

Patterning Nanoscale Ferroic Oxides

Undergraduate Researcher

Gerik J. Zatorski
Vanderbilt University, Nashville, TN

Faculty Adviser

Vinayak P. Dravid
Department of Materials Science and Engineering
Northwestern University

Graduate Student Mentor

Bin Liu
Department of Materials Science and Engineering
Northwestern University

Abstract

Multiferroic materials possess the rare ability to exhibit both ferroelectric and ferromagnetic properties, making them suitable for electronic applications. Patterning a multiferroic composite in an organized array adds functionality, as each nanostructure can hold its own piece of memory characterized by the element's polarization. This paper examines soft-electron-beam lithography (soft-eBL) as a fabrication method to pattern high-density $\text{BaTiO}_3\text{-CoFe}_2\text{O}_4$ (BTO-CFO) multiferroic composite nanostructures. The patterned BTO-CFO is analyzed using optical microscopy, atomic force microscopy (AFM), and scanning-electron microscopy (SEM) methods.

Introduction

The design and manufacture of electronic devices seeks to minimize size while optimizing performance. Multiferroic composites show considerable promise for many electronic devices, as their magnetoelectric nature can be utilized for electronic applications such as actuators, switches, magnetic field sensors, or new types of electronic memory devices.¹ Nanopatterning such multiferroic material leads to an organized array of nanostructures that lends itself to nonvolatile random-access memory applications.² A nanopattern's size partly depends on the dimension of the nanostructures. Because industry demands ever smaller-sized materials, it is essential to test different nanostructure dimensions to find the smallest feature size at which functionality can be maintained.

High-density $\text{BaTiO}_3\text{-CoFe}_2\text{O}_4$ (BTO-CFO) composites can be successfully produced using fabrication methods such as soft electron beam lithography (soft-eBL),³ pulsed-laser deposition (PLD),²⁻⁴ and nanoimprint lithography.⁵ However, fabrication that involves chemical etching can damage the substrate. Optimized for patterning, soft-eBL is one method that does not rely on etching, thereby making damage-free patterning possible for small nanostructures.³

Background

Single-phase multiferroic materials are uncommon. However, composites can replicate multiferroicity through a strain-induced coupling interaction between piezoelectric and magnetostrictive phases.^{1,2,6}

Magnetoelectric coupling is achieved by charging the piezoelectric phase to induce a mechanical deformation, causing the magnetostrictive phase to become magnetized.⁸ In this way, a composite can exhibit a property not inherent in either individual material, also known as a product property.⁶⁻⁸ In fact, the multiferroicity of some composites is synergistic in quality, producing a larger magnetoelectric response than the composite's single-phase counterpart.¹ BTO-CFO composites have a strong multiferroic product property resulting from heteroepitaxy between BTO's perovskite structure and the spinel-structured CFO where the crystalline structures' lattices interlock.⁶ The interlocking of lattices results in shared mechanical deformations. In this way, the heteroepitaxy promotes the multiferroic product property by allowing mechanical deformations to propagate from one phase to the other.

Approach

Using the soft-eBL approach developed by Dravid et al., diverse line structures were patterned onto an e-beam-sensitive layer of poly(methyl methacrylate) (PMMA) on a Si substrate.⁹ Lines were patterned rather than squares or other commonly chosen options because the fabrication of electrodes would require at least one dimension of freedom. Additionally, in determining a viable BTO-CFO nanostructure's smallest possible size, different line structure sizes were used on the same sample to limit the variables. The largest line was 300 nm wide, while the smallest was 30 nm wide. The patterned substrate was then developed in a 1:1 mixture of isopropanol and PMMA-A3 developer solution.

Prior to the addition of solutions, the substrate was cleaned with oxygen plasma for 30 sec (75 W flow rate, 175 mT operating pressure). The patterned holes were then filled with a 0.1 M BTO solution by spin coating at 5000 rpm for 45 sec. As soon as the first spin cycle was completed, a 0.1 M CFO solution was spun onto the samples using the same parameters. However, CFO was not added to some samples so that BTO-only structures and BTO-CFO composite structures could be compared and analyzed. The substrate was then heated on a hot plate for 1 min at 50 °C to gelatinize the solutions and affix them to the substrate. Acetone was then used to dissolve the PMMA resist, thus leaving only the patterned BTO-CFO nanostructures on the Si substrate. Any leftover organic material was removed by annealing the substrate at 950 °C.

