PHASE TRANSFORMATION AND DOMAIN MORPHOLOGY OF STRAIN ENGINEERED $BiFeO_3$ BY SCANNING PROBE MICROSCOPY

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Summary We explore the possibility of inducing and controlling magnetic ordering in misfit strained $BiFeO_3$ film by scanning probe microscopy (SPM). Through careful thermodynamic analysis and phase field simulations, a pathway for field induced transformation from tetragonal to rhombohedral phase has been identified, and it is also demonstrated that the morphology of the rhombohedral phase variants can be regulated, enabling nanoscale control of magnetoelectric coupling in strain engineered $BiFeO_3$ by SPM.

INTRODUCTION

The prospect of manipulating magnetic ordering by electric field in multiferroic materials has generated great excitement in the past a few years, yet such magnetoelectric coupling proves elusive to obtain and difficult to control. Bismuth ferrite (BFO), is one of the rare multiferroic compounds that allows electric manipulation of magnetic ordering at room temperature. It is well known that the structure of epitaxial ferroelectric thin films can be engineered by misfit strain, and this has also been demonstrated in BFO films on $LaAlO_3$ (LAO) substrate, which is close to the so-called morphotropic phase boundary (MPB), where tetragonal-like monoclinic and distorted rhombohedral phases coexist, resulting in higher piezoelectric response than either tetragonal or rhombohedral BFO.[1] Even more interestingly, tetragonal BFO exhibits C-type antiferromagnetism, while distorted rhombohedral BFO is G-type antiferromagnetic. Oxygen octahedra tilting may lead to weak ferromagnetism in rhombohedral BFO, though such mechanism does not exist for tetragonal BFO. As a result, such phase mixture introduces different magnetic orderings in the otherwise homogenous tetragonal BFO films on LAO substrate.

It has been demonstrated that by applying opposite electric fields through a scanning probe microscope (SPM) tip, distorted rhombohedral variants can be erased and reintroduced in the phase mixture region, which in turn changes the underlying magnetic orderings, resulting in magnetoelectric coupling in strain engineered BFO.[2] While this is an exciting development, the process relies on the coexistence of tetragonal and rhombohedral phase mixture, making it difficult to control - the film is predominantly tetragonal-like monoclinic, and the fraction of distorted rhombohedral phase is sensitive to film thickness and other deposition conditions. To overcome such difficulties, we explore the prospect of inducing and controlling different magnetic ordering in the phase pure tetragonal BFO films, using combined theoretical analysis, numerical simulations, and experimental characterizations.

PHASE STRUCTURE AND FIELD INDUCED TRANSFORMATION

Manipulating magnetic ordering in strain engineered BFO films require delicate control of their phase structures, and this can be guided by thermodynamic analysis based on Landau-Devonshire theory modified for epitaxial films. For an epitaxial film under a biaxial misfit strain u_m and an electric field E_i, its potential energy can be written as[3]

$$\begin{aligned} G = \frac{u_{\mathrm{m}}^2}{s_{11}+s_{12}} + \alpha_1(P_1^2+P_2^2) + \alpha_3 P_3^2 + \alpha_{11}(P_1^4+P_2^4) + \alpha_{33}P_3^4 + \alpha_{12}P_1^2P_2^2 \\ + \alpha_{13}(P_1^2+P_2^2)P_3^2 - P_1E_1 - P_2E_2 - P_3E_3 \end{aligned}, \quad (1)$$

where P_1 is polarization component, s_{IJ} is elastic compliance constant, $\alpha_i(T)$ and α_{ij} are dielectric constants as a function of misfit strain, T is temperature. The equilibrium polarization of the thin film can be determined from minimizing the free energy, from which four sets of polarization are obtained, corresponding to four different phase structures, as shown in Fig. 1(a). We first consider the baseline structure of BFO in the absence of electric field, with its misfit-temperature phase diagram shown by the red broken phase boundary in Fig. 1(a), where a MPB between T- and R-phases is observed around -4.3% at room temperature. For epitaxial BFO films on LAO substrate, the misfit strain is calculated to be -4.3%, right at the MPB, suggesting the coexistence of T- and R-phases in the film. If we consider an electric field applied along [111] axis. Quite encouragingly, the MPB does move left toward more compressive misfit strain under an applied electric field of $2\times10^7[111]$ V/m, as shown in Fig. 1(a). This suggests that R-phase BFO is stabilized by an electric field along [111] axis, and thus it is indeed possible to transform the T-phase BFO to R-phase using such an electric field. In order to examine the field induced phase transformation in strain engineered BFO in more detail, we construct the field-misfit phase diagram at room temperature, as shown in Fig. 1(b), with the baseline

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structure assumed to be [00-1] polarized T-phase. It is observed that under a misfit strain of -4.3%, i.e. for film on LAO substrate, T-phase BFO starts convert to distorted R-phase at an electric field of $2.5\times10^{6}[111]$ V/m, and this critical electric field for the phase transformation is further reduced for thicker films with relaxed misfit strain. The polarization and piezoelectric coefficient are also calculated, which agree well with our experimental data, and will be show in our presentation.

