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Epitaxial integration and properties of SrRuO₃ on silicon

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We report the integration of SrRuO₃, one of the most widely used oxide electrode materials in functional oxide heterostructures, with silicon using molecular-beam epitaxy and an SrTiO₃ buffer layer. The resulting SrRuO₃ film has a rocking curve full width at half maximum of 0.01°, a resistivity at room temperature of 250 μΩ cm, a residual resistivity ratio ($\rho_{300\text{ K}}/\rho_{4\text{ K}}$) of 11, and a paramagnetic-to-ferromagnetic transition temperature of ~160 K. These structural, electrical, and magnetic properties compare favorably to the best reported values for SrRuO₃ films on silicon and rival those of epitaxial SrRuO₃ films produced directly on SrTiO₃ single crystals by thin film growth techniques other than molecular-beam epitaxy. These high quality SrRuO₃ films with metallic conductivity on silicon are relevant to integrating multi-functional oxides with the workhorse of semiconductor technology, silicon. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/1.5041940>

SrRuO₃ is one of the most widely used oxide electrode materials in epitaxial oxide heterostructures and related devices.¹ This utility arises from its excellent thermochemical stability,^{2,3} high conductivity at room temperature, and especially because of its close lattice match (SrRuO₃ has a pseudocubic lattice parameter of 3.93 Å) with many functional perovskite oxides. These include multiferroics such as BiFeO₃ (pseudocubic lattice parameter of 3.96 Å),⁴ ferroelectrics such as BaTiO₃ (in-plane lattice parameter of 3.99 Å),⁵ superconductors such as YBa₂Cu₃O_{7-x} (in-plane pseudotetragonal lattice parameter of 3.85 Å),⁶ and piezoelectrics such as Pb(Zr,Ti)O₃ (in-plane lattice parameter 3.905–4.14 Å).^{7,8} SrRuO₃ is often employed in ferroelectric devices,⁹ superconducting multilayers,¹⁰ Josephson junctions,¹¹ electro-optic and magneto-optic devices,¹² Schottky junctions,¹³ ferroelectric tunnel junctions,¹⁴ magnetocaloric devices,¹⁵ resistivity switching devices,^{14,16} magnetoelectric devices,^{17,18} photovoltaic devices,¹⁹ and optoelectronic devices.²⁰ In condensed matter physics, SrRuO₃ also plays an active role in moderately correlated materials physics due to its unusual itinerant ferromagnetism as a 4d transition metal oxide. The transport properties of SrRuO₃ also draw great attention, including its Fermi liquid behavior at low temperature²¹ and bad metallic behavior at high temperature.²² Recently, heterostructures involving SrRuO₃ layers have been shown to exhibit the topological Hall effect²³ and the inverse spin Hall effect,²⁴ indicating its potential for spintronic applications.

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Integration of SrRuO₃ with silicon, the backbone of the electronics industry, is critical for leveraging the extensive existing infrastructure for large-scale semiconductor manufacturing. This will enable the widespread use of SrRuO₃-based multi-functional oxide heterostructures for a wide range of applications.

Unfortunately, directly integrating epitaxial SrRuO₃ on silicon is difficult as the formation of an amorphous SiO₂ layer in the oxidative environment during the growth of SrRuO₃ can impede epitaxial growth, resulting in polycrystalline SrRuO₃ films.²⁵ Polycrystalline SrRuO₃ precludes the epitaxial integration of functional oxide thin films on top of the SrRuO₃ electrode and with it a loss of the optimal properties that epitaxial heterostructures often provide for complex oxide integration.

To achieve epitaxial SrRuO₃ on silicon, various buffer layers that can be epitaxially grown on silicon have been introduced, including yttria-stabilized zirconia (YSZ),^{9,26} SrO,^{27,28} SrTiO₃,^{29,30} and SrTiO₃ on TiN.³¹ Although epitaxy of SrRuO₃ on silicon can be realized via these buffer layers, the quality of the SrRuO₃ films on silicon still cannot compete with typical SrRuO₃ films grown on single-crystal oxide substrates, in terms of both structural perfection [as evaluated by the width of the rocking curve (ω scan) of x-ray diffraction (XRD)] and electrical transport characteristics [as assessed by the residual resistivity ratio (RRR = $\rho_{300\text{ K}}/\rho_{4\text{ K}}$)]. For example, the highest RRR reported for SrRuO₃ films on silicon is ~ 3 ,³¹ indicating significant room for improvement in the transport properties of SrRuO₃ on silicon.

Various growth techniques have been utilized for the growth of SrRuO₃ on conventional single-crystal oxide substrates. These include 90° off-axis sputtering,^{32,33} pulsed-laser deposition (PLD),¹⁰ reactive evaporation,^{34–36} molecular-beam epitaxy (MBE),^{37,38} metal-organic chemical vapor deposition,³⁹ and chemical solution deposition.⁴⁰ For the integration of epitaxial SrRuO₃ with silicon, usually more than one growth technique is involved due to the step for growing the epitaxial buffer layer. For example, in the study of Park *et al.*,⁴¹ the SrTiO₃ buffer layer on silicon was grown by MBE while the SrRuO₃ film was subsequently deposited by off-axis sputtering. Compared with a combination of multiple growth techniques, which typically involves an air exposure of the buffer layer during the transfer of the sample from one growth chamber to the other (assuming that the two growth chambers are not connected under vacuum), an individual growth method for both the buffer layer and the SrRuO₃ film can avoid exposing the buffer layer surface to air and is preferred for the preparation of epitaxial heterostructures. To our knowledge, there is no report of MBE-grown epitaxial SrRuO₃ films on silicon although SrRuO₃ films of very high quality can be grown on single-crystal oxide substrates by MBE.^{38,42}

