Solid State Communications 152 (2012) 241–243

Contents lists available at SciVerse ScienceDirect

Solid State Communications

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

Fast-track communication

The exchange bias in polycrystalline $BiFeO_3/Ni_{81}Fe_{19}$ bilayers on Si substrate with $LaNiO_3$ buffer layer

Xueyong Yuan[a], Xiaobo Xue[b], Xiaona Zhang[c], Zheng Wen[d], Mao Yang[b], Jun Du[b], Di Wu[d], Qingyu Xu[a,*]

[a] Department of Physics, Southeast University, Nanjing 211189, China
[b] Department of Physics, Nanjing University, Nanjing 210008, China
[c] Institute of Microstructure and Property of Advanced Materials, Beijing University of Technology, Beijing 100124, China
[d] Department of Materials Science and Engineering, Nanjing University, Nanjing 210008, China

ARTICLE INFO

Article history:
Received 7 November 2011
Received in revised form
2 December 2011
Accepted 5 December 2011
by A. Pinczuk
Available online 9 December 2011

Keywords:
A. Magnetic films and multilayers
B. Laser processing
D. Exchange and superexchange

ABSTRACT

Single phase polycrystalline $BiFeO_3$ thin films have been grown on Si substrates using $LaNiO_3$ as buffer layers by pulsed laser deposition. A transmission electron microscope shows an amorphous thin layer of $LaNiO_3$ followed by the polycrystalline $LaNiO_3$, which facilitates the crystallization of a $BiFeO_3$ layer in R3c structure and suppression of the impurity phases. NiFe layers were deposited on the $BiFeO_3$ layer by magnetron sputtering. Clear exchange coupling between $BiFeO_3$ and NiFe (with maximum exchange bias field up to 61 Oe) has been observed at room temperature, and the exchange bias field decreases with increasing the NiFe thickness. Our results clearly demonstrate the potential application of polycrystalline $BiFeO_3$ in magnetoelectric coupling based spintronics.

In recent years multiferroic materials have attracted intensive research interests due to the coexistence of ferroelectric and magnetic ordering in a single phase, which opens new opportunities in magnetic data storage, spintronics and high-frequency magnetic devices [1–3]. Among the rare multiferroic materials, $BiFeO_3$ is one of the well-known single-phase multiferroic materials with an ABO_3 structure and a *G*-type antiferromagnetic behavior below Neel temperature $T_N \sim 643$ K and ferroelectric behavior below the Curie temperature $T_C \sim 1103$ K [4]. The coupling between the ferroelectric and antiferromagnetic ordering has been confirmed experimentally by the observation of coupled ferroelectric and antiferromagnetic domains [5], which allows an electric control of the antiferromagnetic spin orientations [6]. Due to the antiferromagnetism in $BiFeO_3$, a sizable magnetic response to the application of electric field cannot be expected. Binek suggested an alternative application of $BiFeO_3$ in spintronics, the magnetization state of the ferromagnetic layer can be manipulated by the applied electric field on the neighboring multiferroic layer through exchange coupling [7].

There have been several reports on the exchange bias using $BiFeO_3$ films as antiferromagnetic layers [8–11]. However, most of the researches are based on the single crystalline $BiFeO_3$ layer epitaxially growing on $SrTiO_3$ substrate [8,9]. In applications, most of the electronic circuits are based on Si. Chu et al. have epitaxially grown single crystalline $BiFeO_3$ on Si substrates by growing single crystalline $SrTiO_3$ layer as buffer layer by molecular beam epitaxy [10], which makes the growing procedure complicated and expensive. Recently, Hauguel et al. reported the growth of polycrystalline $BiFeO_3$ on Pt coated Si substrate, and exchange bias was first observed in the polycrystalline $BiFeO_3$/NiFe bilayers [11]. However, the quality of the $BiFeO_3$ film is not very high because the impurity phases can still be observed. In addition, Pt buffered Si substrates are very costly. Thus, a rather cheap method for the preparation of $BiFeO_3$ film on Si substrates for the exchange bias needs to be explored for large-scale application in the future.

