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Magnetic Phase Formation in Self-Assembled Epitaxial BiFeO₃–MgO and BiFeO₃–MgAl₂O₄ Nanocomposite Films Grown by Combinatorial Pulsed Laser Deposition

Dong Hun Kim,†,‡ XueYin Sun,†,§ Tae Cheol Kim,‡ Yun Jae Eun,‡ Taeho Lee,‡ Sung Gyun Jeong,‡ and Caroline A. Ross†,‡

†Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States
‡Department of Materials Science and Engineering, Myongji University, Yongin 120-728, Republic of Korea
§School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, People’s Republic of China

Supporting Information

ABSTRACT: Self-assembled epitaxial BiFeO₃–MgO and BiFeO₃–MgAl₂O₄ nanocomposite thin films were grown on SrTiO₃ substrates by pulsed laser deposition. A two-phase columnar structure was observed for BiFeO₃–MgO codeposition within a small window of growth parameters, in which the pillars consisted of a magnetic spinel phase (Mg,Fe)₃O₄ within a BiFeO₃ matrix, similar to the growth of BiFeO₃–MgFe₂O₄ nanocomposites reported elsewhere. Further, growth of a nanocomposite with BiFeO₃–(CoFe₂O₄/MgO/MgFe₂O₄), in which the minority phase was grown from three different targets, gave spinel pillars with a uniform (Mg,Fe,Co)₃O₄ composition due to interdiffusion during growth, with a bifurcated shape from the merger of neighboring pillars. BiFeO₃–MgAl₂O₄ did not form a well-defined vertical nanocomposite in spite of having lower lattice mismatch, but instead formed a two-phase film with in which the spinel phase contained Fe. These results illustrate the redistribution of Fe between the oxide phases during oxide codeposition to form a ferrimagnetic phase from antiferromagnetic or nonmagnetic targets.

KEYWORDS: thin film oxide, epitaxy, spinel, perovskite, multiferroic, combinatorial pulsed laser deposition, self-assembled oxide nanocomposite, BiFeO₃

INTRODUCTION

Self-assembled nanocomposite thin films are columnar structures comprising two (or more) codeposited crystalline phases grown epitaxially on a single crystal substrate, and exhibit a remarkable range of functional properties, which can include high-temperature superconductivity, colossal magnetoresistance, ferroelectricity, magnetism, and multiferroicity.¹⁻⁴ Most of the self-assembled nanocomposites reported to date consist of pairs of oxides such as a perovskite (e.g., BiFeO₃, BFO) and a spinel (e.g., CoFe₂O₄, CFO), grown on single crystalline substrates such as (001)-oriented SrTiO₃ (STO). A common morphology is for one phase to grow as pillars within the other,⁵⁻⁸ such as spinel pillars in a perovskite matrix, with both phases epitaxial with the substrate. There are also reports of epitaxial nanocomposite thin films which incorporate other oxide crystal structures such as MgO or ZnO.⁹⁻¹¹ Elastic interactions through the interfaces between the two phases are very important in determining the properties of the nanocomposite. For example, strain transfer at the vertical interface between piezoelectric BiFeO₃ and magnetostrictive CoFe₂O₄ affects the magnetic and ferroelectric properties dramatically and leads to magnetoelectric coupling.⁶,¹⁴⁻¹⁶

Interdiffusion between spinel and perovskite phases has been reported to be small,¹²,¹³ but significant interdiffusion can occur within spinel pillars during deposition, leading to a homogenous pillar composition even if the composition of the arriving flux was changed partway through growth.¹⁷ We showed previously that interdiffusion in spinel pillars was prevented by growing a diffusion barrier such as BFO partway through the film, producing a film consisting of two separated layers of spinel pillars with different compositions.¹⁷

In this paper, we report on the growth of nanocomposites made by combinatorial pulsed laser codeposition of MgO or MgAl₂O₄ (MAO) and a perovskite BFO, with a focus on examining interdiffusion between the two phases during growth, and the deposition conditions that determine which
phase forms. MgO is commonly used as a tunnel barrier material for magnetic tunnel junctions.18,19 MAO has received attention as an alternative barrier material,20,21 and an 8 nm thick MAO layer served as a diffusion barrier preventing Ti migration from an STO substrate into a CFO film.22 MgO and MAO layers are quite well lattice matched to CoFe2O4 or MgFe2O4, suggesting their possible utility as diffusion barriers to be incorporated within nanocomposite films. CFO/MFO nanocomposites have been reported previously.23