Here we report the *in situ* integration of SrRuO₃ thin films on SrTiO₃-buffered (001) Si via MBE. By *in situ*, we mean that the SrRuO₃ film was grown on an SrTiO₃ film on silicon without removing, etching, or post-annealing the SrTiO₃/(001) Si stack outside of vacuum after the SrTiO₃ growth on silicon. The resulting films have the highest structural, transport, and magnetic properties among all SrRuO₃ films on silicon reported to date;^{31,41} these properties are comparable to those of SrRuO₃ films grown directly on perovskite single crystals by thin film growth techniques other than MBE.^{10,32,33,43–46}

Both the SrTiO₃ and SrRuO₃ films were grown in a Veeco Gen10 dual-chamber MBE system on 2" commercial silicon wafers (*p*-type, boron doped, and resistivity > 10 Ω cm). The base pressure of the chamber was in the upper 10⁻⁹ Torr range. Both growth chambers are equipped with *in situ* reflection high-energy electron diffraction (RHEED) systems for monitoring the growth of the SrTiO₃ and SrRuO₃ layers. Substrate temperature is monitored by using either a thermocouple for temperatures below 500 °C or an optical pyrometer with a measurement wavelength of 980 nm for temperatures above 500 °C. Prior to film growth, the silicon substrate was cleaned *ex situ* in an ultraviolet ozone cleaner for 20 min to remove organic contaminants from the surface of the substrate. Molecular beams of strontium, titanium, and ruthenium were generated from elemental sources using a conventional low-temperature effusion cell, a Ti-BallTM,⁴⁷ and an electron-beam evaporator, respectively.

The SrTiO₃ layer was formed in the first growth chamber by the epitaxy-by-periodic-annealing method^{48–50} for its first 2 nm (5 unit cells) and then with a high temperature codeposition (strontium, titanium, and oxygen all supplied simultaneously) growth step at a substrate growth temperature of

580 °C to achieve a total SrTiO₃ film thickness of 14 nm. The stoichiometry of SrTiO₃ was calibrated using shuttered RHEED oscillations, and the growth rate of SrTiO₃ was determined by the RHEED oscillations that occurred when an SrTiO₃ film was codeposited.⁵¹ For each period of the epitaxy-by-periodic-annealing stage, a 2.5 unit-cell-thick layer of SrTiO₃ was first codeposited at 300 °C under an oxygen partial pressure of $\sim 5 \times 10^{-8}$ Torr. Then the substrate temperature was raised to 580 °C in vacuum for the annealing stage to enhance the crystalline quality of the as-grown SrTiO₃ film. During the high temperature codeposition step, the oxygen partial pressure was maintained at $\sim (5-8) \times 10^{-8}$ Torr. The growth of the SrTiO₃ layer on silicon is described in detail elsewhere.⁵⁰

The 14 nm thick SrTiO₃ layer exhibits a rocking curve with a full width at half maximum (FWHM) of 0.01° for the SrTiO₃ 001 peak, indicating that the SrTiO₃ buffer layer is of high crystalline quality. This SrTiO₃ buffer layer serves as an excellent template for the epitaxial growth of SrRuO₃, not only due to the small lattice mismatch [$\sim 0.64\%$ lattice mismatch for (001)_{*p*} SrRuO₃ on (001) SrTiO₃, where the subscript *p* denotes pseudocubic indices], but also due to the high crystalline quality of this 14 nm thick SrTiO₃ layer.

RHEED patterns along the [100] and [110] azimuths of the 14 nm thick SrTiO₃ film at the end of growth are shown in Figs. 1(a) and 1(b), respectively. The sharp streaks indicate that the SrTiO₃ film is epitaxial and smooth. As expected from the codeposition growth of the SrTiO₃ buffer

