Tunable Magnetic Anisotropy in Patterned SrRuO$_3$ Quantum Structures: Competition between Lattice Anisotropy and Oxygen Octahedral Rotation

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Artificial perovskite oxide nanostructures possess intriguing magnetic properties due to their tailorable electron–electron interactions, which are extremely sensitive to the oxygen coordination environment. To date, perovskite oxide nanodots with sizes below 50 nm have rarely been reported. Furthermore, the oxygen octahedral distortion and its relation to magnetic properties in perovskite oxide nanodots remain unexplored thus far. Here, the magnetic anisotropy in patterned SrRuO$_3$ (SRO) nanodots as small as 30 nm are studied. The constituent elements, in particular oxygen ions, are directly visualized via performing atomic resolution electron microscopy and spectroscopy. It is observed that the magnetic anisotropy and RuO$_6$ octahedra distortion in SRO nanodots are both nanodot size-dependent but remain unchanged in the first 3-unit-cell interfacial SRO monolayers regardless of the dots’ size. Combined with first principle calculations, a unique structural mechanism behind the nanodots’ size-dependent magnetic anisotropy in SRO nanodots is unraveled, suggesting that the competition between lattice anisotropy and oxygen octahedral rotation mediates anisotropic exchange interactions in SRO nanodots. These findings demonstrate a new avenue toward tuning magnetic properties of correlated perovskite oxides and imply that patterned nanodots could be a promising playground for engineering emergent functional behaviors.

1. Introduction

Complex oxide heterostructures have a wealth of magnetic states stemming from the specific coupling between spin, charge, orbital, and lattice degrees of freedoms, thereby leading to intriguing applications in emerging spintronic devices.[1–3]

Tremendous efforts have been devoted to looking for novel pathways to tune the magnetic anisotropy in oxide heterostructures through controlling electron–electron correlations.[4,5] On the one hand, one can directly tune the intrinsic magnetocrystalline anisotropy, which derives from the oxygen-coordination environment during material growth.[6] Famous strategies include strain engineering,[7] interface engineering,[8] applying chemical,[9] or physical pressures.[10] On the other hand, magnetic anisotropy is also tailorable after growth by extrinsic contributions such as applying an electric field,[11,12] and controlling the dimensionality.[13] Materials with reduced dimensionality have altered strain fields and reconstructed electronic structures, offering a playground for feasibly engineering magnetic states.[14,15] For instance, Wenisch et al. demonstrated a local control of magnetic anisotropy of (Ga, Mn)As heterostructures by patterning into nanolines.[16] Furthermore, due to electron-system confinements from 3D, nanodots have modified energy levels, presumably giving rise to unique magnetic behaviors.[17,18] To date, most reported nanodots are constructed from standard semiconductors[19] or metals.[20] Patterned nanodots comprising correlated perovskite oxides have rarely been studied because of the difficulty of patterning into small scales. In the latest progress, Laskin and Wang et al. patterned ferromagnetic perovskites to scales of tens of nanometers and found that the magnetic transition temperature ($T_C$) is controllable by changing the size of patterned nanodots.[21] However, the magnetic anisotropy of nanodots fabricated with correlated oxide materials and the underlying fundamental physical mechanisms still remain open questions.

Oxide-perovskite heterostructures are well known for their strong coupling between magnetic properties and centrally coordinated oxygen octahedra, where the deformation of oxygen octahedra influences the magnetic behavior through metal-oxygen-orbital hybridization and rotations of oxygen octahedra change the spin order by breaking the degeneracy of d orbitals.[12,22] Kan et al. demonstrated that the magnetic anisotropy of a correlated ruthenate layer is controllable by an octahedral rotation determined through the atomic-scale design of the oxygen octahedral coupling at the interface.[23] Lee et al.
observed a reversed magnetic configuration in manganite heterostructures resulting from an octahedral deformation rather than a rotation of oxygen octahedra. Although numerous routes for tuning the magnetic anisotropy have been reported, the underlying structural mechanism concerning the respective role of an octahedral deformation and rotation is still under debate, demanding further clarifications. Furthermore, the role of an interfacial anisotropy and a bulk anisotropy in heterostructures also requires in-depth studies. Compared with most reported strategies, in this work, nanodots are fabricated after growth and have fewer additional side effects on the magnetic behavior, making it easier to understand how deformation and rotation of oxygen octahedra influence nanodots’ magnetic properties.

