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Microstructure and properties of sol–gel derived $PbTiO_3/NiFe_2O_4$ multiferroic composite thin film with the two nano-crystalline phases dispersed homogeneously

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ABSTRACT

Ferroelectric/ferrimagnetic $PbTiO_3/NiFe_2O_4$ composite thin films with nano-scale $PbTiO_3$ and $NiFe_2O_4$ phases homogeneously dispersed in each other were synthesized by sol–gel in situ method. The phase structure and morphology of the composite thin films and their dielectric, ferroelectric and ferromagnetic properties were measured respectively in detail. Results show that the ferroelectric/ferrimagnetic composite thin film with $PbTiO_3$ and $NiFe_2O_4$ phases is successfully synthesized at heat-treatment temperature of 850 °C. It is significantly isotropic due to the nanometer scale grain size of the constituent $PbTiO_3$ and $NiFe_2O_4$ phases. A capacitance of 60–100 pF with a good frequency independence over the conventional applied frequency range, ferroelectric hysteresis loops with the applied electric field of 500 kV/cm, a saturation magnetization higher than 4.8 MT, and a coercive field of 5280 A/m with well suitable ferrimagnetic properties are obtained from the thin film with the composition ratio $PbTiO_3/NiFe_2O_4$ of 50/50 post heat-treated at 850 °C. The ferroelectric/ferrimagnetic composite thin film is desirable for multifunctional device application.

1. Introduction

Ferroelectric/ferrimagnetic composite materials containing ferroelectric and ferrimagnetic phases have drawn much attention due to their attractive multifunctional features and potential in device application such as switching, data storage, filters and transducers [1–11]. For miniaturization of an electronic device, ferroelectric/ferrimagnetic composite thin film is an important kind of multifunctional materials. In the last few decades, many studies have been done on it [12–16]. Not only the physical mechanism of ferroelectric/ferrimagnetic composite thin film but also its potential application in microelectronic devices was investigated. It is found that the properties of ferroelectric/ferrimagnetic composite thin film could be modified or controlled by its microstructure [13]. Therefore, much attention has been paid on the preparations. Such as using the sol–gel method and pulsed laser deposition to prepare ferroelectric/ferromagnetic thin films with alternate layers or make ferroelectric system randomly dispersed by ferrite phase [13,15,17]. Actually, with respect to miniaturization for the application in nano devices, isotropic nature in multifunctional composite thin film becomes important. Although there has been research about the nano thin films [18], limited attempt has been done to deal with ferroelectric/ferrimagnetic composite thin film. In this paper, the $PbTiO_3/NiFe_2O_4$ composite thin film with ferrimagnetic and ferroelectric nano-crystalline phases randomly dispersed in each other, which satisfied isotropic requirement of miniaturization, was prepared by sol–gel in situ process. Microstructure and properties of the thin film were investigated. Results show that considerable dielectric and ferrimagnetic properties are satisfactory for application as a multifunctional thin film.

2. Experimental procedures

The sol precursor was prepared with lead acetate ($Pb(CH_3COO)_2{\cdot}3H_2O$), tetrabutyl titanate ($Ti(OC_4H_9)_4$), nickel acetate pentahydrate ($Ni(CH_3COO)_2{\cdot}5H_2O$) and ferricnitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) as raw materials, acetic acid (CH_3COOH) and ethylene glycol monomethyl ether ($CH_3OCH_2CH_2OH$) as solvents. The composition of the raw materials was kept at the mole ratio of Pb:Ti:Ni:Fe of 1:1:1:2 for the final Pb–Ti–Ni–Fe–O thin films containing two phases of $PbTiO_3$ and $NiFe_2O_4$. The thin films were prepared on silicon substrates using the sol precursor by dip coating, followed by a heat-treatment at 550 °C for 8 min plus a post heat-treatment at temperatures of 550 °C, 600 °C, 850 °C, and 950 °C for 1 h, respectively. The microstructure of the composite thin films was measured by X-ray diffraction (XRD) (RIGAKU D/MAX-C, Cu Kα radiation). The morphology of the composite thin films was observed by scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM). The dielectric properties of the composite thin films at room temperature were analyzed by Precision Impedance Analyzer (Agilent 4294A). Temperature dependences of the capacitance of the composite thin films were measured by Precision Impedance Analyzer (Keithley 3330) and temperature control case. For the measurement of capacitance, round-shaped Au electrodes with

