Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) 4031–4034

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Fast ferroelectric domain wall motion in $BiAlO_3$

Jong Yeog Son[a,*], Sung Min Yoon[b]

[a]Department of Applied Physics, College of Applied Science, Kyung Hee University, Suwon 446-701, Republic of Korea
[b]Department of Advanced Materials Engineering for Information & Electronics, Kyung Hee University, Suwon 446-701, Republic of Korea

Received 17 September 2012; received in revised form 25 October 2012; accepted 26 October 2012
Available online 3 November 2012

Abstract

The ferroelectric domain wall motion was investigated in epitaxial $PbTiO_3$ and $BiAlO_3$ thin films on $SrRuO_3/SrTiO_3$ substrates. To determine the switching speeds of two ferroelectric capacitors consisting of $PbTiO_3$ and $BiAlO_3$ thin films, the switching currents of the two capacitors were measured as a function of time. The $BiAlO_3$ thin film showed faster switching behavior than the $PbTiO_3$ thin film. Data from a piezoelectric force microscope study indicated that the high domain wall motion of the $BiAlO_3$ thin film is due to its low activation energy.

Keywords: Ferroelectric thin film; Domain wall speed; Activation energy

1. Introduction

Ferroelectric random access memory (FeRAM) consists of one transistor and one capacitor, and is similar in construction to dynamic RAM (DRAM). When it is used as non-volatile storage, it exhibits much faster operating characteristics than flash memory [1–5]. In FeRAM, ferroelectric thin films such as $Pb(Zr,Ti)O_3$ act as a dielectric medium, determining the operating speed of the FeRAM. The ferroelectric polarization is switchable with a switching time near a few nanoseconds, due to the use of an external electric field [6–9]. Various ferroelectric materials are used in FeRAM applications; established Pb-based materials, as well as new ferroelectric materials such as $BiAlO_3$, $BiAlO_3$, $ZnSnO_3$, $AgNbO_3$, and Bi_2ZnTiO_6, which can be used as substitutes for the Pb-based materials [10–13].

Many researchers have performed studies regarding ferroelectric switching dynamics, though only for established ferroelectric materials such as $BaTiO_3$ and $PbTiO_3$, which show fast ferroelectric switching behaviors within tens of nanoseconds [2]. Theoretical studies of ferroelectric switching dynamics have supported the experimental results, which determine the activation energy and the size of the critical nuclei for established ferroelectric materials such as $BaTiO_3$ and $PbTiO_3$ [14,15]. This information makes it possible to choose a ferroelectric material which will satisfy the demands of manufacturers to scale down the size of devices and increase operating speed. In light of this, it is necessary to study ferroelectric switching behavior for various new ferroelectric materials. Multiferroic $BiAlO_3$ in particular differs from established ferroelectric materials like $BaTiO_3$ and $PbTiO_3$ in that the Al atom of the AlO_6 octahedron in $BiAlO_3$ moves during ferroelectric domain switching [10,16]. In this study, the ferroelectric switching characteristics of heteroepitaxial ferroelectric $PbTiO_3$ and heteroepitaxial multiferroic $BiAlO_3$ thin films were demonstrated. The switching current was measured as a function of time for the $PbTiO_3$ and $BiAlO_3$ capacitors, and the domain wall speed was observed using piezoelectric force microscopy (PFM).

2. Experimental procedures

Epitaxial $PbTiO_3$ and $BiAlO_3$ thin films were deposited on (001) $SrRuO_3$/(100) $SrTiO_3$ substrates using pulsed laser deposition (PLD). For fabrication of the (001) $SrRuO_3$/(100) $SrTiO_3$ substrate, $SrRuO_3$ thin films were also deposited on single crystalline (100) $SrTiO_3$ substrates using PLD. A commercially available 1-inch $SrRuO_3$ target was used for