Here, itinerant ferromagnetic SrRuO$_3$ (SRO, bulk Curie temperature $T_C \approx 160$ K) was selected as a model material for fabricating nanodots. It belongs to a family of quasicubic perovskite oxides. The growth of a single-crystalline SRO thin film on appropriate substrates, e.g., STO, can be achieved routinely. Structural modulations and magnetic behavior of epitaxial SRO thin films on various substrates have been well-documented, which helps to understand the magnetic properties of SRO nanodots. High-quality SRO thin films exhibit a strong magnetocrystalline uniaxial anisotropy, which is highly sensitive to slight variations in stoichiometry, lattice structure, and temperatures. Another interesting point is that the electronic structure of Ru 4d orbitals is controllable by quantum-confinement effects.

Here, we investigate the magnetic anisotropy of 5 × 5 mm$^2$ sized SRO nanodots arrays patterned with electron-beam lithography (EBL) (see the Experimental Section for details). The SRO nanodots size down to 15 nm, nearly an order of magnitude smaller than most previously reported results. As the size of the nanodots decreases, its ferromagnetic behavior is investigated, and the magnetic easy-axis is found to rotate from the out-of-plane (OOP) direction toward the in-plane (IP) direction (see the Experimental Section for details). Scanning transmission electron microscopy (STEM) results indicate that a structural variation in the bulk part of the SRO layer gives rise to the observed alteration of the magnetic anisotropy. First-principle calculations were performed to evaluate the role of competing mechanisms in terms of deformation and rotation of oxygen octahedra.

2. Results

2.1. Microstructure and Magnetic Behaviors

Figure 1a shows a topographic atomic force microscopy (AFM) image of an epitaxial SRO thin film right after growth without noticeable surface contamination by hydrocarbons and/or air dust. The terrace structure with the height of about one unit cell of the SRO lattice is well visible, showing a smooth surface of the SRO thin film. It indicates an excellent epitaxial quality of the SRO thin film. Figure 1b–d corresponds to the topography of the array of nanodots with sizes of 200, 80, and 30 nm, respectively. Nanodots are well arranged on the top of STO substrate, and the shape of nanodots deviates from a rectangle to a circle as the size is smaller than 200 nm. The number of nanodots increases with the decrement of the nanodot size. For nanodot arrays with a dot size below 20 nm, the number of SRO nanodots is on/above the order of magnitude of 10$^3$. Due to inhomogeneity during patterning, i.e., resist thickness variations and substrate charging, defects may appear in the resulting structure, such as missing or distorted nanodots (Figure 1d). This phenomenon becomes more evident for dots as small as 15 nm (see Figure S1, Supporting Information). The probability of such effects increases with reduced nanodot size and spacing, but typically does not exceed several percent of the total number of nanodots for an array of dots with a size above 30 nm.

Cross-sectional TEM specimens of the nanodots were prepared for observing the structural quality and interface coherency with the substrate. Figure 1e displays a high-angle annular dark-field (HAADF) image of the cross-section of a SRO thin film. The SRO thin film is grown on top of STO by perfect layer-by-layer stacking. Since signal intensities of the HAADF image are proportional to the mass of the constituent atoms, the interface between SRO and STO is self-evident. The thin film and the interface are free of any visible defect. STEM results for SRO nanodots in Figure 1f–h shows that after patterning the samples still keep a high epitaxial quality with a clean interface without any detectable defects, revealing that the crystalline structure remains nearly intact during the patterning process. Due to technical limits, the nanodots’ side edge inevitably becomes curved as the nanodot size decreases. The curved shape of the substrate near the nanodot and the shape of the nanodot itself are caused by the nonuniform removal of material during dry etching with Ar ions. During the TEM sample preparation, the nanodot was cut through its center with a lamella thickness of about 20 nm. Therefore, the cross-section provides a projection through almost the entire nanodot.

