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Magnetocapacitance Properties of Multilayered $CoFe_2O_4/BaTiO_3/CoFe_2O_4$ Thin Film by Pulsed Laser Deposition

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$CoFe_2O_4$(CFO)/$BaTiO_3$(BTO)/$CoFe_2O_4$(CFO) multilayered thin films were deposited on Pt/TiO_2/SiO_2/Si substrates by the pulsed laser deposition (PLD) system with KrF excimer laser ($\lambda = 248$ nm). BTO, CFO, BTO/CFO and CFO/BTO/CFO structured thin films were prepared and their crystal structures and microstructures, as well as their magnetic and magneto-electrical properties, were studied. The C-V characteristics of these multilayered thin films with different capacitor structures were obtained to confirm the change in their capacitances under a magnetic field. Finally, the capacitance of the CFO/BTO/CFO thin film as a function of bias voltage under an in-plane magnetic field of 1,000 Oe increased to 951.04 pF at 1 MHz, from 831.90 pF measured under no magnetic field, indicating 14.3% increase in magnetocapacitance.

Keywords : magnetostriction, magnetocapacitance, pulsed laser deposition

1. Introduction

Recently, capacitors with ferroelectric materials have been used in many applications such as electrical devices and information storage devices [1-5]. However, their typical applications have been limited by factors such as charge or spin control only under an electric or a magnetic field.

A multiferroic material, which provides a medium with four states (0, 0, 0, 0), not two states (0, 0), by switching between the ferroelectric and magnetic domains, is expected to overcome such limitations. This implies that magnetic domains can be controlled with an electric field rather than a magnetic field; this type of magnetic domain control has been of high interest for read/write devices [6].

The coupling between a magnetic field and an electric field (ME coupling) is relatively low in a single - phase multiferroic material but it can be increased dramatically in a two - phase ferroelectric and ferromagnetic composite [7]. An ME coupling occurs when an applied magnetic field creates a change in the electric properties of a thin film via interface elastic coupling [7-9].

Ferroelectric and ferromagnetic thin films deposited on the same substrate can have multiferroic properties. These artificial multiferroic films have ferroelectric and ferromagnetic phases, and exhibit a strain-mediated ME coupling which is several times higher than that of single - layer thin films [10, 11].

In this study, we have prepared BTO, CFO, BTO/CFO and CFO/BTO/CFO thin films on Pt/TiO_2/SiO_2/Si substrates and investigated their crystallographic, microstructural, and magnetic properties as well as their magnetocapacitance properties.

2. Experiments

The thin films were deposited on Pt/TiO_2/SiO_2/Si substrates of 12×12 mm^2 size by using a PLD system. The 2 - inch targets of BTO and CFO were fabricated by the conventional solid state method. The base pressure of the chamber was 5.0×10^{-5} torr, and a substrate was located at a distance of 3 cm from the target. We used a KrF excimer laser with 30 ns pulse duration. The BTO thin film was deposited at 9 Hz at pulse energy of 210 mJ, and the CFO thin film at 5 Hz at pulse energy of 190 mJ, while both the target and substrate were rotating at 600 ^{o}C. The fabricated BTO, CFO, BTO/CFO and CFO/BTO/CFO thin films were studied for their crystal, surface, and interface microstructural, as well as magnetic and electrical

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properties. The crystal structures of thin films were characterized by the X-ray diffractometer with Cu-Kα (λ = 1.540562 Å) radiation. The surface morphologies and interface microstructures of the thin films were characterized by using an atomic force microscope (AFM) and field-emission scanning electron microscopy (FE-SEM), respectively. The compositions of the multilayer thin films were identified by energy dispersive x-ray spectroscopy (EDS). Magnetic properties were measured by a vibrating sample magnetometer (VSM). For the measurement of the C-V characteristics, platinum electrodes were patterned and deposited on the tops of these films by DC magnetron sputtering. The C-V characteristics of these multilayered thin films with different capacitor structures were measured with the LCR meter to investigate the change in their capacitances under an external magnetic field.

