as the annealing temperature increases, the ε_r values monotonously increase except for the temperature of 745 °C. The decrease in ε_r for the 745 °C annealed film is mainly due to the existence of more pores and impurity phase. We obtained a high ε_r of 200 from the film annealed at 715 °C. More importantly, even

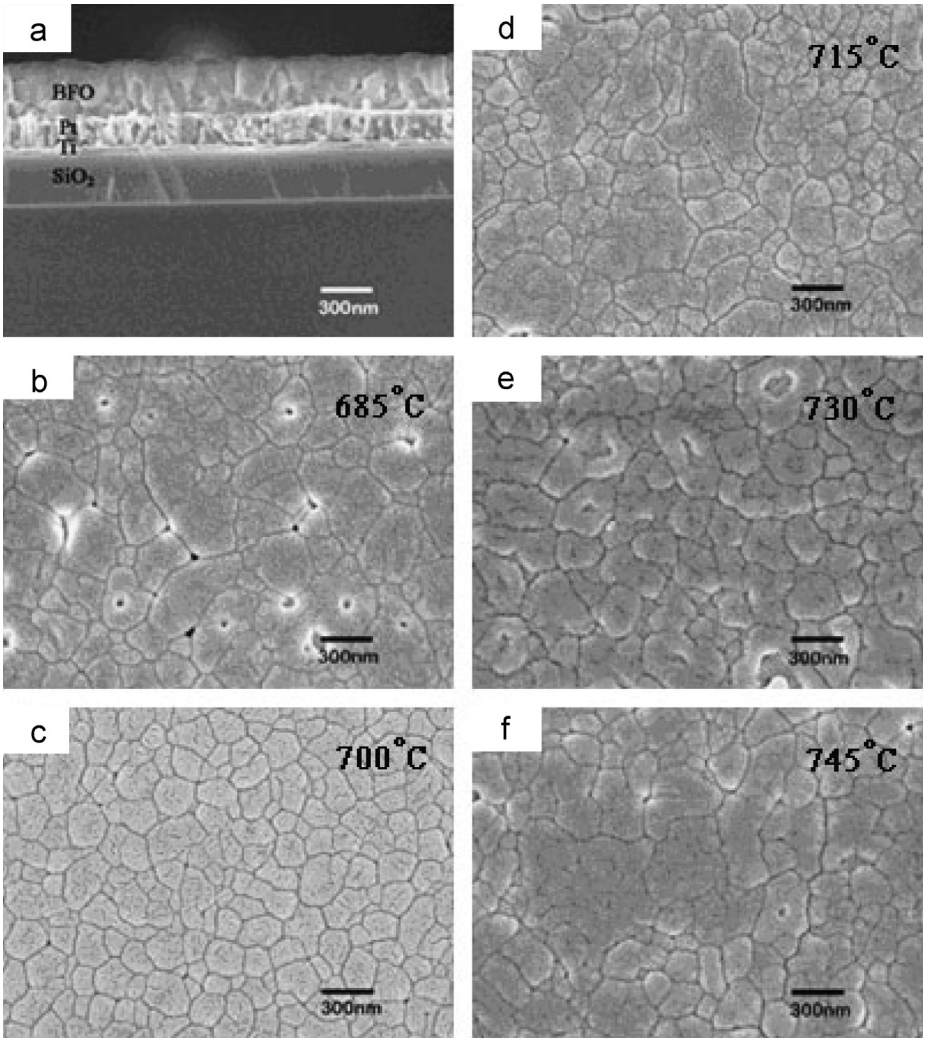

Fig. 2. FESEM images of $BiFeO_3$ thin films: (a) cross-section image of the film annealed at 700 °C, (b)–(f) surface morphologies of the BFO films annealed at 685–745 °C.

if the frequency increases to 1 MHz, the ε_r of the 715 °C annealed film remains quite stable with a very slight decrease, indicating good interfaces between film and electrodes, and the ferroelectricity presented below does not originate from the interface polarisation [14]. The slight decrease in ε_r with increasing frequency is because more polarisations do not have sufficient time to respond with the change of applied electric fields at higher frequencies [15].

