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Influence of epitaxial BiFeO₃ on superparamagnetic behavior of CoFeB thin film

Q. T. Zhang,¹ L. You,² C. H. Wan,¹ Z. H. Yuan,¹ X. Zhang,¹ J. Wang,² and X. F. Han^{1,a)}

¹Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

²School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore

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Superparamagnetic behavior of ultrathin CoFeB film grown on epitaxial BiFeO₃ (BFO) thin film was investigated by using anomalous Hall effect (AHE) at different temperatures. A transition from superparamagnetism to blocked state was observed for CoFeB grown directly on SrTiO₃ (STO) substrate, but absent for CoFeB grown on BFO from 30 K to 300 K. By fitting normalized AHE data with Langevin equation, average grain sizes of the superparamagnetic CoFeB grown on STO and BFO were estimated. Considering the relationship between volume of nanoparticle and blocking temperature (T_B), T_B of CoFeB grown on BFO was above 30 K which was not observed experimentally, indicating that in addition to surface roughness or oxidation, interfacial exchange coupling also played a role in the suppression of T_B . By taking the interfacial exchange coupling between BFO and superparamagnetic CoFeB as an effective field, Bloch equations were introduced to study the relaxation process of superparamagnetic CoFeB. This suppression of T_B was proposed to be attributed to a cooperative effect of interfacial exchange coupling as well as roughness or oxidation between BFO and superparamagnetic CoFeB. © 2015 AIP Publishing LLC.

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I. INTRODUCTION

BiFeO₃ (BFO), as a promising single phase multiferroic material at room temperature, is a potential candidate for realizing electric control of magnetism—the pivot for next-generation memories.^{1–9} Plenty of work has been devoted to understand magnetic properties of BFO^{10–15} and its coupling behaviors with adjacent magnetic materials.^{16–20} Both exchange bias and exchange coupling have been observed in BFO-ferromagnetic (FM) bilayers, which could be modulated by both the types of ferroelectric domain walls¹⁶ and the epitaxial strain states.¹² Most experiments achieved to control the magnetism by electrically tuning the magnitude of exchange bias^{7,8} or switching the magnetic anisotropy of the ferromagnetic layer^{5,6} via interfacial magnetic coupling. Exchange coupling as well as magnetoelectric effects is strongly dependent on interface quality, so it is important to understand interface structure sandwiched by the ferromagnetic layer and BFO. Superparamagnetic nanoparticles formed in ferromagnetic layer adjacent to BFO may lead to abnormal magnetic transport behavior due to thermal fluctuations.²¹ Thus, understanding how BFO influences the superparamagnetism of nanoparticles will shed light on the mechanism of coupling between FM and BFO. In this article, we reported the magnetic properties of the superparamagnetic CoFeB film grown on epitaxial BiFeO₃ at the temperature ranging from 30 K to 300 K. The study of the superparamagnetic CoFeB grown on BFO will be helpful to achieve the electric control of magnetic properties and to

understand the effect of ferroelectric domains configuration on magnetism induced by magnetoelectric coupling.

II. EXPERIMENTAL DETAILS

About 70-nm-thick BiFeO₃ epitaxial film was fabricated on (001)-oriented SrTiO₃ single crystal substrate by pulsed laser deposition (PLD) at 650 °C with a stoichiometric BiFeO₃ target. BFO film was grown under an oxygen partial pressure of 13 Pa and *in situ* annealed in oxygen environment at 10⁴ Pa for 2 h after growth. 1-nm-thick Co₄₀Fe₄₀B₂₀ (CoFeB) film and 5-nm-thick Ta capping layer were grown on epitaxial BFO film and bare SrTiO₃ (STO) substrate using ULVAC magnetron sputter system with a base pressure of 1.0 × 10^{−6} Pa. BFO-FM heterostructure consists of STO(sub.)/BFO(70)/CoFeB(1)/Ta(5) (in nanometer) and CoFeB/Ta was fabricated into Hall bar structure by combined ultraviolet lithography technique and subsequent Ar-ion beam etching. Anomalous Hall effect (AHE) was measured using Keithley 2400 and 2182 in a PPMS system (Quantum Design). It should be noted that resistance of a single BFO Hall bar was above 20 MΩ, which was much larger than that of CoFeB/Ta (less than 1 KΩ), indicating that negligible current flowed through BFO. Therefore, the AHE signals only reflected the magnetic properties of the superparamagnetic CoFeB.

III. RESULTS AND DISCUSSION

The topographic and ferroelectric domains images of BFO film were obtained by atomic force microscopy (AFM) (Fig. 1(a)) and piezoelectric force microscopy (PFM) (Figs.

