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Thin film processing and multiferroic properties of Fe-$BaTiO_3$ hybrid composite

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Abstract: Multiferroic bi-layer Fe/$BaTiO_3$ (BTO) thin films were successfully deposited on Pt(200)/MgO(100) substrates using ion beam sputter deposition (IBSD), and the mutiferroic properties were studied at room temperature. X-ray diffraction (XRD) analyses showed that BTO films were *c*-axis oriented and epitaxially grown on platinum coated MgO substrates, and (110) epitaxial Fe films were subsequently grown on (001) BTO films. Fe/BTO bi-layer films showed good ferroelectric and ferromagnetic properties at room temperature and the multiferroic coupling was observed, which should be attributed to the hybridization of Fe and Ti occurring at the ferromagnetic-ferroelectric interface.

Key words: multiferroic effect; ferroelectricity; magnetic properties; magnetoelectric effect

1 Introduction

Multiferroic effect, which involves two or more of ferroelectric, ferromagnetic, and ferroelastic phenomena, has been the subject of considerable interest due to their multifunctionality, which could provide significant potential for applications as the next-generation multifunctional devices[1−3]. However, the rareness of room temperature multiferroics[4] has led many workers to combine ferroelectric materials with ferromagnetic phases, such as, bulk laminates[5−6], multilayer structures of thick films[7−8], and nanoparticulate film structures[9−10]. In these two-phase systems, magnetoelectric (ME) coupling effects can be considered arising from the interfacial strain-mediated coupling of piezoelectricity and magnetostriction. However, due to the clamping effect of the substrate, the couplings between magnetostrictive and piezoelectric multilayers are expected to be negligible. In order to achieve significant ME effect, novel multiferroic materials of artificial layered structures consisting of different ferroic components using new coupling mechanisms are of particular interest[11−12]. Most recently, motivated by the work of DUAN et al[13], the coupling between elastic components of the ferromagnetic and ferroelectric constituents through the strain is not the only source of a magnetoelectric effect in composite multiferroics, such as interface bonding. Epitaxial thin films analogous to bulk magnetostrictive-piezoelectric composites are of interest in order to understand the role of interfaces on the magnetoelectric effect, to enhance these properties in the films, and to integrate these functional materials into planar technology.

In this paper, we report the preparation and multiferroic properties of bi-layer Fe/$BaTiO_3$ films on a platinum-coated MgO(100) substrate by ion beam sputter deposition (IBSD). Fe and $BaTiO_3$ (BT) are two classical ferroic materials which have well known properties in the bulk form. Perovskite BT(001) and bcc Fe(110) have a very good lattice constant match (a mismatch of only about 1.4%) that allows layer-by-layer epitaxial growth of Fe/BT multilayers with no misfit dislocations.

Among the various sputtering methods, one of the major advantages of IBSD is that the whole process of deposition is, in principle, performed under ultra-high vacuum, so that the contamination from the residual gas can be minimized[14]. Moreover, due to the independent, adjustable ion beam energy and flux and controllable bombardment by secondary low energy ion source, the

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films synthesized by this technique are demonstrated to have very uniform thickness and composition over large area and good process reproducibility[15]. The resultant effect of IBSD is high quality, pinhole-free films, with enhanced adhesion and microstructural control. Typically, the film properties from IBSD exceed those deposited by evaporation or magnetron sputtering[16−18].

2 Experimental

During the ion beam sputtering, the chamber was first pumped down to a base pressure of 2.7×10^{-4} Pa by turbo-molecular pump. In order to deposit BT film, argon gas was bled through the ion source while oxygen was directly bled into the chamber with Ar/O_2 ratio of 1.0, yielding a total pressure of about 7×10^{-2} Pa. The reaction gas O_2 was added to avoid the deficiency of oxygen in the film. The ion beam energy was fixed at 1 000 eV, and the deposition rate was controlled by changing the ion current density. Table 1 shows the detailed deposition conditions. The deposited films were amorphous at a substrate temperature of 400 °C, and post-deposition annealing by conventional tube furnace was performed in oxygen atmosphere at 700 °C for 4 h in order to induce crystallization. After BT deposition, Ar^+ ion beam then irradiated an iron (Fe) target (Furuuchi Chemical, purity >99.99%) to deposit Fe layer directly on top of the BT film. Fe deposition conditions are almost the same as BT deposition, just without introducing the oxygen to prevent the formation of iron oxides. The crystal structure of the deposited film was analyzed by X-ray diffractometer with Cu K_α radiation (λ=1.540 5 Å, D/Max 2000H). The surface morphology and the cross-sectional images of the films were observed by means of field-emission scanning electron microscopy (SEM) (1530YP, Leo Co., Germany). Low signal dielectric properties were measured with an HP 4294A impedance analyzer in the frequency range from 1 kHz to 1 MHz. The ferroelectric and magnetic properties were measured by RT66A standard ferroelectric test unit and vibrating sample magnetometer (VSM) (EV7, ADE, USA), respectively.

