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Three-dimensional heteroepitaxy in self-assembled BaTiO$_3$–CoFe$_2$O$_4$ nanostructures

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Self-assembled BaTiO$_3$–CoFe$_2$O$_4$ complex oxide nanostructures have been synthesized by pulsed laser deposition. A single ceramic target with a molar ratio of 0.62BaTiO$_3$–0.38CoFe$_2$O$_4$ was used. Spinel CoFe$_2$O$_4$ 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$_2$O$_4$ nanopillar arrays embedded in a BaTiO$_3$ matrix. The CoFe$_2$O$_4$ 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. 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. 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$_2$O$_4$ system. BaTiO$_3$–CoFe$_2$O$_4$ is an interesting magnetoelectric system since BaTiO$_3$ is ferroelectric with large piezoelectricity and CoFe$_2$O$_4$ 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. At room temperature, BaTiO$_3$ has a perovskite structure with lattice parameters $a=0.399$ nm and $c=0.404$ nm, while CoFe$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ 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 Ka 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$_2$O$_4$ 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$_2$O$_4$ indicates that the two
phases coexist in the film. The $\phi$ scans of the (202) peak for BaTiO$_3$ phase and (404) peak for CoFe$_2$O$_4$ 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$_2$O$_4$ 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:

$$[100]_{\text{SrTiO}_3} // [100]_{\text{BaTiO}_3} // [100]_{\text{CoFe}_2\text{O}_4}.$$ 

Figure 2(a) is a dark field TEM image obtained using the CoFe$_2$O$_4$ (130) spot from a cross-sectional sample grown at 920°C. The image shows that the CoFe$_2$O$_4$ phase has a columnar structure. The CoFe$_2$O$_4$ 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 $\sim$12. It is interesting that all the pillars grow out of the matrix, forming islands that extend above the surface of the BaTiO$_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$_2$O$_4$ calculated from the XRD and electron diffraction patterns are $c = 0.404$ nm for BaTiO$_3$ and $c = 0.834$ nm for CoFe$_2$O$_4$. 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$_2$O$_4$ along the pillars. Therefore, the calculated height of CoFe$_2$O$_4$ pillars is $\sim 412.8$ 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$_2$O$_4$ 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$_2$O$_4$ 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$_2$O$_4$ nanopillars are homogeneously distributed in the BaTiO$_3$ matrix. The inset is the statistical size distribution of the pillars, which was calculated from a $2 \times 2$ nm$^2$ area of the image; it shows that $\sim 94\%$ 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$_2$O$_4$ in the target. The lateral dimensions of the CoFe$_2$O$_4$ nanopillars increase systematically with increasing growth temperature. The average size of the pillars increases from $\sim 9$ to $\sim 70$ nm as the deposition temperature increases from 750 to 950°C, respectively.
perature. The size evolution of the CoFe$_2$O$_4$ nanopillars
equate kinetic conditions, phase separation is expected due to
diffusion. In bulk, BaTiO$_3$ and CoFe$_2$O$_4$ are essentially line
phases in the film. Another is the difference in Young’s
modulus of the two phases. The volume fraction of the two
phases and the crystal structure of the substrate (i.e., perov-
skite, 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.

In conclusion, self-organized CoFe$_2$O$_3$–BaTiO$_3$ nano-
structures exhibiting three-dimensional heteroepitaxy
have been successfully synthesized by heteroepitaxial
growth. The growth of the pillars is kinetically controlled.
The CoFe$_2$O$_4$ 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 sys-
tems.

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