Self-assembled Epitaxial Ferroelectric Oxide Nanospring with Super-scalability

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Abstract

Oxide nano-springs have attracted many research interests because of their anti-corrosion, high-temperature tolerance, oxidation resistance, and enhanced-mechanic-response from unique helix structures, enabling various nano-manipulators, nano-motors, nano-switches, sensors, and energy harvesters. However, preparing oxide nano-springs is a challenge for their intrinsic nature of lacking elasticity. Here, we developed an approach for preparing self-assembled, epitaxial, ferroelectric nano-springs with built-in strain due to the lattice mismatch in freestanding $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3/\text{BaTiO}_3$ (LSMO/BTO) bilayer heterostructures. We find that these LSMO/BTO nano-springs can be extensively pulled or pushed up to their geometry 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 hetero-structural 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 nano-springs that can be applied to various technologies.

Introduction

Nano-springs can find broad potential applications in sensors, electronics, actuators, and other electro-mechanical nanodevices^{1–5} due to their unique spiral structures, elongation/compression, elasticity and resilience, and harmonic vibration properties. For example, molecules, bio-cells, and micro-fluids can be manipulated by nano-springs precisely for their nano-scale resonance and enhanced mechanical properties through their unique helix structure^{5–7}. The majority of these nano-springs 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 nano-springs have been prepared because oxides are fragile because of their strongly ionic and weakly covalent bonds, defects, and grain boundaries.

In 2005, superlattice structured ZnO nano-springs were fabricated by introducing an abrupt structural transformation due to a rigid lattice rotation or twisting¹¹. Compared with metallic nano-springs, oxide nano-springs are more interesting because of their mechanically-coupled functionality and enhanced mechanic response^{3,12}. For instance, the shape deformation of ferroelectric (FE) nano-springs can be magnified via the spiral structure, resulting in a much greater electric response through the intrinsic electro-mechanical coupling (e.g. piezoelectric) effects or vice versa. The FE nano-springs enable various applications such as voltage-driven nano-motors 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 nano-springs may have strong resilience because of their small plasticity. Recently, we discovered super-elasticity in the FE single-crystal membrane of BaTiO_3 ^{16,17}. This

unusual property hints that ferroelectrics like BaTiO₃ could be suitable materials to prepare oxide nano-springs which may exhibit superior mechanical and electromechanical properties.

In this report, La_{0.7}Sr_{0.3}MnO₃ (LSMO)/BaTiO₃ (BTO) epitaxial ferroelectric nano-springs 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 microscopic (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 nano-springs 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 nano-springs is amplified by their unique helix structure. For example, the LSMO layer experiences a small localized deformation (< 4%), while the LSMO/BTO nano-spring undergoes a giant shape deformation in total (> 500%). Meanwhile, the recovery capability is also enhanced by the small plastic deformation of oxides and the built-in strain between the BTO and LSMO layers. Consequently, the fabrication of FE oxide nano-springs and the discovery of their super-scalability open a door towards broad applications such as voltage-tunable-manipulators/motors/switches, sensors, energy harvesters, etc.^{5,21–24}. This approach can be adapted to various other functional oxides and nano-springs.

Results And Discussion

Epitaxial, high-quality Sr₃Al₂O₆/BTO/LSMO heterostructures were grown by pulsed laser deposition (PLD) on SrTiO₃ (STO) substrates in sequence, as shown in Fig. 1a. The water-soluble Sr₃Al₂O₆ (SAO) layer acts as a sacrificial buffer layer during the lift-off process. Synchrotron-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 (Fig. 1b), comparable with the results obtained from symmetric RSM (002) reflections and θ -2 θ scans (Supplementary Fig.S1 and S2). The *a*- and *c*-axis lattice parameters of the LSMO/BTO/SAO heterostructures are calculated (Supplementary Table S1). The SAO buffer layer was etched with equal velocity in all directions (Fig. 1e) in deionized water, and the LSMO/BTO heterostructure was released, maintaining good heteroepitaxy, as shown in Fig. 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 (Fig. 1d and f).

The LSMO/BTO heterostructured interface was characterized by the aberration-corrected scanning transmission electron microscopy (STEM) (Supplementary Fig. S3, S4). The dislocation spacing is about 40 nm at the interface, and the width of LSMO/BTO nanostripes is 2 ~ 4 μ m (Supplementary Fig. S5, S6). 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 nanostripes coil themselves up into nano-springs because of the built-in strain from the lattice mismatch (Fig. 1g and h). The inside and outside of the nano-springs are LSMO and BTO layers, respectively. Figure 1i presents a relaxed, straight, and left-handed nano-spring lying on a Si substrate, with $\sim 6\ \mu\text{m}$ in diameter, $\sim 2.5\ \mu\text{m}$ in width, and $\sim 12.5\ \mu\text{m}$ in pitch distance (Supplementary Fig. S7). Naturally, the construction technology of bulking structures is universal, especially in epitaxial oxide heterostructures, such as $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{BTO}$ and $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4/\text{PMN-PT}$ (Supplementary Fig. S8). Moreover, the spring geometry parameters can be adjusted by the lattice mismatch, thickness, and patterning process^{25,26}.

In the LSMO/BTO nano-springs, the strain distribution, crystal structure, and polarization are highly coupled. In Fig. 2a, a single LSMO/BTO spring is selected and prepared for cross-sectional TEM imaging (Supplementary Fig. S9). 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 (Fig. 2b and 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 Ti atom relative to the corner Ba atoms. Figure 2e and f show 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 then rotates toward the out-of-plane direction due to the gradually increased compressive strain induced by lattice mismatch when moving towards the BTO/LSMO interface (Fig. 2e). Near the interface, the compressive strain dominates, leading to most polarizations pointing toward the out-of-plane direction (Fig. 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 nano-springs 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 stress¹⁶.