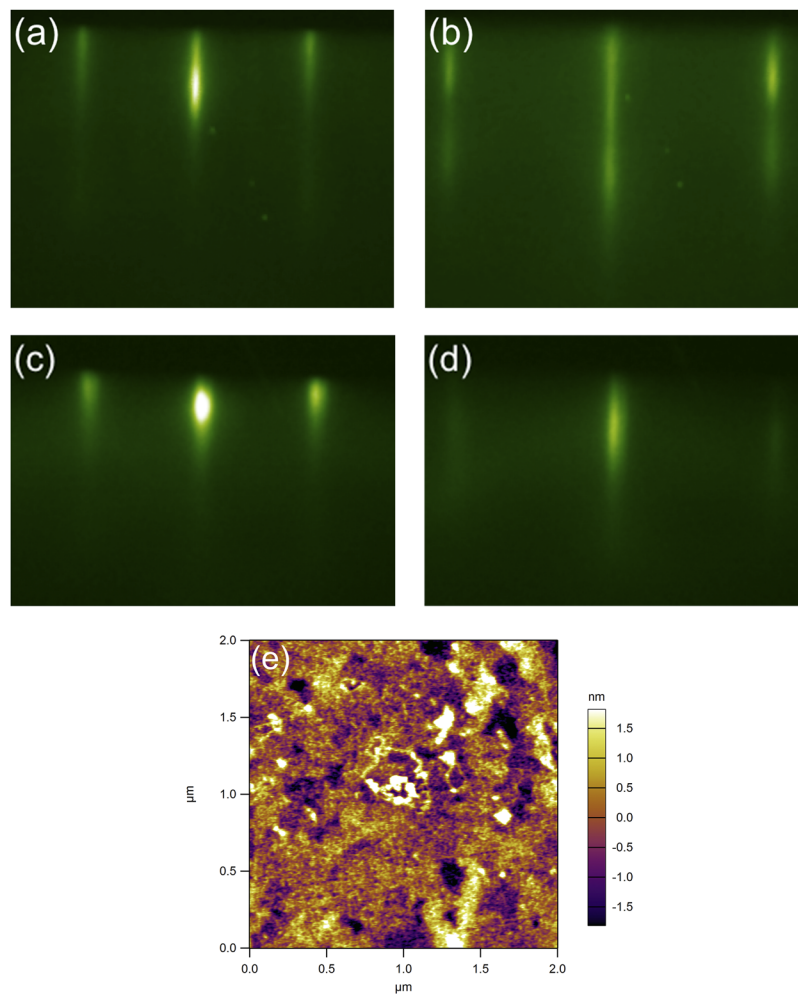


FIG. 1. RHEED patterns of the as-grown 14 nm thick SrTiO₃ film viewed along (a) the [100] azimuth and (b) the [110] azimuth of (001) SrTiO₃ and RHEED patterns of the as-grown 14 nm thick SrRuO₃ film viewed along (c) the [100]_{*p*} azimuth and (d) the [110]_{*p*} azimuth of (001)_{*p*} SrRuO₃. (e) Surface morphology of the same sample by AFM.

layer, the surface of the 14 nm thick (001) SrTiO₃ layer was found to have mixed termination because half-order streaks are not observed along either the [100] azimuth or [110] azimuth,^{49,52} as shown in Figs. 1(a) and 1(b). After the SrTiO₃ growth, SrTiO₃ on silicon was cooled down in vacuum to a substrate temperature below 200 °C, before being transferred in vacuum into the second growth chamber for the SrRuO₃ growth. During this process, no *ex situ* annealing⁴¹ or chemical treatment of the 14 nm thick SrTiO₃ film was involved. After heating up to 660-700 °C in the second chamber for the growth of the SrRuO₃ film under a 1×10^{-6} Torr mixture of ~10% O₃ + 90% O₂, the surface of the 14 nm thick SrTiO₃ became TiO₂-terminated, as is evident from the surface reconstruction that it exhibited shown in Fig. S1 of the [supplementary material](#).⁴⁹ Accordingly, we first deposited a submonolayer amount of SrO to neutralize the surface before the growth of the SrRuO₃ film.

The SrRuO₃ film was grown under adsorption-controlled growth conditions.⁴² Unlike the growth of SrTiO₃, which needs careful calibration to provide 1:1 matched fluxes of strontium and titanium⁵¹ to yield a stoichiometric SrTiO₃ film,⁵³ the stoichiometry of the SrRuO₃ film grown by adsorption-controlled growth is ensured by providing an excess ruthenium flux to the growing film and exploiting thermodynamics to precisely desorb the excess ruthenium in the form RuO_x(g).⁴² We grew the SrRuO₃ film at a substrate temperature of 660-700 °C (measured using the optical pyrometer) and an oxidant (a mixture of ~10% O₃ + 90% O₂) background pressure of 1×10^{-6} Torr. After growth, the film was cooled down under a chamber background pressure of $\sim 2 \times 10^{-7}$ Torr of the same oxidant (a mixture of ~10% O₃ + 90% O₂) until the substrate temperature reached ~150 °C.

The RHEED patterns of the 14 nm thick SrRuO₃ film along the [100]_p and [110]_p azimuths are shown in Figs. 1(c) and 1(d), respectively. These figures show that the SrRuO₃ film is also epitaxial and smooth. The surface morphology of the heterostructure was further examined via *ex situ* atomic force microscopy (AFM) using an Asylum Research MFP-3D in tapping mode, as is shown in Fig. 1(e). The rms roughness of the heterostructure is ~8 Å, which is consistent with the streaky RHEED patterns of the SrRuO₃ film. A height histogram of the AFM image is shown in Fig. S2 of the [supplementary material](#); it exhibits a Gaussian distribution of step heights.

The epitaxial nature and the crystalline quality of the heterostructure were further assessed *ex situ* by XRD with both Rigaku SmartLab and PANalytical X'Pert four-circle x-ray diffractometers utilizing Cu K_{α1} radiation. Figure 2(a) shows the XRD θ -2 θ scan of the same heterostructure characterized in Fig. 1. The appearance of only 00 ℓ reflections indicates that the heterostructure is epitaxial and phase-pure. The intense Bragg peaks reflect the high structural perfection of the perovskite SrTiO₃ buffer layer and the SrRuO₃ film. The thickness fringes indicate that the interfaces of the heterostructure are smooth. Using a Nelson-Riley fit, the out-of-plane lattice parameter of the SrRuO₃ film is found to be 3.935 ± 0.005 Å, which manifests that the SrRuO₃ film is relaxed on the 14 nm thick SrTiO₃ film on silicon. This might originate from the large thermal expansion difference between SrRuO₃ (averaging 1.03×10^{-5} K⁻¹ between 150 °C and 800 °C)⁵⁴ and silicon (averaging 3.7×10^{-6} K⁻¹ between room temperature and 720 °C).⁵⁵ Even though a commensurate film of (001)_p SrRuO₃ is compressively strained to (001) SrTiO₃, the tensile strain induced by the thermal expansion difference to the underlying silicon substrate during the cool-down process can make the lattice parameter of the SrRuO₃ film relax to its bulk value.