Table 1 Deposition condition by ion beam sputtering

Parameter	Value
Substrate	Pt(200)/MgO(100)
Base pressure/Pa	2.7×10^{-4}
Working pressure/Pa	7×10^{-2}
Discharge power	410−460 V, 0.15−0.4 A
Beam power	1 kV, 19−40 mA
Accelerator power	0.1 kV, 0.8−2 mA
Deposition temperature/°C	400
Deposition time/min	30−120
Ar flow/($cm^3\cdot min^{-1}$)	2(BT), 2(Fe)
O_2 flow/($cm^3\cdot min^{-1}$)	2(BT), 0(Fe)

3 Results and discussion

Figure 1 shows the XRD pattern of the bi-layer Fe/BT film. It is seen that the deposited BT film is of single phase and preferentially *c*-axis oriented on Pt(200)/ MgO(100) substrate so that no diffraction peaks from randomly oriented grains or impurity phases can be observed. Since underlying BT layer could wet the Pt(200)/MgO(100) substrate because of the low-energy interface between them, Fe layer was also able to grow epitaxially along (110) planes on top of BT layer without apparent iron oxide phase[19−20].

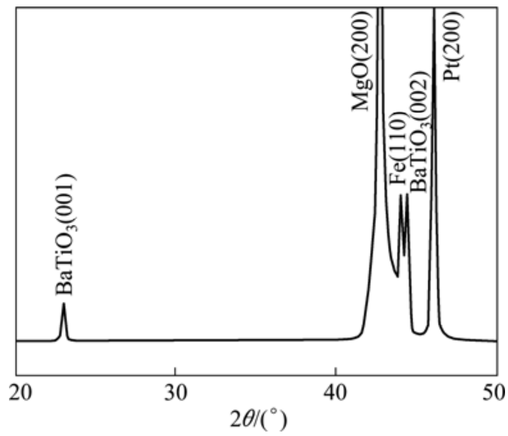

Fig.1 XRD pattern of bi-layer Fe/$BaTiO_3$ thin film on Pt(200)/MgO(100) substrate

SEM images (Fig.2) clearly demonstrate a 2-2 type horizontal heterostructure with sharp interface between the top Fe layer (approximately 280 nm in thickness) and the bottom BT layer (approximately 430 nm in thickness) (Fig.2(c)). Fig.2(a) shows the surface morphology of the BT layer, from which the BT film formed nanoscale island surface via Volmer Webber growth mechanism. The island size is around 50 nm. While the surface image of Fe layer (Fig.2(b)) exhibits much smaller grain size. The morphology of growing islands is dependent on island-substrate interface, deposition rate and temperature.

Figure 3 demonstrates the good coexistence of ferroelectric (Fig.3(a)) and ferromagnetic (Fig.3(b)) behaviors. The ferroelectric loops show that the saturation polarization P_s and remnant polarization P_r for the hetero-structured Fe/BT are about 11 and 3 μC/cm^2, respectively, which is similar to the pure BT film. Due to low deposition temperature, the saturation polarization P_s and remnant polarization P_r values are not so high. The ferromagnetic hysteresis loops, however, show that with insertion of BT layer, the Fe/BT composite films show higher saturation magnetization and smaller coercive