*Corresponding author.
E-mail addresses: jyson@khu.ac.kr (J.Y. Son), sungmin@khu.ac.kr (S.M. Yoon).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.10.253

the ablation. A frequency-tripled (355 nm, ~2 J/cm^2) Nd:YAG laser was used for the deposition, and the distance between the target and the substrate was ~4 cm. For deposition of the epitaxial $BiAlO_3$ thin films, 1-inch $Bi_{1.2}FeO_3$ pellets (in which the Bi concentration was increased because of the Bi volatilization) were used as a PLD target. The base pressure was $\sim 10^{-7}$ Torr, and the oxygen pressure was maintained at 100 mTorr prior to deposition of the $SrRuO_3$ thin films. The substrate temperature was set to 800 °C, with an oxygen partial pressure of 100 mTorr. After the deposition, the thin films were cooled to room temperature in oxygen ambient at 300 Torr.

The thicknesses of the $PbTiO_3$ and $BiAlO_3$ thin films were 100 nm, as measured by a cross-sectional image obtained using scanning electron microscopy (SEM). A c/a ratio of 1.05 was estimated for the $PbTiO_3$ thin film, with a c-lattice constant of 4.14 Å and an a-lattice constant of 3.94 Å. A c-lattice constant of 4.00 Å and an a-lattice constant of 3.94 Å was obtained from the (002) and (110) peaks of the $BiAlO_3$ thin film, producing a c/a ratio of 1.02 [13]. The surface morphology and roughness of the thin films were observed using SEM and an atomic force microscope (AFM). The root mean square roughnesses of the $PbTiO_3$ and $BiAlO_3$ thin films were obtained from the AFM images of the $PbTiO_3$ and $BiAlO_3$ thin films, respectively. RF magnetron sputtering was used to deposit Pt top electrodes on the films in the form of 100 μm dots with a 20 nm thickness. The electrodes were then annealed at 400 °C for 5 min prior to performing the ferroelectric hysteresis loop tests. The ferroelectric hysteresis loop was measured using an RT66A (Radiant Technologies, Inc.) test system.

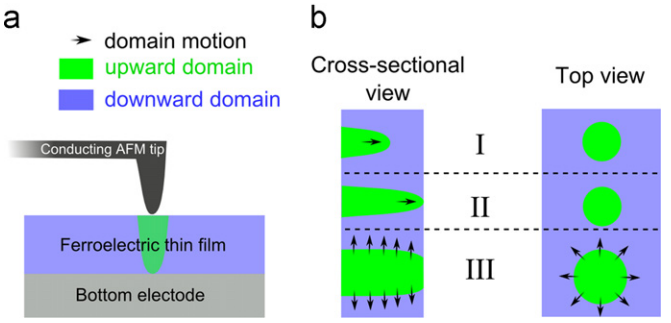

Fig. 1. (a) Ferroelectric domain switching by conducting atomic force microscope (CAFM) tip. (b) Three stages for ferroelectric domain switching: (I) nucleation, (II) growth, and (III) propagation (domain wall motion).

3. Results and discussion

Fig. 1 shows schematic drawings for the ferroelectric domain switching phenomenon of a ferroelectric thin film using a biased conducting AFM tip. There are three stages of ferroelectric domain switching: (I) nucleation, (II) growth, and (III) propagation, as shown in Fig. 1(b). After the nucleation and growth processes, the switched domain propagates around the nucleation in the form of domain wall motion [15,17]. In the case of ferroelectric capacitors, the speed of ferroelectric polarization switching is dependent on the statistical results of random nuclei [18]. In addition, fast domain wall motion allows rapid ferroelectric polarization switching when the number of nuclei are uniform [17,18]. Usually, the PFM observations of the ferroelectric domain switching behavior in thin films give information related to domain wall motion as well as the activation energy of the domain wall motion. Here, the domain wall motions of the $PbTiO_3$ and $BiAlO_3$ thin films were compared.