**EXPERIMENTAL SECTION**

MgO, MgAl2O4 (MAO, the eponymous spinel), CoFe2O4 (CFO, cobalt ferrite), and MgFe2O4 (MFO, magnesium ferrite) targets were prepared by a conventional oxide sintering method. The lattice parameters of the final targets from X-ray diffraction (XRD) were \( a_{\text{MgO}} = 4.213 \pm 0.002 \) Å and \( a_{\text{MgAl2O4}} = 8.081 \pm 0.003 \) Å, which are close to the bulk lattice parameters of \( a_{\text{bulk,MgO}} = 4.213 \) Å (JCPDS # 04-0829) and \( a_{\text{bulk,MgAl2O4}} = 8.083 \) Å (JCPDS # 21-1151). The target preparation process for CFO and MFO was reported elsewhere.23 A Bi-rich Bi\(_{1.2}\)FeO\(_3\) target was prepared by Plasmaterials, CA.

BFO–MgO and BFO–MAO nanocomposite films were deposited by combinatorial pulsed laser deposition (CPLD) using a KrF excimer laser (\( \lambda = 248 \) nm) on SrTiO\(_3\) (001) substrates (STO, \( a_{\text{bulk,STO}} = 3.905 \) Å) at 5 mTorr of oxygen pressure. The substrate temperature during deposition was fixed at 650 °C, which is the optimal condition in our chamber to make stoichiometric BiFeO\(_3\) from the Bi-rich target. Nanocomposite thin films contained excess Bi at low deposition temperatures,24 whereas the volume fraction of BiFeO\(_3\) was reduced at higher deposition temperatures (>700 °C) due to Bi volatility. The laser frequency was 10 Hz and the fluence at the target was 2.6 J/cm\(^2\). CPLD was used to produce a set of samples with a range of composition by alternately ablating two different targets to produce a submonolayer film of tapered thickness from each target, as described elsewhere.25,26 The five 5 mm by 5 mm STO substrates were placed in a row with 18 mm offset between the center of the plume of evaporated material and the substrate rotation axis, and the target-substrate distance was 7 cm. The films were made using cycles
consisting of 500 laser pulses of BFO followed by 200 pulses of MgO or MAO, repeated to build up the desired film thickness.

The phases present in each film were investigated by XRD (PANalytical X’Pert Pro). Top view images of the surface morphology were obtained from scanning electron microscopy (SEM, Helios Nanolab 600). To observe the vertical growth of the nanostructured composites, some samples were etched with 10% dilute hydrochloric acid (HCl) to remove the BFO and reveal the pillars. Composition analysis was carried out using energy dispersive spectroscopy (EDS) in a high resolution transmission electron microscopy (HR-TEM, JEOL JEM 2010F) instrument. Pillars from the nanocomposite were freed by removing the BFO matrix then gathered on a copper mesh coated with a carbon film using a syringe after dispersing them in isopropyl alcohol. In-plane and out-of-plane magnetic hysteresis loops were measured using vibrating sample magnetometry (VSM, ADE model 1660) at a magnetic field of $-10$ to $+10$ kOe at room temperature. The magnetization was calculated for the whole volume of the film instead of normalizing for the volume of the pillar phase.

### RESULTS AND DISCUSSION

Figure 1a–c shows top view SEM images of the BFO–MgO series, which had thicknesses of 80 to 120 nm. As the BFO content increases, the density and areal coverage of the $\sim 20\sim 40$ nm diameter rectangular islands both decrease. Figure 1d–f shows the corresponding top view SEM images after removing the matrix phase in hydrochloric acid for 2 min. The inset in Figure 1f is a 45° tilted image of the nanocomposite after 1 min etch that shows free-standing pillars supported by the remaining matrix. These images show that the BFO–MgO codeposition produces a columnar nanocomposite of islands or pillars in a Bi-rich matrix. Films were grown up to 200 nm thickness and demonstrated columnar structures.

For the MgO-rich sample of Figure 1a, the XRD peak at $2\theta = 43.0^\circ$ corresponds to MgO(002) with an out-of-plane lattice parameter of $4.209 \pm 0.002$ Å (Figure 1g), which is close to that of bulk MgO. An alternative interpretation is that the pillars consist of a spinel phase, $\text{Mg}_x\text{Fe}_{3-x}\text{O}_4$ ($\text{M}_x\text{FO}$) formed by incorporating Fe from the arriving flux. This is plausible because the lattice parameter of $\text{MgFe}_2\text{O}_4$ ($\text{MFO}$) is 8.375 Å, making its (004) peak nearly coincident with that of MgO (002). Peaks from (00l) pseudocubic BFO were not observed, and instead a peak at $2\theta = 32.1^\circ$ corresponds to bismuth oxide $\text{Bi}_2\text{O}_3$ or to BFO (011) that was removed by etching, Figure 1d. The near-bulk lattice parameter of the MgO or $\text{M}_x\text{FO}$ indicates that it is not coherent with the matrix, and the matrix did not form the usual cube-on-cube BFO/STO (001).

