

Multiferroic $\text{CoFe}_2\text{O}_4\text{-Pb}(\text{Zr,Ti})\text{O}_3$ Nanostructures

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Multiferroic $\text{CoFe}_2\text{O}_4\text{-Pb}(\text{Zr,Ti})\text{O}_3$ films were prepared on TiO_2 -terminated (001) Nb-doped SrTiO_3 substrates by using pulsed laser deposition (PLD). The films were epitaxial and exhibited a large in-plane magnetic anisotropy and good ferroelectric properties. A decrease in the magnetization around the ferroelectric Curie temperature indicated magnetoelectric coupling between the magnetostrictive and the piezoelectric phases, which allows interconversion of energy stored in the electric and the magnetic fields and provides great potential for applications as next-generation multi-functional devices.

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I. INTRODUCTION

Multiferroics are single-phase or composite materials that can possess a spontaneous dielectric polarization as a response to an applied magnetic field or a magnetization induced by an external electric field. Such materials have attracted significant attention because of not only their interesting magneto-electrical properties but also

their wide applications in the fields of transducers, sensors and data storage [1–3].

A few single-phase multiferroics, such as Cr_2O_3 and BiFeO_3 can be used only at low temperature due to their low Néel or Curie temperature [4–6]. By combining separate ferromagnetic and ferroelectric phases, the composite offers more possibilities in applications thanks to its multifunctionality [1, 2, 7, 8]. Recently, there has been a revival of multiferroic composites [3, 9–11]. Among them, magnetostrictive materials, for example Terfenol-D and ferrites and piezoelectrics, for example BaTiO_3 and $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT), are particularly interesting due to their large magnetostriction, high piezoelectric properties and high Curie temperature. In these multiferroics, when the magnetostrictive parts are deformed un-

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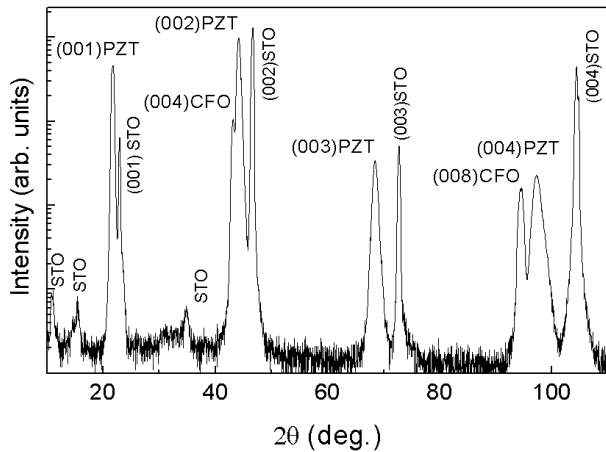


Fig. 1. XRD pattern of a CoFe_2O_4 (280 nm)/PZT (1 μm)/ CoFe_2O_4 (280 nm) film (CFO: CoFe_2O_4 , STO: Nb-doped SrTiO_3 substrate).

der an applied magnetic field, the piezoelectric parts will undergo a forced strain, resulting in an induced electric polarization and *vice versa*.

In this article, we report the properties of epitaxial CoFe_2O_4 /PZT multilayers directly grown on single-crystal (001) Nb-doped SrTiO_3 substrates by using pulsed laser deposition (PLD). Large in-plane magnetic anisotropy and good ferroelectric properties are obtained without using buffered layers. For the first time, a decrease in magnetization around the ferroelectric Curie temperature ($T_{C(E)}$) was observed in this structure, indicating magnetoelectric coupling between the magnetostrictive and the piezoelectric phases. The obtained results will be explained based on the stress in the multilayered structure combined with the magnetostrictive and piezoelectric properties.