In this letter, we report the growth of single phase polycrystalline $BiFeO_3$ film on Si substrate with $LaNiO_3$ buffer layer and the clear exchange bias with maximum value of 61 Oe at room temperature in $BiFeO_3$/NiFe bilayers.

The multilayer structure of $BiFeO_3/Ni_{81}Fe_{19}$ (BFO/NiFe) magnetic heterostructures was deposited on surface oxidized Si (100) substrates by pulsed laser deposition (PLD) for the oxide layers and magnetron sputtering for the metallic layers, with $LaNiO_3$ as buffer layer for $BiFeO_3$ and Ta as capping layer for protecting the NiFe layer from oxidization. It needs to be emphasized that both techniques are widely used in the industry, and our low-cost polycrystalline $BiFeO_3$ film based on Si substrate takes great advantage

---

* Corresponding author. Tel.: +86 2552090600x8308; fax: +86 2552090600 x8203.
E-mail address: xuqingyu@seu.edu.cn (Q. Xu).

0038-1098/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ssc.2011.12.004

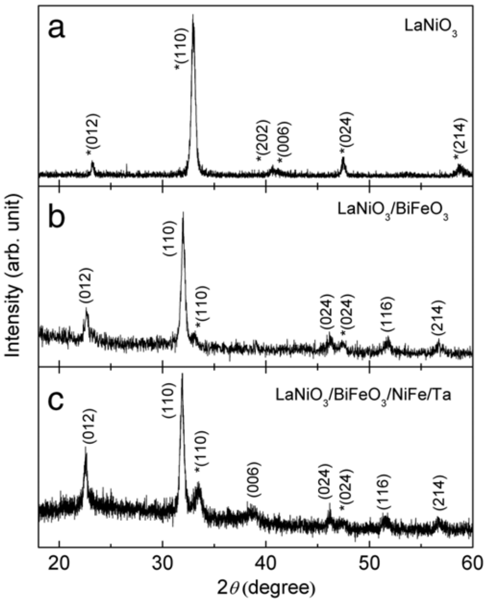

Fig. 1. XRD patterns of (a) $LaNiO_3$ singer layer, (b) $LaNiO_3/BiFeO_3$ bilayer and (c) $LaNiO_3/BiFeO_3$/NiFe/Ta multilayer. The star "*" marks the diffraction peaks from $LaNiO_3$, and the rest are from $BiFeO_3$.

on large-scale applications. The oxide films were fabricated by the PLD system with a KrF eximer laser of 248 nm and a repetition rate of 5 Hz. The laser energy was 300 mJ and target-to-substrate distance was kept at 6 cm. The thickness of the $BiFeO_3$ and $LaNiO_3$ films were controlled by the number of laser pulses. The $LaNiO_3$ buffer layer was grown first at a substrate temperature $T_s = 850\,°C$ in an oxygen pressure $P = 40$ Pa. Then the T_s decreased to 800 °C, and the $BiFeO_3$ was deposited in an oxygen pressure $P = 2$ Pa. After deposition, the heterostructures was annealed for 0.5 h at 550 °C and cooled down to room temperature in an oxygen pressure $P = 1 \times 10^5$ Pa. Then the $BiFeO_3$ films were transferred into a magnetron sputtering chamber, and a thin $Ni_{81}Fe_{19}$ (NiFe) film was deposited on them under a magnetic field of 150 Oe at room temperature, followed by a 5 nm Ta capping layer to prevent oxidation of the NiFe. The argon pressure during deposition was kept at 0.3 Pa, and the base pressure was lower than 8×10^{-6} Pa. The structure of the multilayer films was characterized by X-ray diffraction (XRD) with Cu $K\alpha$ radiation. The surface morphologies of $BiFeO_3$ films were studied by an atomic force microscope (AFM). The microstructures of the films were evaluated by a transmission electron microscope (TEM) using a cross-sectional specimen. The magnetic hysteresis loops were measured by a vibrating sample magnetometer (VSM) at room temperature. The ferroelectric hysteresis loops were measured using a commercial ferroelectric tester (Precision Multiferroic, Radiant Technologies) at room temperature.

