Epitaxial Patterning of Bi$_2$FeCrO$_6$ Double Perovskite Nanostructures: Multiferroic at Room Temperature

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There is an increasing interest in developing and characterizing multifunctional materials, as they exhibit rich physical and chemical properties and offer exciting opportunities, for example, to miniaturize integrated devices and extend the potential of establishing nanoarchitecture concepts.\(^{[1,2]}\) In this context, multiferroic materials\(^{[3]}\) which combine two or more ferroic functionalities are promising for applications in fields such as spintronics and non-volatile data storage.\(^{[4]}\) As recently demonstrated\(^{[5]}\) ferromagnetic–ferroelectric multiferroics can be advantageously used to encode the information in electric polarization and magnetization giving rise to a four logic state memory. The coupling between magnetic and electrical properties leads to additional versatility for related devices, such as electric field-controlled magnetic data storage.\(^{[6]}\) The recent emergence of Bi-based double perovskite thin films, such as Bi$_2$FeCrO$_6$ (BFCO)\(^{[7–9]}\) and Bi$_2$CoMnO$_6$,\(^{[10]}\) with strong magnetic behavior of Bi$_2$FeCrO$_6$ (BFCO)\(^{[7–9]}\) and Bi$_2$CoMnO$_6$,\(^{[10]}\) with strong magnetic behavior and chemical properties and offer exciting opportunities, for example, to miniaturize integrated devices and extend the potential of establishing nanoarchitecture concepts.\(^{[1,2]}\) In this context, multiferroic materials\(^{[3]}\) which combine two or more ferroic functionalities are promising for applications in fields such as spintronics and non-volatile data storage.\(^{[4]}\) As recently demonstrated\(^{[5]}\) ferromagnetic–ferroelectric multiferroics can be advantageously used to encode the information in electric polarization and magnetization giving rise to a four logic state memory. The coupling between magnetic and electrical properties leads to additional versatility for related devices, such as electric field-controlled magnetic data storage.\(^{[6]}\)

However, conventional patterning and lithography techniques applied to these materials with complex multiphase structure and chemical properties and offer exciting opportunities, for example, to miniaturize integrated devices and extend the potential of establishing nanoarchitecture concepts.\(^{[1,2]}\) In this context, multiferroic materials\(^{[3]}\) which combine two or more ferroic functionalities are promising for applications in fields such as spintronics and non-volatile data storage.\(^{[4]}\) As recently demonstrated\(^{[5]}\) ferromagnetic–ferroelectric multiferroics can be advantageously used to encode the information in electric polarization and magnetization giving rise to a four logic state memory. The coupling between magnetic and electrical properties leads to additional versatility for related devices, such as electric field-controlled magnetic data storage.\(^{[6]}\)

Non-conventional patterning techniques, such as microcontact printing,\(^{[13]}\) nanoimprint,\(^{[14]}\) and nanostencil patterning,\(^{[15,16]}\) are being increasingly explored. Compared to traditional methods (e.g., electron-beam lithography and focused ion beam lithography), they are simpler, faster and even cheaper. In addition, they offer a better process flexibility and compatibility with several applications,\(^{[13]}\) as they do not require post-deposition etching processes.

Here we demonstrate the controlled epitaxial growth by pulsed laser deposition (PLD) of ordered arrays of sub-micrometer BFCO multiferroic structures on niobium-doped SrTiO$_3$ (Nb-STO) substrates, through a nanostencil, i.e., a shadow mask with nanometer-scale features. We show that the as-grown structures retain their room temperature multifunctional (ferroelectric and magnetic) character even at submicrometer dimensions. Our work represents an important step towards the successful integration of nanometer-scale multiferroic elements in current microelectronics and future nanoelectronics.

Growth through a nanostencil allows a simpler parallel and resist-free patterning of complex oxides (as opposed to resist-based methods; see Experimental Section). To obtain large arrays (square millimeters) of multiferroic BFCO nanostructures we first optimized the PLD parameters to obtain stoichiometric, epitaxial BFCO multiferroic thin films on single crystal STO substrates\(^{[7–17]}\) and under conditions compatible with stencil technology (e.g., low background pressure). We then proceeded to the fabrication of the epitaxial BFCO nanostructures by nanostenciling, as illustrated in Figure 1a (see Experimental Section for details). Given the stencil is resistant to high temperature (up to 800 °C) and O$_2$,\(^{[18]}\) 3D functional structures with correct stoichiometry and good crystal quality were directly obtained, without the additional steps (e.g., annealing and etching) usually employed in thin film processing. The ordered and well-defined pattern extends over square millimeter surface areas allowing for the investigation of the properties of the resulting features by conventional film characterization techniques, such as X-ray diffraction and vibrating sample magnetometer, as well as local probes.