As shown in Fig. 3(b), the dielectric loss of the BFO films with annealing temperatures from 685 to 730 °C remains low, and the tanδ value of the 715 °C annealed film is only 0.02 at 100 kHz, accompanied by a high ε_r of 194. They are comparable to or even much superior to those data from similar preparation methods reported in the literature [16–19], where the ε_r and tanδ values were reported to be 70–160 and 0.03–0.2, respectively. At low frequencies, the tanδ of the film annealed at 745 °C is very high, which is attributed to the dc conductivity arising from pores and large boundaries in the film according to Iakovlev et al. [20]. Above 300 kHz, because of the dipole inertia, the dielectric loss of all of the films increases with increasing frequencies [21].

Fig. 4 shows the polarisation versus applied electric field hysteresis loops of the $BiFeO_3$ thin films annealed at different temperatures, which were measured at frequencies of 2–3.3 kHz. The films annealed at 685, 700 and 715 °C have a similar remanent polarisation (P_r) of $2P_r$~2.6 μC/cm^2. Due to the low quality and great amount of the impurity phase, the films annealed at 730 and 745 °C could not obtain complete hysteresis loops when they were measured at 8 V, and the $2P_r$ value for the film annealed at 730 °C was reduced to 1.8 μC/cm^2.

Fig. 5 shows the leakage current characteristics of the $BiFeO_3$ thin films annealed at different temperatures. The leakage current density obtained in our work is extremely low (10^{-6} A/cm^2 under an applied electric field of 200 kV/cm), when compared with the BFO films formed similarly on Pt electrodes. The films annealed at 730 and 745 °C have relatively larger leakage current densities, in agreement with the results of the SEM images and the dielectric properties. Fig. 5 indicates that the films annealed at 700 and 715 °C exhibit an asymmetric current–voltage feature in the positive and negative regions, which is speculated to be associated with the accumulation of oxygen vacancies or other defects near the

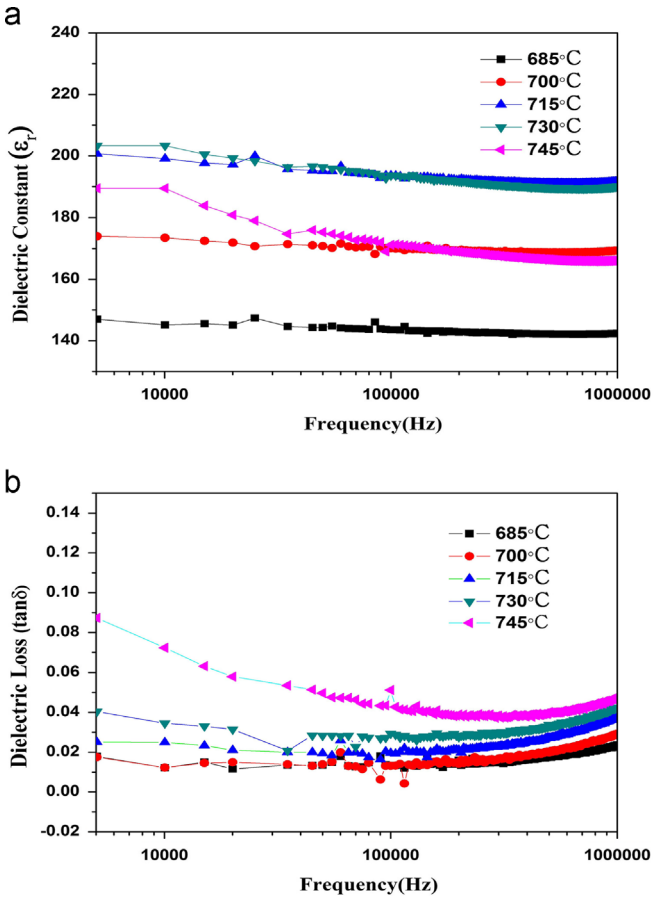

Fig. 3. (a) Relative dielectric constant and (b) dielectric loss tangent of the $BiFeO_3$ thin films annealed at 685–745 °C.