In contrast, the sample in Figure 1b showed peaks from both MgO (002) or $\text{M}_x\text{FO}$ (004) and BFO pseudocubic (00l), Figure 1h. The pillar phase was under out-of-plane compressive strain ($c = 4.187$ Å) compared to the sample of Figure 1(a) due to epitaxy at the vertical interface with BFO. There were two overlapping peaks near $2\theta = 45^\circ$ from the rhombohedral BFO matrix corresponding to $c = 4.065$ Å and $c = 3.995$ Å (compared to bulk pseudocubic $a_{\text{bulk,BFO}} = 3.965$ Å). This is consistent with the SEM image in Figure 1b that indicates two populations of BFO, the material surrounding the dense pillars, and larger BFO regions that cover part of the surface.

In the film with the most BFO, Figure 1c, the diameter and fraction of the pillar phase was much lower. From the X-ray data, Figure 1i, the pillar phase peak could not be distinguished due to its small volume fraction. The major peaks were from rhombohedral BFO grown epitaxially on the STO with out-of-plane lattice parameter of 4.087 Å. A smaller peak from tetragonal BFO also occurs around $39^\circ$, similar to what was seen in low-temperature-deposited BFO–CFO nanocomposites. The lattice mismatch between the pillar phase and the matrix may help stabilize the tetragonal BFO phase.

Figure 2. (a) Top view SEM (b) $\theta$–$2\theta$ XRD pattern of BFO–MgO nanocomposite grown at optimal deposition conditions. (c) In-plane and out-of-plane hysteresis loops of nanocomposite measured by VSM. (d) TEM image and elemental mapping of released pillars on a copper grid.
Unexpectedly, the BFO−MgO nanocomposites showed a magnetic signal measured with VSM at room temperature (Figure S1), though single phase BFO films deposited at the same conditions did not show a magnetic moment (Figure S2). The saturation magnetic moments were 17, 30, and 15 emu cm\(^{-3}\) for the samples of Figure 1a,b,c respectively, calculated over the volume of the film, i.e., not normalized to the pillar volume fraction. The magnetic hysteresis loops were isotropic with low coercivity (<100 Oe). This supports the idea that a ferrimagnetic spinel is present because neither MgO nor BFO has a magnetic signal when grown at this deposition condition (Figure S2), BFO being a canted antiferromagnet. The magnetic signal did not disappear on etching by HCl so is attributed to the pillar phase (Figure S3). To investigate this further, a BFO−MgO nanocomposite was made by alternating ablation of MgO and BFO targets at the optimal ratio obtained from combinatorial PLD. 100 and 250 pulses were incident on the MgO and BFO targets respectively, repeated 200 times to make a 60 nm thick film. In Figure 2a, rectangular nanopillars can be seen with their edges aligned along the (110) directions of STO substrate. This nanocomposite showed XRD peaks corresponding to MgO (002) or M\(_x\)FO (004), and BFO (002) near 2\(\theta\) = 45° with out-of-plane lattice parameter of 4.187 ± 0.002 Å for the pillars and 4.099 ± 0.003 Å for the BFO. These values are closer to each other compared with those of the nanocomposites grown by CPLD. The pillar phase was in out-of-plane compression and the BFO in out-of-plane tension. \(\varphi\) scans shown in Figure S4 demonstrated 4-fold symmetry of BFO and spinel phases indicating epitaxial growth of both phases on the substrate, although some additional peaks were detected.

The in-plane and out-of-plane magnetic hysteresis loops show soft, isotropic magnetic behavior with a saturation magnetization of 20 emu cm\(^{-3}\) averaged over the volume of the entire film. We propose that these nanopillars consist of magnesium ferrite spinel, M\(_x\)FO. MFO has the spinel structure and shows a soft magnetic behavior\(^{28-30}\) with bulk saturation magnetic moment of 130 emu/cm\(^3\)\(^{29}\) and the bulk lattice parameter is 8.375 Å (JCPDS #00-017-0464), close to that of the pillar peak in Figure 2b that corresponds to out-of-plane spinel lattice parameter of 8.374 ± 0.004 Å. The volume fraction of the pillar phase estimated from the area in the top view SEM image is 18±4% which implies a saturation moment for the pillars of 117±26 emu cm\(^{-3}\), close to that of bulk MFO. The low magnetic anisotropy of MFO pillars is a result of the low magnetostriction and low magnetic moment, which produce low magnetoelastic and shape anisotropies, respectively.