The magnetic hysteresis loops ($M(B)$) have been measured to characterize the ferromagnetic properties of materials (see the Experimental Section for details). The overall shape of the hysteresis loops reflects the materials’ magnetic anisotropy. If the angle between the easy axis and the direction of the applied magnetic field is small, the remanent magnetization $M_{rem}$ tends to be close to the saturation magnetization $M_{sat}$, yielding a rectangular-like shape of the hysteresis loop. Figure 1i shows measured hysteresis loops as the unpatterned SRO thin film rotates around the [001] axis relative to the magnetic field ($B$). Four different orientations (10°, 40°, 60°, 90°) of the substrate were applied for the measurement of $M(B)$ curves (see Figure S2, Supporting Information) for the 0° results of SRO grown under similar conditions. The loop shapes deviate from a rectangular shape as the applied magnetic-field direction rotates away from the applied magnetic-field direction. The shape at a tilt angle of 10° is more “rectangular-like” than for larger tilt angles, indicating that the easy axis is almost parallel to the film normal. For a uniaxial magnetic system like SRO, the sample orientation with respect to the applied magnetic field direction yielding the largest remanent-to-saturation-magnetization $M_{rem}/M_{sat}$ ratio indicates the magnetic easy-axis. We observe that the ratio decreases from $M_{rem}/M_{sat}$ at $\alpha = 10^\circ$ to $0.85$ to $M_{rem}/M_{sat}$ at $\alpha = 90^\circ$ with an increasing tilt angle from $\alpha = 10^\circ$ to $\alpha = 90^\circ$, indicating that the epitaxial SRO thin film has an uniaxial perpendicular
magnetic anisotropy. Figure 1j–l corresponds to magnetic hysteresis $M(B)$ loops of an array of 200, 80, and 30 nm sized nanodots patterned from an as-grown SRO thin film, measured in OOP and IP orientations, respectively. For the hysteresis loop of the 200 nm sized nanodots array (Figure 1j), $M_{\text{rem}}/M_{\text{sat}}$ changes from $(M_{\text{rem}}/M_{\text{sat}})_{\perp}=0.51$ in the OOP to $(M_{\text{rem}}/M_{\text{sat}})_{//}=0.32$ in the IP orientation. For the hysteresis loop of the 80 nm sized nanodots array (Figure 1k), we measure $(M_{\text{rem}}/M_{\text{sat}})_{\perp}=0.44$ and $(M_{\text{rem}}/M_{\text{sat}})_{//}=0.12$, which reduces further for nanodots down to 30 nm (Figure 1l), yielding a much weaker magnetic signal of the nanodots. For the 30 nm sized nanodots, only the hysteresis loop in the OOP direction was obtained reproducible with $(M_{\text{rem}}/M_{\text{sat}})_{\perp}=0.39$. To calculate these ratios, the remanent magnetization was determined by linear extrapolation of the magnetization at high magnetic fields equal 0. Since the measurement uncertainty of calculated ratios is relatively large and hard to be precisely determined, the presented ration numbers are used to guide the changing trend of magnetic anisotropy rather than definitive values. The $(M_{\text{rem}}/M_{\text{sat}})_{\perp}$ drops gradually as the nanodots’ size decreases, revealing that the magnetic easy-axis rotates from the OOP direction toward the IP direction, which is sketched in Figure 1m–p for an SRO thin film, 200 nm sized nanodots, 80 nm sized nanodots, and 30 nm sized nanodots, respectively. There is a step at small fields in both IP and OOP loops, which may originate from several mechanisms. Nevertheless, the contribution of magnetic impurity can be fully excluded in this work (see the Experimental Section for detailed explanations). Magnetic hysteresis loops as
a function of the lateral spacing between nanodots suggest that the magnetic interactions within and between nanodots are likely causes (see Figure S3, Supporting Information).

2.2. Lattice Structure and Local Chemistry at the Heterointerface

In order to determine the structure of the epitaxial SRO thin films, we have applied X-ray diffraction (XRD) techniques. Figure 2a shows four reciprocal space maps (RSMs) of a SRO thin film at different φ angle orientations of the substrate, φ = 0°, 90°, 180°, and 270°. b) Line-by-line averaged intensity profiles along the Qz direction for different φ angles, φ = 0° (black), 90° (blue), 180° (red), and 270° (green). c) The corresponding schematic diagram of c), e–i) STEM-EELS elemental mapping at the interface of a 30 nm sized SRO nanodot on a STO substrate. e) HAADF-STEM imaging of a region close to the interface. f) Sr elemental map using the Sr-L2,3 edges. g) Ti elemental map using the Ti-L2,3 edges. h) Ru elemental map using the Ru-L2,3 edges. i) The composite map using the color scheme from f–h). The inset shows the signal intensity profile of Ti and Ru at the interfacial region.

