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Design of Self-Assembled Multiferroic Nanostructures in Epitaxial Films**

demonstrated. All multiferroic nanostructures reported to

date have been limited to CoFe₂O₄ pillars embedded in a fer-

In the present report, we demonstrate that the morpholo-

gies of self-assembled multiferroic nanostructures can be var-

ied over a wide range by modifying the epitaxial stress state in the film. In particular, morphologies ranging from rodlike

(either magnetic or ferroelectric) to lamellar-like were ob-

tained by varying the substrate orientation and phase frac-

tions in epitaxial composite films containing ferrimagnetic

CoFe₂O₄ and ferroelectric PbTiO₃. The approach relies on

the epitaxial stress-controlled self-assembling of the compo-

were deposited on (001), (110), and (111) SrTiO₃ substrates

using pulsed-laser deposition from the composite ceramic tar-

gets (see Experimental section for details). At the typical

growth temperatures (~630 °C), both CoFe₂O₄ (CFO) and

PbTiO₃ (PTO) crystallize with cubic structures having lattice

parameters $a_{\rm CFO}/2 \sim 4.22$ Å and $a_{\rm PTO} = 3.97$ Å, respectively,

which are similar to the lattice parameter of SrTiO₃ (STO),

 $a_{\rm STO} \sim 3.93$ Å; that is, the lattice match among all three com-

ponents is sufficient to enable 3D epitaxy. Indeed, all films, re-

gardless of substrate orientation and phase fractions, con-

tained a mixture of CoFe₂O₄ and PbTiO₃ phases adopting a

cube-on-cube epitaxial relationship with respect to each other

and the substrate, as confirmed by X-ray and electron diffrac-

tion analyses. The interphase boundaries in all cases were ap-

proximately vertical (i.e. perpendicular to the substrate sur-

face) and extended from the top surface to the film/substrate

interface. However, the morphologies of the component

phases varied markedly with the substrate orientation and

phase fractions, as was inferred from the plan-view scanning

electron microscopy (SEM) and transmission electron micros-

on (110) SrTiO₃ featured alternating vertical lamellae of Co-

Fe₂O₄ and PbTiO₃ preferentially aligned along the [100] di-

rection in the film plane (Fig. 1b). The (111)-oriented x = 1/3

films exhibited yet another, labyrinth-like morphology

(Fig. 1c). For the (001) substrate orientation, reversal of the

phase fractions from x = 1/3 to x = 2/3 did not produce any

principal morphological changes: the x = 2/3 films still con-

tained CoFe₂O₄ rods in a continuous PbTiO₃ matrix (Fig. 1d).

Similar to the previous reports on self-assembled nanostructures,^[8,11–13] the PbTiO₃-rich (x = 1/3) films grown on (001) SrTiO₃ contained rodlike pillars of CoFe₂O₄ dispersed in a PbTiO₃ matrix (Fig. 1a). In contrast, the x = 1/3 films grown

copy (TEM) images (Fig. 1).

Multiferroic xCoFe₂O₄-(1-x)PbTiO₃ films (x = 1/3 or 2/3)

roelectric perovskite-type matrix.

nent phases.

By Igor Levin,* Jianhua Li, Julia Slutsker, and Alexander L. Roytburd

Magnetoelectric (ME) materials that exhibit an induction of magnetization by an electric field or an induction of electric polarization by a magnetic field offer increased functionality and entirely new applications for electronic devices.^[1] Examples of potential applications include multistate memories and logic, tunable filters, sensors, and new types of electromechanical devices. The ME response exhibited by all known singlephase materials is either too weak or occurs at temperatures too low for practical exploitation.^[1,2] In contrast, laminated ceramic composites, fabricated from piezoelectric and magnetostrictive components, have been found to exhibit strain-mediated ME responses an order-of-magnitude larger than those observed in single-phase materials.^[3,4] Several types of devices incorporating such composites have been demonstrated.^[5-7] Unfortunately, existing bulk ME composites are not amenable to on-chip integration, which is a prerequisite for incorporation into microelectronic devices. The principal problem in implementing strain-mediated layered ME thin-film composites is related to the strong clamping effects of the substrate, which effectively inhibit the ME response.^[8-10] The clamping can be significantly reduced by generating transversely modulated composite films with interphase boundaries perpendicular to the substrate. Recently, transverse nanostructures have been synthesized using epitaxial self-assembly of CoFe2O4 (ferrimagnetic) and BaTiO₃ (ferroelectric) phases on singlecrystal (001) SrTiO₃ substrates.^[8] These films, which consisted of CoFe₂O₄ nanorods in a BaTiO₃ matrix, were shown to exhibit substantial ME coupling (in contrast to the layered heterostructures), which was attributed to 1) a reduced clamping effect by the substrate, and 2) efficient strain coupling resulting from the nanometer scale of the component phases and coherency of the interfaces. Subsequently, similar self-assembled nanostructures were obtained in composite CoFe₂-O₄-PbTiO₃^[11] and CoFe₂O₄-BiFeO₃ films;^[12] in the latter system, a polarization reversal by the external magnetic field was

