# Microstructural Effects of Chemical Island Templating in Patterned Matrix-Pillar Oxide Nanocomposites

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### **Fabrication Methods and Materials Properties**

 $CoFe_2O_4$ -BiFeO<sub>3</sub> (CFO-BFO) nanocomposite films for this work were grown via pulsed electron deposition (PED, Neocera, Inc.)[1] using a technique that has been described previously.[2] The patterned sample was produced using a directed self-assembly process that has also been described previously.[3] A detailed description of the pulsed electron deposition chamber and process employed in our research group has also previously been published.[4] The reader is referred to these works for an understanding of the growth kinetics of the PED process. An initial film of pure  $CoFe_2O_4$  (CFO) was grown on Nb-doped  $SrTiO_3$  from a stoichiometric CFO target. The film showed a uniform island distribution with thickness of 12.5 nm. This sample was then patterned using the techniques outlined in Ref. 3 to produce the island template shown in Figure 1 of the main paper. The patterned substrate was then loaded into the PED chamber and a CFO-BFO nanocomposite film was grown on the substrate to produce the patterned sample. The growth conditions for these two samples are shown below in Table 1. The temperature of the substrate was determined via a calibration curve obtained using a thermocouple mounted to a sample holder and swept across the set temperatures of the resistive sample heater.

Film	Set	Calibrated	Operating	Gas	Pulse	Pulse	Number of
	Temperature	Substrate	Pressure	Composition	Voltage	Rate	Pulses
	(°C)	Temperature	(Pascal)		(kV)	(Hz)	(thousands)
		(°C)					
CoFe <sub>2</sub> O <sub>4</sub>	700	515	1.6	100% O <sub>2</sub>	8	8	40
CoFe <sub>2</sub> O <sub>4</sub> -	775	577	2.1	100% O <sub>2</sub>	11.5	2.5	37.5
BiFeO <sub>3</sub>					(CFO),	(CFO),	(CFO),
Composite					11.8	5	75 (BFO)
					(BFO)	(BFO)	

Table 1: Growth conditions for sample analyzed in paper.

#### **TEM Sample Preparation**

To prepare the samples for TEM analysis, a dual-beam scanning electron microscope (SEM)/focused ion beam (FIB) system was used to extract a cross-sectioned lamella. An FEI Helios 650[1] system was used for this work with a Ga ion source and a field emission electron gun. The system is equipped with several gas injection system (GIS) sources, which are used to inject a variety of different precursor metalorganic gases for deposition. To deposit these materials, either the SEM or FIB gun is used to crack the precursor gas on the surface of the sample. The system is also equipped with an Oxford Omniprobe<sup>[1]</sup> sample manipulator, which is used during the TEM sample preparation process to lift lamella from the substrate.

Figure S1 shows the progression of the lamella extraction process from a patterned nanocomposite. For the patterned nanocomposite, initial 1  $\mu$ m tall, 1  $\mu$ m diameter Pt metallic pillars were deposited around the array of interest for use as alignment marks using the electron gun with a beam current of 800 pA and 5 kV accelerating voltage. Both patterned and unpatterned nanocomposites were then coated with approximately 100 nm of amorphous carbon using a Gatan Precision Etching and Coating System.<sup>[1]</sup> The carbon serves as a conductive coating to reduce the effects of charging that occur due to the insulating nanocomposite film. The samples were then placed in the dual-beam system for the lift-out process. A 2  $\mu$ m thick initial Pt rectangle with length of 20  $\mu$ m and width of 2  $\mu$ m was deposited along the <110> surface axis using the ion beam source with 30 kV and 0.23 nA beam conditions. This serves as a protective coating during the extraction process. An image of the rectangle on the patterned sample is shown in Figure S1(A). The patterned alignment marks to find the arrays are visible in the image as faint lines of contrast on the surface of the film. The FIB gun is then used to etch a trench into the substrate surrounding the Pt rectangle, with gun conditions set to 30 kV, 9.3 nA. A reduced beam current of 2.5 nA is used to clean any residual material from the trench. The sample is then tilted to undercut the substrate beneath the Pt rectangle. Using the Omniprobe manipulator, a micron scale tip is then mounted to the lamella by depositing Pt using the ion beam source with a beam current of 24 pA at the interface between the probe and lamella. This step is shown in Figure S1(B). With the probe attached, the lamella is then cut from the substrate using the FIB with a beam current of 2.5 nA. The sample is then attached to a Cu TEM grid by depositing Pt with the ion beam source with 80 pA current. The probe is then cut free using the FIB, leaving the lamella attached to the grid. This is shown in Figure S1(C). Finally, a portion of the sample is progressively thinned from its initial 2 µm thickness to less than 100 nm using the ion gun with 230 pA beam current. A view of the final thinned lamella is shown in Figure S1(D).



Figure S1: Preparation process for TEM lamella. A) Deposition of Pt protective barrier along <110> axis. B) Trench milling and Omniprobe attachment to lamella. C) Mounting of lamella on Cu grid. D) View of final thinned lamella.

## **Faulty Templating**

During the EBL process, the effective dose in the resist is dependent on the number of nearby islands also being exposed, due to the significant number of backscattered electrons from a 100 keV electron gun. Near the edges, there are fewer nearby islands being patterned, so the effective dose to the resist is reduced. Thus, the pattern may change in some cases. In Figure S2, it is clear that the center of a separate array on the substrate received a dose that produced large diameter seed islands after etching. The STO substrate was not completely re-exposed, producing a highly defective region with no evidence of CFO pillars. At the corner of the array, ideal pillars were formed due to the reduced dose. This, along with the absence of pillars at the edges of the array in the main text suggests that chemical seeding, rather than topographic, drives the formation of CFO pillars.



Figure S2: SEM image of array of pillars that was overexposed in the center of the pattern but received an ideal dose at the corner.

#### **Energy Dispersive X-ray Spectroscopy Analysis Techniques**

The Energy Dispersive X-ray Spectroscopy (EDS) analysis was performed with an EDAX SiLi detector. The maps were EDS drift corrected spectrum images acquired through the TEM Imaging and Analysis software interface.[1] The energy resolution is 10 eV per channel, 4 second integration time and a shaping time of 25.6 microseconds. A camera length of 0.10 meter and a beam spot size of 6 were used for eds mapping. The beam current with spot size 6 is 0.35 nA. Representative EDS spectra acquired from the substrate, matrix and pillar are shown in Figure S5. It should be noted that Bi is present along the beam path of the pillar, making the signal non-zero for the pillar in Figure S5(C). Additionally, an asterisk in Figure S5(C) denotes the neighboring Co K $\alpha$  and Fe K $\beta$  peaks , which overlap and produce non-zero Co signal in the BFO matrix. The presence of redeposited Cu from the TEM mounting grid was detected in EDS and is likely a product of the FIB sample preparation process. Likewise, we would expect trace amounts of Pt and Ga from the preparation process, but if they are present they do not rise above the noise level in the EDS spectra.



Figure S5: EDS spectra acquired from A) Nb-doped SrTiO<sub>3</sub> substrate; B) BiFeO<sub>3</sub> matrix; C) CoFe<sub>2</sub>O<sub>4</sub> pillar.

- <sup>1</sup> Certain commercial equipment, instruments and materials are identified in this paper in order to specify experimental procedures adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology nor is it intended to imply the materials or equipment identified are necessarily the best available for that purpose.
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