To measure the ferroelectric properties, hysteresis loops of the $PbTiO_3$ and $BiAlO_3$ thin films were observed at a measurement frequency of 10 kHz, as shown in Fig. 2(a). The $PbTiO_3$ and $BiAlO_3$ thin films exhibit high remanent polarizations of 94 μC/cm^2 and 30 μC/cm^2, respectively. To determine the response properties of $PbTiO_3$ and $BiAlO_3$ thin film capacitors to a switching bias, the switching current was measured for a switching bias of 5 V, as shown in Fig. 2(b). A square pulse with a rise time of about 1 ns was used for this switching. Before the measurement of the switching currents as a function of time, a negative bias (−5 V) was applied to the capacitors to define the direction of ferroelectric polarizations in two capacitors. After this process, a positive bias (+5 V) was applied as a switching bias to two capacitors. When the positive bias was applied to the capacitors, the currents of the capacitors were measured as

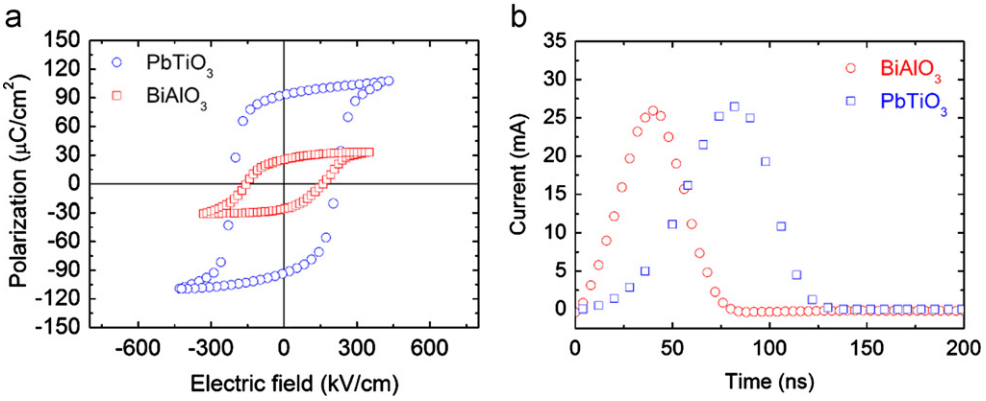

Fig. 2. (a) Hysteresis loops of the $PbTiO_3$ and $BiAlO_3$ thin films and (b) Switching current as a function of time for the $PbTiO_3$ and $BiAlO_3$ thin films.

a function of time. The switching currents as function of time correspond well to the ferroelectric switching time in a ferroelectric capacitor. The $BaAlO_3$ thin film shows faster switching behavior within 125 ns than the $PbTiO_3$ thin film. The area of the switching current curve is proportional to the quantity of ferroelectric polarization charges. The $PbTiO_3$ thin film has a current curve with a larger area than that of the $BiAlO_3$ thin film, which corresponds well to the higher ferroelectric polarization of the $PbTiO_3$ thin film as compared to that of the $BiAlO_3$ thin film.

The surface morphology of the $BiAlO_3$ thin film was observed by AFM, as shown in Fig. 3(a). There are terraces with intervals of about 100 nm, indicating the atomically flat surface of the $BiAlO_3$ thin film. The root mean square (RMS) surface roughness is estimated to be approximately 0.7 nm. The ferroelectric domain structure of the $BiAlO_3$ thin film was also observed by PFM using a 10 kHz ac voltage, applied by the Pt/Ir coated tip ($f_0 \sim 75$ kHz, $k \sim 2$ N/m, Fig. 3(b)). During the PFM measurements, the PFM tip displacement along the out-of-plane direction was

