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# Three-dimensional heteroepitaxy in self-assembled $BaTiO_3-CoFe_2O_4$ nanostructures

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Self-assembled $BaTiO_3-CoFe_2O_4$ complex oxide nanostructures have been synthesized by pulsed laser deposition. A single ceramic target with a molar ratio of $0.62BaTiO_3-0.38CoFe_2O_4$ was used. Spinel $CoFe_2O_4$ and perovskite $BaTiO_3$ phases spontaneously separated during heteroepitaxial growth on a single-crystal $SrTiO_3$ (001) substrate. The nanostructures are epitaxial in-plane as well as out-of-plane, with $CoFe_2O_4$ nanopillar arrays embedded in a $BaTiO_3$ matrix. The $CoFe_2O_4$ 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 $BaTiO_3-CoFe_2O_4$ system. $BaTiO_3-CoFe_2O_4$ is an interesting magnetoelectric system[5,6] since $BaTiO_3$ is ferroelectric with large piezoelectricity and $CoFe_2O_4$ 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, $BaTiO_3$ has a perovskite structure with lattice parameters $a=0.399$ nm and $c=0.404$ nm, while $CoFe_2O_4$ has a spinel structure with a lattice parameter of $a=0.838$ nm or approximately twice the basic building block of $BaTiO_3$. There is a ∼5% lattice mismatch between the two structures. By selecting a suitable substrate with similar crystal structure, such as $SrTiO_3$, 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 $BaTiO_3-CoFe_2O_4$ nanostructured thin films studied in this work were deposited on $SrTiO_3$ (001) substrates using pulsed laser deposition with a KrF ($\lambda=248$ nm) excimer laser. A single ceramic target with molar ratio of $0.62BaTiO_3-0.38CoFe_2O_4$ was used. The substrate temperature was varied in the range of 700–950 °C and a dynamic chamber pressure of 100 m Torr $O_2$ 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 $J/cm^2$. 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 $K\alpha$ 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 $\theta-2\theta$ diffraction spectrum [Fig. 1(a)] shows that the film has $(00l)$ oriented structure with high crystallinity. The spectrum contains three sets of diffraction peaks that can be assigned, respectively, to $(00l)$ spinel $CoFe_2O_4$ and $(00l)$ perovskite $BaTiO_3$ in addition to $(00l)$ reflections from the $SrTiO_3$ substrate. The observation of distinct peaks for $BaTiO_3$ and $CoFe_2O_4$ indicates that the two

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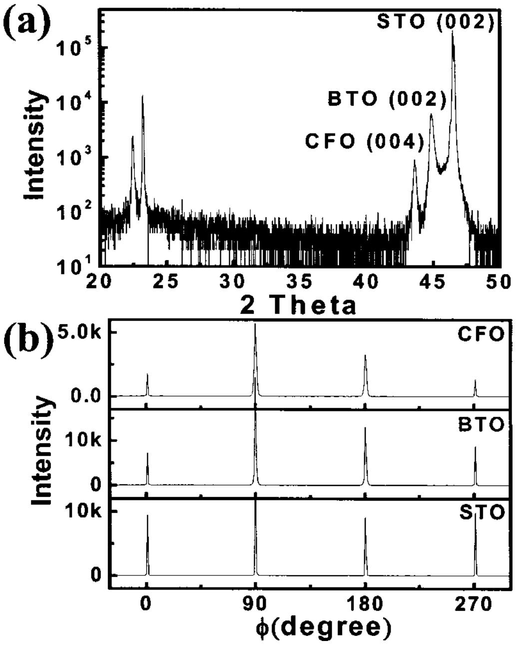

FIG. 1. (a) X-ray $\theta-2\theta$ scan showing $(00l)$ families of peaks, which can be assigned to $CoFe_2O_4$, $BaTiO_3$, and the $SrTiO_3$ substrate. (b) $\phi$-scans using (202) reflection of $BaTiO_3$, (404) reflection of $CoFe_2O_4$, and (202) reflection of $SrTiO_3$ substrate from the same sample.

