Journal of Magnetics 17(2), 78-82 (2012) http://dx.doi.org/10.4283/JMAG.2012.17.2.078

Possibility of Magnetocapacitor for Multilayered Thin Films

Jong Soo Hong, Sung Wook Yoon, Chul Sung Kim, and In-Bo Shim*

Department of Nano and Electronic Physics, Kookmin University, Seoul 136-702, Korea

(Received 16 January 2012, Received in final form 20 January 2012, Accepted 21 January 2012)

CoNiFe(CNF)/$BaTiO_3$(BTO)/CoNiFe(CNF) multilayered thin films were deposited on Pt/Ti/SiO_2/Si substrates by using pulsed laser deposition (PLD) system. We fabricated three different thin films of BTO, BTO/CNF and CNF/BTO/CNF for magneto-capacitor and studied their crystalline structure, surface and interface morphology, and magnetic and electrical properties. When three different structures of multilayered thin film were compared, magnetization of CNF/BTO/CNF thin films was decreased by magnetic and dielectric interaction. Also we confirmed that capacitance of CNF/BTO/CNF multilayered thin film was enhanced as being near tetragonal structure with increasing of c/a ratio because of atomic bonding at interface between BTO dielectric and CNF magnetic materials. Finally, we studied the change of the capacitance of CNF/BTO/CNF multilayered thin film with magnetic field for emergence of magnetocapacitance and suggested a possibility of enhanced capacitance.

Keywords : magnetocapacitance, multilayer thin film, pulsed laser deposition, interface effect

1. Introduction

Capacitors based on ferroelectric perovskites are potentially attractive for applications in nanoscience, such as non-volatile random-access memories and high-permittivity gate dielectrics [1-3]. However, typical applications have demerits with limitation of various properties since controlling of charge and spin is only possible with electric or magnetic field separately. Recently, it become possible to fabricate magnetocapacitor by artificially making ferroelectrics and ferromagnets in nanoscale multilayered thin films [4-6]. It involves the coupling between ferroelectricity and magnetism through interface bonding. The interplay between ferroelectrics (FE) and ferromagnetism (FM) allows a magnetic control of dielectric properties and electric control of magnetic properties [7-9]. More recently, some research efforts have been focused on the fabrication and the investigation of coupling effects of FM/FE/FM multilayers [10-12]. Considering that magneto-electric (ME) effect in multilayer structures comes from the direct elastic-coupling between ferroelectric and ferromagnetic phase, residual strain induced by interfacial lattice mismatch can play an important role in controlling electrical, magnetic and magnetocapacitance [13, 14]. We investigated the effect of distribution of the FM phases and the influence of interfacial layers on the electrical properties of multilayer structure. The strengthened compressive stress enhanced the ferroelectric property of BTO films by reducing structural tetragonality, which was demonstrated by capacitance-voltage measurement. In this paper, we focused on a novel nanostructure of CNF/BTO/CNF multilayered thin films fabricated by PLD, withthe resulting capacitance for energy storage application, and investigated changes of capacitance in ferroelectric material by interfacial crystal deformation and by magnetostriction. Finally, we studied the change of the capacitance in CNF/BTO/CNF multilayered thin film with magnetic field for emergence of magnetocapacitance and suggested a possibility of enhanced capacitance.

*Corresponding author: Tel: +82-2-910-5121
Fax: +82-2-910-5170, e-mail: ibshim@kookmin.ac.kr

2. Experiment Details

The CNF/BTO/CNF multilayered thin films were deposited on Pt/Ti/SiO_2/Si substrate with the size of 12 × 12 mm^2 by using a pulsed laser deposition (PLD) system. The base pressure of the chamber was 2.0×10^{-6} Torr, and a substrate was located at a distance of 3 cm from the target. We have used a LAMBDA PHYSIK KrF (248 nm) excimer laser, with 30 ns pulse duration, operating at 13 Hz and pulse energy of about 2.0 mJ/cm^2 during the rotations of both target and substrate, at temperature of

