Enhanced Magnetism in Epitaxial $SrRuO_3$

A. J. Grutter,[1, 2] F. Wong,[1] E. Arenholz,[3] M. Liberati,[3] A. Vailionis,[4] and Y. Suzuki[1, 2]

[1] *Department of Materials Science and Engineering,*
University of California, Berkeley, CA 94720, USA
[2] *Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*
[3] *Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA*
[4] *Geballe Laboratory for Advanced Materials, Stanford University, Stanford, California, 94305, USA*

(Dated: October 2, 2009)

We have observed enhanced magnetization in epitaxial $SrRuO_3$ thin films compared to previously reported bulk and thin film values of 1.1-1.6 μ_B/Ru ion. The degree of enhancement is strongly dependent on the lattice distortions imposed on the $SrRuO_3$ films by $SrTiO_3$, $(LaAlO_3)_{0.3}(SrTaO_3)_{0.7}$ (LSAT), and $LaAlO_3$ substrates. A larger enhancement of magnetization for coherently strained $SrRuO_3$ films on $SrTiO_3$ and LSAT compared to fully relaxed films on $LaAlO_3$ confirms the importance of the strain state in determining the magnetic ground state of the Ru ion. In particular, $SrRuO_3$ films on (111) $SrTiO_3$ exhibit exhanced moments as high as 3.8 μ_B/Ru ion, thus suggesting the stabilization of a high-spin Ru^{4+} state.

Transition metal complex oxides comprise a fundamentally intriguing and technonologically promising family of materials with a wide range of properties. The tunability of these properties via lattice distortions has been studied in detail in bulk and thin film form. While in the past it has often been difficult to separate out the effects of microstructure and defects from those of strain in epitaxial films, recent advances in atomically precise complex oxide thin film deposition techniques make it possible.

Among the transition metal oxides, $SrRuO_3$ (SRO) is unique in that it is a 4d transition metal oxide that exhibits ferromagnetism and metallic conductivity. It has a distorted perovskite structure with a pseudocubic lattice parameter of 3.93 Å.[1, 2] Bulk $SrRuO_3$ exhibits Curie temperature (T_C) $\approx$ 160 K and a moment of 1.1-1.6 μ_B per Ru^{4+} ion.[1, 3–5] These values are significantly reduced from the low-spin configuration value of 2 μ_B/Ru^{4+} ion. The reduction has been attributed to the delocalization of spin in an itinerant ferromagnet. SRO has also been identified as a technologically promising material as it has been incorporated both as an electrode in oxide devices and a structural template for other oxide films.[6–9]

Recently, layer-by-layer growth of $SrRuO_3$ thin films has enabled the growth of near perfect epitaxial thin films.[10, 11] However, the majority of this work examines films grown on (001) $SrTiO_3$ substrates. There has been some theoretical work that has predicted supressed magnetization for (i) SRO films under compressive epitaxial strain and (ii) SRO films compressed on the (110) plane in comparison with (001) SRO films.[12] Experimentally, remarkably little is known about the effects of the magnitude and symmetry of lattice distortions on the magnetization.[13, 14] Epitaxial growth of SRO films provides model systems to study these distortions and their effects on magnetism.

In this paper we demonstrate that magnetization can be enhanced in SRO films through lattice distortions generated by epitaxial strain. By modifying substrate choice and orientation as well as film thickness, we have systematically varied the magnitude and symmetry of the lattice distortions in SRO films imposed by the substrate. We find magnetization enhanced from bulk values that are consistent with the presence of the maximum spin moment of 2 μ_B for low spin Ru^{4+} ions and a small orbital moment contribution in (001) and (110) SRO films. However, the high moment enhancement of (111) SRO films cannot be explained by a low-spin picture of the Ru^4+ ion, even in the case of perfect alignment of both spin and orbital contributions, thus suggesting the stabilization of a high-spin Ru state.