Figure 2. Lattice structure and local chemistry at the heterointerface between SRO and STO. a) RSMs of an SRO thin film measured around the (103) peak of STO at four different φ angle orientations of the substrate, φ = 0°, 90°, 180°, and 270°. b) Line-by-line averaged intensity profiles along the Qz direction for different φ angles, φ = 0° (black), 90° (blue), 180° (red), and 270° (green). c) The corresponding schematic diagram of c), e–i) STEM-EELS elemental mapping at the interface of a 30 nm sized SRO nanodot on a STO substrate. e) HAADF-STEM imaging of a region close to the interface. f) Sr elemental map using the Sr-L2,3 edges. g) Ti elemental map using the Ti-L2,3 edges. h) Ru elemental map using the Ru-L2,3 edges. i) The composite map using the color scheme from f–h). The inset shows the signal intensity profile of Ti and Ru at the interfacial region.
mixed Ru-Ti-O layer, which is about one unit cell thick. It is worth noting that the HAADF signal profiles are identical for SRO thin films and patterned nanodots on STO substrates. Figure 2e–i shows STEM-EELS results of the elemental distribution of Sr, Ti, Ru at the interface between SRO and STO for a 30 nm sized SRO nanodot at the atomic scale. The Sr-L2,3 map in Figure 2f reveals a homogeneous Sr distribution across the imaged area. The Ti-L2,3 (Figure 2g) and Ru-L2,3 (Figure 2h) intensity maps indicate the different regions of STO and SRO, respectively. The composite image (Figure 2i) of the Sr, Ti, and Ru maps directly visualizes the elemental distribution around the interface. The Ti and Ru signal intensities at the interface (c.f. inset of Figure 2i) confirm a weak intermixing of Ti and Ru within about one unit cell on both sides of the interface, yielding the same chemical distribution as at the interface of SRO thin films on STO substrates. Similar results have been reported at the interface of SRO–STO superlattices, which were grown by pulsed laser deposition (PLD).

2.3. Lattice Anisotropy and Oxygen Octahedral Rotation

Quantitative STEM analysis has been performed to investigate alterations of the lattice anisotropy ($c/a$) and octahedral rotations $\theta = \pi - \alpha$, which are critical factors for influencing the magnetocrystalline anisotropy of SRO nanodots. The $c/a$ values were determined from HAADF images, whereas for the octahedral rotation angles we analyzed ABF images recorded simultaneously. It is worth noting that, since ABF results were acquired in the cross-section orientation, we exclusively have measured amplitudes of rotation angles along the in-plane rotation axis. The 2D $c/a$ maps of the unpatterned SRO thin film, the 80 nm sized nanodots, and the 30 nm sized nanodots are displayed in Figure 3a–c, respectively, using the same color scale. In the SRO part of the unpatterned thin film, we observe an even distribution of the $c/a$ values over the entire SRO layer. In contrast, the SRO part of patterned nanodots displays a maximum of $c/a$ values close to the interface, decreasing while moving toward the surface. The averaged $c/a$ value in the SRO layer becomes smaller as the size of the nanodots reduces (see Figure S6, Supporting Information). To precisely determine the $c/a$ values in the nanodots, we fit Gaussian functions to atomically resolved STEM HAADF images and determine the coordinates of the constituent elements. Figure 3d–f corresponds to $c/a$ values of the first 15 unit cells of the unpatterned SRO thin film, an 80 nm sized nanodot, and a 30 nm sized nanodot. The calculated $c/a$ values using interatomic distances of the A- (Sr) and B-site (Ru/Ti) atoms match well with each other for all studied

![Figure 3. Lattice anisotropy and oxygen octahedral rotation in SRO. a–c) are the 2D $c/a$ maps of the unpatterned SRO thin film, 80 nm sized nanodots, 30 nm sized nanodots, respectively. The vertical arrows denote the interface between SRO and STO. d–f) correspond to the vertically-averaged $c/a$ values of the regions marked by boxes. g–i) depict the relating rotation angles ($\theta = \pi - \alpha$) in the IP ($\theta_1$) and OOP directions ($\theta_2$) in the boxed areas in a–c). The definition of $\alpha_1$ and $\alpha_2$ is shown in the inset of g). The rotation angle $\theta$ denotes a 2D projection of a 3D bonding angle determined from the oxygen positions in the inverted ABF images below the plots. Position 0 represents the surface TiO layer of the STO substrate.](image-url)
samples. Comparing these values to an unpatterned SRO thin film with a constant c/a value of 1.015 ± 0.005, the c/a values of patterned nanodots reach a maximum close to the SRO/STO interface and drop steeply as moving away from the interface. Most importantly, we can observe a clear trend that the smaller the size of the nanodot, the smaller the c/a value at the same distance from the interface, demonstrating that the overall degree of lattice anisotropy is reduced for nanodots with smaller sizes. Nevertheless, the c/a values of the first 3 SRO monolayers remain almost unchanged for all nanodots sizes.