Results

The samples were first analyzed using scanning-electron microscopy (SEM) to see how the BTO-CFO composite formed on the Si substrate prior to annealing. Figure 1a shows BTO and CFO formations in decreasing size from left to right. The gaps to the right of the smallest perceived formations indicate unsuccessful fabrication of the smallest tested nanostructure of 30 nm. It is likely that the BTO and CFO solutions were unable to fill the patterned holes during the spin-coating process. The successful structures are seen as ring structures, indicating

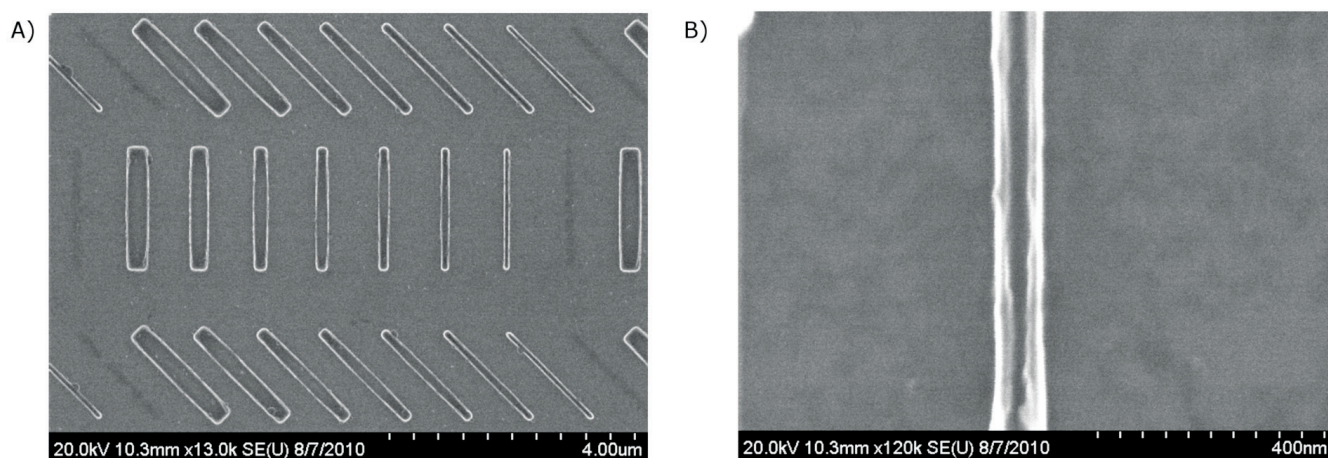


Figure 1. (a) BTO and CFO formations in decreasing size from left to right. (b) SEM image of a single BTO-CFO structure showing that the thickness of the ring is approximately 40 nm.

that the BTO and CFO solutions were pushed to the edge at such high spin speeds. Figure 1b, an SEM image of a single structure, shows that the ring's thickness is approximately 40 nm. If a smaller ring thickness needed to be fabricated, higher spin speeds could be used. The opposite would be true if thicker ring structures were required.

After the annealing process, the height of the nanostructures was measured using atomic force microscopy (AFM). Figures 2a and 2c are AFM images of both the BTO-only and BTO-CFO composite structures. The ring structures are still present in both samples but are more apparent in the BTO-only structure, indicating that an additional spin-coating cycle of CFO filled some of the vacant area in the middle of the ring. The height of a cross section of the BTO-only sample was measured and compared with the height of the composite structures. Figures 2b and 2d show the height of each cross section examined. The inner area of the BTO-only sample was 13.165 nm higher than that of the substrate, while the composite structure had an inner relative height of 65.195 nm. The difference between the two values was about 50 nm, indicating that the CFO formed on top of the BTO layer.

Discussion

The BTO-CFO structures formed on the Si substrate in this study demonstrate that soft-eBL can successfully pattern BTO-CFO composites on Si. At high spin speeds, the spin-coating step of the fabrication process causes the solutions to outline the pattern in a ring structure. Additionally, the soft-eBL method does not damage the substrate and can produce structures as small as 60 nm in order to maximize the density of the nanostructures. This study compared the spatial arrangement of BTO and CFO, but many other physical properties would have to be measured in order to understand the multiferroic nature of the composite structures created using soft-eBL, including their piezoelectric and magnetic properties.

