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 single-phase 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 CoFe$_2$O$_4$ (ferrimagnetic) and BaTiO$_3$ (ferroelectric) phases on single-crystal (001) SrTiO$_3$ substrates.\[8\] These films, which consisted of CoFe$_2$O$_4$ nanorods in a BaTiO$_3$ 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 CoFe$_2$O$_4$–PbTiO$_3$ and CoFe$_2$O$_4$–BiFeO$_3$ films,\[11\] in the latter system, a polarization reversal by the external magnetic field was demonstrated. All multiferroic nanostructures reported to date have been limited to CoFe$_2$O$_4$ pillars embedded in a ferroelectric perovskite-type matrix.

In the present report, we demonstrate that the morphologies of self-assembled multiferroic nanostructures can be varied 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 obtained by varying the substrate orientation and phase fractions in epitaxial composite films containing ferrimagnetic CoFe$_2$O$_4$ and ferroelectric PbTiO$_3$. The approach relies on the epitaxial stress-controlled self-assembling of the component phases.

Multiferroic $x$CoFe$_2$O$_4$–$(1-x)$PbTiO$_3$ films ($x=1/3$ or 2/3) were deposited on (001), (110), and (111) SrTiO$_3$ substrates using pulsed-laser deposition from the composite ceramic targets (see Experimental section for details). At the typical growth temperatures ($\sim630^\circ$C), both CoFe$_2$O$_4$ (CFO) and PbTiO$_3$ (PTO) crystallize with cubic structures having lattice parameters $a_{\text{CFO}} \sim 4.22$ Å and $a_{\text{PTO}} = 3.97$ Å, respectively, which are similar to the lattice parameter of SrTiO$_3$ (STO), $a_{\text{STO}} \sim 3.93$ Å; that is, the lattice match among all three components is sufficient to enable 3D epitaxy. Indeed, all films, regardless of substrate orientation and phase fractions, contained a mixture of CoFe$_2$O$_4$ and PbTiO$_3$ phases adopting a cube-on-cube epitaxial relationship with respect to each other and the substrate, as confirmed by X-ray and electron diffraction analyses. The interphase boundaries in all cases were approximately vertical (i.e. perpendicular to the substrate surface) 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 microscopy (TEM) images (Fig. 1).

Similar to the previous reports on self-assembled nanostructures,\[8,11-13\] the PbTiO$_3$-rich ($x=1/3$) films grown on (001) SrTiO$_3$ contained rodlike pillars of CoFe$_2$O$_4$ dispersed in a PbTiO$_3$ matrix (Fig. 1a). In contrast, the $x=1/3$ films grown on (110) SrTiO$_3$ featured alternating vertical lamellae of CoFe$_2$O$_4$ and PbTiO$_3$ preferentially aligned along the [100] direction 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 contained CoFe$_2$O$_4$ rods in a continuous PbTiO$_3$ matrix (Fig. 1d).

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

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

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In contrast, for the two other substrate orientations, the effect of phase fractions on the nanostructure morphology was very dramatic. For example, the CoFe$_2$O$_4$-rich (110)-substrate films featured irregular-shaped isolated columns of PbTiO$_3$ dispersed in a CoFe$_2$O$_4$ matrix (Fig. 1e), as opposed to a lamellar-like structure for the PbTiO$_3$-rich samples (Fig. 1b). For the (111)-substrate orientation, a labyrinth-like morphology (Fig. 1c) was replaced by cylindrical PbTiO$_3$ nano-rods (20–30 nm in diameter) in a CoFe$_2$O$_4$ matrix for $x = \frac{2}{3}$ (Fig. 1f, Fig. 2). The PbTiO$_3$ 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 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.

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For the (111)-substrate orientation, a labyrinth-like morphology (Fig. 1c) was replaced by cylindrical PbTiO$_3$ nanorods (20–30 nm in diameter) in a CoFe$_2$O$_4$ matrix for $x = \frac{2}{3}$ (Fig. 1f, Fig. 2). The PbTiO$_3$ 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).

High-resolution TEM (HRTEM) imaging of the CoFe$_2$O$_4$/PbTiO$_3$ 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) SrTiO$_3$ orientation confirmed a strong tendency for the PbTiO$_3$ to wet the substrate, thus minimizing the contact between the CoFe$_2$O$_4$ and SrTiO$_3$. This effect can be attributed to an order-of-magnitude smaller lattice misfit between PbTiO$_3$ and SrTiO$_3$ than between CoFe$_2$O$_4$ and SrTiO$_3$. Furthermore, preferential wetting of...
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 \( g(r) \). 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 \( g \). The model incorporated partial relaxation of the epitaxial stresses by introducing misfit dislocations along the interfaces. The equation \( \frac{\partial F}{\partial \eta(r)} = 0 \) 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 \( f(\eta) = f_0(\eta - \eta_0)^2 \), 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 time-dependent 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.
**Experimental**

The $x\text{CoFe}_2\text{O}_4$–$(1-x)\text{PbTiO}_3$ films were deposited on (001), (110), and (111) SrTiO$_3$ 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 $\sim$ 133 Pa) was maintained in the deposition chamber. Films with thicknesses of $\sim$200–230 nm were deposited at a growth rate of 2–3 nm min$^{-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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