3. Results and Discussion

Fig. 1 shows the XRD patterns of the BTO, CFO, BTO/CFO and CFO/BTO/CFO thin films. The XRD patterns confirmed that the prepared films are single-phase without second peaks. The crystal structure of the BTO thin film, as shown in Fig. 1(a), was tetragonal of *P4mm* with lattice constants a_0 = 4.030 Å and c_0 = 4.033 Å. The crystal structure of the CFO thin film, as shown Fig. 1(b), was cubic inverse spinel of *Fd-3m*, with lattice constant a_0 = 8.361 Å. The XRD results in Fig. 1(c) confirmed that the lattice constants of the BTO thin film with CFO underneath changed to a_0 = 4.049 Å and c_0 = 4.021 Å, and the lattice constant of the CFO thin film underneath changed

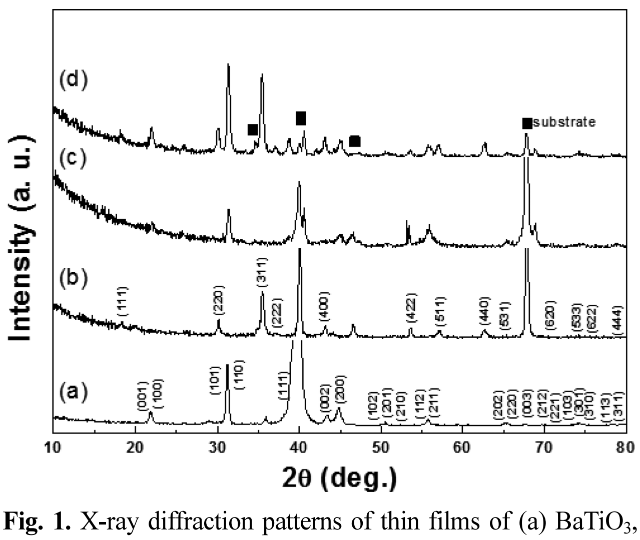

Fig. 1. X-ray diffraction patterns of thin films of (a) $BaTiO_3$, (b) $CoFe_2O_4$, (c) $BaTiO_3/CoFe_2O_4$ and (d) $CoFe_2O_4/BaTiO_3/CoFe_2O_4$ on $Pt/TiO_2/SiO_2/Si$ substrates.

Table 1. Lattice constants of $BaTiO_3$ in thin films of (a) $BaTiO_3$, (b) $BaTiO_3/CoFe_2O_4$ and (c) $CoFe_2O_4/BaTiO_3/CoFe_2O_4$ on $Pt/TiO_2/SiO_2/Si$ substrates.

Lattice constants	a_0 (Å)	c_0 (Å)	*c*/*a* ratio
(a) BTO	4.030	4.033	1.001
(b) BTO/CFO	4.049	4.021	0.993
(c) CFO/BTO/CFO	4.009	4.044	1.009

to a_0 = 8.312 Å. Also we confirmed that the BTO film between the top and bottom CFO layers had lattice constants of a_0 = 4.009 Å and c_0 = 4.044 Å and the lattice constant of both the top and bottom CFO thin films changed to a_0 = 8.407 Å. The *c*/*a* ratios of the BTO thin films of three multilayered capacitor structures are shown in Table 1.

The lattice mismatch [12] between the BTO and the simple cubic platinum substrate with a_0 = 3.920 Å was 2.81% with compressive strain, which is a rather small value. However, the lattice mismatch between the BTO and the CFO in the BTO/CFO structure was 2.65% and that in the CFO/BTO/CFO structure was 4.85%. Considering the fact that the lattice mismatch between the CFO and the Pt substrate is 6.65% with compressive strain, the experimentally observed values are in good agreement with c/a ratios of the BTO thin films, and we expect that the c/a ratios of the BTO thin films will increase with increasing compressive force due to the lattice mismatch between the BTO and the CFO.

From the cross-sectional FE-SEM images (Fig. 2), the thicknesses of the BTO and CFO thin films deposited on the $Pt/TiO_2/SiO_2/Si$ substrates were about 320 and 200