Fig. 1 shows the XRD patterns of $LaNiO_3$ singer layer, $LaNiO_3/BiFeO_3$ bilayer, $LaNiO_3/BiFeO_3$/NiFe/Ta multilayer. It can be seen from the Fig. 1(a), all peaks can be indexed as $LaNiO_3$ in R-3c structure (PDF# 88-0633), and no peak of impure phases were observed. To our knowledge, it is very difficult to get single phase $BiFeO_3$ film by direct deposition on surface oxidized Si substrate. From Fig. 1(b), it can be clearly seen that except for the peaks which can be indexed to $LaNiO_3$, all the other peaks can be indexed to $BiFeO_3$ in the R3c structure (PDF# 86-1518), indicating that $LaNiO_3$ is an effective buffer layer for the crystallization of $BiFeO_3$. After the deposition of NiFe and Ta, similar XRD pattern can be observed, as shown in Fig. 1(c). One needs to be noted that NiFe is too thin (∼5 nm) and Ta is amorphous, thus the diffraction peaks of NiFe and Ta layers cannot be distinguished.

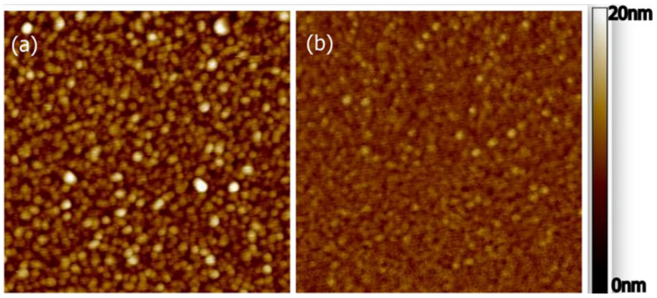

Fig. 2. AFM images (2 μm × 2 μm) of $BiFeO_3$ film (1.5 cm × 1.5 cm) at different regions: (a) center, (b) edge.

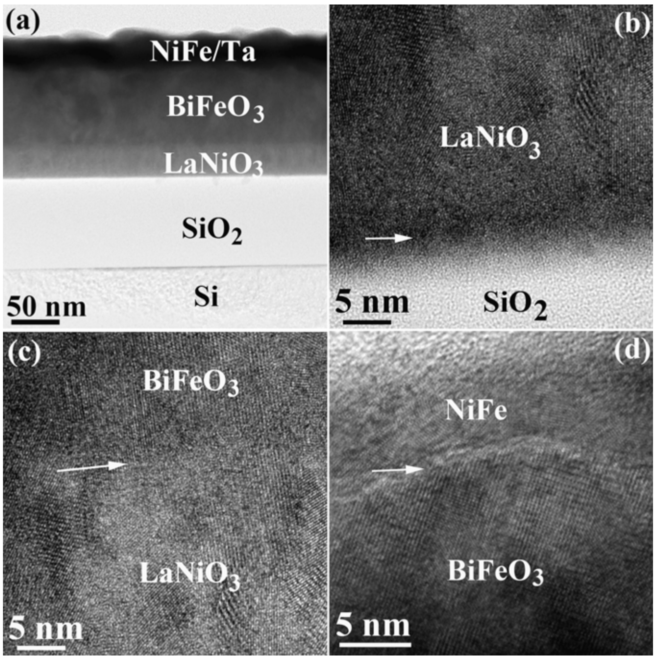

Fig. 3. Cross-sectional TEM images of the $LaNiO_3/BiFeO_3$/NiFe/Ta multilayer on surface oxidized Si (100) substrate: (a) low magnified image, and HRTEM images at the interface of (b) $SiO_2/LaNiO_3$, (c) $LaNiO_3/BiFeO_3$, (d) $BiFeO_3$/NiFe. The white arrow in (b) marks the amorphous thin layer, and in (c) and (d) marks the interface.