II. EXPERIMENTS

Multiferroic CoFe_2O_4 -PZT composites were grown on single-crystal (001) Nb-doped SrTiO_3 substrates by means of PLD using a KrF excimer laser ($\lambda = 248$ nm) with a pulse duration of 25 ns. The CoFe_2O_4 target was prepared from powder obtained by complexometric synthesis [12] and the PZT target was prepared from commercial powder (3N, TRS Ceramic USA). Before deposition, the substrates were chemically treated and annealed at 950 $^\circ\text{C}$ to obtain single TiO_2 termination [13].

The deposition chamber was vacuumed to a background pressure of 5×10^{-6} mbar. The CoFe_2O_4 and the PZT layers were grown at 600 $^\circ\text{C}$ in an oxygen environment at ambient pressures of 0.05 mbar and 0.1 mbar. The PLD system was operated at an energy density of 2.5 J/cm^2 and a laser frequency of 5 Hz for CoFe_2O_4 . These values were 3.5 J/cm^2 and 10 Hz, respectively, for PZT. The target to substrate distance was fixed at

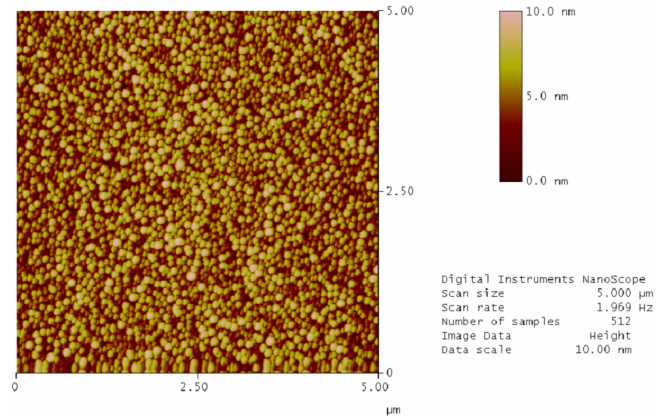


Fig. 2. AFM image of a CoFe_2O_4 (70 nm)/PZT (250 nm)/ CoFe_2O_4 (70 nm) film.

60 mm for CoFe_2O_4 and 47 mm for PZT. After deposition, the films were quickly cooled down to room temperature in 1 bar of oxygen. The film configuration was CoFe_2O_4 /PZT/ CoFe_2O_4 with different thicknesses up to 280 nm for CoFe_2O_4 and 1 μm for PZT.

The crystallographic structure of the films was investigated using an X-ray diffractometer (XRD) with the $\text{Cu } K_\alpha$ wavelength. The thickness of the films was determined using cross-sectional scanning electron microscopy and the surface morphology was analyzed by using atomic force microscopy (AFM). The room-temperature capacitance-voltage (C-V) measurements were performed at a frequency of 10 kHz and with a 50 mV-amplitude ac signal by using a HP 4275A multi-frequency LCR meter. The dielectric constant was calculated from the low-field capacitance. Magnetic hysteresis loops were taken in-plane and perpendicular to the film surface by using a VSM Oxford system at room temperature in magnetic fields from +2400 kA/m (+3 Tesla) to -2400 kA/m (-3 Tesla). The thermomagnetic measurement was carried out using a home made Faraday balance in a magnetic field of 0.05 T.

III. RESULTS AND DISCUSSION

Figure 1 illustrates the typical XRD pattern of the CoFe_2O_4 (280 nm)/PZT (1 μm)/ CoFe_2O_4 (280 nm) film. Analyses revealed that the CoFe_2O_4 /PZT films were epitaxial based on the presence of two sets of (00l) peaks contributed by the CoFe_2O_4 and the PZT layers. AFM images of the first CoFe_2O_4 layer showed a very smooth surface ($rms = 0.5$ nm) following the terrace of the substrate. However, when the PZT layer was deposited, a rough surface with $rms = 2.5$ nm was observed (see Figure 2).

