Enhanced metallic properties of SrRuO3 thin films via kinetically controlled pulsed laser epitaxy

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Abstract

Metal electrodes are a universal element of all electronic devices. Conducting $SrRuO_3$ (SRO) epitaxial (epi-) thin-films have been used extensively in a variety of 'proof-of-concept' electronic devices based on complex-oxides. However, when compared to SRO single crystals, SRO epi-thin films have shown reduced conductivity and Curie temperatures (T_C), which can lead to higher Joule heating and energy loss in devices. Here, we report that high-quality SRO epi-thin films can be synthesized by moderating the growth rate of pulsed laser epitaxy (PLE) with *in-situ* optical spectroscopic monitoring. SRO epi-thin films grown under the moderated conditions, down to ca. 16 nm in thickness, exhibit enhanced conductivity and T_C due to their improved stoichiometry and a strain-mediated increase of the bandwidth of Ru 4*d* electrons. This result

provides a direction for enhancing the physical properties of PLE-grown epi-thin films and paves a way for improved device applications.

Complex-oxide single-crystals with intriguing properties have dawned a new era of the so-called 'functional epitaxial devices' such as non-volatile memories[1-4], high speed switching devices[5-7], piezoelectric nano-generators[8], and ultraviolet lasers[9]. Recent advances in epitaxial (epi-) growth techniques for complex oxides enabled us investigations of high quality ultrathin films with thickness of as thin as a few nanometers, yielding novel electronic and magnetic properties[10]. Exploration of the device applicability requires suitable metal electrodes that maintain such emergent physical properties. Normal metals and alloys such as Pt, Au, Ag, and Cu with high electrical conductivity lack interface cohesion and structural compatibility with epi-complex oxides, which is essential for the fabrication of high performance devices. $SrRuO_3$ (SRO) is one of the most extensively studied and widely used metallic oxides[11,12]. The perovskite structure yields SRO to have excellent chemical stability, which makes it an ideal electrode for epi-oxide heterostructures[13]. However, so far, SRO epi-thin films have shown inferior metallic properties as compared to their bulk counterparts. SRO single crystals typically have a Curie temperature (T_C) around 160-165 K and a room temperature resistivity of ~150 μΩcm (Refs. [14-17]), yet no films have been synthesized which maintain these properties (see Table 1). For example, SRO epi-thin films grown on $GdScO_3$ (GSO) substrates have a significantly higher resistivity of ~650 μΩcm at room temperature and low T_C (100-130 K) (Refs. [18,19]). SRO epi-thin films grown on $SrTiO_3$ (STO) substrates also exhibit a high room-temperature resistivity of ~225 μΩcm and low T_C, which approaches 150 K for thickness above ~25 nm (Refs. [20-22]). Hence, it is essential to ask, "Are the transport properties of SRO epi-thin films inherently inferior to SRO single crystals, or is there a way to enhance the metallic properties in the thin film limit?"

To answer these questions, we have investigated epitaxial thin-films of SRO of various thicknesses (1-65 nm) grown on atomically flat GSO $(110)_o$ substrates (see Fig. S1) using pulsed laser epitaxy (PLE). The pseudo-cubic lattice parameters of SRO and GSO are 3.93 Å and 3.96 Å, respectively. Therefore, SRO epi-thin films grown on GSO substrates will experience in-plane tensile strain of +1.0 % (see Fig. S2). According to our first-principles calculations (see Fig. S3), SRO epi-thin films under tensile strain are expected to exhibit enhanced metallic properties as a result of the increase in the Ru 4*d* electron bandwidth and average exchange energy ($J_{avg.}$). Hence, we have chosen GSO substrates to study the effect of moderated growth on the physical properties of SRO epi-thin films. We have prepared atomically flat GSO $(110)_o$ substrates (from CrysTec GmbH) by annealing at 1000˚C in air[23]. The SRO epi-thin-films are deposited at 600˚C in an oxygen partial pressure of 100 mTorr, with a KrF excimer laser (λ = 248 nm) with a fluence of 1.6 J/cm^2 at 10 Hz using a ruthenium rich polycrystalline target.

