Self-Assembled Epitaxial Ferroelectric Oxide Nanospring with Super-Scalability

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Oxide nanosprings have attracted much research interest because of their anticorrosion, high-temperature tolerance, oxidation resistance, and enhanced-mechanic-response from unique helix structures, enabling various applications like nanomanipulators, nanomotors, nanoswitches, sensors, and energy harvesters. However, preparing oxide nanosprings is a challenge for their intrinsic lack of elasticity. Here, an approach for preparing self-assembled, epitaxial, ferroelectric nanosprings with built-in strain due to the lattice mismatch in freestanding La0.7Sr0.3MnO3/BaTiO3 (LSMO/BTO) bilayer heterostructures is developed. It is found that these LSMO/BTO nanosprings can be extensively pulled or pushed up to their geometrical limits back and forth without breaking, exhibiting super-scalability with full recovery capability. The phase-field simulations reveal that the excellent scalability originates from the continuous ferroelastic domain structures, resulting from twisting under co-existing axial and shear strains. In addition, the oxide heterostructural springs exhibit strong resilience due to the limited plastic deformation nature and the built-in strain between the bilayers. This discovery provides an alternative way for preparing and operating functional oxide nanosprings that can be applied to various technologies.

1. Introduction

Nanosprings can find broad potential applications in sensors, electronics, actuators, and other electromechanical nanodevices[1–5] due to their unique spiral structures, elongation/compression, elasticity, and resilience, and harmonic vibration properties. For example, molecules, biocells, and microfluids can be manipulated by nanosprings precisely for their nanoscale resonance and enhanced mechanical properties through their unique helix structure.[5–7] The majorities of these nanosprings are made of metals or semiconductors,[7–10] which have intrinsic elasticity because of freely transferred electrons in metallic bonds during mechanic deformation or limited flexibility in weakly ionic and extended covalence bonds, respectively. In contrast,
few oxide nanosprings have been prepared because oxides are fragile due to their strongly ionic and weakly covalent bonds, defects, and grain boundaries.

In 2005, superlattice structured zinc oxide nanosprings were fabricated in a vapor-solid growth process by introducing an abrupt structural transformation due to a rigid lattice rotation or twisting.\(^{[18]}\) Compared with metallic nanosprings, oxide nanosprings are more interesting because of their mechanically-coupled functionality and enhanced mechanistic response.\(^{[9,12]}\) For instance, the shape deformation of ferroelectric (FE) nanosprings can be magnified via the spiral structure, resulting in a much greater electric response through the intrinsic electromechanical coupling (e.g., piezoelectric) effects or vice versa. The FE nanosprings enable various applications such as voltage-driven nanomotors and manipulators, sensors, and energy harvesters.\(^{[13–15]}\) Additionally, although traditional metallic springs have good elasticity, their long-term resilience is limited by plastic deformation from freely-transferred electrons that rapidly balance the strain during large deformation. In contrast, the oxide nanosprings may have strong resilience because of their small plasticity. Recently, we discovered super-elasticity in the FE single-crystal membrane of BaTiO\(_3\) (BTO).\(^{[16,17]}\) This unusual property hints that ferroelectrics like BaTiO\(_3\) could be suitable materials to prepare oxide nanosprings, exhibiting superior mechanical, and electromechanical properties.

In this report, La\(_{0.7}\)Sr\(_{0.3}\)MnO\(_3\) (LSMO)/BTO epitaxial ferroelectric nanosprings were fabricated by self-assembly from as-grown epitaxial LSMO/BTO bilayer via a water-peeling off process.\(^{[16,18–20]}\) Under in-situ scanning electron microscope (SEM) manipulation, these ferroelectric springs are pulled and pushed up to their limits back and forth without breaking, demonstrating super-scalability and full recovery capability. The excellent elasticity is originated from the ferroelastic domain structure, which provides displacement tolerance and energy to accommodate axial and shear strain during deformation. The nanosprings sustain the tensile or compressive force, resulting in the FE domain rotations parallel or perpendicular to the force direction. The polarization analysis by transmission electron microscopy (TEM) also confirms the axial strain and the corresponding polarization distortion. In addition, the excellent super-elasticity of the nanosprings is amplified by their unique helix structure. Generally, the single crystal oxide membrane can only withstand small lattice deformation during the uniaxial or biaxial stretching process (<10%).\(^{[20]}\) However, special spiral structures occur shape deformation to avoid breaking chemical bonds. The LSMO/BTO nanospring can undergo a giant shape deformation in total (>500%) while maintaining a small atomic displacement. Meanwhile, the small plastic deformation of oxides and the built-in strain between the BTO and LSMO layers also enhance the recovery capability. Consequently, the fabrication of FE oxide nanosprings and discovering their super-scalability open a door toward broad applications.\(^{[5,21–24]}\) For example, the magnetic and ferroelectric materials are constructed as the multiferroic springs, which can be utilized to various applications such as magnetic or mechanical sensors, transducers, actuators, and magnetoelectric device. This approach can be adapted to various other functional oxides and nanosprings.