The deposition of BFCO on Nb-STO(100) through the hexagonal array of circular apertures of the nanostencil (Figure 1b) results in a regular hexagonal array of rectangular BFCO nanostructures. The average lateral size and pitch of the BFCO nanostructures, 400 and 700 nm, respectively, are related to the aperture size and the distance between pores of the mask (Figure 1c and see Supporting Information, Figure S1). As revealed by atomic force microscopy (AFM), the average height of the BFCO nanoislands is 22–23 nm (see Supporting Information, Figure S1b). The well-defined and completely separated structures retained perfectly the hexagonal architecture with the 700 nm pitch of the circular holes defined in the stencil. The kinetic energy and the surface mobility of the absorbed species are high enough to induce nucleation and crystallization in square-shaped epitaxially oriented nanoislands following the
(111)-oriented Nb-SrTiO$_3$ substrates. As shown in Figure 1e, fully crystallized arrays of BFCO nanoislands were obtained on Nb-STO(111). BFCO nanoislands exhibit {112} oriented facets as previously seen when rhombohedral perovskites are grown at high rates. [24] X-ray diffraction (XRD) revealed that the nanostructures are BFCO pure-phase and have a high degree of orientation on both substrates. [θ–2θ] scans (cf. Figure 2a,b) clearly showed (00$l$) and (hhh) peaks for the BFCO arrays near the STO(100) and (111) substrate reflections, respectively. The presence of the superlattice reflections, indexed $1/2$ $1/2$ $1/2$ and $3/2$ $3/2$ $3/2$ (observed at $2\theta = 19.45^\circ$ and $60.81^\circ$, respectively, in Figure 2b), demonstrates the doubling of the pseudocubic BFCO unit cell as a result of the presence of B-site Fe$^{3+}$ and Cr$^{3+}$ cation ordering along the [111] crystallographic direction. [25] The threefold symmetry observed in the φ-scan measurements (see Supporting Information, Figure S2) confirms the in-plane orientations of the BFCO crystalline islands and thus the epitaxial growth of the BFCO nanostructures on the STO (111) substrate. XRD

To demonstrate the epitaxial growth of the nanostructures, we deposited BFCO through the same nanostencil on (111)-oriented Nb-SrTiO$_3$ substrates. As shown in Figure 1e, fully crystallized arrays of BFCO nanoislands were obtained on Nb-STO(111). BFCO nanoislands exhibit (112) oriented facets as previously seen when rhombohedral perovskites are grown at high rates. [24]

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Figure 1. a) Schematic of the nanostenciling process (PVD stands for physical vapor deposition). b) Scanning electron microscopy (SEM) image of a typical Si$_3$N$_4$ membrane nanostencil. c) SEM image showing a well-defined array of square BFCO nanostructures approximately 400 nm in lateral size that perfectly retained the hexagonal pattern of the shadow mask. d) Detail of an island of about 150 nm in lateral size, formed because of premature clogging of some apertures. e) SEM micrograph displaying a well-defined array of (111)-oriented BFCO nanostructures.
a decrease of the remnant polarization value, a decrease in the ferroelectric to paraelectric phase transition temperature, or an increase in the coercive field as the size of the sample’s geometrical dimensions decreases. Changes in the ferroelectric domain structure were also reported. [27]

The ferroelectric properties of the BFCO nanostructures were investigated by piezoresponse force microscopy (PFM) (see Experimental Section for details) in several randomly chosen areas of the patterned substrate. [27] Typical PFM images of the ferroelectric domains in BFCO epitaxial nanostructures obtained by PLD and nanostenciling on a 0.5% Nb-STO(100) substrate are displayed in Figure 3. In the following, OP and IP stand for the out-of-plane and in-plane components of the PFM signal, respectively, which are simultaneously recorded together with topography (Figure 3a–c). White contrast in the OP-PFM image reveals regions with z-component of spontaneous polarization oriented “upwards” whereas the dark regions denote a polarization component oriented downwards (Figure 3b). For the IP-PFM image (Figure 3c) white/dark contrast stands for opposite lateral (in-plane) components of spontaneous polarization.