650 °C without post-annealing process. Fabricated thin films of three different BTO, BTO/CNF and CNF/BTO/CNF structures were studied for thier crystal, surface and interface microstructure and electrical properties. The crystal structures of BTO, BTO/CNF and CNF/BTO/CNF thin films were characterized by X-ray diffractometry (Philips X'PERT X-ray diffractometer, Cu K_a radiation). The composition of the elements for CNF in the multi-layer thin films was identified using energy dispersive X-ray spectroscopy (EDS). Surface morphology and interface microstructure of thin films were characterized by using an atomic force microscope (AFM) and high resolution transmission electron microscope (HR-TEM), respectively. AFM images were observed by Digital nano Scope III, and TEM observation was investigated by using a JEM-4010 (JEOL Co. Ltd., Japan) transmission electron microscope with an accelerating voltage of 400 kV. The depth distribution of the elements for the CNF/BTO/CNF multilayer thin film was studies by using Auger Electron Spectroscopy (AES). AES depth profiles were measured by a Physical Electronics PHI 700 Auger microprobe using primary electron of 5 kV. The sample was sputtered with 3 kV argon ions, and the corresponding etch rate for SiO_2 was about 10 nm/min^{-1}. For electrical measurements of multilayered thin film with capacitor structure, the dielectric properties and C-V characteristics of the multilayer thin film were obtained from Aglient 4284A LCR meter and analyzed by Agilent 4155C semiconductor parameter analyzer to confirm the change of capacitance for three structures of BTO, BTO/CNF and CNF/BTO/CNF by magnetic field.

3. Results and Discussion

Fig. 1 and Table 1 show X-ray diffraction (XRD) patterns and lattice constants of multilayered thin films for three structures (BTO, BTO/CNF and CNF/BTO/CNF on Pt/Ti/SiO_2/Si substrates). XRD patterns of BTO thin film without top and under layer are shown in Fig. 1(a). Crystal structure of the sample shown in Fig. 1(a) was analyzed to be tetragonal of *P*4*mm* space group with lattice constants of a_0 = 4.010 Å and c_0 = 4.008 Å. From Fig. 1(b), XRD results confirmed that lattice constants of BTO thin film with CNF under layer changed to a_0 = 4.006 Å and c_0 = 4.011 Å. Also we confirmed that BTO with CNF top and under layer have lattice constants of a_0 = 4.003 Å and c_0 = 4.019 Å and is well crystallized with tetragonal structure than samples measured in Fig. 1(a) and (b) do, as shown Fig. 1(c). When three different crystal structures of multilayered thin film were compared, *c*/*a* ratios were increased from 0.996 to 1.004. It confirms that the films grow tetragonally (c-axis direction) due to crystal deformation because atomic radius of CNF is smaller than BTO [15]. Also, nano-sized CoNiFe top and under layers in multilayered thin films could be easily distinguished by using cross-section energy dispersive X-ray spectroscopy (EDS). Table 2 shows EDS results of the multilayered thin films based on CNF. It confirms that all the elements have been precipitated during deposition process and top and under layer containing of the required elements is successfully formed.

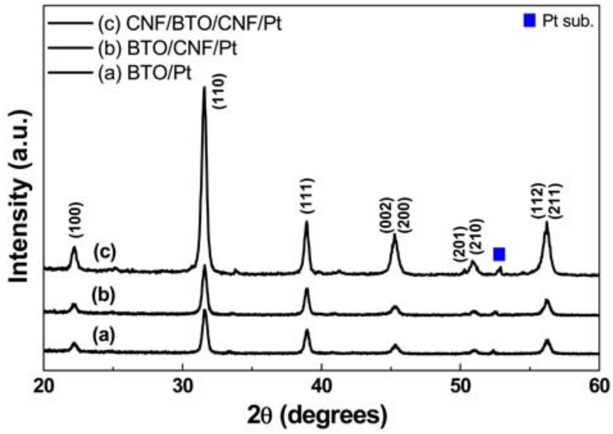

Fig. 1. (Color online) X-ray diffraction patterns of (a) $BaTiO_3$, (b) $BaTiO_3$/CoNiFe and (c) CoNiFe/$BaTiO_3$/CoNiFe thin films deposited at 650 on Pt/Ti/SiO_2/Si substrates by PLD.

Table 1. Parameters of lattice constants for (a) $BaTiO_3$, (b) $BaTiO_3$/CoNiFe and (c) CoNiFe/$BaTiO_3$/CoNiFe thin films deposited at 650 °C on Pt/Ti/SiO_2/Si substrates.

Lattice constants	a_0 (Å)	c_0 (Å)	*c*/*a* ratio
(a) BTO	4.010	4.008	0.996
(b) BTO/CNF	4.006	4.011	1.001
(c) CNF/BTO/CNF	4.003	4.019	1.004

Table 2. EDS elemental abundances of CNF top and under layer of cross-section CoNiFe/$BaTiO_3$/CoNiFe thin films.