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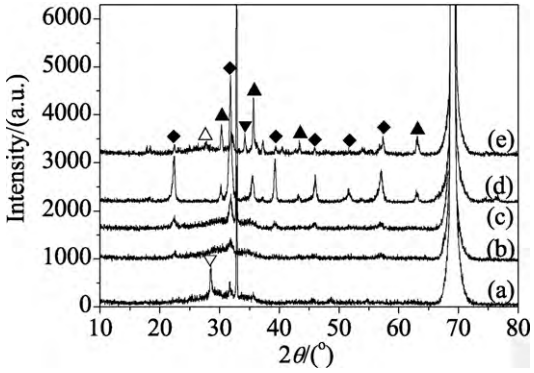

Fig. 1. XRD patterns of the thin film composites rapid heat-treated at 550 °C for 8 min and post heat-treated at (a) room temperature (without post heat-treatment), (b) 550 °C, (c) 600 °C, (d) 850 °C and (e) 950 °C in which the different phase structures are represented by symbols of (♦) $PbTiO_3$,(▲) $NiFe_2O_4$, (▼) $PbFe_{12}O_{19}$, (▽) $Pb_{0.94}Ti_{0.06}O_{1.06}$ and (Δ) TiO_2.

diameters of 0.2 mm and thickness of 100 nm were made by mask method on the thin films. (PVD method used, filament current 1.3 mA, vacuum degree 2.4×10^{-4} Pa, deposition time 20 min) The ferroelectric hysteresis loops were measured by Ferroelectric Charachtorization System (TF Analyzer 1000). Finally, magnetic properties were measured using Physical Property Measurement System (PPMS).

3. Results and discussion

Fig. 1 shows the XRD patterns of $PbTiO_3/NiFe_2O_4$ composite thin films rapidly heat-treated at 550 °C and then post heat-treated at temperatures of 550 °C, 600 °C, 850 °C and 950 °C for 1 h. An unexpected phase $Pb_{0.94}Ti_{0.06}O_{1.06}$ formed in the thin films without post heat-treatment or with post heat-treatment below 550 °C, and $PbTiO_3$ phase formed when post heat-treated at 600 °C. The thin films were composed of $PbTiO_3$ and $NiFe_2O_4$ phases at post heat-treatment temperature of 850 °C while three phases of $PbFe_{12}O_{19}$, $PbTiO_3$ and $NiFe_2O_4$ formed in the thin films with post heat-treatment temperature of 950 °C.

Fig. 2 exhibits the SEM and HRTEM images of the thin films. It shows that the thin films contain round-shaped particles of approximately the same size, yet the particles grew larger from about 80 nm to about 170 nm when the heat-treatment temperature increases from 850 °C to 950 °C. Moreover, for the thin film annealed at 850 °C which possesses actually the typical ferroelectric and ferromagnetic nature, the particles consist of nano-scale grains of both $PbTiO_3$ and $NiFe_2O_4$ phases and the two phases are mixed homogeneously (Fig. 2(c)). The grain size is no more than 15 nm and the thin film thickness is about 1.2 μm (Fig. 2(d)), much larger than the nano grain size. The nano-scale grain size makes the dispersion of the two phases in the thin film uniform and therefore isotropic in multiferroic nature. This contributes to the opportunity of application in multifunctional device, especially in those with the isotropic requirement.

Fig. 3 shows the capacitance–frequency spectrums for the $PbTiO_3/NiFe_2O_4$ composite thin films and $PbTiO_3$ thin films respectively. When the frequency is lower than 5 kHz and the post heat-treatment temperature is 550 °C and 600 °C, the capacitance of the $PbTiO_3/NiFe_2O_4$ composite thin films and $PbTiO_3$ thin films all decrease with increasing frequency. However, when post heat-treatment temperature is 850 °C, discrepancies in frequency dependence of capacitance between the $PbTiO_3/NiFe_2O_4$ composite thin films and $PbTiO_3$ thin films would be observed in the low frequency range (<5 kHz): The capacitance of the $PbTiO_3/NiFe_2O_4$ composite thin film shows a decrease trend while the capacitance of $PbTiO_3$ thin film keeps almost constant with changing frequency. In fact, when the post heat-treatment temperature is below 850 °C, the imperfection of the crystalline phase appears normally