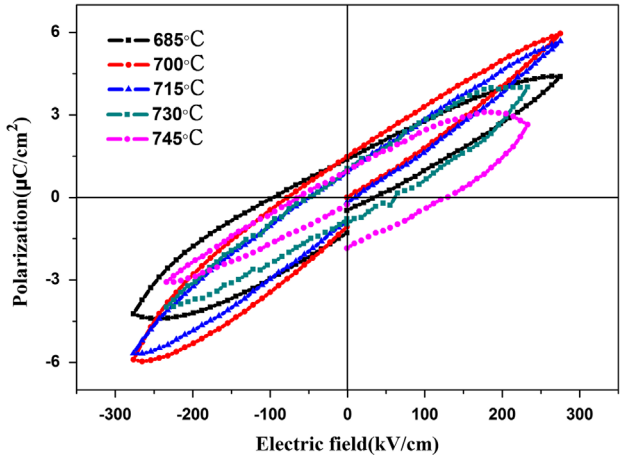

Fig. 4. Ferroelectric hysteresis loops of the BFO films annealed at 685–745 °C.

film/electrode interfaces, where the asymmetric internal electric fields originating from those defects can compensate for the applied voltage and influence the carrier injection [22]. For the same reason, the appearance of irregular leakage current density values in the low voltage region for the films annealed at 685–715 °C is mainly due to injected carriers and the defects in the BFO thin films.

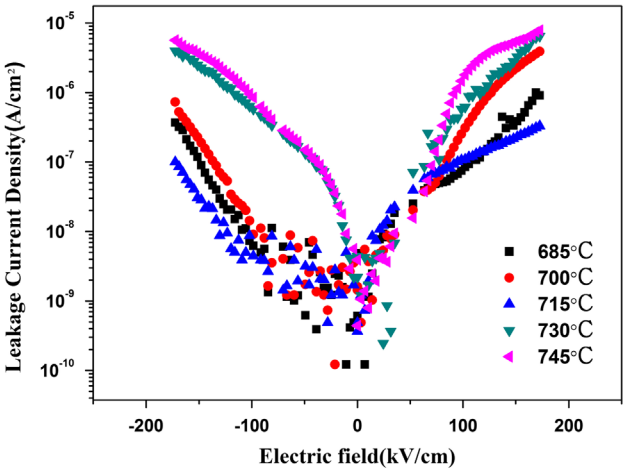

Fig. 5. Leakage current density of the $BiFeO_3$ thin films annealed at 685–745 °C.

4. Conclusions

In summary, multiferroic $BiFeO_3$ thin films were prepared on (111)Pt/Ti/SiO_2/Si substrates via a sol–gel spin-coating method, and a wide range of annealing temperatures from 685 to 745 °C were investigated. The films annealed at approximately 700 °C were well-crystallised in the perovskite phase, whereas higher temperature annealing induced the $Bi_2Fe_4O_9$ impurity phase. The SEM images exhibited granular and uniform surface topographies, as well as homogeneous and dense cross-section morphologies with an average thickness of 300 nm. Compared with other annealing temperatures, the film annealed at 715 °C possessed the highest crystallisation quality and the best electrical properties. As a result, the dielectric constant and the loss tangent at 100 kHz of the 715 °C annealed film were 194 and 0.02, respectively, which are comparable to or even significantly better than the results reported in the literature. Moreover, a very low leakage current density was obtained in our BFO films. The excellent dielectric and electrical properties obtained in this work, most likely stemming from the improved phase purity and microstructure, make the multiferroic BFO thin films good candidates for multifunctional dielectric elements.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant no. 61071017), the Programme for New Century Excellent Talents in University of China (Grant no. NCET-10-0582), the Doctoral Fund of the Ministry of Education of China (Grant no. 20100181120021) and the Programme for Outstanding Young Scientific and Technological Leader of Sichuan Province (Grant no. 2011JQ0021).

References

[1] J. Wang, J.B. Neaton, H. Zheng, V. Nagarajan, S.B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D.G. Schlom, U.V. Waghmare,