Epitaxial SRO thin films were grown by pulsed laser deposition (PLD) on (001), (110), and (111) $SrTiO_3$ (STO) as well as (001) $LaAlO_3$ (LAO), and (La, Sr)(Al, Ta)O_3 (LSAT) substrates. Each substrate places the overlying SRO film under compressive strain with epitaxial strain mismatch ranging from 0.64% in STO and 1.53% in LSAT to 3.56% in LAO. All films were grown at 700 °C in 60 mtorr of O_2 with a laser fluence of 1.29 J/cm^2. To minimize oxygen vacancies, samples were post-annealed at 600 °C for 7 minutes and cooled in atmospheric pressure O_2. Film thicknesses range from 20 to 120 nm. In this paper, we will describe the orientation of the SRO in terms of the pseudocubic lattices parameters $a'_{bulk} = b'_{bulk} = c'_{bulk} =$ 3.93 Å.[15, 16] These lattice parameters are rotated 45 ° from the orthorhombic, nearly cubic lattice parameters a_{bulk} = 5.57 Å, b_{bulk} = 5.53 Åand $c_{bulk} \approx$ 7.84 Å.

All $SrRuO_3$ films exhibited good epitaxy, as indicated by the X-Ray Diffraction (XRD) spectra that showed only $SrRuO_3$ film peaks with the same orientation as the underlying substrates. Films had excellent crystallinity with typical mosaic spreads of approximately 0.06° on (001) STO, 0.11° on 001 LSAT and 0.45° on (001) LAO. Reciprocal space maps (RSM) confirmed the pseudomorphic growth of SRO films on (001), (110), (111) STO substrates in films as thick as 120 nm. Figure 1 shows RSMs of the following reflections and orientations in 120 nm thick SRO films: (103) reflection of (001) SRO, (221) and (310) reflections of (110) SRO, and the (321) reflection

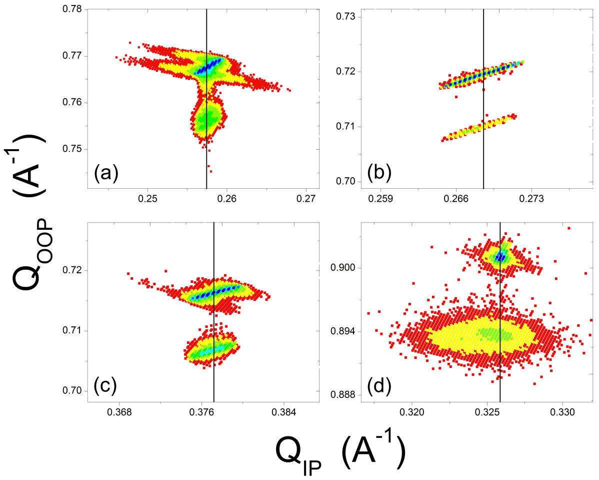


FIG. 1: (color online) RSM of 120 nm thick $SrRuO_3$ films a) (103) reflection of SRO film on (001) STO b) (221) reflection of film on (110) STO c) (310) reflection of film on (110) STO d) (321) reflection of film on (111). The vertical line shows the in-plane lattice parameter of the substrate peak. When this line also passes through the film peak, pseudomorphic epitaxial growth has occurred.

of (111) SRO. The alignment of the substrate and film along the black line is indicative of the coherent matching of the in-plane film and substrate lattice parameters. For SRO films on (001) STO and LSAT, the structural distortions are largely volume preserving tetragonal distortions. Comparable films on (001) LAO are fully relaxed to the bulk value. Thus, the orthorhombic unit cell of SRO is under biaxial strain on the (001) STO substrate that imposes a tetragonal distortion on the unit cell, while films on (110) and (111)-oriented STO experience monoclinic and trigonal distortions of the unit cell, respectively. Therefore, we would expect the out of plane distortion to differ as a function of orientation.

We found that surface morphology was a strong function of sample orientation for a given set of growth conditions. SRO films on (110) and (111) STO had island and columnar morphologies with RMS roughness of 0.6-1.8 nm and 0.6-4.0 nm respectively, much rougher in comparison to their (001) counterpart. All of the (001) films in this study have a step terrace structure consistent with previous work.[17, 18]

The residual resistivity ratios (ρ_{300K}/ρ_{4K}) were obtained from electron transport measurements in the Van der Pauw configuration. The residual resistivity ratios range from 4-5, in agreement with previously reported values for $SrRuO_3$ films deposited by PLD. Although there have been reports of a metal to insulator transition in ultrathin SRO films, these results were most pronounced in films between 4-20 monolayers (1.5-10 nm) thick, with minimal effects in films 20 nm and thicker.[17, 18] Consequently we find that resistivity scales with thickness for all of our films.