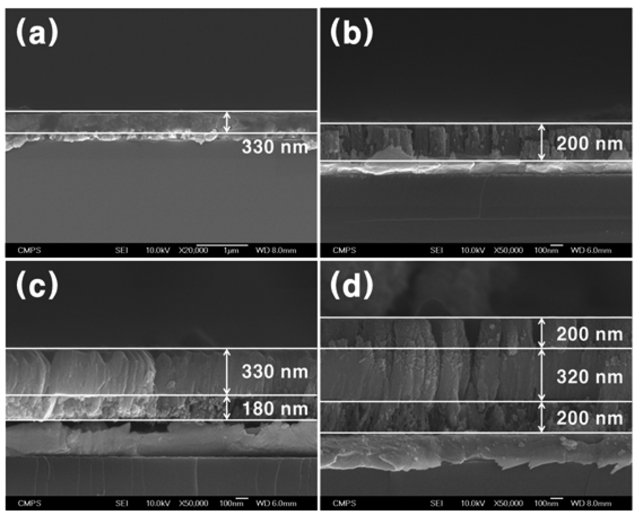

Fig. 2. Cross-sectional FE-SEM images of thin films of (a) $BaTiO_3$, (b) $CoFe_2O_4$, (c) $BaTiO_3/CoFe_2O_4$ and (d) $CoFe_2O_4/BaTiO_3/CoFe_2O_4$ on $Pt/TiO_2/SiO_2/Si$ substrates.

Table 2. Element analysis results of top, middle and bottom layers of $CoFe_2O_4/BaTiO_3/CoFe_2O_4$ multilayered thin film by EDS.

	Element analysis (Atomic %)				
	Ba	Ti	Co	Fe	O
Top layer	–	–	25.08	29.45	45.47
Middle layer	11.57	10.53	–	–	77.89
Bottom layer	–	–	18.73	17.49	63.78

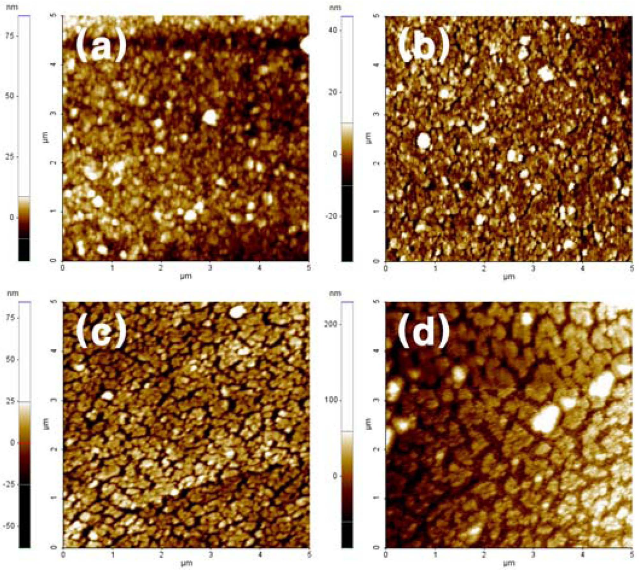

Fig. 3. (Color online) AFM images of surface morphologies of thin films of (a) $BaTiO_3$, (b) $CoFe_2O_4$, (c) $BaTiO_3/CoFe_2O_4$ and (d) $CoFe_2O_4/BaTiO_3/CoFe_2O_4$ on $Pt/TiO_2/SiO_2/Si$ substrates.

nm, respectively. Also, from the EDS analysis shown Table 2, all the elements precipitated during the deposition process, indicating the formation of the top and bottom layers of the CFO/BTO/CFO thin film.

Fig. 3 shows AFM images of the surface topographies of the BTO, CFO, BTO/CFO and CFO/BTO/CFO thin films. The root-mean squared (RMS) values of roughness of the BTO and CFO thin film surfaces were about 3.34 and 5.61 nm, respectively. The interfacial layers are smooth and dense. However, the RMS roughness of the thin films increased with additional layers. The change in the RMS roughness was due to the deposited CFO thin film having a columnar structure, as shown in Fig. 2.

The M-H hysteresis of the thin films was measured by VSM under an applied field of 10 kOe at room temperature. From Fig. 4, the saturated magnetization (M_s) and coercivity (H_c) of the CFO thin film on the Pt substrate are 87.1 emu/cm^3 and 1067.2 Oe, respectively. For the BTO/CFO thin film, these values are 61.8 emu/cm^3 and