N.A. Spaldin, K.M. Rabe, M. Wuttig, R. Ramesh, Epitaxial $BiFeO_3$ multiferroic thin film heterostructures, Science 299 (2003) 1719–1722.
[2] M. Polomska, W. Kaczmarek, Z. Pajak, Electric and magnetic properties of $(Bi_{1-x}La_x)FeO_3$ solid solutions, Physica Status Solidi (A): Applied Research 23 (1974) 567–574.
[3] I. Sosnowska, T.P. Neumaier, E. Steichele, Spiral magnetic ordering in bismuth ferrite, Journal of Physics C—Solid State Physics 15 (1982) 4835–4846.
[4] S. Mandal, C.K. Ghosh, D. Sarkar, U.N. Maiti, K.K. Chattopadhyay, X-ray photoelectron spectroscopic investigation on the elemental chemical shifts in multiferroic $BiFeO_3$ and its valence band structure, Solid State Science 12 (2010) 1803–1808.
[5] A.K. Tagantsev, V.O. Sherman, K.F. Astafiev, J. Venkatesh, N. Setter, Ferroelectric materials for microwave tunable applications, Journal of Electroceramics 11 (2003) 5–66.
[6] A.I. Kingon, J.P. Maria, S.K. Streiffer, Alternative dielectrics to silicon dioxide for memory and logic devices, Nature 406 (2000) 1032–1038.
[7] S.H. Jo, S.G. Lee, S.H. Lee, Structural and pyroelectric properties of sol–gel derived multiferroic BFO thin films, Materials Research Bulletin 47 (2012) 409–412.
[8] Y. Wang, C.W. Nan, Integration of $BiFeO_3$ thin films on Si wafer via a simple sol–gel method, Thin Solid Films 517 (2009) 4484–4487.
[9] L.W. Martin, D.G. Schlom, Advanced synthesis techniques and routes to new single-phase multiferroics, Current Opinion in Solid State and Materials Science 16 (2012) 199–215.
[10] H.R. Liu, Z.L. Liu, Q. Liu, K.L. Yao, Ferroelectric properties of $BiFeO_3$ films grown by sol–gel process, Thin Solid Films 500 (2006) 105–109.
[11] Z. Wen, G.D. Hu, S.H. Fan, C.H. Yang, W.B. Wu, Y. Zhou, X.M. Chen, S.G. Cui, Effects of annealing process and Mn substitution on structure and ferroelectric properties of $BiFeO_3$ films, Thin Solid Films 517 (2009) 4497–4501.
[12] Z.L. Liu, H.R. Liu, G.H. Du, J. Zhang, K.L. Yao, Electric properties of $BiFeO_3$ films deposited on $LaNiO_3$ by sol–gel process, Journal of Applied Physics 100 (2006) 044110.
[13] Y. Wang, Q.H. Jiang, H.C. He, C.W. Nan, Multiferroic $BiFeO_3$ thin films prepared via a simple sol–gel method, Applied Physics Letters 88 (2006) 142503.
[14] C.C. Lee, J.M. Wu, Effect of film thickness on interface and electric properties of $BiFeO_3$ thin films, Applied Surface Science 253 (2007) 7069–7073.
[15] H.R. Liu, Z.L. Liu, K.L. Yao, Improved electric properties in $BiFeO_3$ films by the doping of Ti, Journal of Sol–Gel Science and Technology 41 (2007) 123–128.
[16] A. Huang, S.R. Shannigrahi, Structural and electrical properties of $BiFeO_3$ thin films by solution deposition and microwave annealing, Thin Solid Films 519 (2011) 4793–4797.
[17] X.W. Tang, J.M. Dai, X.B. Zhu, L.H. Yin, R. Ang, W.H. Song, Z.R. Yang, Y.P. Sun, R.L. Zhang, Individual-layer thickness effects on the preferred c-axis-oriented $BiFeO_3$ films by chemical solution deposition, Journal of the American Ceramic Society 93 (2010) 1682–1687.
[18] F. Yan, T.J. Zhu, M.O. Lai, L. Lu, Enhanced multiferroic properties and domain structure of La-doped $BiFeO_3$ thin films, Scripta Materialia 63 (2010) 780–783.
[19] C.H. Yang, G.D. Hu, J.C. Wang, Effect of annealing temperature on electrical properties of metal–ferroelectric ($BiFeO_3$)–insulator ($Bi_2Ti_2O_7$)–silicon capacitors, Microelectronic Engineering 91 (2012) 132–136.
[20] S. Iakovlev, C.H. Solterbeck, M. Kuhnke, M. Es-Souni, Multiferroic $BiFeO_3$ thin films processed via chemical solution deposition: structural and electrical characterization, Journal of Applied Physics 97 (2005) 094901.
[21] M. Cheng, G.Q. Tan, X. Xue, A. Xia, H.J. Ren, Preparation of Nd-doped $BiFeO_3$ films and their electrical properties, Physica B 407 (2012) 3360–3363.
[22] H.L. Zhang, X.M. Chen, T. Wang, F.F. Wang, W.Z. Shi, Structure and electrical properties of $BiFeO_3$ thin films grown on $LaNiO_3$ electrode by chemical solution deposition, Journal of Alloys and Compounds 500 (2010) 46–48.