X-ray absorption (XA) spectroscopy and X-Ray magnetic circular dichroism (XMCD) performed at the Advanced Light Source beamline 4.0.2 and 6.3.1 provide element specific chemical structure and magnetic information, respectively. The XA spectra of the Ru M edge is in good agreement with previously published results for Ru^{4+} in an octahedral environment.[14] Additionally, the spectra did not contain peaks from magnetic contaminants such as Fe, Ni, and Co, although Ba, a common substitutional impurity in Sr compounds, was present in less than 0.2-0.4 At%.[19] However, Ba is nonmagnetic and unlikely to significantly affect the magnetic state of the system in such low concentrations.

XMCD confirmed that the magnetism originates from the Ru^{4+} ions. Additionally, XMCD measurements demonstrated a ratio of orbital to spin moments of approximately 0.1, showing that the source of enhanced magnetization is primarily an increase in the Ru^{4+} spin moment.

SQUID magnetometry measurements showed that the saturated magnetic moment per Ru ion was enhanced relative to bulk values and its magnitude depended on substrate choice, substrate orientation and film thickness. Figure 3 (inset) shows how 50-80 nm thick (001) SRO films coherently strained to the (001) STO and LSAT substrates exhibit larger average magnetic moment per Ru ion compared to fully relaxed (001) SRO films on (001) LAO. For coherently strained films on STO substrates, a closer look at the magnetic moment per Ru ion reveals that (111) SRO films exhibit a significantly higher moment per Ru ion compared to corresponding (001) and (110) SRO films.

In addition to varying the magnitude and symmetry of the lattice distortions imposed by substrate choice, we also studied the evolution of saturation magnetization with increasing film thickness for SRO films grown on (001), (110) and (111) STO. Figure 3 shows that for any given thickness, $M_{S001} < M_{S110} < M_{S111}$. The (111) films show a general trend of decreasing saturation magnetization with increasing thickness which is consistent with a strain induced enhancement of magnetization. The magnetization values for (001) SRO films are consistently lower than those of the (110) SRO films but similar to those reported in the literature. However the magnetization values for (111) SRO films of 2.22-3.77 μ_B/Ru ion exceeds the low spin moment value of 2 μ_B/Ru ion.

From the structural and magnetic data in our SRO films, we believe that the enhanced magnetization is largely determined by the epitaxial strain state. The relationship between magnetization and strain is clearly established by noting that samples on (001) LAO exhibiting full relaxation show smaller magnetic moments consistent with bulk values while larger distortions imposed by (001) LSAT yields higher saturated moment values relative to the smaller distortions imposed by STO (see Figure 3 inset). For coherently strained films on STO, monoclinic distortions on (110) STO and tetragonal distortions on (001) STO give rise to magnetic moments that can be explained in terms of a low spin moment

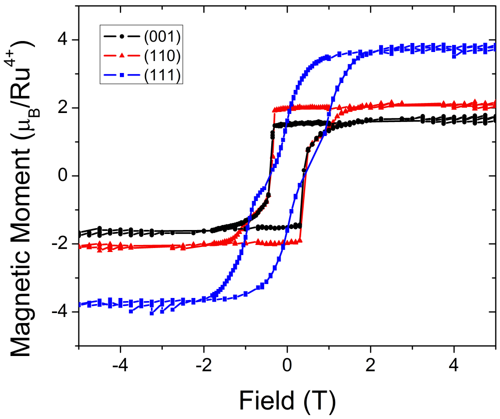
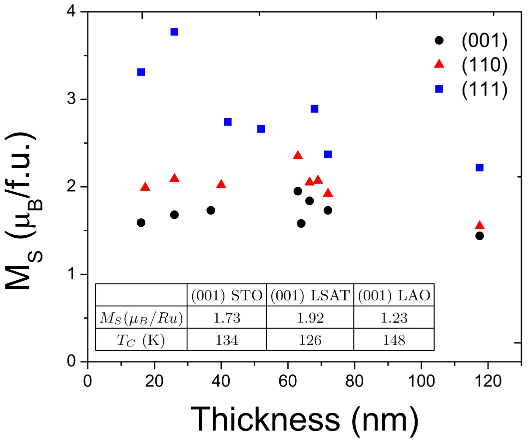


FIG. 2: (color online) Figure 2 -Film thickness vs. M_S in (001), (110), and (111) oriented films on STO. Film thickness was inversely related to saturated moment in (111) films.



