This document is downloaded from DR-NTU (https://dr.ntu.edu.sg)
Nanyang Technological University, Singapore.

Temperature-dependent leakage current characteristics of Pr and Mn cosubstituted BiFeO3 thin films

Wu, Di; Wen, Zheng; Shen, Xuan; Wu, Jingxian; Li, Aidong; Yang, Bin; Wang, Zhu; Chen, Hengzhi; Wang, Junling

2010

Wen, Z., Shen, X., Wu, J., Wu, D., Li, A., Yang, B., et al. (2010). Temperature-dependent leakage current characteristics of Pr and Mn cosubstituted BiFeO3 thin films. Applied Physics Letters, 96.

https://hdl.handle.net/10356/98605

https://doi.org/10.1063/1.3432083

© 2010 American Institute of Physics. This paper was published in Applied Physics Letters and is made available as an electronic reprint (preprint) with permission of American Institute of Physics. The paper can be found at the following DOI: http://dx.doi.org/10.1063/1.3432083. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.

Downloaded on 26 Jan 2022 21:32:20 SGT

Temperature-dependent leakage current characteristics of Pr and Mn cosubstituted $BiFeO_3$ thin films

Zheng Wen,[1] Xuan Shen,[1] Jingxian Wu,[1] Di Wu,[1,a)] Aidong Li,[1] Bin Yang,[2] Zhu Wang,[2] Hengzhi Chen,[2] and Junling Wang[3]

[1]*Department of Materials Science and Engineering and National Laboratory of Solid State Microstructures, Nanjing University, Nanjing, Jiangsu 210093, People's Republic of China*

[2]*Department of Physics, Center for Condensed Matter Science and Technology, Harbin Institute of Technology, Harbin 150080, People's Republic of China*

[3]*School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798*

(Received 15 March 2010; accepted 28 April 2010; published online 20 May 2010)

Leakage current characteristics of $(Bi_{0.86}Pr_{0.14})(Fe_{0.95}Mn_{0.05})O_3$ (BPFMO) thin films are studied at various temperatures from 293 down to 93 K. Space charge limited current and Poole–Frenkel (PF) emission are found to be the dominant mechanism in the low and the high electric fields, respectively. The trap ionization energy at zero-field in BPFMO films is deduced to be around 0.29 eV, which indicates the existence of shallow traps. A negative differential resistivity behavior is observed before the onset of PF emission at 93 K, which is discussed in terms of the competition between electron trapping and field-assisted thermal emission. © *2010 American Institute of Physics*. [doi:10.1063/1.3432083]

As a promising multiferroic material, $BiFeO_3$ (BFO) thin films have shown great potential for applications on high-density ferroelectric random access memories (FeRAMs) due to their large remanent polarization ($Pr \geq 60\ \mu C/cm^2$) at room temperature.[1,2] It is well known that the leakage current characteristics are very critical in FeRAMs applications of ferroelectric films due to its direct relation to power consumption and long-term reliability of the storage elements. Unfortunately, BFO thin films suffer from high leakage currents as the results of the existence of Fe^{2+} and oxygen vacancies,[2–5] hindering its applications in memory devices.

Recently, ion substitutions, using transition metal (TM) ions such as Mn, Ti, Cr, Co, and Cu ions, have been adopted to suppress Fe^{2+} and to decrease the concentration of oxygen vacancies in BFO films.[3,6–11] Especially, Mn-substituted BFO films have exhibited improved breakdown resistance and reduced leakage current densities at high fields.[6–8] Furthermore, cosubstitutions of Bi^{3+} and Fe^{3+} ions with lanthanide ions and TM ions, respectively, have been verified effective to suppress the leakage current and to enhance the overall properties of BFO films.[12–14] For example, Cheng *et al.*[14] observed an increased remanent polarization and an improved fatigue resistance in the La and Nb cosubstituted BFO films in contrast to the La-substituted film. On the other hand, Pr-substituted BFO films and ceramics have been found to show intriguing ferromagnetic hysteresis loops although BFO is antiferromagnetic in itself.[15,16] Therefore, it is interesting to investigate the BFO films cosubstituted with Pr and Mn ions. In this paper, we report on the leakage current characteristics of $(Bi_{0.86}Pr_{0.14})(Fe_{0.95}Mn_{0.05})O_3$ (BPFMO) thin films sandwiched between Pt and indium tin oxide (ITO) electrodes. Current-field characteristics of Pt/BPFMO/ITO capacitors at various temperatures from 293 down to 93 K are analyzed to deduce the conduction mechanisms. The results are discussed in terms of the competition between electron trapping and field-assisted thermal emission, resulting in a space charge limited current (SCLC) in the low field regime, a Poole–Frenkel (PF) emission in the high field regime and a negative differential resistivity (NDR) in between.

