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Three-dimensional heteroepitaxy in self-assembled BaTiO₃-CoFe₂O₄ nanostructures

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Self-assembled BaTiO₃-CoFe₂O₄ complex oxide nanostructures have been synthesized by pulsed laser deposition. A single ceramic target with a molar ratio of 0.62BaTiO₃-0.38CoFe₂O₄ was used. Spinel CoFe₂O₄ and perovskite BaTiO₃ phases spontaneously separated during heteroepitaxial growth on a single-crystal SrTiO₃ (001) substrate. The nanostructures are epitaxial in-plane as well as out-of-plane, with CoFe₂O₄ nanopillar arrays embedded in a BaTiO₃ matrix. The CoFe₂O₄ nanopillars have uniform size and spacing and nearly circular cross section. As the substrate temperature increases from 750 to 950 °C, the average diameter of the pillars increases from ~9 to ~70 nm. © 2004 American Institute of Physics. [DOI: 10.1063/1.1786653]

Nanostructured materials have shown significant promise for a wide range of electronic, optoelectronic, and magnetic applications. The creation of nanostructures with uniform size and spacing in epitaxial heterostructures through self-assembly offers great potential to tailor the physical properties and explore the fabrication of new functional devices. In semiconductor systems, the growth of self-assembled strained coherent island heterostructures has been intensively studied both theoretically and experimentally.¹⁻³ However, such structures have rarely been reported in complex oxide thin films. In the present work, we report on a simple yet general approach to form spinel-perovskite nanostructures by self-assembly in thin film heteroepitaxy.

The approach is based on two concepts. The first is the intrinsic similarity in crystal chemistry between perovskites and spinels, both of which are based on an octahedral oxygen coordination. This leads to crystal lattice parameters that are reasonably commensurate. The second key aspect is the fact that although many of these complex oxides can accommodate considerable cationic solid solution solubility, the perovskite/spinel system behaves like line compounds.⁴ That is, these compounds have very little solid solubility into each other (for example, the spinel in the perovskite). These two aspects then present an interesting opportunity to create perovskite-spinel nanostructures through a spontaneous phase separation process. The two phases in the nanostructure simultaneously can be epitaxial with respect to each other as well as with respect to a common substrate [which, for example, could be a single crystal (001) perovskite]. We illustrate this concept through a prototypical example of the BaTiO₃-CoFe₂O₄ system. BaTiO₃-CoFe₂O₄ is an interesting magnetoelectric system^{5,6} since BaTiO₃ is ferroelectric with large piezoelectricity and CoFe₂O₄ is ferrimagnetic with large magnetostriction. We have recently reported that thin

films of such a system form vertically aligned two-phase nanostructures and show strong magnetoelectric coupling of the order parameters through elastic interactions between the two phases.⁷ At room temperature, BaTiO₃ has a perovskite structure with lattice parameters $a=0.399$ nm and $c=0.404$ nm, while CoFe₂O₄ has a spinel structure with a lattice parameter of $a=0.838$ nm or approximately twice the basic building block of BaTiO₃. There is a ~5% lattice mismatch between the two structures. By selecting a suitable substrate with similar crystal structure, such as SrTiO₃, we present the tantalizing possibility of heteroepitaxy in three-dimensions (i.e., both in-plane as well as out-of-plane) in the film. In the present manuscript we report a detailed study of the structure of the nanocomposite as well as the growth kinetics.

The BaTiO₃-CoFe₂O₄ nanostructured thin films studied in this work were deposited on SrTiO₃ (001) substrates using pulsed laser deposition with a KrF ($\lambda=248$ nm) excimer laser. A single ceramic target with molar ratio of 0.62BaTiO₃-0.38CoFe₂O₄ was used. The substrate temperature was varied in the range of 700-950 °C and a dynamic chamber pressure of 100 m Torr O₂ was maintained during deposition. Films with thickness of ~400 nm were deposited at a growth rate of ~10 nm/min and a laser density of 1.2 J/cm². After the deposition, the samples were cooled to room temperature in 1 atm oxygen ambient at a cooling rate of 5 °C/min. The films were characterized by x-ray diffraction using Cu K α radiation in a Siemens D5000 four-circle diffractometer and by transmission electron microscopy (TEM) using a JEOL 4000FX operating at 300 kV.