^{a)}Electronic mail: xfhan@iphy.ac.cn

FIG. 1. (a) Topographic image of BFO grown on STO, (b) in-plane PFM image, (c) out-of-plane PFM image. The scale bar is 500 nm in length. (d) Polarization directions of BFO are shown schematically with the atomic stacking of STO/BFO heterostructure. The colors of arrows in (d) (yellow, brown, and purple) correspond to the in-plane polarization directions shown in (b) by different color.

1(b) and 1(c)), respectively. Roughness of BFO thin film is about 0.5 nm. The out-of-plane PFM (OP-PFM) image shows little contrast with a yellow tone, indicating uniform out-of-plane polarization direction all over the film, whereas the in-plane PFM (IP-PFM) image exhibits three different tones, a typical signature of multi-domain structure. In our case where BFO was grown on nominal exact STO, four upward polarizations variants out of eight possible ones coexist (Fig. 1(d)). The arrows in Fig. 1(d) indicate the polarization vectors with corresponding color tones (yellow, brown, and purple) shown in Fig. 1(b).

To understand the influence of BFO on the superparamagnetic behavior of CoFeB thin film, anomalous Hall effect, which is proportional to the out-of-plane component of the magnetization, was measured at the temperature ranging from 30 K to 300 K. In Fig. 2, the left panel shows the AHE curves of superparamagnetic CoFeB grown on bare STO substrate at 300 K (a), 210 K (b), 120 K (c) and 30 K (d), whereas the right panel shows those of CoFeB grown on BFO at 300 K (e), 210 K (f), 120 K (g), and 30 K (h), respectively. In the case of STO/CoFeB, paramagnetic-like behavior is observed at room temperature and hysteresis loop is clearly observed as temperature decreased to 30 K. Actually, 180 K is the temperature at which hysteresis loop becomes visible first, indicating the blocking temperature of CoFeB on STO is between 180 K and 210 K. When temperature of

superparamagnetic nanoparticles is below T_B , measurement time is much less than relaxation time of magnetic moment of nanoparticles, magnetization does not flip during measurement and then hysteresis loop appears. However, the hysteresis loop is not observed down to 30 K for CoFeB grown on BFO which consistently behaves as a superparamagnetic film from 30 K to 300 K, demonstrating that the T_B of the superparamagnetic CoFeB film on BFO is lower than 30 K.

To estimate T_B , normalized Hall resistivity ρ_{xy} of CoFeB grown on STO and BFO is rescaled with H/T in Figs. 3(a) and 3(b), respectively. Here, H is applied field and T is temperature. The rescaled magnetization curves of superparamagnetic films measured above T_B are expected to be superimposed on each other.²² In our case (Fig. 3(a)), the magnetization curves of the CoFeB film on STO are roughly superimposed for temperatures ranging from 210 K to 300 K, and hysteresis appears at 180 K, indicating that T_B of CoFeB on STO is between 180 K and 210 K, in agreement with the blocking temperature calculated from data in Figs. 2(a)–2(d). However, it should be noted that several deviations among curves in Fig. 3(a) can be observed, in particular, at high field (saturation field) and near the blocking temperature. These deviations were interpreted in terms of anisotropy effects on the magnetization process which remained as a function of H/T .²³ In the case of CoFeB grown on BFO (Fig. 3(b)), normalized AHE is plotted as a function of H/T which confirms that T_B of CoFeB grown on BFO is below 30 K. Besides, coercivity (H_c) of the CoFeB films on STO is temperature dependent, roughly following $H_c(T) = H_c(0) \times (1 - (T/T_B)^{1/2})$ law (Fig. 3(c)). However, for the CoFeB films on BFO, negligible coercivity has been observed as shown in Fig. 3(c), which also shows that T_B of CoFeB grown on BFO is below 30 K. Intuitively, the reduced blocking temperature might originate from the decrease in the effective volume of the superparamagnetic CoFeB, which is influenced by surface roughness and possible oxidation that occur at the interface of magnetic metal and oxide. We fitted these AHE curves with Langevin equation which can describe paramagnetic and superparamagnetic properties accurately

$$M = N\mu \left[\coth\left(\frac{\mu H}{k_B T}\right) - \frac{k_B T}{\mu H} \right], \quad (1)$$

$$= N\mu L\left(\frac{\mu H}{k_B T}\right), \quad (2)$$

where M is the magnetization of superparamagnetic film, N is the number of nanoparticles, k_B is the Boltzmann constant,

FIG. 2. AHE of 1-nm-thick CoFeB grown on STO (left side) and BFO (right side) at various temperatures ranging from 30 K to 300 K.

FIG. 3. To determine blocking temperature, ρ_{xy} of (a) STO/CoFeB and (b) STO/BFO/CoFeB is scaled with H/T for the temperature ranging from 180 K to 300 K. Besides, H_c versus temperature curve is shown in (c). Fitting AHE curve of STO/CoFeB (up) and STO/BFO/CoFeB (bottom) with Langevin equation at superparamagnetic state in (d).