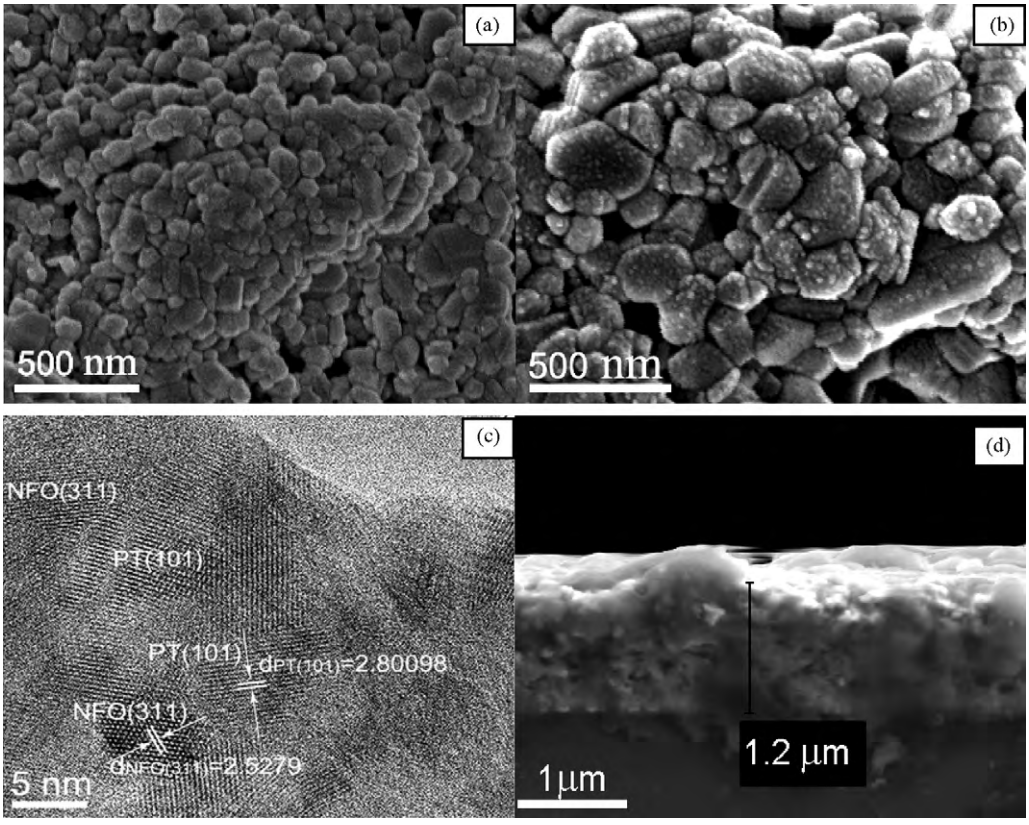

Fig. 2. Photographs for the thin film composites measured by (a) SEM in surface observation after post heat-treated at 850 °C for 1 h, (b) SEM in surface observation after post heat-treated at 950 °C for 1 h, (c) HRTEM after post heat-treated at 850 °C for 1 h and (d) SEM in cross-sectional observation after post heat-treated at 850 °C for 1 h.