A typical x-ray θ - 2θ diffraction spectrum [Fig. 1(a)] shows that the film has (00 l) oriented structure with high crystallinity. The spectrum contains three sets of diffraction peaks that can be assigned, respectively, to (00 l) spinel CoFe₂O₄ and (00 l) perovskite BaTiO₃ in addition to (00 l) reflections from the SrTiO₃ substrate. The observation of distinct peaks for BaTiO₃ and CoFe₂O₄ indicates that the two

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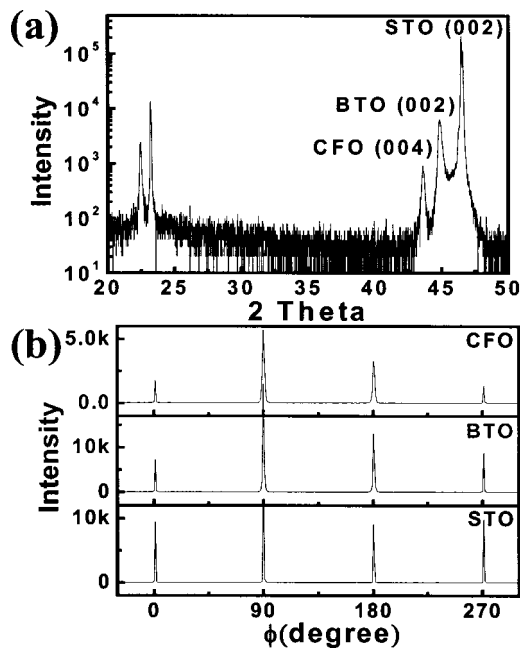


FIG. 1. (a) X-ray θ - 2θ scan showing (00 l) families of peaks, which can be assigned to CoFe₂O₄, BaTiO₃, and the SrTiO₃ substrate. (b) ϕ -scans using (202) reflection of BaTiO₃, (404) reflection of CoFe₂O₄, and (202) reflection of SrTiO₃ substrate from the same sample.

phases coexist in the film. The ϕ scans of the (202) peak for BaTiO₃ phase and (404) peak for CoFe₂O₄ phase of the film as well as (202) peaks for the substrate are presented in Fig. 1(b). The fourfold symmetry indicates a “cube-on-cube” epitaxy of both BaTiO₃ and CoFe₂O₄ on SrTiO₃, as well as an in-plane epitaxy between the two phases in the film. Selected area electron diffraction patterns confirmed the epitaxial growth orientation relationship: [100]SrTiO₃//[100]BaTiO₃//[100]CoFe₂O₄.

Figure 2(a) is a dark field TEM image obtained using the CoFe₂O₄ (130) spot from a cross-sectional sample grown at 920°C. The image shows that the CoFe₂O₄ phase has a columnar structure. The CoFe₂O₄ pillars are separated by the BaTiO₃ matrix and extend through the whole film from the film/substrate interface to the surface (with an aspect ratio of ~12). It is interesting that all the pillars grow out of the matrix, forming islands that extend above the surface of the BaTiO₃ matrix with a height of 10–15 nm as can be seen in Fig. 2(b). This can be explained by the heteroepitaxial growth feature of the film. Namely, the c lattice parameters of BaTiO₃ and CoFe₂O₄ calculated from the XRD and electron diffraction patterns are c =0.404 nm for BaTiO₃ and c =0.834 nm for CoFe₂O₄. There are about 990 unit cells of BaTiO₃ along the film growth thickness of 400 nm. We assume approximately 990/2 units of CoFe₂O₄ along the pillars. Therefore, the calculated height of CoFe₂O₄ pillars is ~412.8 nm, which is in agreement with the experimentally observed value (410–415 nm). The high resolution TEM image in Fig. 2(c) shows that dislocations form at the interface between the CoFe₂O₄ pillars and the BaTiO₃ matrix, which partially relax the lattice mismatch strain between the two phases. However, a residual strain of 0.4% in the CoFe₂O₄ pillars still remains.

Figure 3(a) is a TEM plan view image taken from the sample deposited at 920°C. It shows that the CoFe₂O₄ nanopillars are homogeneously distributed in the BaTiO₃ matrix.

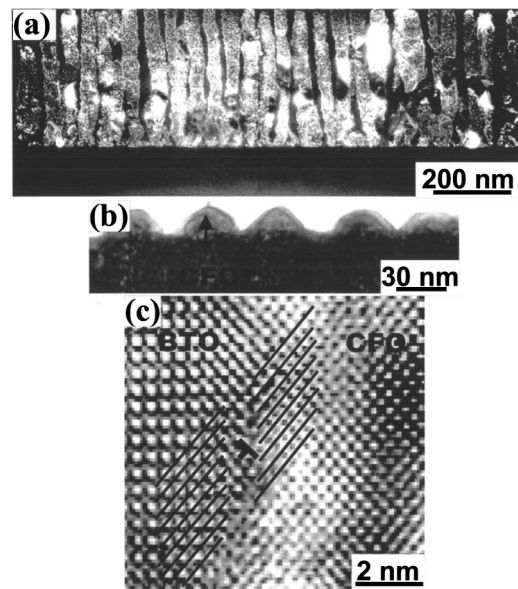


FIG. 2. (a) Cross-section dark field TEM image taken with g =[130] of CoFe₂O₄ (CFO). (b) Cross-section bright field TEM image showing the outgrowth of the CoFe₂O₄ nanopillars. (c) Cross-section high resolution TEM image showing dislocations formed at the interface between a CoFe₂O₄ pillar and the BaTiO₃ (BTO) matrix.