We investigate the mechanical properties of the LSMO/BTO nano-springs in situ using a nano-manipulator introduced inside SEM. The elongation and compression tests of nano-springs are carried out, as shown in Fig. 3. In the compression test, one end of the LSMO/BTO nano-spring is bonded onto a mobile tungsten tip. Under compression, the nano-spring is shortened and twisted while keeping its integrity (Fig. 3a). The length of the nano-spring is decreased from $23.8\ \mu\text{m}$ to $6.6\ \mu\text{m}$, i.e. by 72.3%. After removing the applied stress, the nano-spring returns to its initial state immediately, demonstrating a total elastic deformation during the compression. With the other end of the spring fixed onto lift-out grid, we also pull the nano-spring extensively to reach its limit (from spring structure to concentric winding structure), as shown in Fig. 3b. During the elongation process, the initial dimensions of the nano-spring are $\sim 90\ \mu\text{m}$ in length, $\sim 7.1\ \mu\text{m}$ in diameter, while the length of the nano-spring is increased to $\sim 137.2\ \mu\text{m}$ and the diameter is decreased to $\sim 3.6\ \mu\text{m}$ (Supplementary Video 2). Such a dramatic deformation

results in a 500 % length-diameter aspect ratio change, as shown in Fig. 3e (see Supplementary Fig. S10 and Supplementary Video 3). Additionally, the last image in Fig. 3b shows that once it breaks down, the nano-spring returns to its initial form immediately, indicating a full recoiling capability. 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 nano-springs 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 Supplementary Video 4. In situ mechanical compression tests provide the variation of compressive force vs. displacement shown in Fig. 3d. Upon linear approximation, the Hooker coefficient of the spring is calculated as 0.45 N/m, which is higher than that of SiGe/Si/Cr nano-spring²⁷.

Figure 4a,b and e,f show the strain component distribution ε_z and the ferroelectric/ferroelastic domain structures of nano-springs from the phase-field simulations under compression and elongation along the z-axis, respectively. The ferroelectric strip domains around the surface of the nano-springs can be obtained since the complex strain field of mixed bending and twisting is induced by the uniaxial compression and tension (Supplementary Fig. S12-13). When the nano-spring is compressed (stretched), the ε_z on the outer surface is mainly tensile (compressive) strain, and the ε_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 and g show the domain structure and polarization states on the outer surface of the nano-spring under compress and elongation tests, respectively. And Fig. 4d and h show the corresponding polarization component P_θ and strain distribution ε_θ along the middle line on the outer surface of the nano-spring, respectively (The θ -axis comes from the natural coordinate system introduced to the middle line of the outer surface, which is detailed in the Supplementary Materials). It is observed that when the super-elastic BTO thin films are twisted into the self-assembled nano-springs, the electromechanical coupling behavior is different from the direct correlation between polarization and strain in the previous ferroelectric thin film state (Supplementary Fig. S14g-i, S15g-i). The same relationship between polarization components P_r , P_φ and strain components ε_r , ε_φ can be obtained in Supplementary Fig. S14 and S15. The ferroelectric nano-spring system shows a very different domain structure and polarization orientation under compression and elongation compared with the corresponding thin film²⁸. The simulated results corroborate the experimental observation that these nano-springs present excellent elasticity and recovering capability under both elongation and compression (Supplementary Fig. 11). The corresponding domain evolution shows that the polarization is strongly coupled with the bending or twisting strain²⁹⁻³¹, arising from the ferroelectric nature of the nano-springs.

Conclusions

The self-assembled LSMO/BTO oxide nano-springs 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 nano-springs can be adapted to the fabrication of other oxide nano-springs, paving the way towards multifunctional nano-devices for broad applications, such as voltage-driven nano-manipulators based on mechanically-coupled electrical response or vice versa.

Declarations

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Figures

Figure 1

Synthesis and crystal structure of LSMO/BTO nano-springs. (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 the heterostructure with the PDMS support layer during the peel-off process. (f) SEM image of the LSMO/BTO heterostructured belts on the PDMS support layer. (g) Sketch of LSMO/BTO nano-springs. (h) and (i) SEM images of right- and left-handed LSMO/BTO nano-springs on PDMS and Si, respectively.

Figure 2

Micro- and nanostructures of the LSMO/BTO nano-springs. (a) SEM image of an LSMO/BTO nano-spring, 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) and (f) Atomic displacement and polarization arrow map overlaid on STEM-HAADF images of the BTO layer near the surface and the interface, respectively.

Figure 3

Mechanical behaviors of the LSMO/BTO nano-springs. In situ SEM images of the LSMO/BTO nano-springs during the compressive process (a) and tensile process (b), respectively. (c) In situ TEM images of an LSMO/BTO nano-spring undergoing compression test. (d) Mechanical force as a function of displacement measured by TEM during the loading process in (c). (e) Length-diameter aspect ratio of the LSMO/BTO nano-spring measured by SEM during the tensile process. The data was collected from Supplementary Movie 3.

Figure 4

Ferroelectric/ferroelastic domains, polarization orientations, and strain components of a nano-spring under compression and elongation from the phase-field simulations. (a) The strain components ϵ_z , the domain of (b) the whole nano-spring and (c) the outer surface of the nano-spring under compress test, and (d) the corresponding polarization component P_θ and strain distribution ϵ_θ along the middle line of the outer surface. (e) The strain components ϵ_z , the domain of (f) the whole nano-spring and (g) the outer surface of the nano-spring under elongation test, and (h) the corresponding polarization component P_θ and strain distribution ϵ_θ along the middle line of the outer surface.

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