In order to control the deposition rate, we have used a variety of laser spot sizes (0.16-0.41 mm^2) by changing the aperture size in our laser optics. In general, a larger (smaller) laser spot size produces a larger (smaller) PLE plume; therefore by changing the size of the laser spot, we can effectively control the deposition rate (for technical details, see Ref. 24). Note that the deposition rates we have used are between 150-800 pulses/u.c. (0.027-0.005nm/sec), which are significantly slower than the typical deposition rates (10-50 pulses/u.c.) of conventional pulsed laser deposition. Figure 1 shows that the deposition rate can be controlled by keeping our growth parameters fixed and only changing the laser spot size. Using an isotropic slab model[25] with the complex dielectric functions of a SRO thin-film and a GSO substrate, as shown in Figs. 1 (a) and 1 (b), respectively, the real-time thickness of SRO epi-thin-films was monitored using *in-situ* optical spectroscopic ellipsometry[25] and the deposition rate was determined for each laser spot size. Figure 1 (c) shows the SRO *in-situ* film thickness as a function of time with the laser spot sizes of 0.16 mm^2, 0.30 mm^2, and 0.41 mm^2, respectively. The total thickness of the SRO thin films was also confirmed from the interference fringes in the x-ray diffraction (XRD) θ-2θ scans. Figure 1 (d) shows the room temperature optical conductivity spectrum of a SRO epi-thin film, which is consistent with a reference spectrum[26].

SRO thin films display a change in the crystal structure above 16 nm. Figure 2 (a) shows the XRD θ-2θ scans for our SRO epi-thin films, which reveal the out-of-plane $(hk0)_o$ reflections of the orthorhombic phase. The inset of Fig. 2 (a) shows a rocking curve of a 16 nm-thick SRO epi-thin film, which has a full width at half maximum (FWHM) value of 0.06 °, indicating good crystallinity of the film. GSO substrates typically reveal FWHM values around 0.05 °. XRD reciprocal space maps (RSM) around the GSO 620 and 260 reflections (see Fig. S4) show that all of the film peaks are located in the same position along the $[1\text{-}10]_o$ in-plane direction indicating the films are coherently strained. However, for films below 16 nm, we have observed that the SRO 620 and 260 peaks appear in different positions along the $[110]_o$ out-of-plane direction while thicker films have peaks at the same position. D. Kan, *et al.* (Ref. 18) have reported a similar result for their SRO films grown on GSO substrates. This change in RSM indicates a structural change from an orthorhombic (monoclinic) to a tetragonal phase as the SRO thin-film thickness is increased above 16 nm. Cross-sectional scanning transmission electron microscopy images of a 65 nm-thick SRO thin-film are shown with the beam along the $[1\text{-}10]_o$ (Fig. 2 (b)) and the $[001]_o$ (Fig. 2 (c)) directions, respectively. A sharp interface (red arrows) is observed between the GSO substrate and SRO epi-thin film, and there are no indications of misfit dislocations or defects.

The resistivity and T_C of thicker SRO thin films are similar to SRO bulk single crystals. The dc-transport behavior of SRO epi-thin films is shown in Figure 3 as a function of temperature ($\rho(T)$). While a 1 nm thick film is insulating, SRO epi-thin films with increased thickness show a clear metallic behavior. Note that $\rho(T)$ is significantly reduced above ca. 16 nm and it is very similar to that of a single crystal[17]. Moreover, the room temperature resistivity values of our SRO epi-thin films are smaller than any previous reports of SRO single crystals and thin-films, as summarized in Table 1. The seemingly surprising improvement over the single crystal resistivity is in agreement with our first-principles calculations, which suggest an enhanced conductivity of SRO under tensile strain (see Fig. S3). SRO is an itinerant ferromagnet described by Ru 4*d* conduction bands using the Stoner model. The "kink" visible in the $\rho(T)$ data is due to the suppression of spin scattering as SRO transitions to a ferromagnetic state and represents the T_C of SRO epi-thin films. The T_C is estimated by taking the first derivative of the resistivity ($d\rho/dT$), as shown in the inset of Fig. 3 and Figs. S5, 6. The T_C values of our SRO epi-thin films are close to (or higher than) the previously reported values of SRO single crystals (Refs. 14-16) and compressive-strained SRO thin films (Ref. 20-22).