The rocking curves of both the SrTiO₃ 001 and the SrRuO₃ 001_p peaks were measured, together with that of the Si 004 peak. Figure 2(b) shows that the FWHM of the SrTiO₃ 001 peak is 0.01°; this FWHM is comparable to single crystal SrTiO₃ substrates.⁵⁶ With a FWHM of the SrRuO₃ 001_p peak of 0.01°, the 14 nm thick SrRuO₃ film on SrTiO₃ on silicon has the narrowest rocking curve ever reported for SrRuO₃ films on silicon;^{28,41} this FWHM is comparable to most SrRuO₃ films grown on single-crystal oxide substrates.^{34,38,43,44} Representative rocking curve FWHM values of SrRuO₃ films reported in the literature are summarized in comparison with our result for SrRuO₃ on silicon in Fig. S3(a) of the [supplementary material](#). The in-plane orientation relationship between the film and the silicon substrate was confirmed with a ϕ scan: (001) SrTiO₃ || (001)_p SrRuO₃ || (001) Si and [100] SrTiO₃ || [100]_p SrRuO₃ || [110] Si, as is shown in Fig. 2(c).

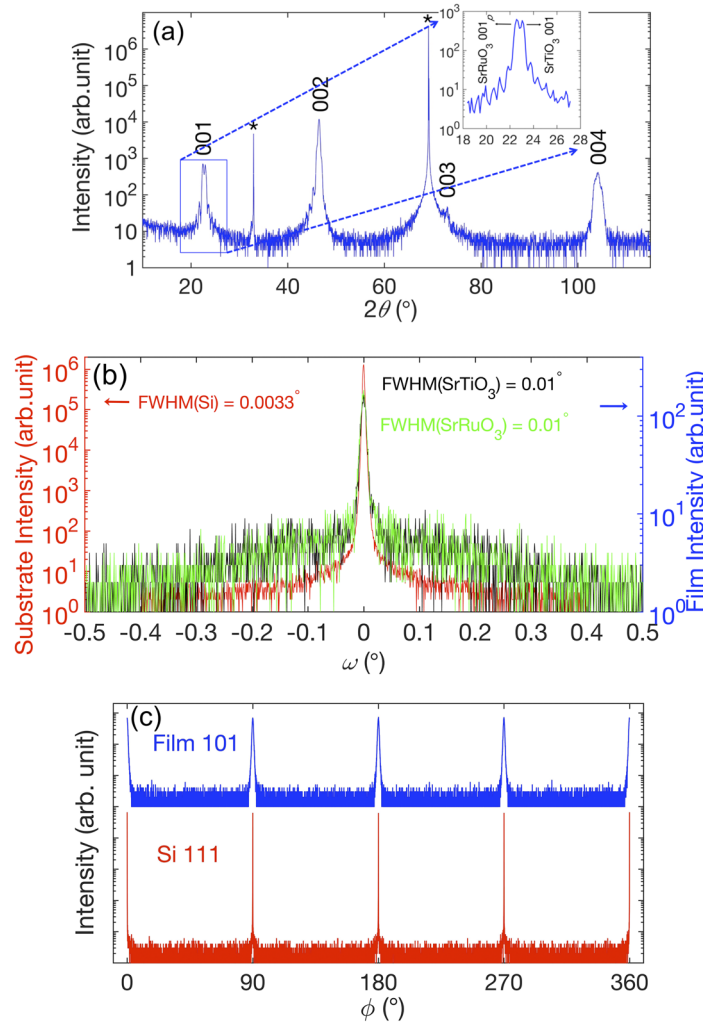


FIG. 2. (a) XRD θ - 2θ scan of the 14 nm thick SrRuO₃ film on 14 nm thick SrTiO₃ film on silicon. Peaks from the silicon substrate are indicated with an asterisk. Thickness fringes manifest that the interfaces of the heterostructure are smooth. The inset shows an enlarged view of the 001_p film peak. (b) Rocking curves of the SrTiO₃ 001 and the SrRuO₃ 001_p peaks of the same heterostructure. These peaks both have FWHMs of 0.01°. The rocking curve of the Si 004 peak is overlaid with those of the films. (c) ϕ scans of the same sample indicate that the in-plane epitaxial relationship is cube-on-cube with the [100]_p direction of the perovskite film aligned with the [110] direction of the Si (001) surface. The FWHM of the film ϕ scan is 0.92°. The ϕ scans are offset from each other along the vertical axis for clarity.

The resistivity (ρ) vs. temperature (T) of the same sample was measured in a standard four-probe van der Pauw geometry with wire-bonded contacts made using aluminum wire in a Quantum Design physical property measurement system (PPMS). The result is shown in Fig. 3(a). The RRR is ~ 11 , which is the largest RRR reported for SrRuO₃ films on silicon;^{31,57} it is comparable to the RRR values of SrRuO₃ films grown on single-crystal oxide substrates by PLD^{43–45} but is inferior to those of SrRuO₃ films grown on single-crystal oxide substrates by MBE.⁴² A general comparison of the RRRs of SrRuO₃ films in the literature is summarized in Fig. S3(b) of the [supplementary material](#).

The linear relationship between resistivity and T^2 for temperatures below 10 K [Fig. 3(c)] is consistent with the Fermi liquid behavior observed in SrRuO₃ films grown on single-crystal SrTiO₃ substrates by reactive evaporation.²¹ There is a clear kink observed at ~ 160 K in Fig. 3(a), indicating the change in the scattering rate due to the paramagnetic-to-ferromagnetic transition. The paramagnetic-to-ferromagnetic transition temperature is approximately given by the temperature at