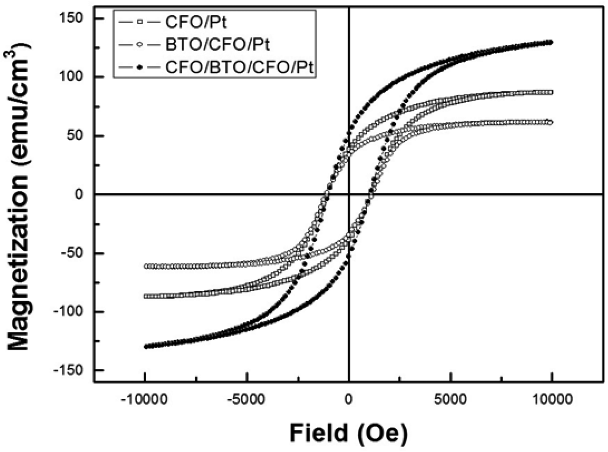

Fig. 4. M-H hysteresis of $CoFe_2O_4$, $BaTiO_3/CoFe_2O_4$ and $CoFe_2O_4/BaTiO_3/CoFe_2O_4$ thin films on $Pt/TiO_2/SiO_2/Si$ substrates at room temperature.

1131.9 Oe. The magnetization and coercivity of the multilayered thin film with top and bottom layers is 129.6 emu/cm^3 and 1023.6 Oe, respectively. The Hc of BTO/CFO is larger than those of CFO and CFO/BTO/CFO.

The C-V curves showed the capacitances of the BTO, CFO, BTO/CFO and CFO/BTO/CFO thin films (Fig. 5). The C-V curves were measured as a function of bias voltage at 1 MHz under an in-plane magnetic field of 1000 Oe. The capacitances of the BTO and CFO thin films did not change under the applied magnetic field. However, the capacitances of the BTO/CFO and CFO/BTO/CFO multilayered thin films increased by as much as 3.42 and 119.14 pF, respectively, indicating that the magnetocapacitances [13] of the BTO/CFO and CFO/BTO/CFO multilayered thin films increased by 0.4 and 14.3%, respectively.

The multilayered thin films of BTO and CFO studied here combined the ferroelectricity of BTO and the ferromagnetism of CFO to produce a magnetoelectric coupling effect under interfacial stress. When a magnetic field was applied to these thin films, stress was generated by the CFO due to its magnetostriction [7, 14-16]. Such a stress can create an electric field in the BTO in turn due to its piezoelectricity. We confirmed that the capacitance of BTO was affected by the stress because the CFO layer experienced a compressive stress due to magnetostriction effect and that crystal deformation was generated at the interfaces between the BTO and the top and bottom layers of CFO.