Further evidence that the pillars are spinel not MgO comes from their morphology. The pillar shape resembles those of CFO−BFO nanocomposites. The rectangular prismatic shape and top surface faceted structure with four tilted (111) planes is characteristic of spinel pillars in a perovskite matrix, originating from the lowest surface energy (111) planes of spinel.\(^6\) In contrast, simulation results show that the lowest surface energy planes of MgO are (100) planes.\(^{31}\)

STEM-EDS elemental mapping also supports the identification of M\(_x\)FO pillars. The top left image in Figure 2d shows
the TEM images of agglomerated nanoparticles collected on a TEM grid after etching in HCl solution, and the other panels in Figure 2d show Mg, Fe, and O mapping of the same area. The composition analysis reveals that there is no detectable Bi, but Fe is present throughout the pillars. The small pillar size compared to the beam size precluded an accurate measurement of Mg:Fe ratio.

The pillar structure and the magnetic hysteresis of the BFO−MgO nanocomposite are similar to those of BFO−MFO nanocomposites reported previously.23 The spinel phase forms in the BFO−MgO nanocomposite because MFO is thermodynamically stable,32 and MFO has also been observed to form at the interface between an MgO substrate and an iron oxide thin film.33 However, other nanocomposites containing MgO have been grown, such as (La0.7Ca0.3MnO3)−MgO,34 CoFe2O4−MgO,11 and ZnO−MgO.35 This suggests that the low stability of BFO contributes to the formation of MxFO in the BFO−MgO codeposition. Formation of MxFO would leave excess Bi, but Bi or Bi2O3 peaks were not detected by XRD except in the sample of Figure 1a, and it is likely that excess Bi is lost from the film due to its volatility.

We now discuss a “triple-layer” nanocomposite consisting of CFO/MgO/MFO in a BFO matrix, designated BFO−(CFO/MgO/MFO), which was fabricated to investigate the effects of inserting an MgO layer within a spinel pillar. We have already shown in nanocomposite BFO−(CFO/BFO/MFO), where layers of CFO and MFO pillars were separated by a thin BFO layer, that any direct contact between the CFO and MFO pillars led to interdiffusion producing (Co1−xMgx)Fe2O4 pillars of uniform composition.17 Therefore, it was interesting to see whether MgO could fulfill the function of a diffusion barrier in a spinel pillar.

First, a magnetically hard BFO−CFO nanocomposite was grown on a STO (001) substrate, then 20 nm thick BFO−MgO was grown, and finally a soft magnetic BFO−MFO nanocomposite layer was grown. Samples were made in a single run in the same chamber equipped with four targets without breaking vacuum. Figure 3a shows the top view SEM image of the BFO−(CFO/BFO/MFO) trilayer nanocomposite. The XRD pattern shows BFO and a single peak for spinel and/or MgO, Figure 3b.
In the plane view, faceted rectangular pillars line up along the [110] directions of the STO substrate resembling Figure 2a. However, after etching in HCl solution for 3 min (Figure 3c), the nanopillars are seen to grow from two or three roots connected by a wider midsection. The roots correspond to the BFO–CFO growth, the midsection to BFO–MgO, and the top to BFO–MFO. The BFO–MgO layer is assumed to grow as BFO–M,M FO as discussed above, resulting in a higher pillar volume fraction that caused the small CFO pillars to expand and merge. Then growth of the top CFO–MFO layer leads to narrowing of the pillars. The growth sequence suggests that the pillars should consist of three chemically different layers, but compositional analysis with EDS mapping shows a uniform cation distribution throughout the whole pillar to produce a spinel phase of (Co1−M,M)Fe2O4 (Figure 3d). This exhibited magnetic hysteresis loops with intermediate magnetic behavior between that of hard magnetic CFO and soft magnetic MFO (Figure 3e),17 in which both shape and magnetoelastic anisotropy promote an out-of-plane easy axis. The anisotropy was lower than that of a BFO–CFO nanocomposite. Therefore, growing a layer of BFO–MgO did not provide an effective diffusion barrier within the spinel pillars due to the formation of M,M FO instead of MgO from the arriving Mg flux. In the all-spinel pillar, cation interdiffusion took place as seen in bilayer spinel pillars.17

We finally describe the growth of nanocomposites made from BFO–MAO. Figure 4a,b,c shows top-view SEM images of 100 nm thick BFO–MAO nanocomposites grown by CPLD using BFO and MAO targets and Figure 4d,e,f shows their SEM images after etching. MAO did not form well-defined pillars as seen in the BFO–CFO or BFO–MFO cases7,25,31 even though the lattice mismatch between BFO (2abulk,BFO = 7.930 Å) and MAO (abulk,MAO = 8.083 Å) is smaller than in BFO–CFO or BFO–MFO.