Based on the fitted coordinates of the oxygen positions, Figure 3g–i presents the IP ($\theta_1 = \pi - \alpha_1$) and OOP ($\theta_2 = \pi - \alpha_2$) angles between neighboring RuO$_6$ octahedra for the first 15 unit cells of an unpatterned SRO thin film, an 80 nm sized nanodot, and a 30 nm sized nanodot. For the unpatterned SRO thin film, the angles $\theta_1$ and $\theta_2$ remain unchanged at a value of 0°, since the STO substrate fully strains the SRO lattice. The rotation of the oxygen octahedra appears in SRO nanodots due to the patterning. For smaller nanodots, the SRO lattice has a higher degree of freedom for strain relaxation, deviating the rotation angles of RuO$_6$ octahedra more from 0°. For 80 nm sized nanodots, the rotation angles show a slight increase to around 2°. In contrast, the octahedral rotations in 30 nm sized nanodots are more prominent with an angle of ~15°, which is similar to bulk SRO. As moving away from the interface, the OOP plane rotation occurs earlier than the IP rotation due to a gradual IP strain relaxation. Interestingly, the RuO$_6$ octahedra of the first 3 unit cells exhibit identical results on rotation angles with a value of 0° for both $\theta_1$ and $\theta_2$. It implies that the crystal structure of the fully strained first 3-unit-cell layers is too robust to be modified by the patterning process.

2.4. First-Principles Calculations

To probe the physical origin of the nanodots' magnetic anisotropy, the magnetic moment and the magnetocrystalline anisotropy energy (MAE) of Ru in SRO were calculated within a $2 \times 2 \times 2$ supercell (i.e., Sr$_9$Ru$_8$O$_{24h}$) using VASP (Vienna Ab-initio Simulation Package), which is based on the density-functional theory (DFT). The influences of the lattice anisotropy (c/a) and the oxygen octahedral rotation are examined according to the experimentally measured values in Figure 3. Considering the experimental data and previously reported calculations on the SRO system,[40–42] an effective Hubbard parameter $U_{\text{eff}} = 3$ eV is adopted for our calculations. Here, we define the total energy difference by considering the spin-quantization axis is IP ($E_{ij}$) and OOP ($E_{ij}$) as MAE, i.e., $\text{MAE} = E_{ij} - E_{ij}$. Thus, a positive (negative) value of MAE indicates the OOP (IP) to be the easy axis.

Figure 4b,c presents the first-principles calculation results, where the magnetic moment and the MAE of Ru are shown for different c/a ratios (c/a = 1.0, 1.01, 1.02) and various oxygen octahedral rotation angles ($\theta = 0°, 4°, 10°$). The magnetic moment per Ru atom (Figure 4b) slightly increases with increasing c/a ratio and is also subtly influenced by $\theta$. Nevertheless, the magnetic moment remains around 1.4 $\mu_B$ per Ru atom irrespective of the c/a ratio and $\theta$. In contrast, the MAE (Figure 4c) is highly dependent on the c/a ratio and $\theta$. The MAE is 0 for c/a = 1 and no octahedral rotation ($\theta = 0°$). Once a strain is applied along the c axis (c/a > 1), the MAE increases with c/a and reaches 0.6 meV Ru$^{-1}$ for c/a = 1.02 and $\theta = 0°$. However, the MAE decreases with an increase of $\theta$. An oxygen octahedron rotation of 10° even leads to an IP easy axis, i.e., a negative
MAE, for $c/a \leq 1.01$. These results indicate the competitive role of the $c/a$ ratio and $\theta$ on the MAE, i.e., a high $c/a$ ratio increases the OOP MAE, while a large $\theta$ decreases it. Therefore, both the smaller $c/a$ ratio and the large $\theta$ in 30 nm sized nanodots (Figure 3f,i) synergetically reduce the OOP MAE more, compared to the larger $c/a$ ratio and smaller $\theta$ in 80 nm sized nanodots (Figure 3e,h). This explains the larger deviation of the easy axis from the OOP direction in 30 nm sized nanodots.