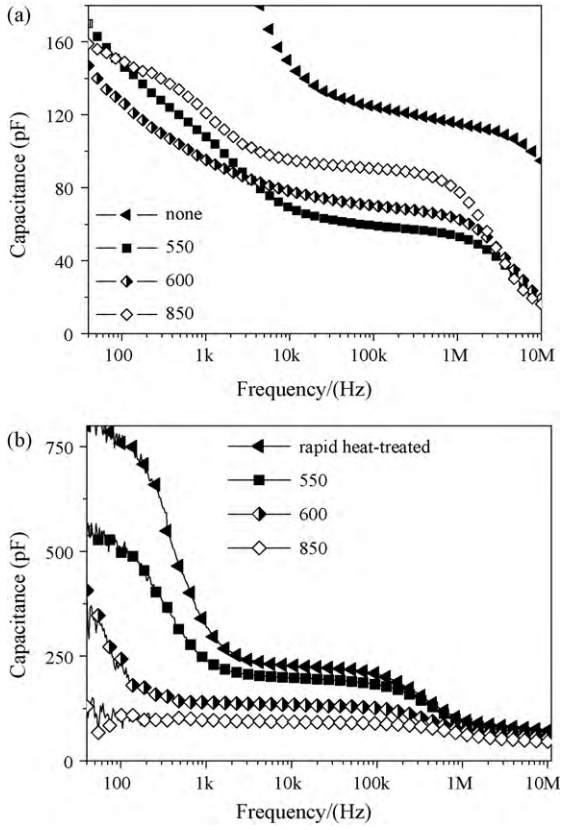

Fig. 3. Dependence of capacitance on frequency for (a) the $PbTiO_3/NiFe_2O_4$ composite thin films and (b) $PbTiO_3$ thin films rapid heat-treated at 550 °C for 8 min initially and post heat-treated at different temperatures finally for 1 h.

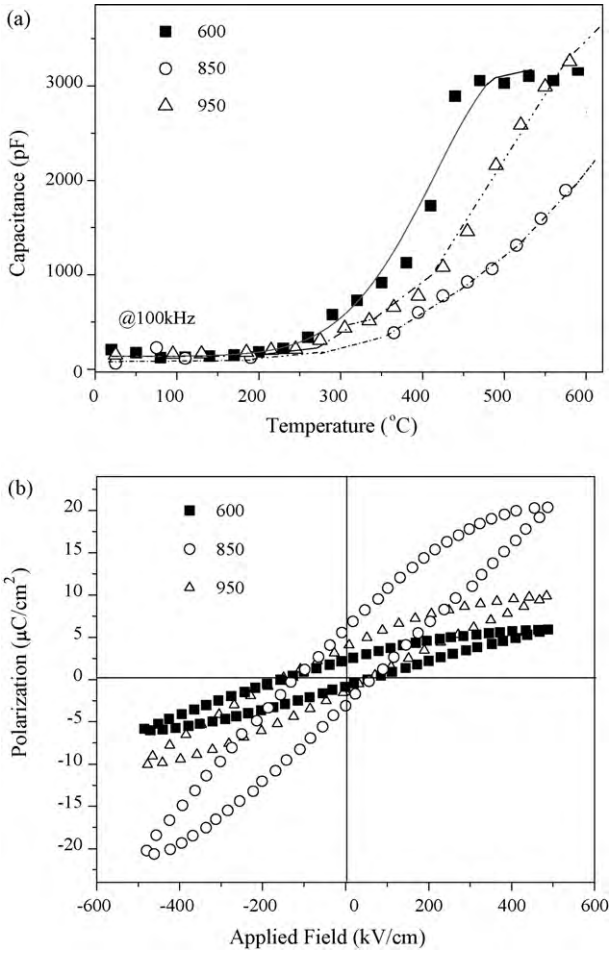

Fig. 4. (a) Temperature dependence of the capacitance and (b) ferroelectric hysteresis loops of the $PbTiO_3/NiFe_2O_4$ thin films rapidly heat-treated at 550 °C for 8 min initially and then annealed at 600 °C, 850 °C, 950 °C for 1 h finally.

in the $PbTiO_3$ thin films, which makes the deficiencies increase in the $PbTiO_3$ thin films and thus the space charge polarizations increase in the $PbTiO_3$ thin films. According to Maxwell-Wagner effect, the space charge polarization contributes to the increase in capacitance at low applied frequency [19–21]. Thus the capacitance of the $PbTiO_3$ thin films post heat-treated at 550 °C and 600 °C at low frequency are both high. However, when the post heat-treatment temperature increases to 850 °C, the perovskite phase forms perfectly in the $PbTiO_3$ thin films. The space charge polarization would decrease and the capacitance would keep almost stable over the low applied frequency range. In comparison, for the $PbTiO_3/NiFe_2O_4$ composite thin films, when post heat-treatment temperature is 850 °C, other than the appearance of imperfection mentioned above in $PbTiO_3$ thin films, boundaries mismatching between $PbTiO_3$ and $NiFe_2O_4$ phases would occur despite of the high calcination temperature. As a result, the space charge polarization still appears. Therefore, the capacitance of the $PbTiO_3/NiFe_2O_4$ composite thin film post heat-treated at 850 °C is high at low frequency. The difference of dielectric behavior between the $PbTiO_3/NiFe_2O_4$ composite thin films and the $PbTiO_3$ thin films appears. Practically, there is no affect on application of the composite thin films since the frequency in application of most multifunctional devices is generally above 5 kHz, thus the $PbTiO_3/NiFe_2O_4$ composite thin films are still applicable in device use. In conclusion, the capacitance of the composite thin films is in the range of 60–100 pF. The thin films are applicable as a ferroelectric/ferrimagnetic composite in multifunctional device.