T is the temperature of sample, H is the applied magnetic field, and μ is the magnetic moment of single domain ($\mu = M_s \cdot V$, V is the volume of nanoparticle and M_s is the saturation magnetization). By fitting Langevin equation with normalized AHE data of CoFeB grown on BFO and STO, the average volume of CoFeB nanoparticles could be estimated as 20 nm^3 and 110 nm^3 , respectively. Assuming the characteristic measurement time is 100 s, the relationship between the volume of nanoparticles and the blocking temperature is expressed as follows:²⁴

$$K_{\text{eff}} \cdot V = 25k_B \cdot T_B, \quad (3)$$

T_B of CoFeB on STO which is between 180 K and 210 K should be about five times higher than that of CoFeB grown on BFO, indicating that T_B of CoFeB grown on BFO was $35 \pm 3 \text{ K}$. Experimentally, however, the hysteresis loop of CoFeB grown on BFO remained far from appearance at 30 K. Therefore, possible exchange coupling between the spins of CoFeB and BFO should be taken into consideration. According to the experimental results, an in-plane exchange coupling induced by BFO impeded the magnetizations of CoFeB to rotate towards out-of-plane direction.

Remanent magnetization of a superparamagnetic system is zero because the time used to measure the magnetization of nanoparticles is much longer than relaxation time of the nanoparticles. When the temperature is below T_B , the measurement time becomes shorter than the relaxation time of magnetic moment of superparamagnetic particles, as a result, hysteresis appears. Bloch equations could be applied to phenomenologically describe the process of relaxation as well as decoherence of magnetization of a small superparamagnetic particle in applied magnetic field. In our case, this model was employed to study the relaxation process of superparamagnetic CoFeB with an effective field from BFO when the external magnetic field was reduced to zero. The interfacial exchange coupling between BFO and the superparamagnetic CoFeB was taken into account as an effective field which lies in the (001) plane, such as [100] direction which can be expressed as $(B_x, 0, 0)$. The resulting Bloch equations are expressed by the following equations:

$$\frac{dM_x(t)}{dt} = -\frac{M_x(t)}{T_2}, \quad (4)$$

$$\frac{dM_y(t)}{dt} = \gamma \cdot B_x \cdot M_z - \frac{M_y(t)}{T_2}, \quad (5)$$

$$\frac{dM_z(t)}{dt} = -\gamma \cdot M_y \cdot B_x - \frac{M_z(t) - M_0}{T_1}, \quad (6)$$

where γ is the gyromagnetic ratio, $M(t) = (M_x(t), M_y(t), M_z(t))$ is the magnetization, M_0 is the steady state magnetization, T_1 is the spin-lattice relaxation time, and T_2 is the spin-spin relaxation time. In the Bloch equations, $\gamma \cdot B_x$ can be expressed by $1/T_0$ for simplicity. When $1/T_0$ tends to be infinite or very large value, the Bloch equation describes the case with very small effective field. While $1/T_0$ tends to small (0.25, 0.5), the Bloch equation describes the case with large effective field. Combining initial condition ($M(t=0)$)

FIG. 4. CoFeB magnetization relaxes with different effective fields. CoFeB magnetization with large effective field ($1/T_0 = 0.25$) induced by BFO relaxes faster in z direction than the case without effective in-plane field ($1/T_0 = 1000$). Tendency is clear that a large effective field leads faster relaxation.

$= (0, 0, 1)$, the Bloch equations were solved with different effective fields which are indicated by $1/T_0$ ($1/T_0 = 0.25, 0.5, 1, 1000$). In Fig. 4, CoFeB magnetization with large effective field ($1/T_0 = 0.25$) induced by BFO relaxes faster in z direction than the case without effective in-plane field ($1/T_0 = 1000$). Results in Fig. 4 indicate that magnetization of CoFeB (M_z) coupling with BFO relaxes to zero in a faster speed than CoFeB without the effective field. Thus, it is suggested that interfacial exchange coupling as well as roughness or oxidation function together to result in the suppression of blocking temperature in CoFeB grown on BFO.

IV. CONCLUSIONS

In summary, ultrathin CoFeB films were prepared on epitaxial BFO or directly on STO substrates. Anomalous Hall effect was investigated at different temperatures to study the magnetic properties of the superparamagnetic CoFeB films. A transition from superparamagnetism to blocked state was observed in CoFeB grown on STO substrate, but not for superparamagnetic CoFeB grown on BFO from 30 K to 300 K. With the aid of Langevin equation and Bloch equations, this suppression of T_B was proposed to result from a cooperative effect of interfacial exchange coupling as well as roughness or oxidation between BFO and CoFeB. This work could be helpful to achieve the electric control of magnetic properties and to understand the effect of ferroelectric configuration on magnetism.

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