The T_C values gradually increase as the thickness is increased, reach a maximum (~ 163 K) at 16 nm, and remain constant above this thickness. Figure 4 (a) shows the estimated T_C's as a function of thickness. Note that these T_C values are significantly higher than previously reported T_C's for SRO epi-thin films under compressive (open triangles)[20] and tensile (open squares) strain[18], as shown in Fig. 4 for comparison. Although the room temperature resistivity and T_C of our films are enhanced from other SRO epi-thin films, the residual resistivity ratio (RRR) remains low (see Table 1 and Fig. S7). This is likely due to the appearance of a metal-toinsulator-like transition at low temperatures (< 20K) in SRO thin-films, which has been observed in previous studies, but its origin is not fully understood at this moment.

To investigate the discrepancy in the enhanced metallic properties observed in our SRO epi-thin films compared to that of other thin film reports, we have performed a test growth of a 15 nm-thick SRO thin film with an increased laser fluence of ~3.0 J/cm^2. Note that the optimal SRO thin films are grown at ~1.6 J/cm^2. The XRD θ-2θ scan of the test-grown SRO thin film shows a slight increase in the out-of-plane lattice parameter (decrease in 2θ values) compared to an optimal 16 nm-thick SRO thin film, as shown in Fig. 4 (b), while the FWHM of the two thin-films rocking curves is very similar. Surprisingly, the $\rho(T)$ data display that the 15 nm-thick SRO thin-film grown at the high fluence (~3.0 J/cm^2) has a significantly higher resistivity, as shown in Fig. 4 (c), and a significantly lower T_C (~ 133 K) than those from the 16 nm-thick SRO thin-film. In order to verify the effects of the moderated growth rate on the properties of SRO thin-films, we also have grown a 5 nm-thick SRO epi-thin film using an extremely slow growth rate (~800 pulses per unit-cell). This films resistivity is reduced compared to a 6 nm-thick SRO epi-thin film, which is grown at the rate of ~200 pulses per unit-cell (Fig. S8). Hence, moderated PLE techniques, i.e. controlled growth rate and laser spot size, are the key for the enhanced transport properties of SRO epi-thin films.

It is well known that Ru vacancies can be formed in SRO thin-films due to the volatile nature of the Ru atom. According to Dabrowski *et al.*[27], Ru vacancies have a profound impact on the metallic and magnetic properties of SRO thin-films, i.e. decreasing T_C down to 86 K for only a 6 % change in Ru site occupancy. Therefore, we consider that the laser fluence in PLE may affect the stoichiometry of SRO epi-thin films. Unfortunately, because the change in stoichiometry is so small, microscopic characterization measurements are not capable of resolving the differences in our films. However, the transport and magnetic properties of SRO epi-thin films can be significantly affected as shown above. [high-lighted part may be moved over here] [Also, ohnish's paper on the effect fluence and our Scientiic report paper's discovery can be discussed to mention the same thing can happen here, indirectly implying the importance of kinetic growth control.]

It is also known that structural distortions and symmetry mismatch across interface boundaries, and other interfacial effects can deteriorate electrical properties of complex-oxide thin-films and heterostructures[28-30]. However, in our SRO epi-thin films grown on GSO substrates, the moderated growth rate seems to have a more significant effect on their transport properties than the interfacial contributions (see Fig. S7).