2. Result and Discussion

Epitaxial, high-quality LSMO/BTO/Sr\(_3\)Al\(_2\)O\(_6\) (SAO) heterostructures were grown by pulsed laser deposition (PLD) on SrTiO\(_3\) (STO) substrates in sequence as shown in Figure 1a. The water-soluble SAO layer acts as a sacrificial buffer layer during the lift-off process. Synchrontron-based reciprocal space mapping (RSM) shows asymmetric RSM (–103) reflections with the four-fold splits, which verifies the fully epitaxial growth of LSMO, BTO, SAO, and STO (Figure 1b), comparable with the results obtained from symmetric RSM (002) reflections and \(\theta-2\theta\) scans (Figures S1 and S2, Supporting Information). The a- and c-axis lattice parameters of the LSMO/BTO/SAO heterostructures are calculated (Table S1, Supporting Information). The SAO buffer layer was etched with equal velocity in all directions (Figure 1e) in deionized water, and the LSMO/BTO heterostructure was released, maintaining good heteroepitaxy, as shown in Figure 1c. While the LSMO/BTO heterostructures were transferred onto the polydimethylsiloxane (PDMS) support, they broke and self-assembled into regular nanostripes along the [110] crystallographic direction of BTO (Figure 1d,f).

The LSMO/BTO heterostructured interface was characterized by the aberration-corrected scanning transmission electron microscopy (STEM) (Figures S3 and S4, Supporting Information). The dislocation spacing is about 40 nm at the interface, and the width of LSMO/BTO nanostrings is \(\approx 2–4\) \(\mu\)m (Figures S5 and S6, Supporting Information). These results indicate that the accumulation of mismatch stress is released by breaking the ionic bond at the mismatch dislocation during the peel-off processing. With desorption from the PDMS support, the LSMO/BTO nanostrings coil themselves up into nanosprings because of the built-in strain from the lattice mismatch (Figure 1g,h). The inside and outside of the nanosprings are LSMO and BTO layers, respectively. Figure 1i presents a relaxed, straight, and left-handed nanospring lying on a Si substrate, with \(\approx 6\) \(\mu\)m in diameter, \(\approx 2.5\) \(\mu\)m in width, and \(\approx 12.5\) \(\mu\)m in pitch distance (Figure S7, Supporting Information). Naturally, the fabrication of spiral structures with built-in strain due to the lattice mismatch is universal, especially in epitaxial oxide heterostructures, such as Mn\(_{0.5}\)Zn\(_{0.5}\)Fe\(_2\)O\(_4\)/BTO and Mn\(_{0.3}\)Zn\(_{0.7}\)Fe\(_2\)O\(_4\)/PMN-PT (Figure S8, Supporting Information). Moreover, the spring geometry parameters can be adjusted by the lattice mismatch, thickness, and patterning process.\(^{[25,26]}\)

In the LSMO/BTO nanosprings, the strain distribution, crystal structure, and polarization are highly coupled. In Figure 2a, a single LSMO/BTO spring is selected and prepared for cross-sectional TEM imaging (Figure S9, Supporting Information). The LSMO (34 nm thick) and BTO (36 nm thick) layers are distinguished in the curved LSMO/BTO heterostructure by low-resolution cross-sectional STEM-HAADF (high-angle annular dark-field) imaging (Figure 2b,c). Figure 2d shows the high-resolution STEM-HAADF image of the LSMO/BTO interface along the [100] direction, confirming the epitaxial interface. To assess local variations of polarization, we map the off-center displacement of the Ti atom relative to the corner Ba atoms. Figure 2e,f shows the atomic displacement and polarization arrow overlaid on the STEM-HAADF images focused on the interface of BTO/LSMO and the surface of the BTO layer, respectively. In the BTO layer, the tensile strain near the surface
zone gives rise to polarization along the in-plane direction, which rotates toward the out-of-plane direction due to the gradually increased compressive strain induced by lattice mismatch when moving toward the BTO/LSMO interface (Figure 2e). Near the interface, the compressive strain dominates, leading to most polarizations pointing toward the out-of-plane direction (Figure 2f). Here, the nearly continuous polarization rotation is originated from atomic displacement and lattice tilting along the z-direction. These results suggest that the local polarization lamination and rotation in the BTO layer of the nanosprings are very different from the bent BTO film in which large bending can promote the local polarizations to merge and transform into in-plane direction under normal stress.[16]