Fig. 2 shows the surface morphologies of $BiFeO_3$ films at different regions: (a) center of the $BiFeO_3$ films; (b) edges of the $BiFeO_3$ films. Though the substrates rotated during the film deposition in the PLD chamber, the laser path was fixed. The intensity of the laser power was not very uniform, i.e. stronger inside and weaker outside. Thus the deposition rates of the film in the center and edge of the substrates were slightly different and the thickness near the center of the film was a little larger consequently, which causes the roughness varying from center to edge regions consequently. The values of the root mean square roughness (rms) for the center and the edge were 2.2 nm and 1.0 nm, respectively, which is much smaller than that (9 nm) of $BiFeO_3$ film deposited on Pt buffered Si substrates by magnetron sputtering [11], indicating high quality of our polycrystalline $BiFeO_3$ film on $LaNiO_3$ buffered Si substrates. The center and edge regions in the $BiFeO_3$ film show similar morphologies of granular structure with granular size of about 50 nm.

Since TEM is very useful to characterize the microstructure, the interfaces of $SiO_2/LaNiO_3$, $LaNiO_3/BiFeO_3$ and $BiFeO_3$/NiFe in the $LaNiO_3/BiFeO_3$/NiFe/Ta multilayer were carefully investigated by TEM. Fig. 3(a) shows the TEM images of multilayers. $LaNiO_3$, $BiFeO_3$, NiFe/Ta layers can be clearly distinguished due to different contrasts, from which the thickness of the $BiFeO_3$ layer and $LaNiO_3$ layer can be determined to be about 80 nm and 30 nm,

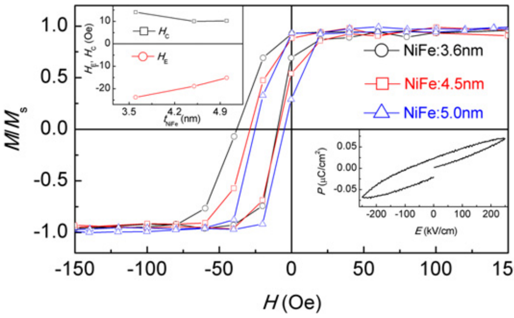

Fig. 4. Magnetic hysteresis loops of the Si/SiO_2/$LaNiO_3$/$BiFeO_3$/NiFe/Ta multilayer at room temperature. The top left inset shows the NiFe thickness dependence of H_E and H_C, and the right bottom inset shows the ferroelectric hysteresis loop for $BiFeO_3$ film measured at 20 kHz at room temperature.

respectively. Fig. 3(b)–(d) show the high resolution TEM (HRTEM) images. Fig. 3(b) shows the interface between SiO_2 and $LaNiO_3$. An amorphous thin layer with thickness of about 5 nm can be clearly seen, followed by the polycrystalline $LaNiO_3$ layer, as can be seen from the randomly oriented lattice fringes. Similar phenomenon has been observed at the interface of epitaxial $SrTiO_3$ films on Si substrates [12–14]. There is no abrupt interface found between the $LaNiO_3$ and $BiFeO_3$ layers in Fig. 3(c), and some lattice fringes from the crystals in $LaNiO_3$ layer extend to the $BiFeO_3$ layer, suggesting the possible epitaxial growth of $BiFeO_3$ grains on the $LaNiO_3$ buffer layer, since both of them have a perovskite structure and similar lattice parameters. The spacing of the lattice fringe in the NiFe layer close to the interface is about 2.08 Å, which corresponds to the (111) planes of metallic NiFe. Thus the possible oxidation of NiFe by $BiFeO_3$ at the interface is negligible.