Fig. 4(a) shows the capacitance dependence on temperature of the composite thin films. It is found that the capacitance of the thin films keeps almost stable below 300 °C but starts to increase rapidly above 300 °C. The maximum value of the capacitance of the 600 °C sintered thin films appears at about 490 °C. As the curie point of $PbTiO_3$ is 490 °C [22], the increase in the capacitance of the composite thin films near 490 °C indicated a probable transition of perovskite $PbTiO_3$ phase in the composite thin film from ferroelectric to paraelectric. Thus the $PbTiO_3$ phase in the composite thin film still keeps ferroelectric nature at room temperature. However, the normal decrease in capacitance above 490 °C does not occur. This is attributed to the $Pb_{0.94}Ti_{0.06}O_{1.06}$ formed stably in the thin film near 550 °C (Fig. 1(a)). Further, when the post sintering temperature increases to 850 °C, the Curie temperature seems to be higher than 600 °C (Fig. 4(a)) according to the evidence that the capacitance curve starts to rapidly increase with temperature at a higher temperature than that of 600 °C treated sample. But when the heat-treatment temperature for the sample increases to 950 °C, according to the capacitance curve which starts to rapid increase with temperature at a lower temperature than that of 850 °C treated sample but still higher than that of 600 °C treated sample, the Curie temperature seems to decrease to about 600 °C. As is known, the radius of Ti^{4+} is close to Fe^{3+}, thus the replacement of Ti^{4+} ion by Fe^{3+} ion and the corresponding appearance of oxygen vacancies in $PbTiO_3$ occur. When post heat-treatment temperature increases to 950 °C, a new phase $PbFe_{12}O_{19}$ forms (Fig. 1) and cost part of the Fe^{3+} ions in the system, causing the decrease of the content of Fe^{3+} ions which could be dissolved into $PbTiO_3$ phase. So the content of Fe^{3+} ions dissolved in $PbTiO_3$ decreases. The decrease in Fe^{3+} ion concentration could answer for the decrease in Curie temperature. That is to say Fe^{3+} ion concentration plays the major

role although the increase in Pb loss may also cause the change in Curie temperature [23]. This can be seen further for the thin film below 850 °C at which Pb loss is generally believed small. When post heat-treatment temperature increases from 600 °C to 850 °C, the Curie temperature increases. It exhibits opposite change trend with increasing temperature and thus with increasing Pb loss [23]. In conclusion, the composite thin film is a little different from general dielectric thin film. Despite of this difference, the composite thin film still exhibits usual dielectric behavior which is almost the same as that of the single $PbTiO_3$ thin film, especially at normal application temperature, being completely acceptable in normal usage.

The ferroelectric hysteresis loops of the $PbTiO_3/NiFe_2O_4$ composite thin films are shown in Fig. 4(b). The saturation polarization P_s first increases from 6 μC/cm^2 to 21 μC/cm^2 and then decreases to 10 μC/cm^2 . Meanwhile, the remanent polarization P_r increases from 2.5 μC/cm^2 to 5.8 μC/cm^2 and then decreases to 4 μC/cm^2 , and the coercive force changes little with increasing heat-treatment temperature. In fact, when the heat-treatment temperature increases to 850 °C, the crystalline phase content of the ferroelectric $PbTiO_3$ phase in the composite system increases and when heat-treatment temperature increases to 950 °C, it decreases (Fig. 1). The amount of electric dipoles therefore exhibits similar heat-treatment temperature dependence, causing the simultaneous response in remnant and saturation polarization. It can then be seen that the tendency of the changes is related with the crystalline phase formation in the composite system. Yet still, the $PbTiO_3/NiFe_2O_4$ composite thin film exhibites almost the same ferroelectric behavior as that of the $PbTiO_3$ thin film [24], giving the applied electric field of 500 kV/cm without breakdown.