We investigate the mechanical properties of the LSMO/BTO nanosprings in situ using a nanomanipulator introduced inside SEM. The elongation and compression tests of nanosprings are carried out, as shown in Figure 3. One end of the LSMO/BTO nanospring is bonded onto a mobile tungsten tip in the compression test. Under compression, the nanospring is shortened and twisted while keeping its integrity (Figure 3a). The length of the nanospring is decreased from 23.8 to 6.6 µm, i.e., by 72.3%. After removing the applied stress, the nanospring immediately returns to its initial state, demonstrating a total elastic deformation during the compression test. With the other end of the spring fixed onto the lift-out grid, we also pull the nanospring extensively to reach its limit.

Figure 1. Synthesis and crystal structure of LSMO/BTO nanosprings. a) Sketch of LSMO/BTO/SAO heterostructure grown on an STO substrate. b) Synchrotron XRD RSM for the heterostructure on STO near the −103 reflection. c) RSM of the transferred heterostructure on Si near the (−103) reflection. d) Sketch of LSMO/BTO heterostructured belts. e) Optical photographs of LSMO/BTO/SAO/STO with the PDMS support layer during the peel-off process in water. f) SEM image of the LSMO/BTO heterostructure belts on the PDMS support layer. g) Sketch of LSMO/BTO nanosprings. h,i) SEM images of right- and left-handed LSMO/BTO nanosprings on PDMS and Si, respectively.
(from spring structure to concentric winding structure), as shown in Figure 3b. During the elongation process, the initial dimensions of the nano-spring are \( \approx 90 \, \mu m \) in length, \( \approx 7.1 \, \mu m \) in diameter, while the length of the nano-spring is increased to \( \approx 137.2 \, \mu m \) and the diameter is decreased to \( \approx 3.6 \, \mu m \) (Video S2, Supporting Information). Such a dramatic deformation results in a 500% length-diameter aspect ratio change, as shown in Figure 3e (Figure S10; and Video S3, Supporting Information). Additionally, the last image in Figure 3b shows that the nano-spring returns to its initial form immediately, indicating a full recoiling capability once it breaks down. It is well-known that oxides are brittle with poor flexibility and elasticity due to their strong ionic or extended covalent bonds. However, these elongation and compression tests reveal that the ferroelectric oxide nanosprings made of LSMO/BTO exhibit strong super-elasticity and super-scalability. A custom-built in situ TEM holder is used to measure the Hooker coefficient. Figure 3c shows the TEM bright-field images of the initial state and the mechanically loaded state, and a continued compressing manipulation can be found in Video S4 (Supporting Information). In situ mechanical compression tests provide the variation of compressive force versus displacement shown in Figure 3d. Upon linear approximation, the Hooker coefficient of the spring is calculated as approximately 0.45 N/m, which is higher than that of SiGe/Si/Cr nanospring.\(^{[27]}\)

Figure 2. Micro- and nanostructures of the LSMO/BTO nanosprings. a) SEM image of an LSMO/BTO nanospring, with the yellow box indicating the cross-sectional TEM sample location. b) Low resolution cross-sectional STEM-HAADF image of the curved LSMO/BTO heterostructure. c) Magnified STEM-HAADF image of LSMO/BTO. d) High-resolution STEM-HAADF image of the LSMO/BTO interface. e,f) Atomic displacement and polarization arrow map overlaid on STEM-HAADF images of the BTO layer near the surface and the interface, respectively.