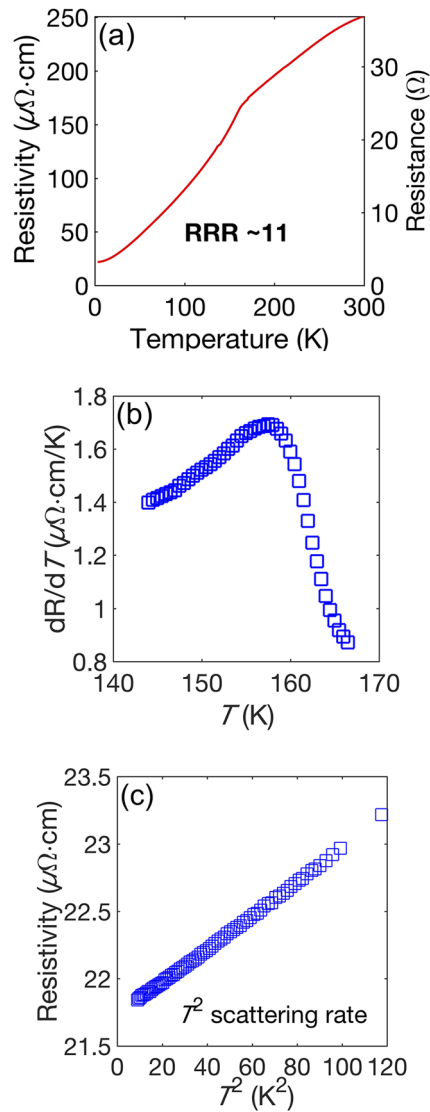


FIG. 3. Transport properties of the 14 nm thick SrRuO₃ film of the same sample. (a) The SrRuO₃ film exhibits a resistivity of $\sim 250 \mu\Omega \cdot \text{cm}$ at room temperature and metallic behavior at low temperature. (b) The derivative of the resistivity as a function of T indicates that the paramagnetic-to-ferromagnetic transition temperature is at ~ 160 K. (c) In the low-temperature regime, resistivity scales linearly with T^2 , indicating the Fermi liquid behavior at low temperature for the SrRuO₃ film.

which the derivative of the temperature-dependent resistivity is maximal, as is shown in Fig. 3(b). The transition temperature of ~ 160 K is close to that of bulk SrRuO₃ single crystals,⁵⁸ which indicates that the 14 nm thick SrRuO₃ film is relaxed on the SrTiO₃-buffered silicon. A comparison of the Curie temperatures of SrRuO₃ films in the literature is summarized in Fig. S3(c) of the [supplementary material](#).

The magnetic properties of the same sample were measured with a superconducting quantum interference device (SQUID) from Quantum Design. The sample was cooled under a 0.1 T field, and the in-plane (along $[100]_p$) and out-of-plane magnetization was measured as a function of temperature. The result is shown in Fig. 4(a). The in-plane and out-of-plane magnetic hysteresis loops measured at 10 K are shown in Fig. 4(b). Both loops show similar hysteresis with a large squareness (a ratio between the remanent and saturation magnetization) implying strong magnetocrystalline anisotropy of the SrRuO₃ film. The in-plane and out-of-plane saturation magnetization at 10 K is $\sim 0.75 \mu_B$ and $\sim 0.61 \mu_B$ per ruthenium atom, respectively. These values are again comparable to the results from

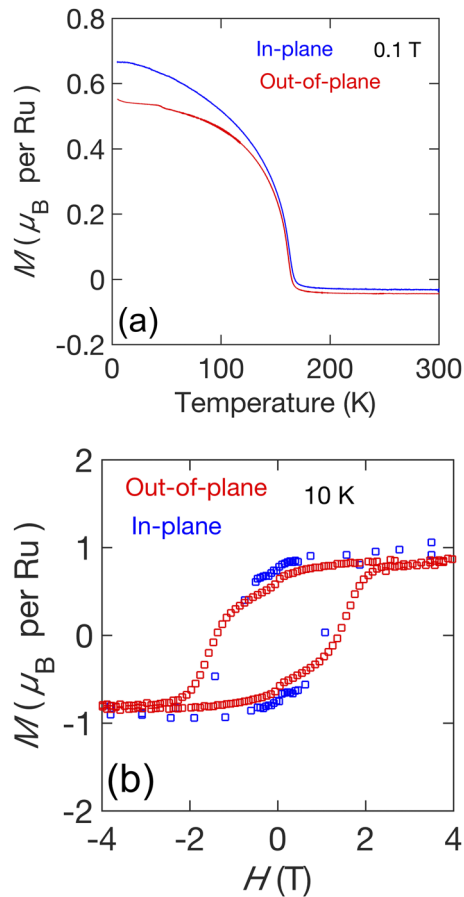


FIG. 4. (a) The in-plane and out-of-plane magnetization as a function of temperature measured on the same sample cooled under 0.1 T. (b) In-plane and out-of-plane magnetic hysteresis loops measured at 10 K. For the in-plane measurement, H is along the $[100]_p$ of SrRuO_3 , and for the out-of-plane measurement, H is along the $[001]_p$ of SrRuO_3 .

SrRuO_3 films grown directly on SrTiO_3 single crystals^{59,60} and are among the highest for SrRuO_3 films on silicon.³¹

The $\text{SrRuO}_3/\text{SrTiO}_3$ and SrTiO_3/Si interfaces in the same sample were examined by high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) using a Titan microscope operated at 300 keV. As is shown in Fig. 5(a), the interface between the 14 nm thick SrRuO_3 layer and the 14 nm thick SrTiO_3 layer is abrupt on the atomic scale. White, cyan, and green circles indicate strontium, ruthenium, and titanium atoms, respectively. Figures S4(a) and S4(b) of the [supplementary material](#) show the microstructure and thickness uniformity of the same sample at lower magnification. These HAADF-STEM images indicate that the SrTiO_3 buffer layer and the SrRuO_3 film both exhibit a high degree of crystalline perfection and that the sample is uniform over a large scale. There is an amorphous SiO_2 layer between the SrTiO_3 film and the silicon substrate, which originates from the diffusion of oxygen through the SrTiO_3 layer during the growth of either the SrTiO_3 or the SrRuO_3 film. This amorphous layer is typical for epitaxial SrTiO_3 films grown on silicon and is seen in other related studies.^{61–64}