BPFMO thin films were deposited onto ITO/glass substrates using chemical solution deposition. The precursor solutions were prepared by dissolving $Bi(NO_3)_3 \cdot 5H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Mn(CH_3COO)_2 \cdot 2H_2O$, and $Pr(NO_3)_3 \cdot 6H_2O$ in acetic acid. Ethylene glycol was added for adjusting the viscosity. Citrate acid was added as the chelating agent. The final concentration was adjusted to 0.2 mol/l. The BPFMO films were deposited by spin coating at 4000 rpm for 30 s, pyrolyzed at 400 °C for 10 min in flowing O_2 and annealed at 525 °C for 5 min in flowing N_2. These steps were repeated several times to increase film thickness. Then a final annealing at 525 °C for 30 min in flowing N_2 was performed to achieve better crystallinity. The final film thickness is about 300 nm. In preparing BFO films, N_2-annealing is often used.[17,18] It has been proved effective to suppress secondary phases, which is prone to appear in O_2-annealed films. Pt top electrodes of 200 μm in diameter were sputter-deposited with a shadow mask. These films were characterized by x-ray diffraction (XRD) using a Rigaku Ultima III diffractometer with Cu $K\alpha$ radiation. Hysteresis loops and leakage currents were measured using a Precision Premier II ferroelectric tester (Radiant Technologies).

Figure 1(a) shows XRD pattern of the BPFMO film. This pattern can be indexed using a distorted rhombohedral $R3c$ structure.[19] The film is of a single phase and no peaks from secondary phases can be detected. Thus, the influence of impurities on the electric properties can be ruled out. A well-saturated hysteresis loop measured at 5 kHz is shown in the inset of Fig. 1(a). As shown in Fig. 1(b), leakage current density of the BPFMO film decreases monotonically with decreasing temperature. One may notice that the leakage current characteristics of BPFMO film are symmetric under positive and negative bias although the top and bottom electrodes are of different materials. Thus, the predominant con-

a)Electronic mail: diwu@nju.edu.cn.

 © 2010 American Institute of Physics

Downloaded 19 Jun 2011 to 155.69.4.4. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions

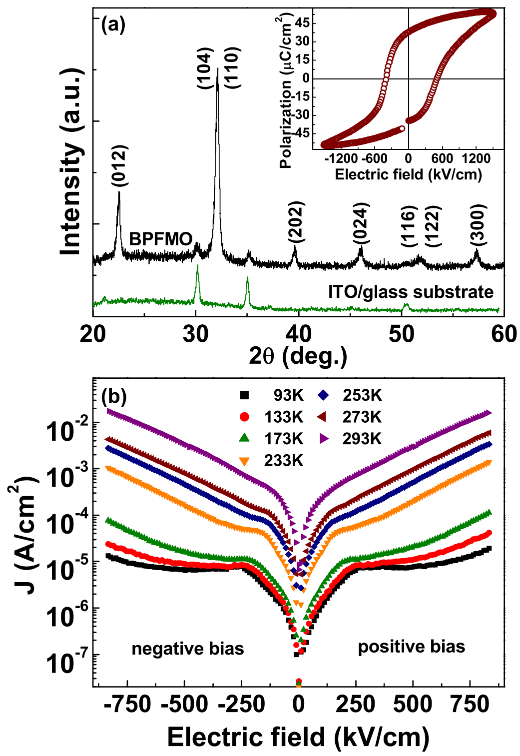

FIG. 1. (Color online) (a) XRD pattern of the BPFMO film. The inset is a room temperature hysteresis loop. (b) Leakage currents of the BPFMO film as functions of electric field at various temperatures.