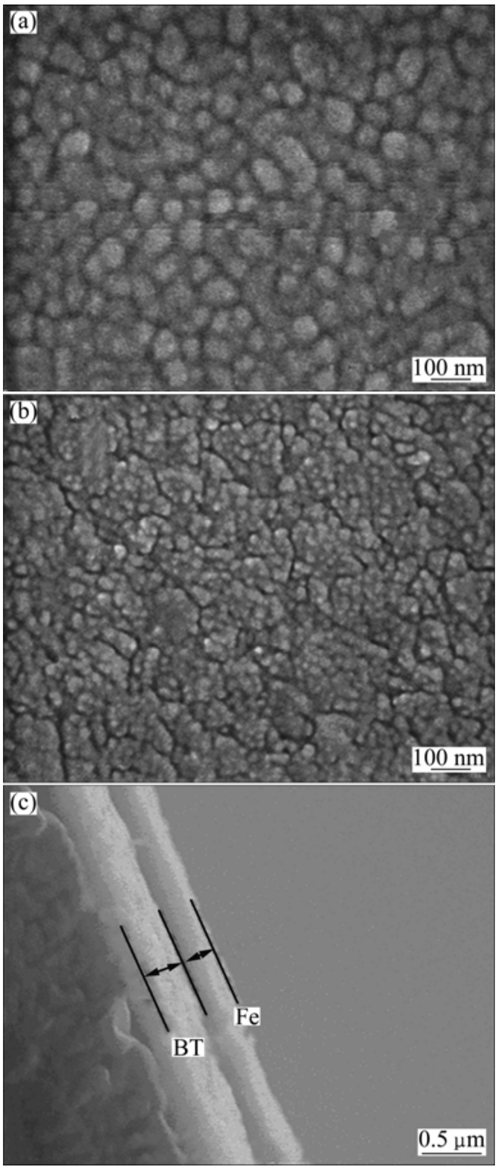

Fig.2 SEM surface micrographs of BT(001) film (a), Fe(110)/BT(001) film (b), and cross-section image of Fe(110)/BT(001) film (c)

field than the pure Fe film. For example, the saturation magnetization M_s and coercive field H_c values are 720 emu/cm^3 (or 90 T/m) and 18 Oe (or 1 432 A/m), respectively, while they are only 608 emu/cm^3 (or 76 T/m) and 37 Oe (or 2 940 A/m) for pure Fe film. This is indicative of an obvious multiferroic coupling at the ferroelectric-ferromagnetic interface, which is in accordance with the prediction of DUAN et al[13], i.e. interface bonding-induced magnetoelectric effect. The presence of ferroelectricity in $BaTiO_3$ seems to cause the magnetic moments of Fe and Ti atoms near interface to deviate from their values in the paraelectric state. This is due to the change in the strength of bonding between the Fe and Ti atoms induced by ferroelectric displacement. Displacement of atoms at the interface caused by ferroelectric instability alters the overlap between atomic orbits at the interface which affects the interface magnetization[13]. The upward polarization makes Ti atoms move away from the bottom interface and towards the top interface. This causes the Fe-Ti bond length to be shorter and, hence, the overlap between the Fe 3d and Ti 3d orbits to be stronger at the top interface compared to the bottom interface. Thus, ferroelectric instability enhances the induced magnetic moment on top Ti atoms. This exciting observation demonstrates a new mechanism for the multiferroic coupling which deserves further investigation.

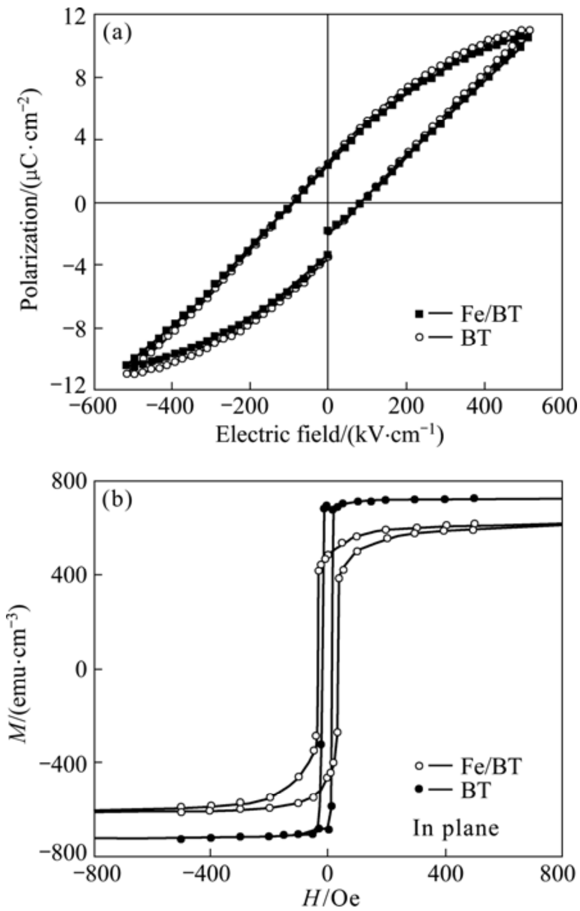

Fig. 3 Ferroelectric hysteresis loops (a) and in-plane magnetic hysteresis loops (b) of Fe(110)/BT(001) film and pure Fe(110) film

4 Conclusions

Epitaxial Fe(110)/BT(001) films were successfully deposited on Pt(200)/MgO(100) substrate by IBSD. The Fe(110)/BT(001) films show the coexistence of ferroelectric and ferromagnetic properties. The enhanced magnetization of Fe(110)/BT(001) film compared with pure Fe(110) film demonstrates the interfacial multiferroic coupling caused by the interface hybridization of Ti and Fe, which reveals a new mechanism for multiferroic effect.

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