Supporting Information

Effects of pillar size modulation on the magneto-structural coupling in self-assembled $BiFeO_3$-$CoFe_2O_4$ heteroepitaxy

Tahta Amrillah,[a,b] Yu-Xun Chen,[b,c] My Ngoc Duong,[b] Wildan Abdussalam,[d] Firman Mangasa Simanjuntak,[e] Chia-Hao Chen,[c] Ying-Hao Chu,[b,f] and Jenh-Yih Juang[b]

[a]*Department of Physics, Faculty of Science and Technology, Airlangga University, Surabaya 60115, Indonesia.*

[b]*Department of Electrophysics, National Chiao Tung University, Hsinchu 30010, Taiwan.*

[c]*National Synchrotron Radiation Research Center (NSRRC), Hsinchu, 30076, Taiwan.*

[d]*Helmholtz-Zentrum Dresden-Rossendorf, Bautzner Landstrae 400, Dresden 01328, Germany*

[e]*World Premier Institute-Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

[f]*Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30010, Taiwan*

*) Authors to whom correspondence should be addressed.

Email: *tahta.amrillah@fst.unair.ac.id, jyjuang@nctu.edu.tw*

Materials and method of fabrication

For each PLD process of the BFO–CFO composite films, we use one single target contain 80% vol. of BFO and 20% vol. of CFO, whereas the (001)-oriented LAO substrate is placed on the sample holder equipped with heater. Meanwhile, for the deposition of BFO and CFO single layer, we use 99.9% of BFO and CFO targets respectively. The targets were purchased from Ultimate Materials Technology co. ltd. All samples were growth using target-substrate distance about 5 cm and oxygen pressure of 100 mTorr. The detail of the growth conditions for each sample are listed as follows:

1. 50 nm-thick of BFO-CFO composites having small pillars were deposited employing a KrF laser energy of 250 mJ and laser pulses with a repetition rate of 10 Hz for 18000 pulses while the substrate was kept at 620 °C.
2. 50 nm-thick of BFO-CFO composites having medium pillars were deposited employing a KrF laser energy of 250 mJ and laser pulses with a repetition rate of 10 Hz for 18000 pulses while the substrate was kept at 670 °C.
3. 50 nm-thick of BFO-CFO composites having large pillars was deposited employing a KrF laser energy of 250 mJ and laser pulses with a repetition rate of 5 Hz for 36000 pulses while the substrate was kept at 700 °C.
4. 100 nm-thick of BFO and CFO single layers were deposited employing a KrF laser energy of 275 mJ and with a repetition rate of 10 Hz for 36000 pulses, while the substrate was kept at 620 °C.

We note that the laser energy gave no significant effect to the formation of CFO pillars. Thus, the laser energy range of 250-275 mJ can be used to grow BFO-CFO nanocomposite samples. On the other hand, substrate temperature holds an important role in determining the size of CFO pillars. Moreover, although the film's surface morphology becomes rougher with increasing of substrate temperatures, reasonably smooth film surface can be obtained by reducing the repetition rate. Lower pulse repetition rate is expected to give more time for the growing islands to coalescence before the arrival of the next deposit.[1] As a result, good shape of CFO pillars as well as improved film surface quality can be achieved during the self-assembling process. The film thickness was evaluated by observing the growth rate using ex-situ AFM measurement right after growing process of the reference samples. Thickness was also checked independently using cross-sectional TEM image as depicted in Fig. S1. A strong relation between the growth rate and the thickness of the samples was observed.

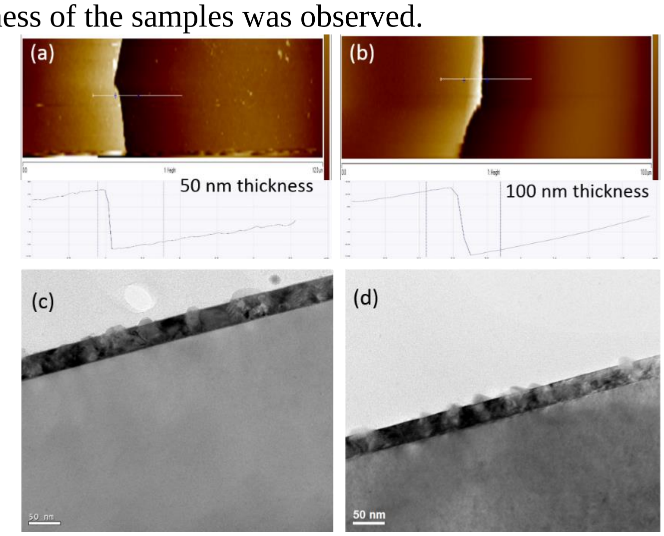

Figure S1. The thickness of the samples observed using (a)-(b) AFM and (c)-(d) cross-sectional TEM.

Method of materials characterization

Equipment model and measurement apparatus/condition are as follow;

1. XRD: A Bruker D2 X-ray diffractometer equipped Cu Kα1 radiation ($\lambda = 1.5406$ Å). The samples were measured using conventional symmetrical Bragg-Brentano configuration ($\theta/2\theta$).
2. AFM: Veeco Multimode 8, under ScanAsyst mode.
3. TEM: FEI Tecnai F20 equipped with high-angle annular dark field detector. The diffraction patterns were acquired at a JEOL-2010 microscope operating at 200 kV. Meanwhile, the cross-section samples were prepared using a standard ion milling technique.
4. XPS: The sample is placed on pure Tantalum or Tungsten holder by copper conductive tape with conductive silver glue being painted on sample edges. After 30 min drying, the sample is transferred into UHV chamber. In order to prevent the pillar structure from damaging, we did not clean the sample surface. The measurements were carried out at room temperature in UHV chamber (1×10^{-9} torr) using SPECs Phoibos 150 hemispherical energy analyzer system in Fixed Analyzer Transmission mode. The tool is equipped with the Al Kα X-ray source of 1486.6 eV (300W). All spectra were calibrated by Au 4f 7/2 with a binding energy of 84 eV. The details of parameters for acquisitions are given in Table S1.