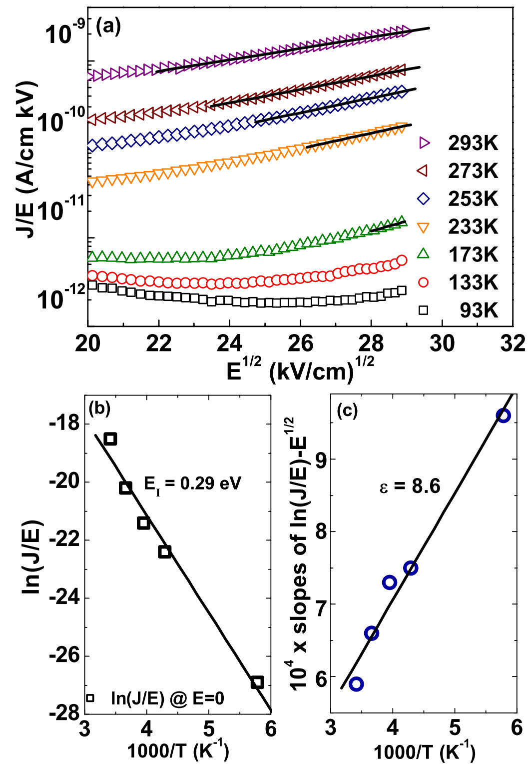

FIG. 3. (Color online) (a) Log(J/E) plotted against $E^{1/2}$ for leakage currents at high fields at various temperatures; (b) a plot of ln(J/E) (at $E=0$) vs $1000/T$; and (c) slopes of $\ln(J/E)-E^{1/2}$ curves vs $1000/T$.

duction mechanisms of Pt/BPFMO/ITO capacitor should be bulk-limited, such as SCLC and PF emission.[20–22]

Figure 2 shows low field leakage current density (J) of the BPFMO film as functions of electric field (E) at various temperatures. The J-E curves can be fitted well by the modified Langmuir–Child law[3,23]

$$J = \alpha E + \beta E^2. \tag{1}$$

The coefficients α and β, obtained from the fitting, are plotted against measurement temperatures in the inset of Fig. 2. With decreasing temperature, both α and β decreases, which indicates that both Ohmic and space charge limited contributions decrease. However, it can be found that α decreases much faster than β as temperature decreases from 293 to 133 K. At 93 K, α reduces to zero and a pure SCLC characteristic is observed. This indicates that the bulk-generated carriers are gradually exceeded by the injected electrons with the decrease in temperature.[3]

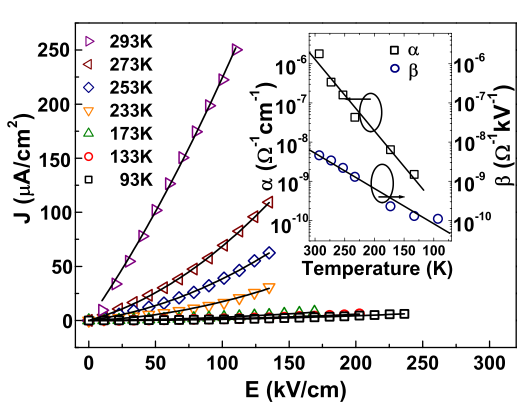

FIG. 2. (Color online) J-E curves of the Pt/BPFMO/ITO capacitor at low fields. The solid lines are fits to the data according to the modified Langmuir–Child law; the inset shows the variation in fitting parameters α and β as functions of temperature.

PF emission has been observed frequently as a dominant conduction mechanism in BFO-based thin films under high electric fields.[4,5] PF emission obeys[24]

$$\frac{J}{E} = c \exp\left\{-\frac{1}{k_B T}\left[E_I - \left(\frac{q^3 E}{\pi \epsilon_0 \epsilon}\right)^{1/2}\right]\right\}, \tag{2}$$

where c is a constant; E_I is the trap ionization energy; k_B is the Boltzmann's constant; q is the unit of electronic charge; ϵ_0 is the dielectric permittivity of vacuum; and ϵ is the optical-frequency dielectric constant of the film. As shown in Fig. 3(a), where J/E is presented against $E^{1/2}$ in a semilog plot, the data from 293 to 173 K fit well to the PF emission when E is above 500 kV/cm with the onset electric field of PF emission increasing with the decrease in temperature. The leakage current characteristics at 133 and 93 K do not fit to the PF emission. It is well known that PF effect is the thermal emission of electrons overcoming the Coulomb barrier between electrons and positively charged traps with the help of the applied field.[24] Thus, at low temperatures, higher electric field is required to activate trapped electrons to have a contribution to the conduction. At 133 and 93 K, the onset of PF emission may likely exceed the maximum field reached in this work (830 kV/cm).