A series of NiFe thin films with different thickness were deposited on the $BiFeO_3$ films. The corresponding magnetic hysteresis (M–H) loops are shown in Fig. 4. Obviously, the center position of M–H loops exhibit a shift (exchange bias field, H_E) toward negative fields and a concurrent enhancement of coercivity (H_C) in comparison with the free NiFe layer. The values of H_E and H_C are 23.8 Oe, 18.9 Oe, 15.1 Oe and 14.0 Oe, 10.0 Oe, 10.1 Oe when the thickness of the NiFe layer is 3.6 nm, 4.5 nm and 5.0 nm, respectively. For comparison, single NiFe films with the same thicknesses were made under the same conditions, which show no exchange bias and a very small coercive field of about 0.5 Oe. The left top inset of Fig. 4 displays the NiFe thickness dependence of H_E and H_C. This indicates that the exchange bias field decreases with increasing the NiFe thickness from 3.6 to 5.0 nm, which is consistent with the conventional inverse relationship with the thickness of the ferromagnetic layer [15,16]. This dependence reveals the interface nature of the exchange bias effect and reflects the origin of exchange bias as a competition between the Zeeman energy of the ferromagnetic layer and antiferromagnetic/ferromagnetic interface coupling energy [17]. The enhancement of the coercive field of NiFe films is more complicated, which is strongly affected by the grown quality of ferromagnetic and antiferromagnetic layers, micro-structure and defect distribution near the interface. Further studies reveal that besides the ferromagnetic layer thickness, the exchange bias effect is also affected by the $BiFeO_3$ layer thickness. The maximum value of H_E in the $BiFeO_3$/NiFe bilayer can be achieved as 61 Oe with the NiFe and $BiFeO_3$ layer thickness to be 3.6 nm and 40 nm respectively.

Though an overwhelming literature about the mechanism of exchange bias based on the $BiFeO_3$ has emerged [18,19], the physical origin of exchange bias are still being proposed, debated, and tested. To further explore the mechanism of exchange bias based on the $BiFeO_3$, we also did a series of follow-up works, such as: the dependence of exchange bias on the $BiFeO_3$ thickness, the dependence of exchange bias on the temperature, the angular dependence of the exchange bias and asymmetrical magnetization reversal, the exchange bias training effect and etc., which are in preparation for another paper.

The ferroelectric hysteresis loop of $BiFeO_3$ film prepared under the same conditions was also measured at room temperature at 20 kHz, as shown in the right bottom inset of Fig. 4. However, the polarization is small, which is due to the fact that the film was seriously leaking and thus a large enough electric field could not be applied. Further investigations are being performed to suppress the leakage current and improve the ferroelectric properties of the $BiFeO_3$ films consequently.

In conclusion, single phase polycrystalline $BiFeO_3$ film has been successfully grown on surface oxidized Si substrates by employing $LaNiO_3$ as a buffer layer, and the exchange biased $BiFeO_3$/NiFe bilayers were prepared by combination of PLD and magnetron sputtering techniques. An obvious exchange bias effect was observed at room temperature and the exchange bias field decrease with increasing the NiFe layer thickness. Although the physical origin responsible for the exchange bias effect in $BiFeO_3$/ferromagnetic bilayers needs further study, the present results are promising for continued studies of $BiFeO_3$ based multiferroic magnetic devices and eventual production of electrically tunable magnetic devices.

Acknowledgments

This work is supported by National Key Projects for Basic Researches of China (2010CB923401, 2010CB923404, 2009CB929503) the National Natural Science Foundation of China (51172044, 11074112, 91022001 and 11174131), the National Science Foundation of Jiangsu Province of China (BK2011617), NCET-09-0296, the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, and Southeast University.