Note that despite the high crystalline perfection and electrical characteristics, opportunities remain to further improve the quality of SrRuO_3 films on SrTiO_3 -buffered silicon. For example, the FWHM of the ϕ scan is relatively large, indicating a considerable amount of in-plane mosaic spread of the SrRuO_3 film. Also, SrRuO_3 samples with less surface roughness are needed for applications where interfaces are critical. Finally, the temperatures used for the deposition of high quality SrRuO_3 films (in our study as well as in the work by others on single-crystal perovskite substrates)

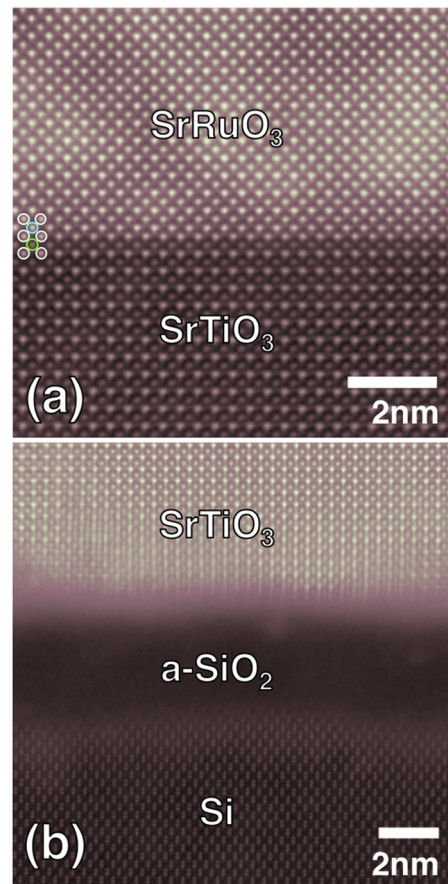


FIG. 5. HAADF-STEM images of the same sample characterized in Figs. 1–4. The interface between the SrRuO₃ layer and the SrTiO₃ layer is shown in (a). An amorphous SiO₂ layer is evident between the SrTiO₃ film and the silicon substrate in (b). This is due to the oxygen diffusion through the SrTiO₃ film during the film growth.

are too high to be compatible with underlying complementary metal-oxide-semiconductor (CMOS) circuitry.

In summary, we have integrated SrRuO₃ films on SrTiO₃-buffered silicon with a film quality similar to SrRuO₃ films grown on single-crystal oxide substrates via thin film growth techniques other than MBE. This integration paves the way toward integrating multi-functional devices of record-performance on the workhorse of semiconductor technology, silicon.

See [supplementary material](#) for additional details on the surface termination of the SrTiO₃ buffer layer, AFM height histogram, comparison of rocking curve FWHM, RRR, and Curie temperature of our sample with those of representative results from the literature, and additional STEM images of the sample.