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2044

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Figure 1. SEM images revealing the morphologies of the xCoFe₂O₄-(1-x)PbTiO₃ films grown epitaxially on differently oriented SrTiO₃ substrates. a-c) x = 1/3, d-f) x = 2/3. a,d) (001) SrTiO₃; b,e) (110) SrTiO₃; c,f) (111) SrTiO₃. The bright and dark regions correspond to PbTiO₃ and CoFe₂O₄, respectively. In (e), the PbTiO₃ appears as the brightest regions (inclusions), whereas the darker areas represent the CoFe₂O₄ (matrix); the grayscale variations inside the CoFe₂O₄ result from the CoFe₂O₄ surface topography.

In contrast, for the two other substrate orientations, the effect of phase fractions on the nanostructure morphology was very dramatic. For example, the $CoFe_2O_4$ -rich (110)-substrate films featured irregular-shaped isolated columns of PbTiO₃ dispersed in a $CoFe_2O_4$ matrix (Fig. 1e), as opposed to a lamellar-like structure for the PbTiO₃-rich samples (Fig. 1b).

For the (111)-substrate orientation, a labyrinth-like morphology (Fig. 1c) was replaced by cylindrical PbTiO₃ nanorods (20–30 nm in diameter) in a CoFe₂O₄ matrix for x = 2/3 (Fig. 1f, Fig. 2). The PbTiO₃ nanorods exhibited facets having {112} traces in the film plane (Fig. 2); slower growth rates yielded rods having a well-defined triangular prism shape (Fig. 3). Clearly, epitaxial self-assembly provides a promising



Figure 2. a,b) Cross-sectional and plan-view diffraction contrast images of the x = 2/3 films on the (111) SrTiO₃ showing the PbTiO₃ rods (bright) in the CoFe₂O₄ matrix (dark). c) Low-magnification high-resolution TEM image showing faceting of the PbTiO₃ nanorods.



Figure 3. SEM image of the triangular-shaped PbTiO₃ rods in the CoFe₂O₄ matrix for the x = 2/3 film grown on (111) SrTiO₃ at a slower rate than that used for the film shown in Fig. 2.

approach for generating arrays of ferroelectric nanorods in the lattice-matched matrix (not necessarily magnetic). The <111> nanorods should be particularly interesting for ferroelectric compounds crystallizing with a rhombohedral-like structure so that the direction of polarization would be parallel to the rod axis. Additionally, composite epitaxial nanostructures containing ferroelectric nanorods can provide excellent samples for studying the effects of constraints on ferroelectric phase transitions in low dimensions.

The PbTiO₃/CoFe₂O₄ interfaces in all films were strongly faceted on the {111} planes while maintaining the average vertical orientation. For example, in the PbTiO₃-rich nanostructures on (001) SrTiO₃, the $\{111\}$ facets alternated about the vertical (110) planes (Fig. 4a and b). Note that these facets intersect the film surface along the (110) traces, giving a false appearance of (110) faceting in the plan-view images. Similar {111} faceting occurred in the nanostructures grown on (110) and (111) SrTiO₃, with the facets being inclined at 90° and 70° to the substrate, respectively (e.g., Fig. 4c). In fact, the lamellae in the (110)-oriented films consisted of segments parallel to the two nonequivalent <112> directions in the film plane aligned at ±35° with respect to the in-plane [100] direction (Fig 4c). An example of the $\{111\}$ faceting in the CoFe₂O₄rich nanostructures is shown in Fig. 4d. Apparently, the orientation of the interfaces was determined by superposition of two effects: 1) coupled eutectic-like growth of the composite film, which supports a vertical alignment of the interfaces, and 2) minimization of the elastic and interfacial energies, which promotes faceting on the favorable crystallographic planes.

High-resolution TEM (HRTEM) imaging of the CoFe₂O₄/ PbTiO₃ interfaces revealed misfit dislocations which were separated by distances larger (on average by 20–25 %) than those expected for complete relaxation of the epitaxial strain; that is, these interfaces are semicoherent, implying the existence of nonrelaxed epitaxial stresses. Imaging of the film/substrate interface for the (001) SrTiO₃ orientation confirmed a strong tendency for the PbTiO₃ to wet the substrate, thus minimizing the contact between the CoFe₂O₄ and SrTiO₃. This effect can be attributed to an order-of-magnitude smaller lattice misfit between PbTiO₃ and SrTiO₃ than between Co-Fe₂O₄ and SrTiO₃. Furthermore, preferential wetting of

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Figure 4. a,b) Cross-sectional dark-field and phase-contrast images of the CoFe₂O₄ rods in the x = 1/3 films grown on (001) SrTiO₃. c) Plan-view dark-field image of the x = 1/3 film grown on (110) SrTiO₃. d) Plan-view dark-field image of the x = 2/3 film grown on (111) SrTiO₃. CoFe₂O₄ and PbTiO₃ are imaged as bright and dark regions, respectively. All images reveal strong faceting of the PbTiO₃/CoFe₂O₄ interfaces on the {111} planes.