The MAO-rich nanocomposite (Figure 4a) showed micro-meter-sized islands that had facets along STO {100}. XRD patterns, Figure S5a, clearly showed one film peak corresponding to MAO (004) whose lattice parameter was 8.098 ± 0.004 Å, but no BFO or B2O3 peak. The etching had little effect on the morphology indicating that BFO or B2O3 were not present at the top surface.

As the BFO content increased, Figure 4b, the numbers of islands increased, and etching removed some of the island material to produce an irregular surface. XRD showed two phases corresponding to MAO (8.088 ± 0.004 Å) and BFO (3.947 ± 0.004 and 3.975 ± 0.002 Å), Figure S5b. In Figure 4c with greater BFO content, BFO covered most of the surface and small diameter pillars were present, revealed by etching. The XRD pattern displayed BFO peaks that had out-of-plane lattice parameters of 4.027 ± 0.003 and 3.952 ± 0.004 Å, Figure S5c. In both samples of Figure 4b,c, the BFO peaks (Figures S5b,c) did not disappear on etching suggesting interdiffusion may have led to a more etch-resistant matrix phase.

The nanocomposites all showed magnetic phases with in-plane easy axis even though the spinel unit cell parameters were characteristic of nonmagnetic MAO rather than M,M FO. We presume the magnetism originates from a partly substituted (Mg, Al, Fe)2O3 spinel phase. Consequently, the excess Mg or Al is present in the perovskite phase, yielding for example B(Fe,Al)O3 with higher etch resistance than BFO. (The end member BiAlO3 can form a perovskite structure.)56 The averaged saturation magnetization for the three samples was similar, 20–25 emu cm−3 despite the different volume fractions of spinel, which may indicate a lower Fe content in the spinel made at lower BFO fraction counteracting the higher volume fraction to give similar average magnetization. The films showed magnetic anisotropy, in comparison with the isotropic behavior of the BFO–MgO (Figure S1). This is assumed to originate from the different morphology, composition and/or magnetostriction and lattice strain of the (Mg, Al, Fe)2O3 spinel phase in the BFO–MAO nanocomposites compared to the M,M FO in the BFO–MgO nanocomposites.

**CONCLUSION**

In summary, self-assembled two-phase nanocomposite films were made by codeposition of BFO–MgO and BFO–MAO and phase formation was investigated. The BFO–MgO formed a nanocomposite consisting of spinel M,M FO pillars in a BFO matrix within a very small window of deposition parameters, with little or no rocksalt MgO. The pillars contributed a magnetic signal consistent with the volume fraction and the saturation magnetization of MFO. A multilayer nanocomposite, BFO–(CFO/MgO/MFO), showed related behavior in which the pillars had a spinel structure throughout, with interdiffusion leading to a uniform composition of (Co,Mg,Fe)2O4. The pillars had interesting bifurcated structures due to the merger of smaller pillars into larger ones, and the magnetic properties were intermediate between those of magnetically hard CFO and soft MFO pillars. In contrast, codeposition of BFO with an aluminum spinel, MAO, in which there is a lower lattice mismatch between the pure bulk phases, grew as a two-phase film but did not produce clearly defined crystallographic pillars under the deposition conditions used here. Fe incorporation in the MAO led to a magnetic moment, and incorporation of Al or Mg into the BFO matrix increased its etch resistance. These results show that intermixing of the arriving flux from two targets leads to formation of phases not present in the targets, and in particular the growth of Fe-containing spinel phases leads to magnetic properties in nanocomposites made from nonferromagnetic targets.

**ASSOCIATED CONTENT**

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b10676.

Magnetic hysteresis data of BFO–MgO and BFO, and X-ray diffraction data of BFO–MgO and BFO–MAO samples (PDF).

**AUTHOR INFORMATION**

*Corresponding Author*

C. A. Ross. E-mail: caross@mit.edu.

**Notes**

The authors declare no competing financial interest.

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