	(001) STO	(001) LSAT	(001) LAO
$M_S(\mu_B/Ru)$	1.73	1.92	1.23
T_C (K)	134	126	148

FIG. 3: (color online) Film Magnetization vs. Applied field measured with a SQUID magnetometer. Samples were 24 nm thick (001), (110), and (111) oriented SRO films on STO.

value of 2 μ_B/Ru ion combined with a small orbital contribution. The consistently larger values observed for the (110) films compared to the (001) films is at odds with previous theoretical calculations.[12]

For trigonally distorted samples on (111) STO, the moment is a very strong function of in-plane strain of the samples. Figure 3 shows that as the in-plane lattice parameters relax, the M_S decreases. The Ru saturation moment values for the trigonally distorted (111) SRO films on STO far exceed 2 μ_B and are extremely difficult to reconcile within a low spin moment plus small orbital moment picture. These results suggest the presence of Ru magnetic moment values well beyond that of the typical low spin (2 μ_B/Ru^{4+}) configuration. In the absence of magnetic impurities, we may invoke the stabilization of the high spin (4 μ_B/Ru^{4+}) configuration to explain the enhanced Ru moment in the (111) SRO films. If this is indeed the case, this would be the first known high-spin state of Ru^{4+}.

According to theoretical calculations, compressive expitaxial strains are predicted to give rise to the suppression of magnetization. One possible explanation for the enhancement of magnetization could be strain induced octahedral tilt instabilities that give rise to reduced covalency via changes in bond angle. Theoretically, an increase in bond angle away from 180° could reduce the covalency of the Ru-O bonds, thus giving rise to more localized moment. However, given the thickness range of our epitaxial (111) films, it is extremely difficult to measure changes in bond angles in single crystalline films.

In summary, we have demonstrated the importance of the magnitude and symmetry of lattice distortions in achieving enhanced magnetism in epitaxial SRO films. Tetragonally distorted (001) SRO films exhibit saturation magnetization values consistent with previous bulk and thin film studies. Monoclinically distorted (110) SRO films achieve higher saturation magnetization values consistent with the maximum spin moment value of 2 μ_B/Ru ion for the low spin configuration. Trigonally distorted (111) SRO films exhibit even higher saturated moment values which are beyond the range consistent with a low-spin configuration of Ru.

We would like to thank J. Rondinelli and N. Spaldin for fruitful discussions, and K. M. Yu for his assistance in RBS data collection. This work and the Advanced Light Source are supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

---

[1] Allen et al., Phys. Rev. B **53**, 4393 (1996)
[2] C. W. Jones et al., Acta Cryst. **C45**, 365 (1988)
[3] S. N. Bushmeleva et al., J. Magn. Magn. Mater. **305**, 491 (2006)
[4] A. Kanbayasi, J. Phys. Soc. Jpn. **41**, 1876 (1976)
[5] P.S. Anil Kumar et al., Physica B **269**, 356 (1999)
[6] Z. G. Ban et al, Appl. Phys. Letters **84**, 4848 (2004)
[7] H. Tanaka et al., Jap. J. of Appl. Phys., **47**, 7527 (2008)
[8] Y. Hikita et al., Phys. Rev. B 77, 205330 (2008)
[9] K. Maki et al., Appl. Phys. Letters **82**, 1263 (2003)
[10] J. C. Jiang et al., Appl. Phys. Letters **72**, 2963 (1998)
[11] A. Vailionis et al., Appl. Phys. Letters **91**, 071907 (2007)
[12] A. T Zayak et al., Phys. Rev. B **77**, 214410 (2008)
[13] A. Vailionis et al., Appl. Phys. Letters **93**, 051909 (2008)
[14] B. W. Lee et al., J. of Appl. Phys. **104**, 103909 (2008)
[15] Q Gan et al., Appl. Phys. Letters **72**, 978 (1998)
[16] C. B. Eom et al., Science **258**, 1766 (1992)
[17] Toyota et al., Appl. Phys. Letters **87**, 162508 (2008)
[18] Herranz et al., Phys. Rev. B **67**, 174423 (2003)
[19] V. Seeman et al., Phys. Stat. Sol. (b) **102**, 459 (1980)