Figure 4a,b and e,f shows the strain component distribution \( \varepsilon_z \) and the ferroelectric/ferroelastic domain structures of nanosprings from the phase-field simulations under compression and elongation along the \( z \)-axis, respectively. The ferroelectric strip domains around the surface of the nanosprings can be obtained since the complex strain field of mixed bending and twisting is induced by the uniaxial compression and tension (Figures S12 and S13, Supporting Information). Moreover, the shear strain from mixed bending and twisting mainly concentrates on the outer surface and edge of the BTO layer (Figure S14, Supporting Information). When the nanospring is compressed (stretched), the \( \varepsilon_z \) on the outer surface is mainly tensile (compressive) strain, and the \( \varepsilon_z \) on the inner surface is mainly compressive (tensile) strain, which results in the polarization of the outer surface deflected parallel (perpendicular) to the \( z \)-axis, while the polarization of the inner surface deflected perpendicular (parallel) to the \( z \)-axis. Figure 4c,g shows the domain structure and polarization states on the outer surface of the nanospring under compress and elongation tests, respectively. And Figure 4d,h shows the corresponding polarization component \( P\theta \) and strain distribution \( \varepsilon_\theta \) along the middle line on the outer surface of the nanospring, respectively (The \( \theta \)-axis comes from the natural coordinate system introduced to the middle line of the outer surface, which is detailed in the Supporting Information). It is observed that when the super-elastic
BTO thin films are twisted into the self-assembled nanosprings, the electromechanical coupling behavior is different from the direct correlation between polarization and strain in the previous ferroelectric thin film state (Figures S15g–i and S16g–i, Supporting Information). The same relationship between polarization components $P_r$, $P_{\phi}$ and strain components $\epsilon_r$, $\epsilon_{\phi}$ can be obtained in Figures S15 and S16 (Supporting Information). The ferroelectric nanospring system shows a very different domain structure and polarization orientation under compression and elongation compared with the corresponding thin film.[28] The simulated results corroborate the experimental observation that these nanosprings present excellent elasticity and recovering capability under both elongation and compression (Figure S11, Supporting Information). The corresponding domain evolution shows that the polarization is strongly coupled with the bending or twisting strain,[29–31] arising from the ferroelectric nature of the nanosprings. As for the strain distribution, the strain at the interface between the two layers is smaller than that of the BTO and LSMO layers, indicating that stress is released at the interface. Strain distribution at the LSMO/BTO nanospring interface is simulated, as shown in Figure S17 (Supporting Information).

3. Conclusion

In conclusion, self-assembled LSMO/BTO oxide nanosprings show excellent elasticity. They can be stretched or compressed up to their geometric limit without breaking down, achieving a giant scalability of 500%. The ferroelectric/ferroelastic domain switching associated with highly coupled strain and polarization provides the tolerance for shape deformation and the energy for recovery. The method for preparing the LSMO/BTO nanosprings can be adapted to the fabrication of other oxide nanosprings, paving the way toward multifunctional nanodevices for broad applications, such as voltage-driven nanomanipulators based on mechanically-coupled electrical response or vice versa.

4. Experimental Section

Thin Film Deposition: BTO, LSMO and SAO targets were prepared by the conventional solid-state method. These targets were used to fabricate the LSMO/BTO/SAO/STO (001) heterostructures by a PLD system with a KrF excimer laser of 248 nm wavelength. Base pressure was below $1 \times 10^{-6}$ Torr. The target-substrate distance was fixed at 50 mm. First, 30–40 nm SAO thin films were deposited as a sacrificial
layer with an energy density of 1.8 J cm\(^{-2}\), a repetition rate of 3 Hz, and a substrate temperature of 800 °C. Then, the BTO and LSMO films were grown at 750 °C and 2 Hz. During the growth of BTO and LSMO, oxygen gas partial pressures were maintained at 100 and 200 mTorr, respectively.

After deposition, the samples were in situ annealed at 750 °C for 10 min and then slowly cooled to room temperature.

**Fabrication of LSMO/BTO Nanospring**: The SAO sacrificial layer was completely and quickly removed in deionized water at room temperature. The PDMS as a supporting layer should be coated on the LSMO/BTO heterostructures during etching SAO. While the LSMO/BTO heterostructures are transferred on PDMS, they were broken and self-assembled into regular nanostripes along [110] crystal direction of BTO. The dynamic releasing process is shown in Movie S1 (Supporting Information). After that, with desorption from the PDMS, LSMO/BTO nanostripes coil themselves up into nanosprings due to the large lattice mismatch between LSMO and BTO.

**Structure and Performance Characterizations**: The RSM of the films was investigated by using a high-resolution synchrotron X-ray, which was recorded with the 14B beamline of the Shanghai Synchrotron Radiation Facility (SSRF). XRD measurements were performed using a PANalytical Empyrean diffractometer. The morphology was characterized by atomic force microscopy (Bruker, Dimension Icon). Cross-sectional samples for TEM observations were prepared by the focused ion beam technique (FIB, Tescan LYRA 3). Meanwhile, the in situ SEM experiments were conducted by the double beam system in FIB. In situ TEM experiments of nanospring were performed F30 (FEI Tecnai) with in situ mechanical sample holder (PI-95, HYSTRON, USA). Moreover, the microstructure of films and springs was imaged using a probe aberration-corrected scanning transmission electron microscopy (Cs-STEM, Themis Z G2 300kV, FEI).

**Supporting Information**

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

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.
Keywords
elasticity, ferroelectrics, freestanding oxides, polarization, spring

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