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- ¹ G. Koster, L. Klein, W. Siemons, G. Rijnders, J. S. Dodge, C. B. Eom, D. H. A. Blank, and M. R. Beasley, *Rev. Mod. Phys.* **84**, 253 (2012).
- ² W. Bensch, H. W. Schmalle, and A. Reller, *Solid State Ionics* **43**, 171 (1990).
- ³ H. N. Lee, H. M. Christen, M. F. Chisholm, C. M. Rouleau, and D. H. Lowndes, *Appl. Phys. Lett.* **84**, 4107 (2004).
- ⁴ F. Kubel and H. Schmid, *Acta Crystallogr., Sect. B: Struct. Sci.* **46**, 698 (1990).
- ⁵ R. H. Buttner and E. N. Maslen, *Acta Crystallogr., Sect. B: Struct. Sci.* **48**, 764 (1992).
- ⁶ T. Siegrist, S. Sunshine, D. W. Murphy, R. J. Cava, and S. M. Zahurak, *Phys. Rev. B* **35**, 7137 (1987).
- ⁷ R. J. Nelmes and W. F. Kuhs, *Solid State Commun.* **54**, 721 (1985).
- ⁸ S. Teslic and T. Egami, *Acta Crystallogr., Sect. B: Struct. Sci.* **54**, 750 (1998).
- ⁹ C. B. Eom, R. B. Van Dover, J. M. Phillips, D. J. Werder, J. H. Marshall, C. H. Chen, R. J. Cava, R. M. Fleming, and D. K. Fork, *Appl. Phys. Lett.* **63**, 2570 (1993).
- ¹⁰ X. D. Wu, S. R. Foltyn, R. C. Dye, Y. Coulter, and R. E. Muenchausen, *Appl. Phys. Lett.* **62**, 2434 (1993).
- ¹¹ L. Antognazza, K. Char, T. H. Geballe, L. L. H. King, and A. W. Sleight, *Appl. Phys. Lett.* **63**, 1005 (1993).
- ¹² L. Klein, J. S. Dodge, T. H. Geballe, A. Kapitulnik, A. F. Marshall, L. Antognazza, and K. Char, *Appl. Phys. Lett.* **66**, 2427 (1995).
- ¹³ T. Fujii, M. Kawasaki, A. Sawa, H. Akoh, Y. Kawazoe, and Y. Tokura, *Appl. Phys. Lett.* **86**, 012107 (2005).
- ¹⁴ J. Rodríguez Contreras, H. Kohlstedt, U. Poppe, R. Waser, C. Buchal, and N. A. Pertsev, *Appl. Phys. Lett.* **83**, 4595 (2003).
- ¹⁵ S. Thota, Q. Zhang, F. Guillou, U. Lüders, N. Barrier, W. Prellier, A. Wahl, and P. Padhan, *Appl. Phys. Lett.* **97**, 112506 (2010).
- ¹⁶ C. H. Ahn, T. Tybell, L. Antognazza, K. Char, R. H. Hammond, M. R. Beasley, Ø. Fischer, and J.-M. Triscone, *Science* **276**, 1100 (1997).
- ¹⁷ X. Martí, F. Sánchez, J. Fontcuberta, M. V. García-Cuenca, C. Ferrater, and M. Varela, *J. Appl. Phys.* **99**, 08P302 (2006).
- ¹⁸ J. M. Rondinelli, M. Stengel, and N. A. Spaldin, *Nat. Nanotechnol.* **3**, 46 (2007).
- ¹⁹ S. Y. Yang, L. W. Martin, S. J. Byrnes, T. E. Conry, S. R. Basu, D. Paran, L. Reichertz, J. Ihlefeld, C. Adamo, A. Melville, Y.-H. Chu, C.-H. Yang, J. L. Musfeldt, D. G. Schlom, J. W. Ager, and R. Ramesh, *Appl. Phys. Lett.* **95**, 062909 (2009).
- ²⁰ H. J. Liu, J. C. Wang, D. Y. Cho, K. T. Ho, J. C. Lin, B. C. Huang, Y. W. Fang, Y. M. Zhu, Q. Zhan, L. Xie, X. Q. Pan, Y. P. Chiu, C. G. Duan, J. H. He, and Y. H. Chu, "Giant photoresponse in quantized SrRuO₃ monolayer at oxide interfaces," *ACS Photonics* **5**, 1041 (2018).
- ²¹ A. P. Mackenzie, J. W. Reiner, A. W. Tyler, L. M. Galvin, S. R. Julian, M. R. Beasley, T. H. Geballe, and A. Kapitulnik, *Phys. Rev. B* **58**, R13318 (1998).
- ²² L. Klein, J. S. Dodge, C. H. Ahn, G. J. Snyder, T. H. Geballe, M. R. Beasley, and A. Kapitulnik, *Phys. Rev. Lett.* **77**, 2774 (1996).
- ²³ J. Matsuno, N. Ogawa, K. Yasuda, F. Kagawa, W. Koshibae, N. Nagaosa, Y. Tokura, and M. Kawasaki, *Sci. Adv.* **2**, e1600304 (2016).
- ²⁴ M. Wahler, N. Homonnay, T. Richter, A. Müller, C. Eischmidt, B. Fuhrmann, and G. Schmidt, *Sci. Rep.* **6**, 28727 (2016).
- ²⁵ K. Watanabe, M. Ami, and M. Tanaka, *Mater. Res. Bull.* **32**, 83 (1997).
- ²⁶ S. Y. Hou, J. Kwo, R. K. Watts, J.-Y. Cheng, and D. K. Fork, *Appl. Phys. Lett.* **67**, 1387 (1995).
- ²⁷ T. Higuchi, Y. Chen, J. Koike, S. Iwashita, M. Ishida, and T. Shimoda, *Jpn. J. Appl. Phys., Part I* **41**, 6867 (2002).
- ²⁸ T. Higuchi, Y. Chen, J. Koike, S. Iwashita, M. Ishida, and T. Shimoda, *Jpn. J. Appl. Phys., Part II* **41**, L481 (2002).
- ²⁹ J. Wang, H. Zheng, Z. Ma, S. Prasertchoung, M. Wuttig, R. Droopad, J. Yu, K. Eisenbeiser, and R. Ramesh, *Appl. Phys. Lett.* **85**, 2574 (2004).
- ³⁰ L. W. Martin, Y. H. Chu, Q. Zhan, R. Ramesh, S. J. Han, S. X. Wang, M. Warusawithana, and D. G. Schlom, *Appl. Phys. Lett.* **91**, 172513 (2007).
- ³¹ M. Zheng and W. Wang, *ACS Appl. Mater. Interfaces* **8**, 14012 (2016).
- ³² C. B. Eom, R. J. Cava, R. M. Fleming, J. M. Phillips, R. B. vanDover, J. H. Marshall, J. W. P. Hsu, J. J. Krajewski, and W. F. Peck, *Science* **258**, 1766 (1992).
- ³³ Q. Gan, R. A. Rao, C. B. Eom, J. L. Garrett, and M. Lee, *Appl. Phys. Lett.* **72**, 978 (1998).
- ³⁴ L. Klein, J. S. Dodge, C. H. Ahn, J. W. Reiner, L. Mieville, T. H. Geballe, M. R. Beasley, and A. Kapitulnik, *J. Phys.: Condens. Matter* **8**, 10111 (1996).
- ³⁵ M. Izumi, K. Nakazawa, Y. Bando, Y. Yoneda, and H. Terauchi, *J. Phys. Soc. Jpn.* **66**, 3893 (1997).
- ³⁶ L. Klein, Y. Kats, A. F. Marshall, J. W. Reiner, T. H. Geballe, M. R. Beasley, and A. Kapitulnik, *Phys. Rev. Lett.* **84**, 6090 (2000).
- ³⁷ W. Tian, J. H. Haeni, D. G. Schlom, E. Hutchinson, B. L. Sheu, M. M. Rosario, P. Schiffer, Y. Liu, M. A. Zurbuchen, and X. Q. Pan, *Appl. Phys. Lett.* **90**, 022507 (2007).
- ³⁸ D. E. Shai, C. Adamo, D. W. Shen, C. M. Brooks, J. W. Harter, E. J. Monkman, B. Burganov, D. G. Schlom, and K. M. Shen, *Phys. Rev. Lett.* **110**, 087004 (2013).
- ³⁹ N. Okuda, K. Saito, and H. Funakubo, *Jpn. J. Appl. Phys., Part I* **39**, 572 (2000).
- ⁴⁰ D. Yang, X. Tang, R. Wei, Z. Hui, W. Song, X. Zhu, and Y. Sun, *J. Alloys Compd.* **682**, 154 (2016).
- ⁴¹ J. W. Park, S. H. Baek, C. W. Bark, M. D. Biegalski, and C. B. Eom, *Appl. Phys. Lett.* **95**, 061902 (2009).
- ⁴² H. P. Nair, Y. Liu, J. P. Ruf, N. J. Schreiber, S. Shang, D. J. Baek, B. H. Goodge, L. F. Kourkoutis, Z. Liu, K. M. Shen, and D. G. Schlom, *APL Mater.* **6**, 046101 (2018).
- ⁴³ O. Tsuyoshi and T. Kazunori, *Appl. Phys. Express* **4**, 025501 (2011).
- ⁴⁴ D. Kan, R. Aso, H. Kurata, and Y. Shimakawa, *J. Appl. Phys.* **113**, 173912 (2013).
- ⁴⁵ J. Thompson, J. Nichols, S. Lee, S. Ryee, J. H. Gruenewald, J. G. Connell, M. Souri, J. M. Johnson, J. Hwang, M. J. Han, H. N. Lee, D.-W. Kim, and S. S. A. Seo, *Appl. Phys. Lett.* **109**, 161902 (2016).
- ⁴⁶ F. Chu, Q. X. Jia, G. Landrum, X. D. Wu, M. Hawley, and T. E. Mitchell, *J. Electron. Mater.* **25**, 1754 (1996).
- ⁴⁷ C. D. Theis and D. G. Schlom, *J. Vac. Sci. Technol., A* **14**, 2677 (1996).