3. Discussion

The magnetization results have unambiguously demonstrated the tunable magnetic anisotropy in patterned SRO nanodot arrays. Since the magnetocrystalline anisotropy in SRO plays a huge role in its overall magnetic anisotropy,\(^{25}\) the effects of surface and shape anisotropy are insignificant here. We attribute the variable magnetic anisotropy of fabricated nanodot arrays to the altered intrinsic magnetocrystalline anisotropy. Generally, the effective uniaxial anisotropy energy $K_u$ in a heterostructure can be described as the following relation:\(^{43,44}\)

$$K_u = K_v + K_i/t$$  (1)

where $K_v$ and $K_i/t$ correspond to the volume anisotropy energy and the contribution from the interface in a ferromagnetic layer with a thickness $t$. For as-grown SRO thin films with perpendicular uniaxial magnetic anisotropy, the contributions from the volume magnetocrystalline anisotropy $K_v$ and the interfacial crystalline anisotropy $K_i/t$ cannot be decoupled, because STEM results reveal that the lattice structure controlling the magnetocrystalline anisotropy remains unchanged throughout the SRO layer. Nevertheless, the role of $K_v$ and $K_i/t$ can be rationally separated for differently sized SRO nanodots. STEM studies identify a 3-unit-cell thick interfacial SRO layer, whose lattice anisotropy and octahedral rotations are stabilized by the symmetry mismatch,\(^{45}\) and show constant values regardless of the nanodots size. In this scenario, $K_i/t$ does not contribute to the magnetic anisotropy in SRO nanodots. In contrast to the interfacial contribution $K_i/t$, we observe a gradual variation of the volume anisotropy energy $K_v$ closely related to the size of SRO nanodots. Octahedral distortions in SRO nanodots are gradually altered while moving away from the interface. Furthermore, the degree of octahedral distortions at the same distance from the interface increases as the size of the SRO nanodots reduces, because the IP biaxial strain relief is more prominent in smaller nanodots. It unveils that $K_i$ plays a dominating role in tuning the magnetic anisotropy of patterned SRO nanodot arrays. Although the cation/anion stoichiometry in perovskite oxides generally affects the RuO$_6$ octahedral rotation,\(^{27}\) its effect can be excluded here, because no apparent changes of the composition of the SrRuO$_3$ can be observed after nanopatterning via energy-dispersive X-ray spectroscopy (EDS) studies. (see Figures S7 and S8, Supporting Information).

The influence of magnetocrystalline anisotropy concerning lattice anisotropy and oxygen octahedral rotations is generally a paradox in perovskite heterostructures. Ru$^{4+}$ ions in SRO are usually considered to be in the low-spin state.\(^{46}\) In fully-strained SRO/STO heterostructures, the RuO$_6$ octahedron is IP compressed, inducing an increased tetragonality. On the one hand, the RuO$_6$ crystal field is modified, enhancing the energy of the lateral 4$d$ orbitals and the occupancy of the perpendicular 4$d$ orbitals. On the other hand, the orbital hybridization between Ru 4$d$ and O 2$p$ states is weakened along the $c$ axis, reducing the exchange interaction in this direction. Obviously, the RuO$_6$ crystal-field effect is dominative, which gives rise to a perpendicular magnetic anisotropy in the SRO thin film (Figure 3d,g). In contrast, the structural origin of the magnetic anisotropy in SRO nanodots is size-dependent. When patterning the SRO thin film to nanodots with a relatively large size, the IP strain relaxation leads to a noticeable change of the lattice anisotropy but usually negligible oxygen octahedral rotations. For instance, 80 nm sized nanodots show an apparent decrease of the lattice anisotropy and minimal octahedral rotations of about $2^\circ$ in the SRO layer (Figure 3e,h). Hence, the lattice-anisotropy-induced RuO$_6$ crystal-field effects dominate the magnetic anisotropy of large-sized SRO nanodots. However, oxygen octahedral rotations are crucial in controlling the magnetic anisotropy for nanodots as small as 30 nm. We found that the Ru-O-Ru rotation angles change from $2^\circ$ for 80 nm sized nanodots to $15^\circ$ for 30 nm sized nanodots (Figure 3i). At the same time, only a slight change of the lattice anisotropy is observed (Figure 3f). DFT calculations have also explained this mechanism, implying that tuning octahedral rotation angles in heterostructures with a minor lattice mismatch is a practical pathway to engineer magnetic behaviors.