SrTiO₃ by PbTiO₃ is supported by the existence of favorable {111} orientations (inclined at 54° to the substrate) for the CoFe₂O₄/PbTiO₃ interfaces. The film/substrate interface was semicoherent with misfit dislocations.

The observed morphological changes as a function of substrate orientation and phase fractions conform to the predictions of phase-field modeling, which assumed that the two phases self-assemble during growth to minimize the sum of elastic and interfacial energies. A 3D phase-field model described the nanostructures as a continuous field of the order parameter $\eta(r)$. The equilibrium arrangements of phases were determined by minimizing the free energy, F, which included both interfacial (isotropic) and elastic (anisotropic) energy terms, with respect to η . The model incorporated partial relaxation of the epitaxial stresses by introducing misfit dislocations along the interfaces. The equation $\partial F/\partial \eta(r) = 0$ was solved using a relaxation procedure that considered a virtual phase transformation from the unstable initial phase ($\eta = 0$) to a two-phase state corresponding to the two minima of the specific free energy $f(\eta) = f_0(\eta - \eta^2)^2$, where $\eta_{01} = -1$ and $\eta_{02} = 1$ and f_0 is the specific free energy at $\eta = 0$. The time evolution of the phase field of the order parameters, as described by the timedependent Landau–Ginzburg equation, was solved using the microelasticity approach.^[14–16]

The calculated morphologies correctly predict the effect of substrate orientation on the nanostructure architectures. In particular, even such nontrivial morphological changes as lamellar to labyrinth (Fig. 5a,b), with substrate orientation varying from (110) to (111), and labyrinth to rod (Fig. 5c,d), with the PbTiO₃ fraction decreasing from 2/3 to 1/3, were reproduced. This strikingly consistent agreement between the experimental and calculated data, obtained despite the assumption of thermodynamic equilibrium, provides strong support for the dominant role of elastic interphase interactions in defining the morphologies of the nanostructures. In particular, the modeling showed that the morphologies are determined by the symmetry of the in-plane stress state, as dictated by the substrate orientation. A complete account of theoretical modeling of morphologies in self-assembled nanostructures is outside the scope of this communication and will be reported separately.

In summary, the results of this study demonstrate that the epitaxial self-assembly of two largely immiscible phases on a single-crystal substrate is driven by the elastic interactions that, under the appropriate growth conditions, dominate over the kinetic factors and determine the resulting phase morphology and arrangement. In that case, the morphological characteristics of the nanostructures can be controlled by modifying the stress state in the film, which can be accomplished, for example, by using different substrate orientations and phase fractions. We demonstrated that multiferroic nanostructures containing either magnetic or ferroelectric nanorods can be obtained by the appropriate choice of substrate orientation. Ultimately, our combined experimental and modeling results suggest that the rational design of epitaxial composite functional nanostructures is feasible.



Figure 5. xCoFe₂O₄–(1-x)PbTiO₃ nanostructures simulated using phase-field modeling. a,b) x = 1/3; c,d) x = 2/3. a,c) Substrate: (110) SrTiO₃; b,d) substrate (111) SrTiO₃. Bright and dark regions correspond to Co-Fe₂O₄ and PbTiO₃, respectively. Note the good agreement with the corresponding phase morphologies in Fig. 1b,e,c,f.



Experimental

The *x*CoFe₂O₄–(1–*x*)PbTiO₃ films were deposited on (001), (110), and (111) SrTiO₃ substrates using pulsed laser (KrF excimer) deposition from the composite ceramic targets having fixed preselected x = 1/3 and x = 2/3 compositions. The substrate temperature was kept at 630 °C, and simultaneous growth on differently oriented substrates was used to ensure similar growth conditions. A dynamic oxygen pressure of 100 mTorr (1 torr ~133 Pa) was maintained in the deposition chamber. Films with thicknesses of ~200–230 nm were deposited at a growth rate of 2–3 nm min⁻¹ using a laser density of 1.6 J cm⁻². The structures of the samples were characterized using X-ray diffraction and scanning and transmission electron microscopy. The samples for TEM were prepared using conventional sectioning, grinding, and polishing, followed by Ar ion-thinning until perforation.

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