Element analysis (Normalized)			
CNF (top and under layer)	Co	Ni	Fe
Atomic percent (%)	59.45	7.80	5.98
Weight percent (%)	52.24	6.56	7.46

The morphology and microstructure of the interfacial multilayered thin film was studied by cross-sectional HR-TEM. The microstructure of interface layers plays an important role for the atomic bonding behavior [16]. Fig. 2 shows the cross-sectional morphology of multilayered thin films with BTO and CNF top and under layers on Pt substrate. Also it was confirmed that thicknesses of CNF and BTO deposited on Pt/Ti/SiO_2/Si substrate were 25 nm

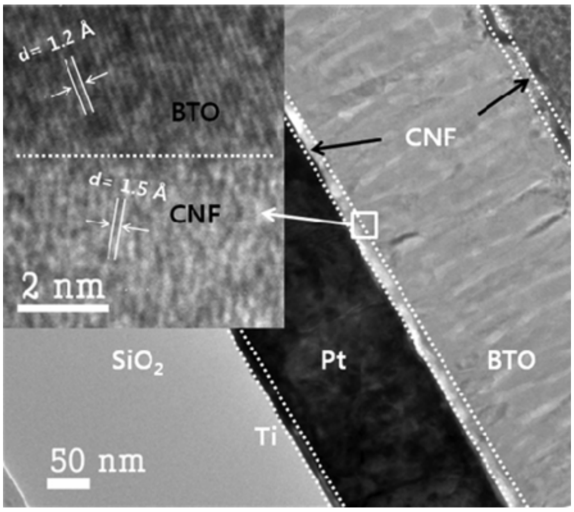

Fig. 2. HR-TEM images of the CoNiFe/$BaTiO_3$/CoNiFe thin films (cross-section). The inset image shows the interface between BTO and CNF layer.

and 300 nm, respectively and clear interfacial structure between CNF and BTO were shown in the inset of Fig. 2. We investigated surface morphology and roughness of each layer in the multilayered thin film as well as the interfacial layer. The AFM images shown in Fig. 3 reveal the homogeneous and uniform microstructures in the thin films. From Fig. 3(a), it is obvious that the surface morphology of CNF under layer on Pt/Ti/SiO_2/Si substrate has many cluster grains with average size of about 260 nm, and the root mean square (rms) roughness of the film surface is 9.48 nm. From Fig. 3(b), it can be seen that the surface morphology of the BTO thin film on CNF/Pt/Ti/SiO_2/Si substrates have the cluster grain size around 200 to 220 nm and the rms roughness of the film surface is 16.38 nm. From AFM images, it is seen that the interfacial layers are smooth and dense. To confirm atomic concentration and diffusion layer for chemical elements of interface layer, AES depth profiles of CNF/BTO/CNF

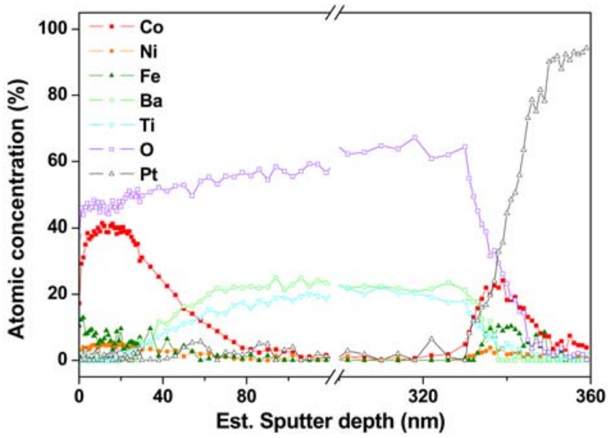

Fig. 4. (Color online) AES depth profiles of CoNiFe/$BaTiO_3$/CoNiFe multilayer thin films. The depth scales were calculated using weighted sputter rates of the pure components.

multilayer thin film were measured, as shown in Fig. 4. Also the depth scales were calculated using weighted sputter rates of the pure components. In the Auger spectra recorded during depth profiling, different peak shapes were identified by factor analysis and linear least squares fit to spectra obtained on pure Co, Ni, Fe and oxide layer of Ba and Ti. AES depth profiles proved that the multilayered thin film showed no diffusion layer at the CNF top layer/BTO interface and BTO/CNF under layer interface. However, we have noticed Pt diffusion because Pt was detected at the interface between CNF under layer and Pt substrate.