We have focused so far on the differences in the lattice structure and magnetic anisotropy as a function of the nanodot size. Interestingly, SRO nanodots also have a complicated lattice structure that evolves with increasing distance from the interface. The first atomic layers close to the interface have a lattice structure with a large $c/a$ ratio, whereas the lattice relaxes further away from the interface, and the $c/a$ ratio decreases. SRO is a unique ferromagnet with a large ratio of the magnetocrystalline anisotropy energy and the exchange energy.\(^{25}\) This implies that the direction of the magnetization can change at very small length scales.\(^{47}\) Therefore, it can be expected that the nanodots have a complicated magnetic structure, where the magnetization follows the local magnetocrystalline anisotropy energy landscape. Thus, we expect the magnetization within a single nanodot to be oriented relatively out-of-plane close to the interface and more in-plane at the top of nanodots. The unique magnetic properties of SRO in combination with the range of crystal structure variation possible within nanodots makes these nanodots an intriguing playground to engineer novel magnetic configurations for potential applications. Furthermore, in principle, one can design the magnetic behavior in a desired way via nanopatterning when building nanodevices with oxide heterostructures. Via the maintained interfacial magnetic anisotropy, one can also build interface-based nanodevices, in which the magnetic properties are stable during the nanopatterning process.

4. Conclusion

This work presents a flexible control of the SRO layer’s magnetic anisotropy from the OOP direction to the film plane by
patterning the film to SRO nanodots with different sizes. STEM results demonstrate that the magnetic anisotropy modulation in SRO nanodots makes use of controlling volume anisotropy rather than the interfacial magnetocrystalline anisotropy confined within the first 3 unit cell SRO monolayer. The roles of lattice anisotropy and oxygen octahedral rotations on the magnetic anisotropy of the SRO nanodot array are size-dependent, which is revealed by combining STEM studies and DFT calculations. The method presented is not limited to SRO/STO heterostructures, but can be extended to a broad range of heterostructures. One can design the epitaxial layer’s magnetic order by selecting a proper substrate and then engineer the magnetic states by patterning them into an array of nanodots with different sizes. Controlling the shape of nanodots is also an exciting topic, which may lead to emergent magnetic phases, e.g., vortex states or skyrmion phases.

5. Experimental Section

Epitaxial Growth of SRO Thin Films: Epitaxial SRO thin films were grown on TiO2-terminated (100)-oriented STO substrates (Shinkosha) by PLD using a stoichiometric, polycrystalline target (Lesker). The growth temperature was 680 °C, the oxygen pressure was 0.08 mbar, the laser fluence was 2.5 J/cm², the laser frequency was 1 Hz, and the growth rate was 0.05 monolayer per pulse. The growth mode is a layer-by-layer growth as evidenced by the observation of corresponding RHEED oscillations.

Fabrication of SRO Artificial Atoms: The SRO nanodots were fabricated by patterning as-grown epitaxial SRO thin films with electron beam lithography (EBL) in a class-100 (ISO 5) cleanroom, which enables to make custom shapes by irradiating a suitably sensitive resist material with a focused beam of electrons. The resist material used in this work is poly(m-ethyl styrene-co-a-chloroacrylate methylether) (CSAR, Aliresei GmbH, Germany), which provides superior resolution and requires a smaller exposure dose than the commonly-used resist poly(methyl methacrylate) (PMMA). Electron beam exposure was performed with a design layout using a 100 keV electron beam lithography system (JBX6300, JEOL Co. Ltd.). A hard mask of a thin layer of amorphous α-Al2O3 was then deposited on the top by PLD. Afterward, the resist layer was lifted off by chemically dissolving it in a remover solution, leaving the only hard mask on the top of the SRO layer. The SRO nanodots were finally obtained by dry etching with a flux of ionized argon to pattern the SRO layer (see Figure S9 for the fabrication process of SRO nanodots, Supporting Information).

Magnetic Measurements: The magnetic properties of the samples were measured using a Quantum Design MPMS SQUID magnetometer equipped with the reciprocating sample option (RSO) head. The most frequently used measurement parameters were: 4 cm of oscillation amplitude with a frequency of 0.5−1 Hz and 10 oscillation cycles per data point. The typical sensitivity of such a measurement is on the order of 10−12−10−11 Am2 (2−10−4 emu), depending on the experimental conditions. The preparation for the magnetic measurements was done using nonmagnetic tweezers and without contact with any magnetic substance. Since the patterned nanostructure on 5 x 5 mm² substrates fit into the setup of the SQUID measurements, no cutting was applied to the samples. The M(H) loops of a bare STO substrate show paramagnetic flat lines without features, proving that no magnetic impurities exist in the initial STO substrates (see Figure S10, Supporting Information). For all samples, the thickness of the SrRuO3 film is equal to 12 nm (i.e., 32 unit cells of SrRuO3). Bare Every sample was measured twice at different steps of the fabrication process: directly after the film growth and then after being patterned into nanodots. The curves were measured in the range of −6 T to +6 T with a step size of 0.1 T. For further data analysis, the linear paramagnetic contribution from the STO substrate was subtracted first. The magnetization was then normalized to the estimated total number of Ru atoms present in the nanodots. From large area SEM and AFM scans, the coverage of the substrate was estimated. The thickness and shape of the nanodots were inferred from the TEM data. Combining these data allowed to calculate the approximate total number of Ru atoms on the substrate. Finally, the magnetic signal has been normalized to the estimated amount of Ru.