The C-V characteristics of the CoFe_2O_4 /PZT films showed a well-defined butterfly shape, which indicates their ferroelectric behavior, as presented in Figure 3

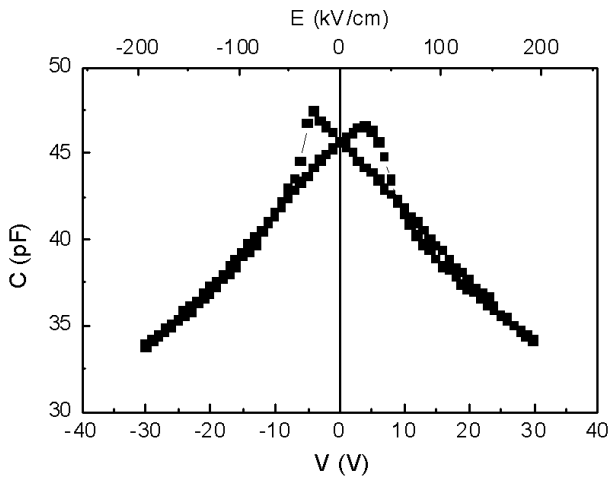


Fig. 3. C-V curve of a CoFe_2O_4 (280 nm)/PZT (1 μm)/ CoFe_2O_4 (280 nm) film.

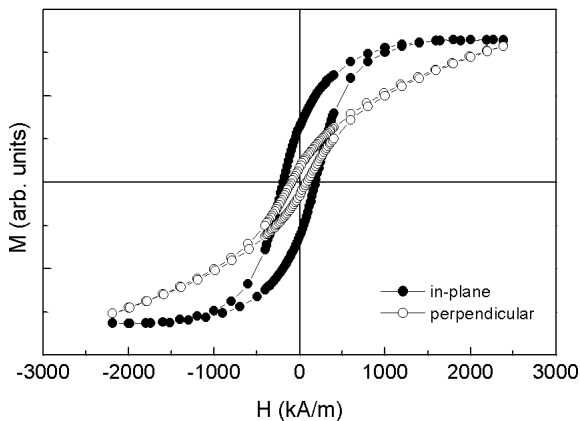


Fig. 4. Magnetic hysteresis loops of a CoFe_2O_4 (280 nm)/PZT (1 μm)/ CoFe_2O_4 (280 nm) film.

for the film having a configuration of CoFe_2O_4 (280 nm)/PZT (1 μm)/ CoFe_2O_4 (280 nm). The dielectric constant, derived from the capacitance value at zero applied voltage, is around 800. This dielectric constant is close to that of bulk PZT. The leakage current of the CoFe_2O_4 /PZT films measured at an applied voltage of 30 V and a frequency of 10 kHz was low, in the range of 10^{-4} A/cm².

The in-plane and perpendicular magnetic hysteresis loops of the CoFe_2O_4 (280 nm)/PZT (1 μm)/ CoFe_2O_4 (280 nm) film are represented in Figure 4. The film exhibits a large in-plane magnetic anisotropy with a coercivity of 200 kA/m. This magnetic anisotropy can be explained in terms of the stress in the film, which originates from the lattice mismatch between the CoFe_2O_4 layer and the substrate and between the CoFe_2O_4 layers and the PZT layer. Since the lattice parameter of cubic CoFe_2O_4 is 8.39 Å, layers grown on a Nb-doped SrTiO_3 substrate ($a = b = c = 3.91$ Å) and a PZT layer ($a = b = 4.03$ Å, $c = 4.14$ Å) are under compression in the film

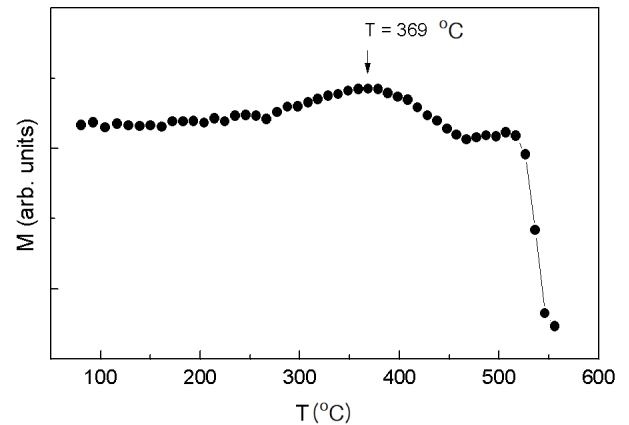


Fig. 5. Temperature dependence of the in-plane magnetization of a CoFe_2O_4 (280 nm)/PZT (1 μm)/ CoFe_2O_4 (280 nm) film.

plane. Due to the negative magnetostriction, a strong in-plane stress anisotropy will be induced.