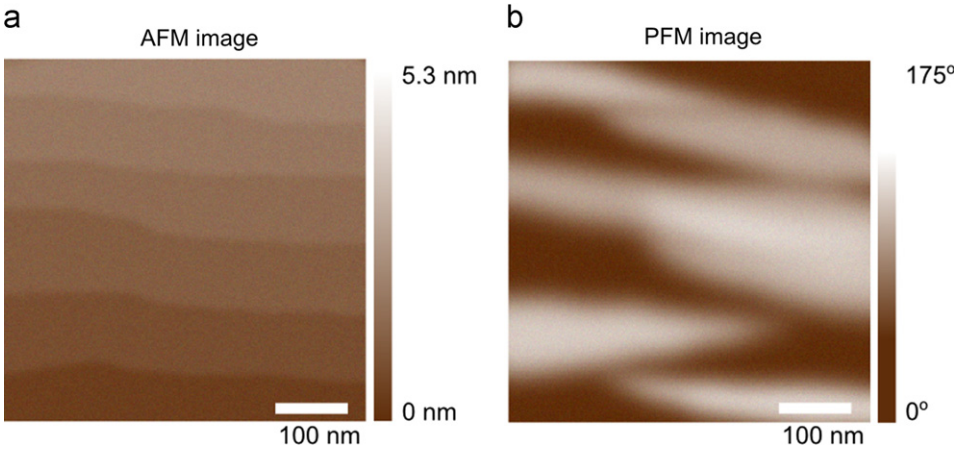

Fig. 3. (a) An AFM image of the $BiAlO_3$ thin film. (b) A PFM image of the $BiAlO_3$ thin film.

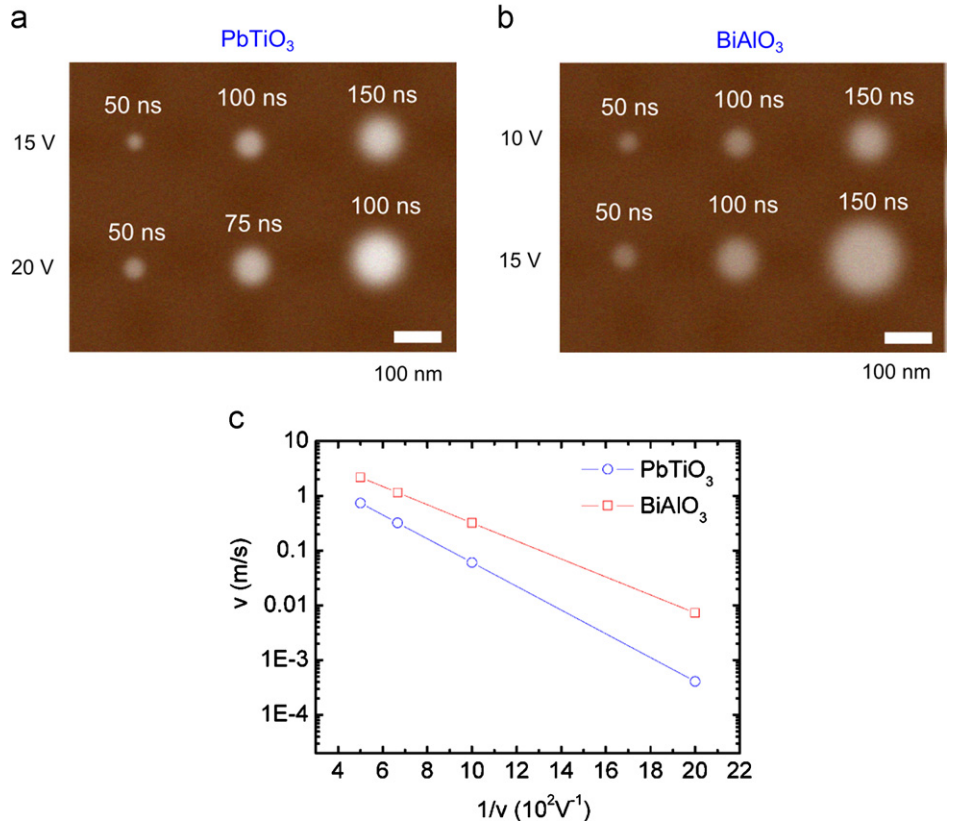

Fig. 4. PFM images of the ferroelectric polarization bits in the (a) $PbTiO_3$, (b) $BiAlO_3$ thin films and (c) Domain wall speeds as a function of applied bias voltage for the $PbTiO_3$ and $BiAlO_3$ thin films.

recorded using a lock-in amplifier, and the d_{33} was obtained from the slope of the resulting displacement as a function of an applied bias at the PFM tip. $BiAlO_3$ exhibits a stripe domain structure. The polarized domains properly correspond to the rectangular surface morphology with different polarization directions and magnitudes. The pattern size of the $BiAlO_3$ thin film is larger than that of the $PbTiO_3$, indicating that the $BiAlO_3$ has lower domain wall energy than that of the $PbTiO_3$ [19].