Figure 3(b) shows an Arrhenius plot of the J/E values extrapolated to $E=0$. The zero-field trap ionization energy E_I of BPFMO is estimated to be about 0.29 eV from the slope of the linear fit. It has been reported that PF trap ionization energy for BFO ranges from 0.65 to 0.80 eV.[4,5] The smaller zero-field E_I in this work indicates the existence of shallow traps in the band gap of BPFMO. Clark *et al.*[25] has reported

Downloaded 19 Jun 2011 to 155.69.4.4. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions

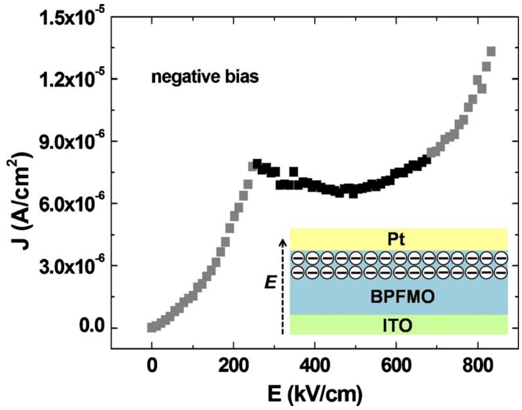

FIG. 4. (Color online) The NDR in the *J-E* curve under negative bias at 93 K. The inset shows the depletion layer near the cathode schematically.

that energy levels associated with shallow oxygen vacancies including V_o, $(V_{o^{1-}})^{\cdot}$, and $(V_{o^{2-}})^{\cdot\cdot}$, are of 0.2–0.4 eV below the bottom of the conduction band in BFO. Simmons[26] has proposed a model taking into account the coexistence of shallow traps and deep donors in insulated thin films. It was deduced that the potential attenuation due to the image force interaction in PF emission will be reduced by a factor of 2 due to such coexistence. Using this model, the ϵ of BPFMO can be determined to be about 8.6 from the slopes of the linear fit to the $\ln(J/E)-E^{1/2}$ plot, as shown in Fig. 3(c). This value is larger than that of BFO as reported by Iakovlev and coworkers.[27]

Figure 4 shows the NDR behavior observed in BPFMO film at 300–500 kV/cm at 93 K. The NDR have also been observed in $SrBi_2Ta_2O_9$ and $Pb(Zr,Ti)O_3$ films.[28–30] This behavior can be attributed to the existence of a near cathode depletion region in ferroelectric thin films induced by electron trapping.[21,29–31] As schematically depicted in the inset of Fig. 4, the negatively charged depletion layer screens the applied field and reduces the density of injected electrons from the cathode. At low applied fields, trapping process is dominant, which generates a SCLC behavior. With the increase in the applied field, the screening gets stronger as the depletion layer widens and may finally cause a decrease in current density, i.e., $\Delta J/\Delta E<0$. The NDR occurs. As the applied field further increases, field-assisted emission process may be dominant. This results in a PF emission character. Therefore, the NDR occurs only in the transition region from SCLC to PF emission, where there is a competition between electron trapping by positively charged defects and emitting by the PF effect. It is also worth noting that the NDR behavior cannot be observed at higher temperatures. The trapped electrons can be readily emitted with the assistance of the applied field at high temperatures, resulting in a decrease in the depletion layer thickness near cathode. Thus, the screening cannot reach the threshold to induce NDR.

In summary, the leakage current mechanisms of Pt/BPFMO/ITO thin-film capacitors are investigated at various temperatures from 293 down to 93 K. SCLC and PF emission are found to be dominant in low and high electric fields, respectively. A small zero-field ionization energy of 0.29 eV is obtained, which indicates the existence of shallow traps in BPFMO film. The onset field of PF emission is found to increase with the decrease in temperature. The NDR behavior is observed in the transition region between SCLC and PF emission mechanisms. These can be understood considering the competition between electron trapping and field-assisted thermal emission.

This work was jointly sponsored by the Natural Science Foundation of China (Grant Nos. 50872050 and 10704021), the State Key Program for Basic Research of China (Grant No. 2009CB929503) and an open project of the National Laboratory of Solid State Microstructures.