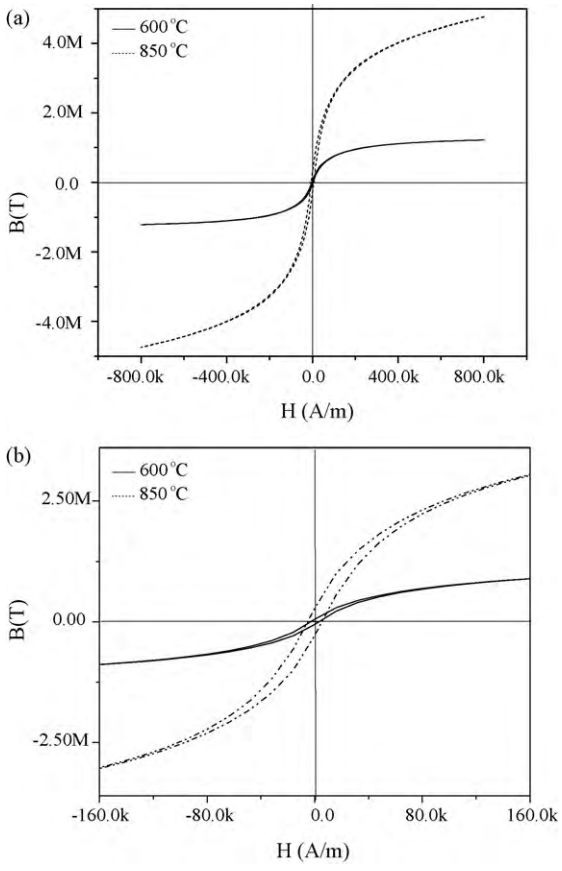

Fig. 5. (a) In-plane room temperature magnetic hysteresis loops of the $PbTiO_3/NiFe_2O_4$ thin films annealed at 600 °C (the solid line) and 850 °C (the dashed) and (b) the amplified loops of (a).

The magnetic hysteresis loops of the thin films changing with the post heat-treatment temperature is shown in Fig. 5. The $PbTiO_3/NiFe_2O_4$ composite thin films exhibit good magnetic hysteresis loops. The saturation magnetization increases from about 1.2 MT to higher than about 4.8 MT and the coercive field from 3200 A/m to 5280 A/m with increasing heat-treatment temperature. Meanwhile, the relative initial permeability increases from about 2.13 to 4.26. In fact, magnetic dipoles increase with the increase of $NiFe_2O_4$ crystalline phase in the composite and thus the heat-treatment temperature. The magnetization and initial permeability of the $PbTiO_3/NiFe_2O_4$ composite thin films therefore increase with the temperature. Furthermore, the influence of pinning effect of the non-magnetic phase $PbTiO_3$ on the turning of the magnetic domains increases with increasing $PbTiO_3$ phase content. Actually in the 600 °C and 850 °C samples, the main phase is PTO other than NFO phases. It implies that the pinning effect would be mainly from the $PbTiO_3$ phase. From Fig. 1 it can be seen that the crystalline phase of PTO in the samples increases significantly from 600 °C to 850 °C although the NZFO phase is also increased with increasing temperature. The pinning effect will thus increase with increasing heat-treatment temperature. The coercive force of the magnetic phase of $NiFe_2O_4$ therefore increases with increasing temperature. For the thin film heat-treated at 850 °C, a saturation magnetization higher than 4.8 MT and a coercive field of 5280 A/m are revealed respectively. These values are comparative to the reported values for the $NiFe_2O_4$ thin film [25], which means that this composite thin film should be accepetble in using for related ferroelectric and ferromagnetic bifunctional devices.

4. Conclusions

Biphase $PbTiO_3/NiFe_2O_4$ composite thin films were successfully prepared by sol–gel in situ method. $NiFe_2O_4$ grains were homogeneously dispersed in $PbTiO_3$ on a nanometer scale in the composite, making the thin film isotropic. The $PbTiO_3/NiFe_2O_4$ composite thin films show good dielectric, ferroelectric and ferrimagnetic properties at conventional applied temperature. A capacitance of 60–100 pF with a good frequency independence over the conventional applied frequency range, ferroelectric hysteresis loops with the applied electric field of 500 kV/cm, a saturation magnetization higher than 4.8 MT, and a coercive field of 5280 A/m with well suitable ferrimagnetic properties are obtained from the thin film with the composition ratio $PbTiO_3/NiFe_2O_4$ of 50/50 post heat-treated at 850 °C. The thin films are satisfactory as a candidate of high quality ferroelectric/ferrimagnetic thin film composite in multifunctional device application especially in isotropic requirement of miniaturization.