To determine the domain wall speeds of the $PbTiO_3$ and $BiAlO_3$ thin films, PFM images of the ferroelectric polarization bits were observed after domain switching with various bias voltages in the range of 5–20 V, and switching times in the range of 50–200 ns. Fig. 4 shows the PFM images of the ferroelectric polarization bits for the $PbTiO_3$ and $BiAlO_3$ thin films. The ferroelectric polarization bits linearly increase with switching time. The domain wall speed, v, can be defined by $v=l/2t$, where l is the size of a switched domain defined by the full width at half maximum of the potential for switched domains, and t is the pulse width. An l value of 74 nm was observed between two ferroelectric nanobits of the $PbTiO_3$ for a time range of 50–150 ns when a bias of 20 V was applied. The domain wall of the ferroelectric bit formed by a switching condition of 50 ns and 20 V moves and becomes similar in size to the ferroelectric bit formed by the switching condition of 100 ns. Thus, it is possible to evaluate the domain wall speed for the bias of 20 V as 0.74 m/s. For a bias of 20 V, the domain wall speeds of the $PbTiO_3$ and $BiAlO_3$ thin films are estimated to be 0.74 and 2.18 m/s, respectively. The $BiAlO_3$ thin film shows a faster domain wall speed than the $PbTiO_3$ thin films.

To evaluate the activation fields for domain wall motion, the domain wall speeds are depicted as a function of the applied bias voltages for the $PbTiO_3$ and $BiAlO_3$ thin films, as shown in Fig. 4. The activation field for the domain wall motion can be obtained from Merz's law, which defines the domain wall speed as $\sim\exp((-R/k_BT)(E_0/E)^{\mu})$, where $R/(k_BT)^{1/\mu}E_0$ is the activation field, k_B is the Boltzmann constant, R is the characteristic energy, μ is the dynamical exponent, and E_0 is the applied electric field [20]. For the calculation of the activation field, we use a bias of 5 V to approximate a uniform electric field of 1 MV/cm, although the electric field induced at the KFM tip is not uniform (Bessel function). Activation energies of 0.87 and 0.70 MV/cm were estimated for the $PbTiO_3$ and $BiAlO_3$ thin films, respectively. Based on these data, we infer that the faster domain wall motion of the $BiAlO_3$ thin film is due to the lower domain wall energy.

4. Summary

Epitaxial $PbTiO_3$ and $BiAlO_3$ thin films were fabricated on $SrRuO_3/SrTiO_3$ substrates using PLD. The $PbTiO_3$ and $BiAlO_3$ thin films showed ferroelectric polarizations of approximately 50 and 29 $\mu C/cm^2$, respectively. The switching behavior of the thin film was observed to be faster for $BiAlO_3$ when compared to $PbTiO_3$. The fast domain wall motion and switching current are a function of the lower activation energy of $BiAlO_3$ thin film.

References

[1] H. Kohlstedt, Y. Mustafa, A. Gerber, A. Petraru, M. Fitsilis, R. Meyer, U. Bottger, R. Waser, Current status and challenges of ferroelectric memory devices, Microelectronic Engineering 80 (2005) 296.

[2] J.F. Scott, C.A. PazdeAraujo, Ferroelectric memories, Science 246 (1989) 1400.

[3] I. Jung, J.Y. Son, A nonvolatile memory device made of a graphene nanoribbon and a multiferroic $BiFeO_3$ gate dielectric layer, Carbon 50 (2012) 3854.