[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, and R. Ramesh, Science **299**, 1719 (2003).
[2]J. Dho, X. Qi, H. Kim, J. L. MacManus-Driscoll, and M. G. Blamire, Adv. Mater. (Weinheim, Ger.) **18**, 1445 (2006).
[3]X. Qi, J. Dho, R. Tomov, M. G. Blamire, and J. L. MacManus- Driscoll, Appl. Phys. Lett. **86**, 062903 (2005).
[4]G. W. Pabst, L. W. Martin, Y. H. Chu, and R. Ramesh, Appl. Phys. Lett. **90**, 072902 (2007).
[5]H. Yang, M. Jain, N. A. Suvorova, H. Zhou, H. M. Luo, D. M. Feldmann, P. C. Dowden, R. F. DePaula, S. R. Foltyn, and Q. X. Jia, Appl. Phys. Lett. **91**, 072911 (2007).
[6]S. K. Singh, H. Ishiwara, and K. Maruyama, Appl. Phys. Lett. **88**, 262908 (2006).
[7]S. K. Singh, H. Ishiwara, K. Sato, and K. Maruyama, J. Appl. Phys. **102**, 094109 (2007).
[8]T. Kawae, Y. Terauchi, H. Tsuda, M. Kumeda, and A. Morimoto, Appl. Phys. Lett. **94**, 112904 (2009).
[9]Z. Wen, G. Hu, S. Fan, C. Yang, W. Wu, Y. Zhou, X. Chen, and S. Cui, Thin Solid Films **517**, 4497 (2009).
[10]J. K. Kim, S. S. Kim, W.-J. Kim, A. S. Bhalla, and R. Guo, Appl. Phys. Lett. **88**, 132901 (2006).
[11]H. Naganuma, J. Miura, and S. Okamura, Appl. Phys. Lett. **93**, 052901 (2008).
[12]T. Kawae, H. Tsuda, and A. Morimoto, Appl. Phys. Express **1**, 051601 (2008).
[13]S. K. Singh, K. Maruyama, and H. Ishiwara, Appl. Phys. Lett. **91**, 112913 (2007).
[14]Z. Cheng, X. Wang, S. Dou, H. Kimura, and K. Ozawa, Phys. Rev. B **77**, 092101 (2008).
[15]B. Yu, M. Li, Z. Hu, L. Pei, D. Guo, X. Zhao, and S. Dong, Appl. Phys. Lett. **93**, 182909 (2008).
[16]P. Uniyal and K. L. Yadav, J. Phys.: Condens. Matter **21**, 405901 (2009).
[17]J. K. Kim, S. S. Kim, and W. J. Kim, Integr. Ferroelectr. **76**, 103 (2005).
[18]V. R. Singh, A. Dixit, A. Garg, and D. C. Agrawal, Appl. Phys. A: Mater. Sci. Process. **90**, 197 (2007).
[19]I. Sosnowska, R. Przenioslo, P. Fischer, and V. A. Murashov, J. Magn. Magn. Mater. **160**, 384 (1996).
[20]D. Wu, A. Li, and N. Ming, J. Appl. Phys. **97**, 106110 (2005).
[21]J. F. Scott, *Ferroelectric Memories* (Springer, Berlin, 2000).
[22]S. J. Clark and J. Robertson, Appl. Phys. Lett. **90**, 132903 (2007).
[23]R. H. Tredgold, *Space Charge Conduction in Solids* (Elsevier, Amsterdam, 1966).
[24]J. Frenkel, Phys. Rev. **54**, 647 (1938).
[25]S. J. Clark and J. Robertson, Appl. Phys. Lett. **94**, 022902 (2009).
[26]J. G. Simmons, Phys. Rev. **155**, 657 (1967).
[27]S. Iakovlev, C.-H. Solterbeck, M. Kuhnke, and M. Es-Souni, J. Appl. Phys. **97**, 094901 (2005).
[28]K. Watanabe, A. J. Hartmann, R. N. Lamb, and J. F. Scott, J. Appl. Phys. **84**, 2170 (1998).
[29]A. K. Maity, J. Y. Lee, A. Sen, and H. S. Maiti, Jpn. J. Appl. Phys., Part 1 **43**, 7155 (2004).
[30]H. D. Chen, K. R. Udayakumar, K. K. Li, C. J. Gaskey, and L. E. Cross, Integr. Ferroelectr. **15**, 89 (1997).
[31]J. F. M. Cillessen, M. W. J. Prins, and R. M. Wolf, J. Appl. Phys. **81**, 2777 (1997).

Downloaded 19 Jun 2011 to 155.69.4.4. Redistribution subject to AIP license or copyright; see http://apl.aip.org/about/rights_and_permissions