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References

[1] A.S. Fawzi, A.D. Sheikh, V.L. Mathe, J. Alloys Compd. 493 (2010) 601–608.
[2] Y. Zhou, J.C. Zhang, L. Li, Y.L. Su, J.R. Cheng, S.X. Cao, J. Alloys Compd. 484 (2009) 535–539.
[3] H. Zheng, Y.L. Dong, X. Wang, W.J. Weng, G.R. Han, N. Ma, P. Du, Angew. Chem. Int. Ed. 48 (2009) 8927–8930.
[4] Y.B. Kamble, S.S. Chougule, B.K. Chougule, J. Alloys Compd. 476 (2009) 733–738.
[5] P. Uniyal, K.L. Yadav, J. Alloys Compd. 492 (2010) 406–410.
[6] J.Q. Huang, P.Y. Du, L.X. Hong, Y.L. Dong, M.C. Hong, Adv. Mater. 19 (2007) 437–440.

[7] S. Narendra Babu, S.V. Suryanarayana, T. Bhimasankaram, J. Alloys Compd. 473 (2009) 418–422.
[8] C.E. Ciomaga, C. Galassi, F. Prihor, I. Dumitru, L. Mitoseriu, A.R. Iordan, M. Airimioaei, M.N. Palamaru, J. Alloys Compd. 485 (2009) 372–378.
[9] B.K. Bammannavar, L.R. Naik, R.B. Pujar, B.K. Chougule, J. Alloys Compd. 477 (2009) L4–L7.
[10] K. Ramam, M. Lopez, K. Chandramouli, J. Alloys Compd. 488 (2009) 211–216.
[11] L.N. Su, P. Liu, Y. He, J.P. Zhou, L. Cao, C. Liu, H.W. Zhang, J. Alloys Compd. 494 (2010) 330–335.
[12] R.Y. Zheng, X.S. Gao, J. Wang, S. Ramakrishna, J. Am. Ceram. Soc. 91 (2008) 463–466.
[13] H.C. He, J.P. Zhou, J. Wang, C.W. Nan, Appl. Phys. Lett. 89 (2006) 052904.
[14] Y.L. Dong, X. Wang, X.Y. Chai, W.J. Weng, G.R. Han, P.Y. Du, Surf. Rev. Lett. 15 (2008) 7–11.
[15] H. Zheng, J. Wang, S.E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S.R. Shinde, S.B. Ogale, F. Bai, D. Viehland, Y. Jia, D.G. Schlom, M. Wuttig, A. Roytburd, R. Ramesh, Science 303 (2004) 661–663.
[16] Y.L. Dong, P.Y. Du, W.J. Weng, G.R. Han, G.L. Zhao, J. Electroceram. 21 (2008) 327–330.
[17] H.J. Ryu, P. Murugavel, J.H. Lee, S.C. Chae, T.W. Noh, Y.S. Oh, H.J. Kim, K.H. Kim, J.H. Jang, M. Kim, C. Bae, J.-G. Park, Appl. Phys. Lett. 89 (2006) 102907.
[18] A.U. Ubale, S.C. Shirbhate, J. Alloys Compd. 497 (2010) 228–233.
[19] J.Q. Huang, L.X. Hong, G.R. Han, W.J. Weng, P.Y. Du, Acta Phys. Sinicha. Ed. 55 (2006) 3664–3669.
[20] Y. Zhi, A. Chen, J. Appl. Phys. 91 (2002) 794–797.
[21] Z.H. Chen, J.Q. Huang, Q. Chen, C.L. Song, G.R. Han, W.J. Weng, P.Y. Du, Scripta. Mater. 57 (2007) 921–924.
[22] D. Bersani, P.P. Lottici, A. Montenero, S. Pigoni, J. Mater. Sci. 31 (1996) 3153–3157.
[23] Y.A. Shevchuk, S.K. Korchagina, V.V. Gagulin, V.V. Bogatko, Inorg. Mater. 33 (1997) 970–972.
[24] S.D. Cheng, C.H. Kam, Y. Zhou, W.X. Que, Y.L. Lam, Y.C. Chan, W.S. Gan, Thin Solid Films 375 (2000) 109–113.
[25] P. Samarasekara, F.J. Cadieu, Jpn. J. Appl. Phys. Part 1 40 (2001) 3176–3179.