[4] B. Kam, X. Li, C. Cristoferi, E.C.P. Smits, A. Mityashin, S. Schols, J. Genoe, G. Gelinck, P. Heremans, Origin of multiple memory states in organic ferroelectric field-effect transistors, Applied Physics Letters 101 (2012) 033304.

[5] M.J. Polking, M.-G. Han, A. Yourdkhani, V. Petkov, C.F. Kisielowski, V.V. Volkov, Y. Zhu, G. Caruntu, A. Paul Alivisatos, R. Ramesh, Ferroelectric order in individual nanometre-scale crystals, Nature Materials 11 (2012) 700.

[6] K. Iijima, Y. Tomita, R. Takayama, I. Ueda, Preperation of c-axis oriented $PbTiO_3$ thin films and their crystallographic, dielectric, and pyroelectric properties, Journal of Applied Physics 60 (1986) 361.

[7] M. Shimizu, H. Fujisawa, H. Niu, K. Honda, Growth of ferroelectric $PbZr_xTi_{1-x}O_3$ thin films by metalorganic chemical vapor deposition (MOCVD), Journal of Crystal Growth 237–239 (2002) 448.

[8] Y.-H. Shin, J.-Y. Son, B.-J. Lee, I. Grinberg, A.M. Rappe, Order and disorder character of $PbTiO_3$, Journal of Physics: Condensed Matter 20 (2008) 015224.

[9] J.H. Cho, S.H. Bang, J.Y. Son, Q.X. Jia, Control of epitaxial growth for $SrBi_2Ta_2O_9$ thin films, Applied Physics Letters 72 (1998) 665.

[10] 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.

[11] M.R. Suchomel, A.M. Fogg, M. Allix, H. Niu, J.B. Claridge, M.J. Rosseinsky, Bi_2ZnTiO_6: a lead-free closed-shell polar perovskite with a calculated ionic polarization of 150 $\mu C/cm^{-2}$, Chemistry of Materials 18 (2006) 4987.

[12] D. Fu, M. Endo, H. Taniguchi, T. Taniyama, M. Itoh, $AgNbO_3$: a lead-free material with large polarization and electromechanical response, Applied Physics Letters 90 (2007) 252907.

[13] J.Y. Son, C.S. Park, Y.H. Shin, Epitaxial $BiAlO_3$ thin film as a lead-free ferroelectric material, Applied Physics Letters 92 (22) (2008) 222911.

[14] Y.H. Shin, V.R. Cooper, I. Grinberg, A.M. Rappe, Development of a bond-valence molecular-dynamics model for complex oxides, Physical Review B 71 (5) (2005) 054104.

[15] Y.H. Shin, I. Grinberg, I.W. Chen, A.M. Rappe, Nucleation and growth mechanism of ferroelectric domain-wall motion, Nature 449 (2007) 881.

[16] F. Kubel, H. Schmid, Structure of a ferroelectric and ferroelastic monodomain crystal of the perovskite $BiFeO_3$, Acta Crystallographica B46 (1990) 698.

[17] J.Y. Jo, S.M. Yang, T.H. Kim, H.N. Lee, J.G. Yoon, S. Park, Y. Jo, M.H. Jung, T.W. Noh, Nonlinear dynamics of domain-wall propagation in epitaxial ferroelectric thin films, Physical Review Letters 102 (2009) 045701.

[18] D.J. Kim, J.Y. Jo, Y.S. Kim, T.K. Song, Inhomogeneous domain nucleation and growth in disordered ferroelectric capacitors observed by modified piezoresponse force microscopy, Journal of Physics D: Applied Physics 43 (39) (2010) 395403.

[19] G. Catalan, H. Bea, S. Fusil, M. Bibes, P. Paruch, A. Barthelemy, J.F. Scott, Fractal dimension and size scaling of domains in thin films of multiferroic $BiFeO_3$, Physical Review Letters 100 (2008) 027602.

[20] W.J. Merz, Domain Formation and Domain Wall Motions in Ferroelectric $BaTiO_3$ Single Crystals, Physical Review 95 (1954) 690.