This work dismisses the notion that SRO epi-thin films are inherently inferior to single crystals, which has become a generally accepted problem in the solid state community. By monitoring and controlling the deposition rate, we have discovered that it is possible to achieve SRO epi-thin films with metallic properties similar to SRO single crystals by reducing the deposition rate below ~160 pulses per u.c (~ 1.5 nm/min). Our results show that through precise control of stoichiometry (moderated PLE) and the application of an appropriate tensile strain, it is possible to develop epi-thin film electrodes for functional oxide devices which do not hinder the functionality of the device as a result of degraded metallic properties.

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Table 1 | Transport properties of $SrRuO_3$ thin-films and single crystals.

	ρ (2 K) (μΩcm)	ρ (300 K) (μΩcm)	RRR	T_C (K)
This report, SRO/GSO (tensile strain), $t > 15$ nm	25-30	125-140	5-6	160-163
SRO single crystals[14-17]	1-15	150-200	20-192	160-165
SRO/STO (comp. strain)[20,21] (1-50 u.c.)	25-80	225-300	2-14	130-150
SRO/GSO (tensile strain)[18] (27-64 u.c.)	350-375	650-700	2-4	100-130

Figure Captions

FIG 1. Real-time monitoring of the epi-thin film thickness via *in-situ* optical spectroscopic ellipsometry. Schematic of the sample geometry with the associated *in-situ* real (blue) and imaginary (red) dielectric functions as a function of photon energy for **(a)** SRO epi-thin film and **(b)** GSO substrate, collected after and before deposition, respectively. **(c)** Real time thickness of a SRO epi-thin film extracted from the *in-situ* spectroscopic ellipsometry data using a single slab model during the growth. The red arrows indicate the start and stop point for deposition and the red asterisks represent when the deposition is stopped to change the laser spot size. **(d)** Comparison of room-temperature optical conductivity spectrum of our SRO epi-thin film to the data previously reported for SRO (Ref. 26).

FIG 2. X-Ray Diffraction patterns and cross-sectional High Resolution Scanning Transmission Electron Microscopy images obtained for films of $SrRuO_3$ deposited on $GdScO_3$ (110) substrates. **(a)** Out-of-plane θ-2θ XRD patterns for SRO films around the $(220)_o$ peak, of thickness ranging from 6-65 nm. The inset shows a typical rocking curve for all of the films in this thickness range. **(b,c)** High resolution Scanning Transmission Electron Microscopy images of cross-sections with the beam along the $(1\text{-}10)_o$ **(b),** and $(001)_o$ **(c),** directions.

FIG 3. *dc*-Transport data for $SrRuO_3$ films of various thicknesses. Resistivity, $\rho(T)$, as a function of temperature for films of 1, 6, 16 and 32 nm thickness. For comparison we have also included digitized data from our references, for SRO single crystals (Ref. 17). The inset shows the derivative of the resistivity as a function of temperature for our 16 nm sample as well as the digitized data for single crystals (Ref. 17) and a SRO/STO (compressive strain) film (Ref. 20). We can clearly see that the T_C and resistivity of our 16 nm sample is similar to the values reported for single crystals, and significantly improved from SRO/STO.

FIG 4. Effects of moderated deposition rate on the Curie temperature (T_C) and physical properties. **(a)** The Curie temperature versus the film thickness is shown as red filled circles. The open triangles and squares represent previously reported values for SRO/STO (Ref. 20) and SRO/GSO (Ref. 18) films (compressive and tensile strain), respectively. The T_C reaches a maximum of ~163 K at 16 nm and remains essentially constant above this thickness. This value is significantly higher than previous reports for SRO films under compressive or tensile strain, and is even comparable to the values for single crystals. The green shaded area highlights the thickness region where the conductivity and T_C become maximum and comparable to single crystals (black dashed lines). **(b)** Comparison of the XRD θ-2θ data of two films grown at 350 pulses per unit cell but with different laser fluence. The red curve shows the 16 nm film (~1.6 J/cm^2) and the black curve shows the 15 nm film (~3 J/cm^2). **(c)** Comparison of the $\rho(T)$ data for the same two samples.

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