   Table S1. XPS acquisitions parameters

Parameter	Co 2p	Fe 2p	O 1s	Bi 4f
Dwell Time	0.1	0.1	0.1	0.1
Scans	15	10	10	5
Pass Energy	40	40	20	25
Energy Step	0.1	0.1	0.1	0.1

   Moreover, since the composition of carbon in the sample is not our main object in XPS measurement, we did not acquire the spectra of C 1s. Nevertheless, by surveying the XPS spectra, we find out that the ratio of oxygen and carbon is around 4:1.

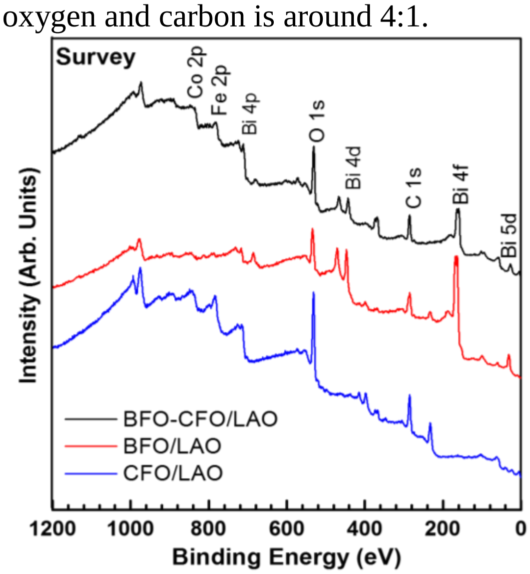

   Figure S2. Full scan XPS spectra of BFO-CFO/LAO nanocomposite (black line), BFO/LAO single layer (red line) and CFO/LAO single layer (blue line).

5. SQUID: A Quantum Design® magnetic property measurement system (MPMS) equipped with a superconducting quantum-interference device (SQUID) magnetometer was conducted using magnetic fields up to 2.5 T applied along the in-plane (IP) and out-of-plane (OOP) directions of the samples at 300 K.

The in-plane orientation of CFO and BFO in the composite films

Figure S3 shows the phi-scans results of the small and large CFO pillars samples, respectively. We found that the observed diffraction peaks of phi-scan on {220} plane of BFO and LAO exhibit 4-fold symmetry corresponding to their cubic symmetries. However, the diffraction peak of CFO is difficult to obtain due to our limitation of our XRD equipment. Nevertheless, we found that the BFO phase exhibited good epitaxial relationships with the LAO substrate, with $[100]_{BFO}$ // $[100]_{LAO}$, in agreement with XRD and TEM results. The phi-scan results of small and large CFO pillars samples are largely identical, indicating that such significant strain induced by CFO phase to the BFO phase in the large CFO pillars sample does not change the crystallographic direction of BFO phase. It is conceived that the crystalline structure of BFO phase might have been distorted it remains of cubic symmetry.

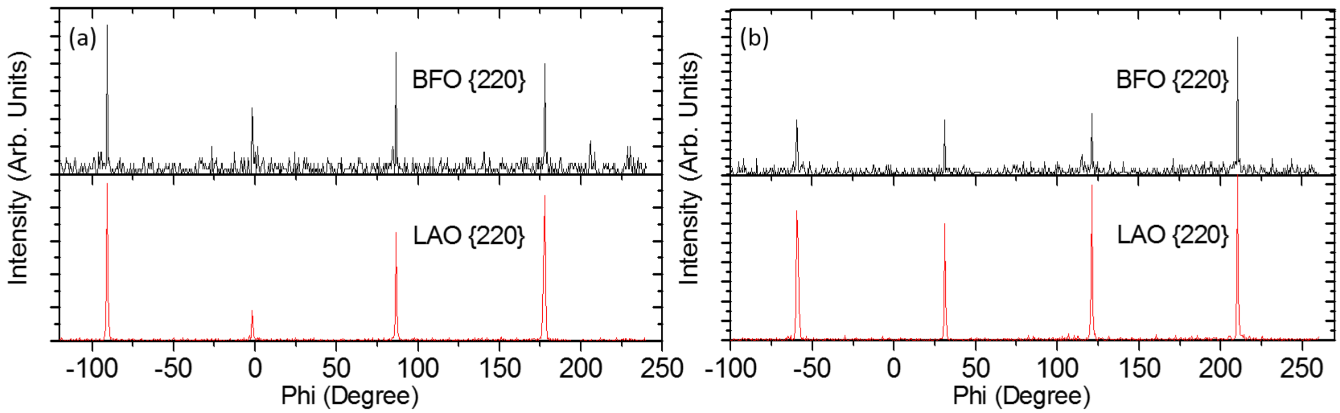

Figure S3. In-plane orientation of BFO and CFO phase in the BFO-CFO/LAO nanocomposite films. (a) Small and (b) large CFO pillars samples.

References

1. L. Guan, D. M. Zhang, X. Li, and Z. H. Li, Nuclear Instruments and Methods in Physics Research B, 2008, **266**, 57–62.