The presence of both IP and OP components of polarization is consistent with the fact that the spontaneous polarization (P_s) lies along one of the [111] directions of the rhombohedral distorted BFCO unit cell. The ferroelectric domain structure presents a rather complex configuration, and on average one ferroelectric domain extends over several tens of nanometers. The observed piezoelectric hysteresis loops confirm the

Ferroelectricity, ferro-, antiferro-, and ferrimagnetism all exhibit finite-size effects: Below a critical dimension, referred to as the superparaelectric, respectively superparamagnetic critical size, the considered property is suppressed. Size effect predictions, both for magnetic and for ferroelectric materials, suggest that for both magnetism and ferroelectricity this is attributable to the increasing role of the depolarization field and the weakening of long range cooperative interactions. [26] More specifically for ferroelectrics, studies have shown that possible manifestations of the above mentioned “finite-size effect” are

Figure 2. X-ray diffraction spectra of a) (001) and b) (111)-oriented BFCO nanostructures. c) Electron diffraction pattern of a 350 nm BFCO nanostructure along the [010] direction and d) high-resolution cross-section TEM image of the epitaxial BFCO layer taken along the [010] direction.
of the BFCO nanostructures. The saturated magnetization is estimated to be around 2.6 Bohr magneton ($\mu_B$) per site (see Experimental Section) corresponding to 5.2 $\mu_B$ per Fe-Cr pair, about 2.7 times higher than the 1.91 $\mu_B$ per Fe-Cr pair magnetization observed in epitaxial continuous BFCO films.\textsuperscript{[8]} This unexpectedly large magnetization observed in the BFCO nanostructures compared to that of continuous films is a very interesting size effect that is currently under further investigation.

The global magnetic investigations were complemented with MFM measurements (Figure 4b,c), performed in a magnetic field oriented perpendicular to the substrate (see Supporting Information). The value of the applied magnetic field during the measurement (250 Oe) is higher than the coercive field of the structures, but lower than that of the magnetic tip (400 Oe). The structures exhibit a uniform contrast, clearly different from that of the substrate (Figure 4b). By reversing the direction of the external magnetic field the MFM contrast was inverted (Figure 4c), demonstrating that the structures are magnetically polarizable.\textsuperscript{[29]}

The presence of magnetism in the BFCO islands, at room temperature, is explained by the existence of B-site cation ordering (in the $A_2BB'O_6$ double perovskite structure) which causes the formation of a spontaneous magnetic moment characteristic of the ferromagnetic Fe and Cr d-orbitals under 180° superexchange interaction. Since both Fe and Cr ions are formally in the 3+ ionic states (see Supporting Information, Figure S3), BFCO is an example of such a d$^5$-d$^3$ orbital combination, and the magnetic coupling between Fe$^{3+}$ and Cr$^{3+}$ was predicted to be either ferrimagnetic (FiM) or ferromagnetic (FM) in terms of superexchange.\textsuperscript{[10]} The existence of this cationic ordering in BFCO nanostructures is proved by structural analysis performed on the patterned STO(111) substrate (Figure 2b). The magnetization of 5.2 $\mu_B$ per Fe-Cr pair for the epitaxial nanostructure experimentally measured and reported here is intermediate between a ferromagnetic and an antiferromagnetic coupling.

In summary, we demonstrated the controlled epitaxial growth of sub-micrometer BFCO structures by PLD through a miniature shadow mask. In comparison to conventional resist-based lithographic patterning, nanostenciling is a rapid versatile approach for direct epitaxial growth of submicrometer structures of complex functional materials where high temperatures are required during deposition to ensure good functional properties at room temperature. Nanostenciling yields damage-free submicrometer epitaxial BFCO structures which retain their multiferroic character. We established that the epitaxial growth and shapes of the nanostructures can be controlled varying the crystal orientation of the underlying substrate, to obtain square-shaped structures on Nb:STO(100)
were mechanically clamped and temporarily fixed onto Nb-doped (100)- and (111)-oriented SrTiO$_3$ substrates. It was desirable that the gap between the sieve and substrate be as small as possible and as uniform as possible over the whole shadowed area, which was achieved using a proper mechanical fixture for the stencil–substrate assembly.

**Pulsed Laser Deposition (PLD):** The assembled substrate–stencil was mounted in a vacuum chamber of a PLD system in front of a rotating target. A KrF Lumonics PM-800 excimer laser ($\lambda = 248$ nm, pulse duration = 13.4 ns) was employed for ablation with the laser beam at a 45° incidence angle with respect to the BFCO target surface and a laser fluence of 2 J cm$^{-2}$. The BFCO target was acquired from MTI Corporation. Depositions were carried out in 1 Pa of O$_2$ ambient pressure at a substrate temperature of 650°C, with a laser repetition rate of 8 Hz.

**Analysis of the Microstructure and Crystallography:** Stencils and nanostructure morphologies were investigated using SEM. Determination of the crystal structure of the BFCO nanostructures was performed using long acquisition time XRD (PANalytical X’Pert MRD 4-circle diffractometer). HR TEM (JEOL JEM-2100F) and SAED analysis were also employed to characterize the structural properties of the BFCO nanostructures.