References

[1] N.A. Spaidin, M. Fiebig, Science 309 (2005) 391.
[2] Y.H. Chu, L.W. Martin, M.B. Holcomb, M. Gajek, S.J. Han, Q. He, N. Blake, C.H. Yang, D. Lee, W. Hu, Q. Zhan, P.L. Yang, A. Fraile-Rodrìguez, A. Scholl, S.X. Wang, R. Ramesh, Nature Mater. 7 (2008) 478.
[3] H.H. Kim, J.H. Dho, X. Qi, S.K. Kang, J.L. Macmanus-Driscoll, D.J. Kang, K.N. Kang, M.G. Blamire, Ferroelectrics 333 (2006) 157.
[4] J. Wang, J.B. Neaton, V. Nagaragan, 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, Science 299 (2003) 1719.
[5] G. Catalan, H. Béa, S. Fusil, M. Bibes, P. Paruch, A. Barth élémy, J.F. Scott, Phys. Rev. Lett. 100 (2008) 027602.
[6] T. Zhao, A. Scholl, F. Zavaliche, K. Lee, M. Barry, A. Doran, M.P. Cruz, Y.H. Chu, C. Ederer, N.A. Spaldin, R.R. Das, D.M. Kim, S.H. Baek, C.B. Eom, R. Ramesh, Nature Mater. 5 (2006) 823.
[7] Ch. Binek, B. Doudin, J. Phys.: Condens. Matter 17 (2005) L39.
[8] H. Béa, M. Bibes, S. Cherifi, F. Nolting, B. Warot-Fonrose, S. Fusil, G. Herranz, C. Deranlot, E. Jacquet, K. Bouzehouane, A. Barthélémy, Appl. Phys. Lett. 89 (2006) 242114.
[9] J. Dho, X. Qi, H. Kim, J.L. MacManus-Driscoll, M.G. Blamire, Adv. Mater. 18 (2006) 1445.
[10] L.W. Martin, Y.H. Zhu, Q. Zhan, R. Ramesh, Appl. Phys. Lett. 91 (2007) 172513.
[11] T. Hauguel, S.P. Pogossian, D.T. Dekadjevi, D. Spenato, J.P. Jay, M.V. Indenbom, J.B. Youssef, J. Appl. Phys. 110 (2011) 073906.
[12] X. Hu, H. Li, Y. Liang, Y. Wei, Z. Yu, D. Marshall, J. Edwards Jr., R. Droopad, X. Zhang, A.A. Demkov, K. Moore, J. Kulik, Appl. Phys. Lett. 82 (2003) 203.
[13] G.J. Yong, Rajeswari.M. Kolagani, S. Adhikari, W. Vanderlinde, Y. Liang, K. Muramatsu, S. Friedrich, Appl. Phys. Lett. 108 (2010) 033502.
[14] G.J. Yong, Rajeswari M. Kolagani, B.P. Hoffmann, S. Adhikari, Y. Liang, V.N. Smolyaninova, Appl. Phys. Lett. 109 (2011) 063913.
[15] V. Baltz, J. Sort, S. Landis, B. Rodmacq, B. Dieny, Phys. Rev. Lett. 94 (2005) 117201.
[16] G. Malinowski, M. Albrecht, I.L. Guhr, J.M.D. Coey, S. van Dijken, Phys. Rev. B 75 (2007) 012413.
[17] S. Polisetty, S. Sahoo, C. Binek, Phys. Rev. B 76 (2007) 184423.
[18] D. Lebeugle, A. Mougin, M. Viret, D. Colson, J. Allibe, H. Béa, E. Jacquet, C. Deranlot, M. Bibes, A. Barthélémy, Phys. Rev. B 81 (2010) 134411.
[19] L.W. Martin, Y.H. Chu, M.B. Holcomb, M. Huijben, P. Yu, S.J. Han, D. Lee, S.X. Wang, R. Ramesh, Nano Lett. 8 (2008) 2050.