Fig. 5 shows in-plane magnetic hysteresis loop of CNF, BTO/CNF and CNF/BTO/CNF thin films at room temperature. From Fig. 5(a), the saturated magnetization and coercivity of CNF under layer on Pt substrate are 223.74 emu/cm^3 and 93.52 Oe, respectively. Fig. 5(b) shows magnetization of BTO/CNF thin film with CNF under layer is 96.90 emu/cm^3. Magnetization of multilayered thin films with top and under layer is 66.55 emu/cm^3, as

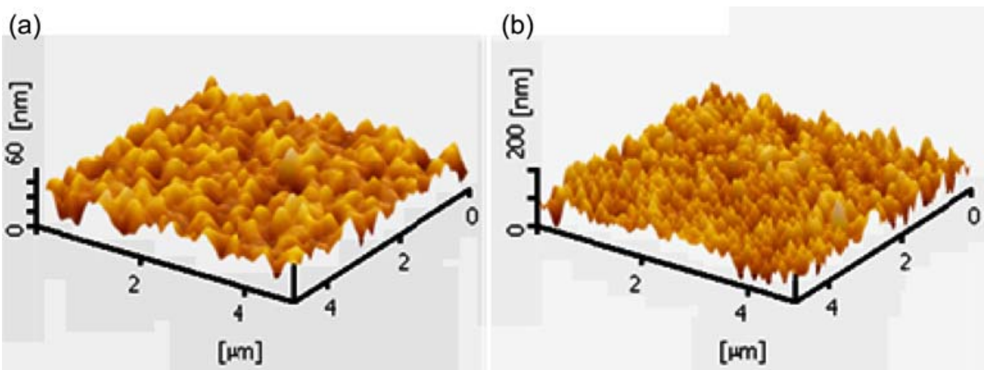

Fig. 3. (Color online) AFM images of surface morphologies of (a) CoNiFe under layer and (b) $BaTiO_3$/CoNiFe (with CNF under layer) thin films on Pt/Ti/SiO_2/Si substrates.

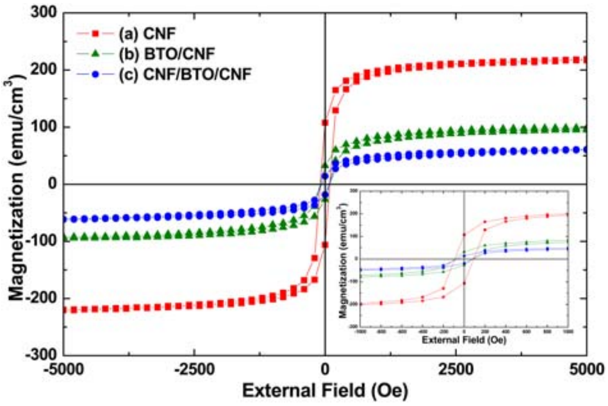

Fig. 5. (Color online) Magnetic hysteresis loops of (a) CoNiFe, (b) $BaTiO_3$/CoNiFe and (c) CoNiFe/$BaTiO_3$/CoNiFe thin films grown on Pt/Ti/SiO_2/Si substrates with the magnetic field parallel to the film planes. The inset graph shows the magnified curve.

shown in Fig. 5(c). Consequently, we confirmed that CNF, BTO/CNF and CNF/BTO/CNF thin films show ferromagnetic behavior at room temperature and the saturation magnetization was decreased by fabricating thin-film capacitor structure with CNF top and under layer. We confirmed that atomic bonding at interface between dielectric and magnetic materials resulted in decreasing of magnetization [17]. This indicates that the rotation of the axis of spin is blocked by magnetic field because of the electron orbital in magnetic material is strongly combined by lattice.

The dc-biasd field dependence of capacitance density at room temperature was measured to evaluate the capacitance of the CNF/BTO/CNF multilayer thin film. Top platinum (Pt) electrodes of 200 μm diameter were deposited through a shadow mask onto the thin films by DC sputter. The measurement were conducted by applying a small ac signal of 0.5 V with frequency of 1 MHz while the dc field was swept from positive bias to negative bias. The potential of the multilayer thin films to be used in magnetocapacitor depends on the ability to change the capacitance by means of an applied voltage. In Fig. 6 C-V curves of the multilayer thin films shows the dependence of the capacitance density at room temperature as a function of bias voltage. As expected, during the sweep up and down processes, the C-V curves showed butterfly loops with the presence of ferroelectric domain, which was the typical characteristic of ferroelectric materials. The capacitance densities of three structures are (a) 377, (b) 624, and (c) 1423 nF/cm^2, respectively, at 1 MHz and zero field. Also dielectric constants at room temperature are 128, 223 and 485, respectively. A dielectric constant value of 600 has been reported for BTO thin film on Pt

