Multiferroic BaTiO$_3$-CoFe$_2$O$_4$ Nanostructures

H. Zheng et al.

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We report on the coupling between ferroelectric and magnetic order parameters in a nanostructured BaTiO$_3$-CoFe$_2$O$_4$ ferroelectromagnet. This facilitates the interconversion of energies stored in electric and magnetic fields and plays an important role in many devices, including transducers, field sensors, etc. Such nanostructures were deposited on single-crystal SrTiO$_3$ (001) substrates by pulsed laser deposition from a single Ba-Ti-Co-Fe-oxide target. The films are epitaxial in-plane as well as out-of-plane with self-assembled hexagonal arrays of CoFe$_2$O$_4$ nanopillars embedded in a BaTiO$_3$ matrix. The CoFe$_2$O$_4$ nanopillars have uniform size and average spacing of 20 to 30 nanometers. Temperature-dependent magnetic measurements illustrate the coupling between the two order parameters, which is manifested as a change in magnetization at the ferroelectric Curie temperature. Thermodynamic analyses show that the magnetoelastic coupling in such a nanostructure can be understood on the basis of the strong elastic interactions between the two phases.

Ferroelectromagnets, which display simultaneous magnetic and electric ordering, have recently stimulated much scientific and technological interest (1). The coexistence of magnetic and electric subsystems engenders the material with the “product” property (i.e., the composite exhibits properties that are not available in the individual component phases), thus allowing an additional degree of freedom in the design of actuators, transducers, and storage devices. However, the choice of single-phase materials exhibiting coexistence of strong ferro/ferrimagnetism and ferroelectricity is limited (2, 3). Van Suchtelen et al. proposed that composites of piezoelectric and magnetostrictive phases can be electromagnetically coupled via a stress mediation (4). Subsequent theoretical and experimental work has focused on bulk ceramics (5–8). In a film-on-substrate geometry, such composites can be created in two extreme forms. Figure 1, A and B, shows a “multilayer” geometry consisting of alternating layers of the ferroelectric phase (e.g., perovskite BaTiO$_3$) and the ferro/ferrimagnetic phase (e.g., spinel CoFe$_2$O$_4$). When the magnetoelastic coupling is purely through elastic interactions, the effect in a multilayer structure will be negligible due to the clamping effect of the substrate (9). Therefore, we focus our efforts on creating and analyzing a vertically aligned structure. Moshnyaga et al. (10) have used an approach that creates three-dimensional nanoscale clusters of La-Ca-Mn-O (LCMO, perovskite) embedded in an insulating MgO (rocksalt structure) matrix. They have demonstrated the tuning of the transport properties of the LCMO nanoclusters through a mechanical coupling with the surrounding MgO regions. Figure 1, C and D, illustrates a heterostructure consisting of nanopillars of the ferro/ferrimagnetic phase embedded in a ferroelectric matrix. The intrinsic similarities in crystal chemistry (i.e., oxygen coordination chemistry) between the perovskite and spinel families lead to lattice dimensions that are compatible. For example, the perovskites have a lattice parameter of ~4 Å, which is generally within 5% of the basic building block of the spinels. Consequently, this presents the tantalizing possibility of heteroepitaxy in three dimensions (i.e., both in-plane as well as out-of-plane).
where $\phi_p$ ($\phi_m$) is the specific free energy of uniform ferroelectrics (ferro/ferrimagnetics); $H$ and $E$ are magnetic and electric fields. It is clear from Eq. 4 that a strong magnetoelectric coupling requires a strong interphase elastic interaction.

Self-assembled BaTiO$_3$-CoFe$_2$O$_4$ nanocomposites were formed from a 0.65BaTiO$_3$-0.35CoFe$_2$O$_4$ target by pulsed laser deposition. SrRuO$_3$ was chosen as the lattice-matched SrTiO$_3$ substrate. (Fig. 2A) X-ray ($\theta$ = 2θ) scan showing only the (002) type peaks, corresponding to CoFe$_2$O$_4$, BaTiO$_3$, SrRuO$_3$, and the SrTiO$_3$ substrate. (B) AFM topography image of the film showing a quasi-hexagonal arrangement of the CoFe$_2$O$_4$ nanopillars. (C) TEM planar view image showing the CoFe$_2$O$_4$ nanostructures in the BaTiO$_3$ matrix. (D) Electron diffraction pattern of (C), illustrating the in-plane heteroepitaxy between CoFe$_2$O$_4$ and BaTiO$_3$.