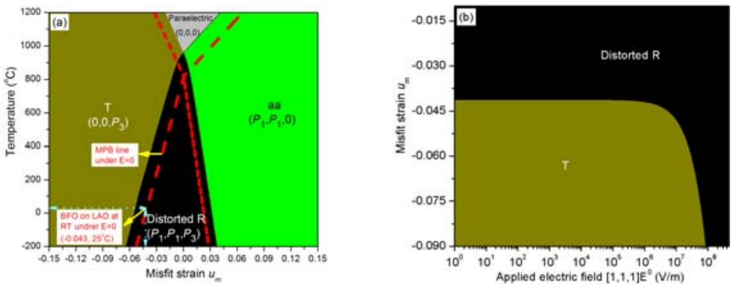

Fig. 1 Phase structure of strain engineered BFO (a) misfit-temperature phase diagram, in the absence of electric field (red broken line), and with an applied electric field (solid line); (b) field-misfit phase diagram at room temperature.

NANOSCALE CONTROL BY SCANNING PROBE MICROSCOPY

Conductive SPM tip has been widely used to manipulate ferroelectric domain structures, in-plane electric field also exists away from the SPM tip in addition to the out-of-plane component, making it possible to utilize such in-plane electric field to induce phase transformation in T-phase BFO. We calculate the distribution of electric field induced by an SPM tip using image charge model, and develop a phase field method to simulate the formation of R-phase variants in T-phase matrix with characteristic function $\lambda_k(\mathbf{x})$ and magnetic $\mathbf{m}$ as order parameters. The evolution of characteristic function is assumed to follow linear kinetic relation, and that of magnetic spins is governed by Landau-Lifshitz-Gilbert type of rotational dynamics.[4] The representative morphologies involving 4, 3, and 2 R-phase variants are shown in Fig. 2(a-d). All these R-phase patterns have been observed in experiment, including rosette structure (a), U-shaped structure (b), parallel pair (c), and L-shaped pair (d), as highlighted in the AFM topography image in Fig. 2(e). Also, the resulting magnetic ordering of rosette R-phase structure in tetragonal matrix is shown in Fig. 2(f), where only spins of one sublattice of R-phase is given. By breaking rotational symmetry of tip-induced electric field as suggested by phase field simulation, the morphology of distorted rhombohedral variants has been delicately controlled and regulated, which will be show in our presentation. These simulations demonstrate the possibility of delicate control and regulation of magnetic ordering and magnetoelectric coupling in strain engineered BFO film by SPM tip, which is accomplished indirectly through controlling and regulating field induced phase transformation by SPM tip.

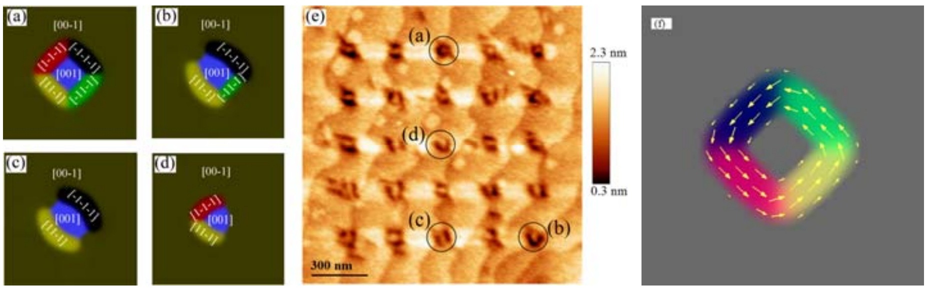

Fig. 2 Morphology of R-phase variants in T-phase matrix induced by SPM tip; (a-d) phase field simulations; (e) AFM topography image; and (f) magnetic ordering corresponding to (a).

CONCLUSIONS

We have demonstrated electric-field control of magnetic ordering in strain engineered BFO film through combined theoretical analysis, numerical simulations and experimental characterizations. The magnetic R-phase BFO can be induced in T-phase matrix by SPM tip, and its morphology can be controlled and regulated by symmetry breaking. These points to a novel pathway to nanoscale control of magnetoelectric coupling in strain engineered BFO film.

References

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