4. Conclusion

BTO, CFO, BTO/CFO and CFO/BTO/CFO thin films

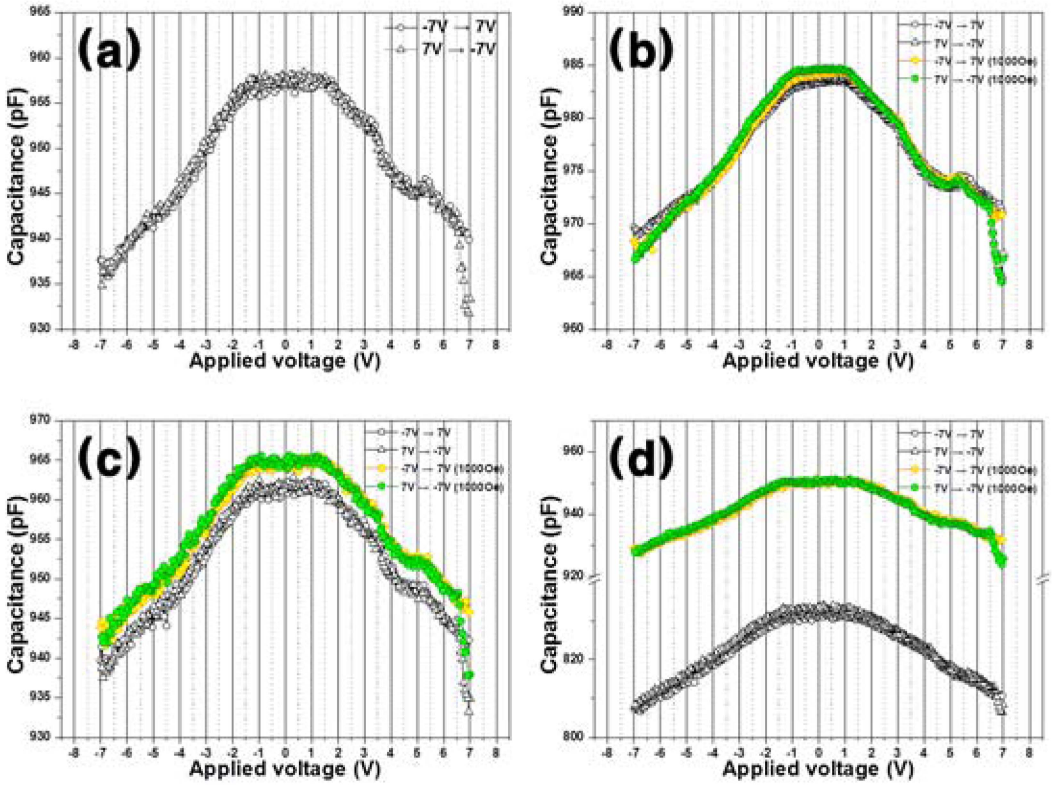

Fig. 5. (Color online) C-V curves of (a) $BaTiO_3$, (b) $CoFe_2O_4$, (c) $BaTiO_3/CoFe_2O_4$ and (d) $CoFe_2O_4/BaTiO_3/CoFe_2O_4$ thin films on $Pt/TiO_2/SiO_2/Si$ substrates under applied magnetic field.

were deposited on $Pt/TiO_2/SiO_2/Si$ substrates by PLD. The XRD patterns confirmed that the prepared thin films were single-phase with cubic inverse spinel (CFO) and tetragonal (BTO) structures. The thicknesses of the BTO and CFO thin films deposited on the $Pt/TiO_2/SiO_2/Si$ substrates were about 320 nm and 200 nm, respectively. By adding CFO multilayers, the capacitances of BTO/CFO and CFO/BTO/CFO multilayered thin films were increased by 3.42 and 119.14 pF, indicating that magnetocapacitances of the BTO/CFO and CFO/BTO/CFO multilayered thin films were increased by 0.4 and 14.3%, respectively. This result is due to the change in the c/a ratio in the BTO thin film, which can be explained by the lattice mismatch between BTO and CFO. Our study suggests that the capacitance of a multilayered CFO/BTO/CFO thin film can be tuned by applying a magnetic field.

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References

[1] C. A. P. Dearaujo, J. D. Cuchiaro, L. D. Mcmillan, M. C. Scott, and J. F. Scott, Nature **374**, 627 (1995).
[2] J. F. Scott, Science **315**, 954 (2007).
[3] D. B. Strukov, G. S. Snider, D. R. Stewart, and R. S. Williams, Nature **453**, 80 (2008).
[4] J. H. Jung, C. Y. Chen, B. K. Yun, N. Lee, Y. S. Zhou, W. Jo, L. J. Chou, and Z. L. Wang, Nanotechnology **23**, 375401 (2012).
[5] O. Guillon, J. Chang, S. Schaab, and S.-J. L. Kang, J. Am. Ceram. Soc. **95**, 2277 (2012).
[6] C. Chappert, A. Fert, and F. N. Van Dau, Nature Mater. **6**, 813(2007).
[7] 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, and R. Ramesh, Science **303**, 661 (2004).
[8] Y. Zhang, J. Liu, Y. Lin, and C.-W. Nan, J. Phys. D **42**, 135413 (2009).
[9] T. N. Narayanan, B. P. Mandal, A. K. Tyagi, A. Kumarasiri, X. B. Zhan, M. G. Hahm, M. R. Anantharaman, G.

Lawes, and P. M. Ajayan, Nano Lett. **12**, 3025 (2012).
[10] H. Ko, K. R. Choi, S.-I. Park, I.-B. Shim, S. J. Kim, and C. S. Kim, J. Magn. **13**, 163 (2008).
[11] J. S. Hong, S. W. Yoon, C. S. Kim, and I.-B. Shim, J. Magn. **17**, 78 (2012).
[12] S. C. Jain, A. H. Harker, and R. A. Cowley, Philos. Mag. A **75**, 1461 (1997).
[13] K. T. McCarthy, A. F. Hebard, and S. B. Arnason, Phys. Rev. Lett. **90**, 117201 (2003).
[14] J. Zhu, L. X. Zhou, W. Huang, Y. Q. Li, and Y. R. Li, J. Cryst. Growth **311**, 3300 (2009).
[15] Y. Wu, J. Wan, J.-M. Liu, and G. Wang, Appl. Phys. Lett. **96**, 152902 (2010).
[16] I. Kagomiya, Y. Hayashi, K.-i. Kakimoto, and K. Kobayashi, J. Magn. Magn. Mater. **324**, 2368 (2012).