Figure 5 shows the temperature dependence of the in-plane magnetisation of the CoFe_2O_4 (280 nm)/PZT (1 μm)/ CoFe_2O_4 (280 nm) film. The magnetic phase is clearly seen to exhibit an ordering temperature of about 530 °C. In addition, an anomaly in the in-plane magnetisation curve is observed at 369 °C, close to the PZT Curie temperature ($T_{C(E)} = 360 - 390$ °C) and can be understood as a magnetoelectric coupling between the magnetostrictive and the piezoelectric parts in this two-phase nanostructure. At temperatures higher than $T_{C(E)}$, CoFe_2O_4 is compressed in plane due to the lattice mismatch with cubic PZT. For temperatures below $T_{C(E)}$, the tetragonal distortion in the PZT lattice further increases this deformation in the CoFe_2O_4 layers and results in a decrease in the magnetization as the temperature passes through $T_{C(E)}$. This effect cannot be observed in thinner CoFe_2O_4 /PZT films as a consequence of the in-plane piezo-deformation being clamped by the substrate, thus preventing any deformation in the magnetic layers.

IV. CONCLUSION

Epitaxial multilayered CoFe_2O_4 /PZT multiferroics have been successfully grown on a Nb-doped SrTiO_3 substrate. The two-phase nanostructures have a large in-plane magnetic anisotropy, reasonable ferroelectric properties and especially, good magnetostrictive-piezoelectric coupling. Previously, this coupling could only be observed in bonding laminated or nanostructured composites. The result obtained in multilayered nanostructure facilitates the interconversion of energy stored in the electric and the magnetic fields and provides great potential for practical applications. It opens a novel approach to prepare multilayered multiferroics for applications in

Micro-Electro-Mechanical Systems (MEMS) and Nano-Electro-Mechanical Systems (NEMS).

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REFERENCES

- [1] T. H. O'Dell, *Electronics and Power* **11**, 266 (1965).
- [2] J. Van Suchetelene, *Philips Research Report* **27**, 28 (1972).
- [3] K. Uchino, in *Comprehensive Composite Materials: Piezoelectric Composites*, Vol. 5 (Elsevier, Amsterdam, 2000), p. 523.
- [4] D. N. Astrov, *Sov. Phys. -JETP* **11**, 708 (1960).
- [5] G. T. Rado and V. J. Folen, *Phys. Rev. Lett.* **7**, 310 (1961).
- [6] I. H. Ismailzade, V. I. Nesternko, F. A. Mirishli and P. G. Rustamov, *Phys. Status Solidi* **57**, 99 (1980).
- [7] J. van den Boomgaard, D. R. Terrell, R. A. J. Born and H. F. J. I. Giller, *J. Mater. Sci.* **9**, 1705 (1974).
- [8] J. van den Boomgaard and R. A. J. Born, *J. Mater. Sci.* **13**, 1538 (1978).
- [9] M. I. Bichurin, V. M. Petrov, Yu. V. Kiliba and G. Srinivasan, *Phys. Rev. B* **66**, 13404 (2002).
- [10] 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).
- [11] N. H. Duc and D. T. Huong Giang, to be published in *J. Alloys Compd.*
- [12] P. D. Thang, G. Rijnders and D. H. A. Blank, *J. Magn. Magn. Mater.* **295**, 251 (2005).
- [13] G. Koster, B. L. Kropman, G. J. H. M. Rijnders, D. H. A. Blank and H. Rogalla, *Appl. Phys. Lett.* **73**, 2920 (1998).