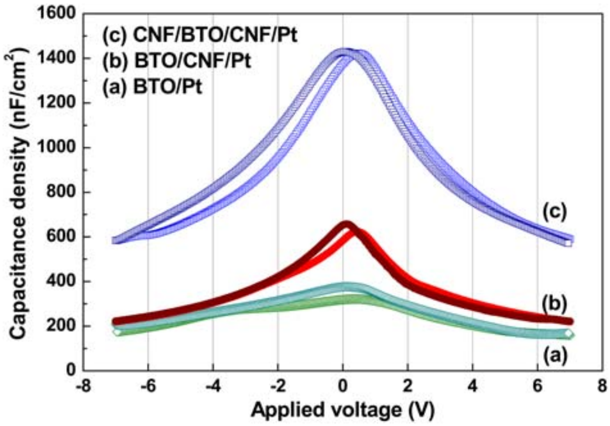

Fig. 6. (Color online) *C-V* characteristics of (a) $BaTiO_3$, (b) $BaTiO_3$/CoNiFe and (c) CoNiFe/$BaTiO_3$/CoNiFe thin films at 1 MHz.

substrate prepared by the PLD technique [18]. We confirmed that multilayer thin film with the CNF top and bottom layer enhanced the capacitance. This indicates that atomic bonding at interface generates the changes in lattice constants a_0 and c_0. The crystallization of multilayer thin films may influence the electric properties. Also an atomic displacement is expected to increase the dielectric properties.

Finally, we studied the tunability of the capacitance value of BTO, fabricated as CNF/BTO/CNF thin film, with applied magnetic field. From Fig. 7, the enhancement of the capacitance density as a function of bias voltage is confirmed for the CNF/BTO/CNF thin film with parallel applied magnetic field of 500 Oe, which increased from 1431 to 1462 nF/cm^2 at 1MHz and zero field. According to a general Le Chatelier's principle [19], it is known that the effect of stress on magnetization is

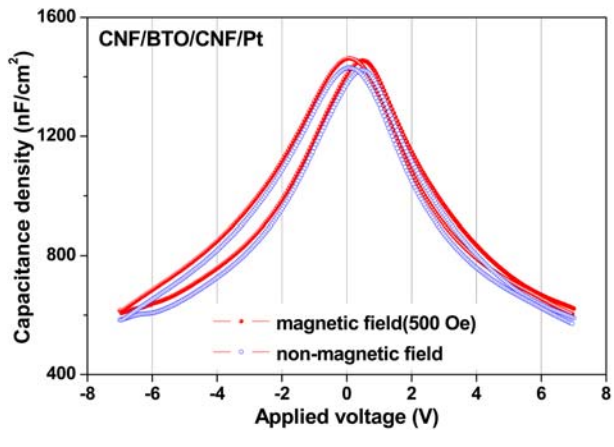

Fig. 7. (Color online) *C-V* characteristics of CoNiFe/$BaTiO_3$/CoNiFe (with CNF top and under layer) multilayer thin films on applied magnetic field of 500 Oe at 1 MHz.

mainly generated from the magneto-strictive materials. We confirmed that the capacitance is affected by the stress because CNF layer is deformed compressively by magnetostriction effect and crystal deformation generates at BTO interface of CNF top and under layer with atomic bonding by interface effect.

4. Conclusion

To fabricate magnetocapacitor, multilayered thin films were deposited on Pt (111) substrates by using pulse laser deposition (PLD) system with thicknesses of 25 nm and 300 nm for CoNiFe and $BaTiO_3$, respectively. Capacitance of CNF/BTO/CNF multilayered thin film enhanced as being near tetragonal structure with increasing of *c*/*a* ratio because BTO was combined with CNF material, having lattice constant smaller than that of BTO. Also we studied the change of capacitance of CNF/BTO/CNF multilayered thin film with magnetic field for emergence of magneto-capacitance. We confirmed that the order of dielectric polarization was changed by generating strain in dielectric material combined with magnetic material by the magneto-striction and interface effect. We suggest a possibility of enhanced capacitance and show overcoming the limitation of separate control of charge and spin either by electric or magnetic field in magnetocapacitors.

Acknowledgment

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) grant funded by the Ministry of Education, Science and Technology (2010-0022468) and by the Korea government (MEST) (R11-2005-048-00000-0) and in part by research program 2009 of Kookmin University in Korea.

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