**Atomic Force Microscopy (AFM), Piezoelectric Force Microscopy (PFM), and Magnetic Force Microscopy (MFM):** AFM, PFM, and MFM measurements were performed using a Veeco Enviroscope AFM equipped with Co/Cr coated cantilevers (NSC 36) from MicroMasch. For PFM, an oscillating testing voltage of 0.5 V was applied between the tip and the conductive substrate on which the structures were deposited. Hysteresis measurements were obtained using an auxiliary digital-to-analog converter of the computer-controlled lock-in amplifier by sweeping an additional direct current (DC) bias voltage between chosen maximum and minimum values. For MFM, the two-pass technique was employed (lift mode with a height of 50 nm) with resonant frequency detection and no voltage applied to the tip or sample. To apply a magnetic field, a permanent magnet was placed below the sample, the field intensity being adjusted by setting the sample elevation above the magnet. Reversal of the field direction was achieved by rotating the permanent magnet by 180° and placing the opposite magnetic pole beneath the sample.[9]

**Vibrating Sample Magnetometer (VSM):** Macroscopic magnetic hysteresis loops were measured at room temperature using a VSM (Model EV9 from ADE Technologies). A maximum saturating field of 10 kOe was applied parallel to the film plane and then decreased to −10 kOe in steps of 500 Oe and back up to 10 kOe. The field steps were decreased to 50 Oe around the zero field range for better resolution. An average factor of 20 measurements per field point provided an absolute sensitivity of about $10^{-6}$ emu. The observed hysteresis clearly indicates the presence of an ordered magnetic phase. To ensure that the ferro- or ferrimagnetic signal originated from the BFCO nanostructures, the magnetic responses of the sample holding rods and of bare substrates (without BFCO) were also measured and subtracted. The magnetic moment $m$ of BFCO (in $\mu_B$ per f.u. or Bohr magneton per formula unit) was calculated using the following formula: $m = M \times V \times 10^{-15}$, where $M$ is the magnetization in emu cm$^{-3}$ ($1 \text{ emu} = 1$ electromagnetic unit = 0.001 A m$^2$), $V$ is the volume of the unit cell of BFCO, $\mu_B = e/ m$, is a Bohr magneton = 9.27 × 10$^{-24}$ A m$^2$, and f.u. stands for a formula unit of Bi$_2$FeCrO$_6$.

**Experimental Section**

**Stencil Properties and Positioning:** Nanostencils were acquired from Aqua Marijn Filtration (The Netherlands). Stenciling experiments were conducted using laser interference lithography-based stencil masks, with built-in 500 nm thick Si$_3$N$_4$ nanosieves with circular apertures. The stencils had hexagonal arrays of pores (350 nm in diameter) with a periodicity of 700 nm and were patterned on 14 free-standing, low-stress (LS-Si$_3$N$_4$) membranes (2 mm in length and 100 µm in width each, 100 µm apart). The 0.5 µm Si$_3$N$_4$ membranes were prepared on single crystalline Si(100) wafers 380 µm thick and the stencil’s dimension was 5 × 5 mm$^2$ with an active area of $2 \times 2.7$ mm$^2$. The stencils and triangular-shaped islands on Nb:STO(111). The observations of an unexpectedly large magnetization of $5.2 \mu_B$ per Fe-Cr pair in the BFCO nanostructures is an interesting indication of a size effect. These results constitute an important step towards the successful integration of nanometer-scale multiferroic elements (working at room temperature or above) in future nanoelectronic devices. They may pave the way towards novel reconfigurable logic spintronic architectures and data storage technology, such as a multi-state nonvolatile memory.

**Figure 4.** a) IP and OP room temperature magnetic hysteresis loops for the whole patterned area of BFCO structures recorded by VSM. The inset is a zoom around the origin evidencing the remnant magnetization and coercive field of the nanostructure array. MFM measurements performed in a magnetic field ($\pm$250 Oe) showing the magnetic switching of BFCO patterned structures: b) Applied magnetic field pointing out from the substrate. c) Change in the MFM contrast of the BFCO islands upon reversing the direction of the magnetic field. Images (b) and (c) show different areas of the sample.
Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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[22] According to this theory, BFO completely wets the (001) oriented perovskite substrate and follows a “layer-by-layer” growth mode. Since the crystal structure of BFCO is similar to that of BFO, we assume that this also holds for BFCO, and that after a wetting layer is formed in the area defined by the stencil’s aperture, “cube on cube” epitaxial growth occurs.
[23] The SEM microscopy image in Figure 1d shows a detail of an island of ≈150 nm in lateral size, formed because of premature clogging of some apertures (most probably caused by droplets retained on the top-side of the membrane). These so-called “accidents” indicate that smaller initial apertures could lead to even smaller islands with epitaxial registry.  
[29] It is challenging to study local magnetism in non-conductive structures since the MFM tips are conductive, and an electrostatic interaction is always present between the tip/cantilever and the sample. This effect is typically superimposed on the magnetic interaction. There is an induced magnetic moment in each BFCO island that is switched by the applied magnetic field.