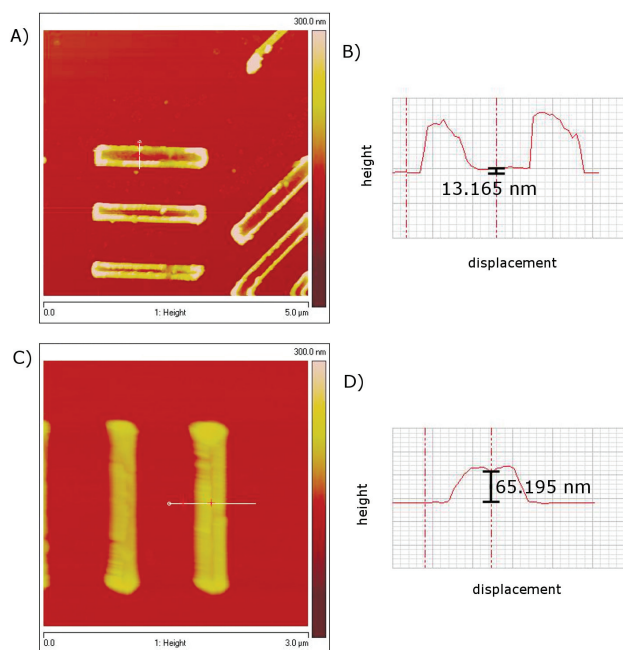


Figure 2. (a) AFM image of the BTO-only structure. (b) Graph showing heights of cross sections of the BTO-only structure. (c) AFM images of the BTO-CFO composite structure. (d) Graph showing heights of cross sections of the BTO-CFO composite structure.

Conclusions

Multiferroic composites show considerable promise for many electronic devices. This study focused on patterning BTO-CFO multiferroic composites using soft-eBL. The BTO ring structures that formed on the substrate were subsequently filled with CFO. The next step would be to examine the multiferroic tendencies of the composite structures created by the high spin speeds involved in the soft-eBL process; magnetic-force microscopy and piezoresponse-force microscopy can be used to test the magnetic and ferroelectric properties of the ring structures.

In this study, BTO-CFO composite structures were affixed to a Si substrate. However, an epitaxial layer deposited between the substrate

and the composite could enhance the magnetoelectric response. SrTiO₃ could be a suitable substitute for Si because, like BTO, it has a perovskite structure.

Acknowledgements

This research was supported primarily by the Nanoscale Science and Engineering Research Experience for Undergraduates (REU) Program under National Science Foundation (NSF) award number EEC-0647560. Any opinions, findings, conclusions, or recommendations expressed in this material are those of the authors and do not necessarily reflect those of the NSF.

References

- 1 Yan, L.; Yang, Y.; Wang, Z.; Xing, Z.; Li, J.; Viehland, D. *J. Mater. Sci.* **2009**, *44*, 5080–5094.
- 2 Ma, W.; Hesse, D.; Gosele, U. *Nanotechnology* **2006**, *17*, 2536–2541.
- 3 Pan, Z.; Alem, N.; Sun, T.; Dravid, V. P. *Nano Lett.* **2006**, *6*, 2344–2348.
- 4 Zhang, Y.; Deng, C.; Ma, J.; Lin, Y.; Nan, C. *Appl. Phys. Lett.* **2008**, *92*, 062911.
- 5 Suzuki, N.; Tanaka, H.; Yamanaka, S.; Kanai, M.; Lee, B. K.; Lee, H. Y.; Kawai, T. *Small* **2008**, *4*, 1661–1665.
- 6 Zheng, H.; Wang, J.; Lofland, S. E.; Ma, Z.; Mohaddes-Ardabili, L.; Zhao, T.; Salamanca-Riba, L.; Shinde, S. R.; Ogale, S. B.; Bai, F.; Viehland, D.; Jia, Y.; Schlom, D. G.; Wuttig, M.; Roytburd, A.; Ramesh, R. *Science* **2004**, *303*, 661–663.
- 7 Kumar, A.; Katiyar, R. S.; Premnath, R. N.; Rinaldi, C.; Scott, J. F. *J. Mater. Sci.* **2009**, *44*, 5113–5119.
- 8 Liu, G.; Nan, C.; Sun, J. *Acta Materialia*. **2006**, *54*, 917–925.
- 9 Donthu, S.; Pan, Z.; Myers, B.; Shekhawat, G.; Wu, N.; Dravid, V. P. *Nano Lett.* **2005**, *5*, 1710–1715.