XRD Measurements: XRD data have been measured in-house on the Empyrean set-up (Cu Kα line, λ = 1.541 Å) and at the Max Planck Institute beam line which is part of the synchrotron radiation facility ANKA (Ångströmquelle Karlsruhe, KIT, Germany, λ = 1.541 Å). The step size for Qx and Qy in acquired RSM maps were 0.001 Å⁻¹.

STEM Investigations: STEM specimens were prepared by focused ion beam (FIB) followed by NanoMill at liquid-N₂ temperature. The way, the central part of SRO nanodots was prepared, enables to perform STEM investigations with high precision.[44] STEM studies were conducted using a spherical aberration-corrected STEM (JEM-ARM200F, JEOL Co. Ltd.) equipped with a cold field emission gun and a DCOR probe Cs-corrector (CEOS GmbH) operated at 200 kV. The STEM images were obtained by JEOL ADF and BF detectors with a convergent semiangle of 20.4 mrad. The corresponding collection semiangles for HAADF imaging were 70–300 mrad and for ABF imaging 11–22 mrad. In order to make precise measurements of lattice constants and octahedral rotation angles, ten serial frames were acquired with a short dwell time (2 µs per pixel), aligned, and added afterward to improve the signal-to-noise ratio (SNR) and minimize the image distortion of HAADF and ABF images. EELS acquisition was performed by a Gatan GIF Quantum ERS imaging filter with dual-LiHe acquisition capability with a convergent semiangle of 20.4 mrad and a collection semiangle of 111 mrad. Dual EELS spectrum imaging was applied with the dispersion of 1 ev per channel by a 2048 pixel wide detector for simultaneously acquiring the spectrum image of the Sr-La, Ti-La, and Ru-La edges. The raw spectrum image data were denoised by applying a principal component analysis (PCA) with the multivariate statistical analysis (MSA) plugin (HREM Research Inc.) in Gatan DigitalMicrograph and then smoothed using a spatial filter in Gatan DigitalMicrograph. c/a maps were calculated with the lattice-deformation results obtained using a Geometric Phase Analysis (GPA).[45] The c/a value for each unit cell was measured with the Matlab-based image-quantification tool StatSTEM.[46] The Oxygen Octahedra Picker tool was employed for measuring the octahedral rotation angles in IP and OOP directions.[47,48]

First Principle Calculations: The core-electron interaction is described by the projector augmented wave potential, in which the Sr (1s²2s²2p⁶), Ru (4d⁵5s²), and O (2s²2p⁴) shells are taken as valence electrons. Owing to the epitaxial growth of the thin SRO film on SrTiO3 (STO) substrate, the in-plane lattice parameters of the epitaxial SRO film are determined by the experimental value (a = b = 3.905 Å) of the bulk STO system.[49] The cut-off energy is set to 500 eV and the convergence criteria for the total energy is 5 × 10⁻⁹ eV for self-consistent calculations. Moreover, the influence of the oxygen octahedral rotation is studied using a 2 x 2 x 2 SRO super cell (i.e., SrₓRu₁₋ₓO₂₊₂₊₂). The 3D Brillouin zone is sampled with a 5 x 10 x 10 x 5 x 5 Monkhorst-Pack k-point mesh for a five-atom unit cell and a 40-atom super cell, respectively. The local density approximation (LDA) is adopted for the exchange-correlation function. In addition, to account for the strong correlations in d-orbitals of Ru, LDA+U with rotationally invariant approach introduced by Dudarev et al. is applied.[50] In this way, the effective Hubbard parameter (Uₘ⁺ = U − J) is used, where U and J are the strength of the effective on-site Coulomb energy and exchange interactions of Ru 4d states, respectively. The MAE was calculated by the energy difference corresponding to magnetization along different crystal axes. In detail, a collinear spin-polarized self-consistent calculation is performed to obtain the converged charge densities. Then by reading these charge densities, noncollinear nonself-consistent calculations with spin–orbit coupling are carried out to obtain the total energy as a function of spin-quanization axes.
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

lattice anisotropy, magnetic anisotropy, oxygen octahedral rotation, quantum structures, scanning transmission electron microscopy, SrRuO₃

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