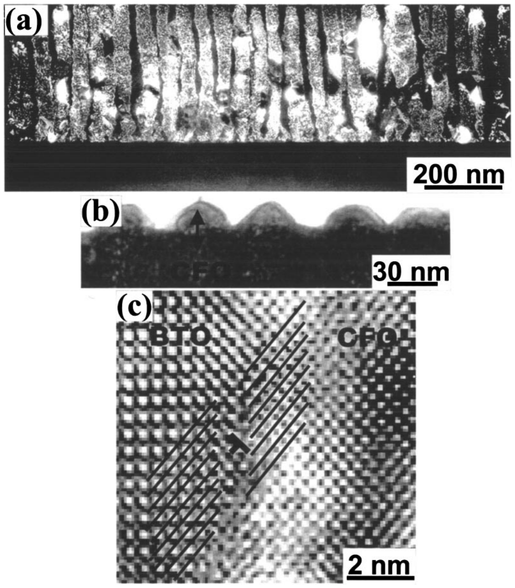

FIG. 2. (a) Cross-section dark field TEM image taken with $g=[130]$ of $CoFe_2O_4$ (CFO). (b) Cross-section bright field TEM image showing the outgrowth of the $CoFe_2O_4$ nanopillars. (c) Cross-section high resolution TEM image showing dislocations formed at the interface between a $CoFe_2O_4$ pillar and the $BaTiO_3$ (BTO) matrix.

phases coexist in the film. The $\phi$ scans of the (202) peak for $BaTiO_3$ phase and (404) peak for $CoFe_2O_4$ 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 $BaTiO_3$ and $CoFe_2O_4$ on $SrTiO_3$, 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: $[100]SrTiO_3//[100]BaTiO_3//[100]CoFe_2O_4$.

Figure 2(a) is a dark field TEM image obtained using the $CoFe_2O_4$ (130) spot from a cross-sectional sample grown at 920 °C. The image shows that the $CoFe_2O_4$ phase has a columnar structure. The $CoFe_2O_4$ pillars are separated by the $BaTiO_3$ 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 $BaTiO_3$ 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 $BaTiO_3$ and $CoFe_2O_4$ calculated from the XRD and electron diffraction patterns are $c=0.404$ nm for $BaTiO_3$ and $c=0.834$ nm for $CoFe_2O_4$. There are about 990 unit cells of $BaTiO_3$ along the film growth thickness of 400 nm. We assume approximately 990/2 units of $CoFe_2O_4$ along the pillars. Therefore, the calculated height of $CoFe_2O_4$ 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 $CoFe_2O_4$ pillars and the $BaTiO_3$ matrix, which partially relax the lattice mismatch strain between the two phases. However, a residual strain of 0.4% in the $CoFe_2O_4$ pillars still remains.

Figure 3(a) is a TEM plan view image taken from the sample deposited at 920 °C. It shows that the $CoFe_2O_4$ nanopillars are homogeneously distributed in the $BaTiO_3$ matrix. The inset is the statistical size distribution of the pillars, which was calculated from a $2\times2\ \mu m^2$ 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 $CoFe_2O_4$ in the target. The lateral dimensions of the $CoFe_2O_4$ 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-

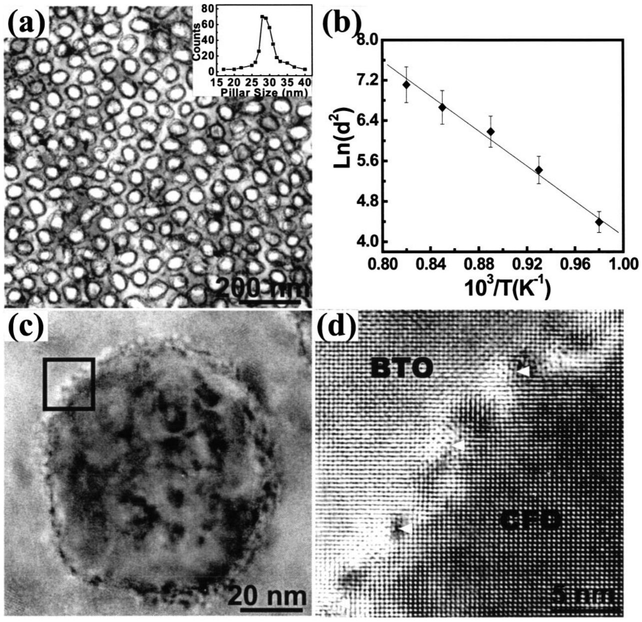

FIG. 3. (a) Plan view TEM image of the film grown at 920 °C with the inset of statistic size distribution of the pillars. (b) Lateral dimension of the $CoFe_2O_4$ nanopillars vs temperature. (c) In-plane high resolution TEM image of one $CoFe_2O_4$ pillar embedded in the $BaTiO_3$ matrix grown at 950 °C. (d) Magnified segment of the interface between the $CoFe_2O_4$ pillar and the $BaTiO_3$ 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 $\leqslant 950\,°\mathrm{C}$ 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-dimemensional 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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