**Fig. 2.** (A) X-ray ($\theta$ = 2θ) scan showing only the (002) type peaks, corresponding to CoFe$_2$O$_4$, BaTiO$_3$, SrRuO$_3$, and the SrTiO$_3$ substrate. (B) AFM topography image of the film showing a quasi-hexagonal arrangement of the CoFe$_2$O$_4$ nanopillars. (C) TEM planar view image showing the CoFe$_2$O$_4$ nanostructures in the BaTiO$_3$ matrix. (D) Electron diffraction pattern of (C), illustrating the in-plane heteroepitaxy between CoFe$_2$O$_4$ and BaTiO$_3$.

**Fig. 3.** (A) Polarization–electric field hysteresis loop showing that the film is ferroelectric with a saturation polarization $P_s$ ~ 23 $\mu$C/cm$^2$. (B) Small-signal piezoelectric $d_{33}$ hysteresis loop for a 50-µm-diameter capacitor. (C) Out-of-plane (red) and in-plane (black) magnetic hysteresis loops depicting the large uniaxial anisotropy. (D) Magnetization versus temperature curve measured at $H = 100$ Oe, which shows a distinct drop in magnetization at the ferroelectric Curie temperature for the vertically self-assembled nanostructure (red curve); the multilayered nanostructure (black curve) shows negligible change in magnetization.

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tocrystalline anisotropy is expected between [001] and [100] directions for CoFe2O4. The experimentally measured magnetic anisotropy should arise primarily from the magnetoelastic coupling. The first source of stress is the mismatch between the CoFe2O4 and BaTiO3 lattices at the growth temperature ($T_g$). High-resolution TEM images (fig. S1) show that part of this mismatch is accommodated by the formation of interface dislocations. The second source of stress is the lattice distortion in the CoFe2O4 as a consequence of the cubic-tetragonal structural distortion in the BaTiO3 matrix below the ferroelectric Curie temperature ($T_c$). This contribution decreases the compression along the axis of the CoFe2O4 lattice. This compressive strain in the CoFe2O4 lattice can be related to the magnetic anisotropy through its magnetostrictive effect. The stress in the CoFe2O4 is given by $\sigma_{01} = Y_{011} e_{011}$, in which $Y$ is Young's modulus (~141.6 GPa ($T_c$)) and $e_{011}$ is the strain along the [001] direction. The magnetoelastic energy associated with it is $e_{11} / H_{11002}$.

In summary, an epitaxial CoFe2O4-BaTiO3 ferroelectromagnetic nanocomposite was made by a simple self-assembly technique. This system shows a strong coupling of the order parameters through the heteroepitaxy of the two lattices. This approach is general—we have been able to create similar structures of other spinel-perovskite systems such as cobalt ferrite/bismuth ferrite and cobalt ferrite/lead titanate—and as such should impact a broad range of materials research.

References and Notes

Crosstalk Between the EGFR and LIN-12/Notch Pathways in C. elegans Vulval Development

Andrew S. Yoo,* Carlos Bais,‡* Iva Greenwald‡*

The Caenorhabditis elegans vulva is an important paradigm for cell-cell interactions in animal development. The fates of six vulval precursor cells are patterned through the action of the epidermal growth factor receptor—mitogen-activated protein kinase (EGFR-MAPK) inductive signaling pathway, which specifies the 1° fate, and the LIN-12/Notch lateral signaling pathway, which specifies the 2° fate. Here, we provide evidence that the inductive signal is spatially graded and initially activates the EGFR-MAPK pathway in the prospective 2° cells. Subsequently, this effect is counteracted by the expression of multiple new negative regulators of the EGFR-MAPK pathway, under direct transcriptional control of the LIN-12-mediated lateral signal.

The six vulval precursor cells (VPCs) are consecutively numbered P3.p to P8.p (Fig. 1A). Each VPC has the potential to adopt one of three fates, termed 1°, 2°, or 3°. Descendants of the 1° cells constitute the vulva; the 3° cell daughters join the major hypodermal syncytium.

The lin-12 mutation (~ lin-12 alleles) results in a failure to form the vulva (~ lin-23 alleles). In these mutants, the 2° cells adopt the 3° fate, which is believed to be a result of inhibitory influences from the hypodermal syncytium.

Genetic and cell-ablation experiments have led to different models of inductive signaling (~ lin-12). One model proposes that the inductive signal forms a morphogen gradient from the anchor cell, such that a high level of inductive signal causes the 1° fate, whereas a lower level helps specify the 2° fate (~ lin-23). An alternative model proposes that VPC patterning is achieved by a “sequential induction,” such that the inductive signal activates LET-23 only in P6.p, leading to a lateral signal that then induces P5.p and P7.p to adopt the 2° fate and transcribe genes encoding the lateral signal (~ lin-23). The lateral signal activates the receptor LIN-12/Notch in the two neighboring VPCs, P5.p and P7.p, causing them to adopt the 2° fate. Without activation of either the inductive or lateral signaling pathways, P3.p, P4.p, and P8.p adopt the 3° fate, believed to be a result of inhibitory influences from the hypodermal syncytium.

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