The inset is the statistical size distribution of the pillars, which was calculated from a $2 \times 2 \mu\text{m}^2$ area of the image; it shows that ~94% of the pillars are within the size range of 25–35 nm. The volume fraction of the nanopillars calculated using the plan view TEM image is about 40%, which is in agreement with the 38% fraction of CoFe₂O₄ in the target. The lateral dimensions of the CoFe₂O₄ nanopillars increase systematically with increasing growth temperature. The average size of the pillars increases from ~9 to ~70 nm as the deposition temperature increases from 750 to 950°C, respec-

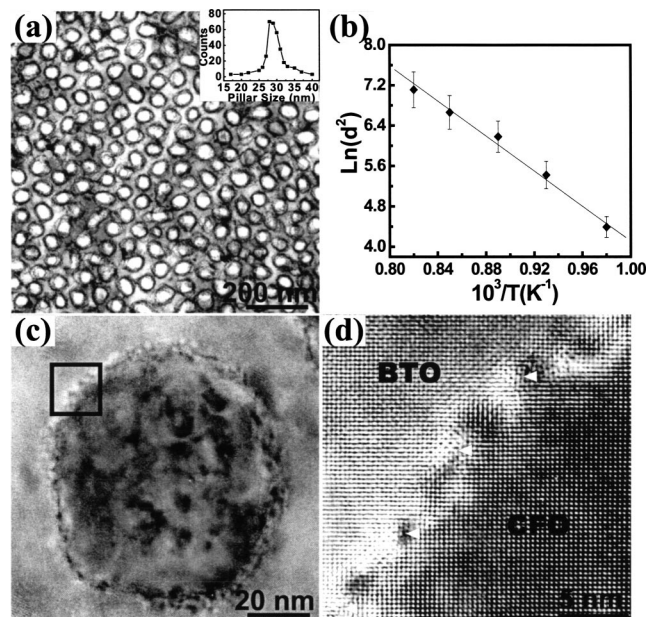


FIG. 3. (a) Plan view TEM image of the film grown at 920°C with the inset of statistic size distribution of the pillars. (b) Lateral dimension of the CoFe₂O₄ nanopillars vs temperature. (c) In-plane high resolution TEM image of one CoFe₂O₄ pillar embedded in the BaTiO₃ matrix grown at 950°C. (d) Magnified segment of the interface between the CoFe₂O₄ pillar and the BaTiO₃ matrix from (c).

tively. No phase separation was observed at 700°C at the growth rate of 10 nm/min. Deposition temperatures in this study were restricted to $\leq 950^\circ\text{C}$ due to the operating temperature limit of our heater. In the temperature range of 750–950°C, the temperature dependence of the lateral dimensions of the nanopillars can be fitted to an Arrhenius behavior, which suggests a diffusion controlled growth mechanism, see Fig. 3(b). Plan view high resolution TEM images show that in the temperature range studied all the pillars are single crystals with sharp interfaces with the matrix. Figure 3(c) is a high resolution TEM image of one CoFe_2O_4 pillar embedded in the BaTiO_3 matrix, which was taken from the sample grown at 950°C. A periodic dislocation array was found at the interface [Fig. 3(d)], which relaxes the lattice mismatch strain between the two phases. It is interesting to note that the nanopillars have fairly circular cross section with very small microfaceting even at the high growth temperature [Fig. 3(c)]. Faceting does not occur in this system probably because of the increase in interfacial energy that would be produced by sharp corners.

The formation of self-organized epitaxial arrays of CoFe_2O_4 columns in a BaTiO_3 matrix in thin films is a process directed by both thermodynamic equilibrium and kinetic diffusion. In bulk, BaTiO_3 and CoFe_2O_4 are essentially line compounds with very small mutual solubilities.⁴ Given adequate kinetic conditions, phase separation is expected due to the thermodynamic instability of the solutions at the growth temperature. The size evolution of the CoFe_2O_4 nanopillars with growth temperature in the present case, with fine pillars at low temperature and coarser pillars at higher temperature, indicates that the growth of the pillars is kinetically controlled by surface diffusion during growth.^{8,9} It is a very interesting question as to why CoFe_2O_4 forms pillars in this system. There are several factors that have to be considered to answer the question. One is the lattice mismatch of the film to substrate, and the lattice mismatch between the two phases in the film. Another is the difference in Young's

modulus of the two phases.¹⁰ The volume fraction of the two phases and the crystal structure of the substrate (i.e., perovskite, or spinel) could also play a role. In order to identify which is the drive force to the formation of the nanopillar structure (as well as the phase that forms the nanopillar), systematic studies are required; such studies are in progress and the results will be published in future publications.¹¹

In conclusion, self-organized CoFe_2O_4 – BaTiO_3 nanostructures exhibiting three-dimensional heteroepitaxy have been successfully synthesized by heteroepitaxial growth. The growth of the pillars is kinetically controlled. The CoFe_2O_4 nanopillars have a narrow size distribution and are homogeneously distributed in a BaTiO_3 matrix. This approach to the formation of self-assembled nanostructures is generic, and can be applied to other perovskite-spinel systems.

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