- ⁴⁸ H. Li, X. Hu, Y. Wei, Z. Yu, X. Zhang, R. Droopad, A. A. Demkov, J. Edwards, K. Moore, W. Ooms, J. Kulik, and P. Fejes, *J. Appl. Phys.* **93**, 4521 (2003).
- ⁴⁹ M. P. Warusawithana, C. Cen, C. R. Sleasman, J. C. Woicik, Y. Li, L. F. Kourkoutis, J. A. Klug, H. Li, P. Ryan, L. P. Wang, M. Bedzyk, D. A. Muller, L. Q. Chen, J. Levy, and D. G. Schlom, *Science* **324**, 367 (2009).
- ⁵⁰ Z. Wang, D. Baek, B. Goodge, M. Zachman, X. Huang, X. Bai, C. M. Brooks, H. Paik, A. B. Mei, J. D. Brock, J. P. Maria, L. F. Kourkoutis, and D. G. Schlom (unpublished).
- ⁵¹ J. H. Haeni, C. D. Theis, and D. G. Schlom, *J. Electroceram.* **4**, 385 (2000).
- ⁵² K. Iijima, T. Terashima, Y. Bando, K. Kamigaki, and H. Terauchi, *J. Appl. Phys.* **72**, 2840 (1992).
- ⁵³ C. M. Brooks, L. F. Kourkoutis, T. Heeg, J. Schubert, D. A. Muller, and D. G. Schlom, *Appl. Phys. Lett.* **94**, 162905 (2009).
- ⁵⁴ S. Yamanaka, T. Maekawa, H. Muta, T. Matsuda, S. Kobayashi, and K. Kurosaki, *J. Solid State Chem.* **177**, 3484 (2004).
- ⁵⁵ Y. S. Touloukian, R. K. Kirby, R. E. Taylor, and T. Y. R. Lee, "Thermophysical properties of matter," in *Thermal Expansion-Nonmetallic Solids*, The TPRC Data Series (Plenum, NY, 1977), Vol. 13.
- ⁵⁶ D. G. Schlom, L. Q. Chen, X. Q. Pan, A. Schmehl, and M. A. Zurbuchen, *J. Am. Ceram. Soc.* **91**, 2429 (2008).
- ⁵⁷ M. Zhu, X. Dong, Y. Chen, F. Xue, J. Lian, L. Xiao, G. Ding, and G. Wang, *Ceram. Int.* **42**, 13925 (2016).
- ⁵⁸ G. Cao, S. McCall, M. Shepard, J. E. Crow, and R. P. Guertin, *Phys. Rev. B* **56**, 321 (1997).
- ⁵⁹ M. Zheng, X. Li, W. Xiao, W. Wang, and H. Ni, *Appl. Phys. Lett.* **111**, 152405 (2017).
- ⁶⁰ S. Woo, S. A. Lee, H. Mun, Y. G. Choi, C. J. Zhung, S. Shin, M. Lacotte, A. David, W. Prellier, T. Park, W. N. Kang, J. S. Lee, S. W. Kim, and W. S. Choi, *Nanoscale* **10**, 4377 (2018).
- ⁶¹ D. B. Fenner, A. M. Viano, D. K. Fork, G. A. N. Connell, J. B. Boyce, F. A. Ponce, and J. C. Tramontana, *J. Appl. Phys.* **69**, 2176 (1991).
- ⁶² Y. Chen, J. Koike, T. Higuchi, S. Iwashita, M. Ishida, and T. Shimoda, *Jpn. J. Appl. Phys., Part II* **40**, L1305 (2001).
- ⁶³ S. Abel, T. Stöferle, C. Marchiori, C. Rossel, M. D. Rossell, R. Erni, D. Caimi, M. Sousa, A. Chelnokov, B. J. Offrein, and J. Fompeyrine, *Nat. Commun.* **4**, 1671 (2013).
- ⁶⁴ R. Guo, Z. Wang, S. Zeng, K. Han, L. Huang, D. G. Schlom, T. Venkatesan, Ariando, and J. Chen, *Sci. Rep.* **5**, 12576 (2015).

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