Effect of microstructure on the electronic transport properties of epitaxial CaRuO$_3$ thin films

Gopi Nath Daptary,$^1$ Chanchal Sow,$^1$ Suman Sarkar,$^1$ Santosh Chiniwar,$^1$ P. S. Anil Kumar,$^1$ Anomitra Sil,$^2$ and Aveek Bid$^{1,*}$

$^1$Department of Physics, Indian Institute of Science, Bangalore 560012, India  
$^2$Center For Nano Science And Engineering, Indian Institute of Science, Bangalore 560012, India

We have carried out extensive comparative studies of the structural and transport properties of CaRuO$_3$ thin films grown under various oxygen pressure. We find that the preferred orientation and surface roughness of the films are strongly affected by the oxygen partial pressure during growth. This in turn affects the electrical and magnetic properties of the films. Films grown under high oxygen pressure have the least surface roughness and show transport characteristics of a good metal down to the lowest temperature measured. On the other hand, films grown under low oxygen pressures have high degree of surface roughness and show signatures of ferromagnetism. We could verify that the low frequency resistance fluctuations (noise) in these films arise due to thermally activated fluctuations of local defects and that the defect density matches with the level of disorder seen in the films through structural characterizations.

I. INTRODUCTION

Complex perovskite oxides of the 4d transition ruthenates have attracted interest in condensed matter physics due to the strong correlation between their electronic structure, magnetic structure and transport properties [1–4]. Of special interests are the members of the Ruddlesden-Popper series [5] of ruthenates $A_{n+1}Ru_nO_{3n+1}$ where $n$ denotes the number of Ru-O layers between two alternative layers of A-O. The interest in these materials stems from the fact that their band structure is very strongly influenced by lattice distortions. A classic example is the case of SrRuO$_3$ and CaRuO$_3$ which are the infinite dimensional members ($n$ = ∞) of the Ruddlesden-Popper series. At low temperatures SrRuO$_3$ is a ferromagnetic metal. Iso-structural and iso-electronic CaRuO$_3$ on the other hand is at the border between metal and non-metal. Until recently, it was thought that CaRuO$_3$ had no magnetic order. Recent experiments have shown that this is not necessarily true. Depending on its growth parameters CaRuO$_3$ thin films can show signatures of either long range magnetic order like that in SrRuO$_3$ or short range interactions, possibly a spin-glass like state [6, 7]. The transport properties of CaRuO$_3$ thin films are equally intriguing. Conventional Fermi-liquid behaviour does not hold well in CaRuO$_3$ [8, 9]. The temperature range over which this non-Fermi liquid like behaviour sets in and the exact values of the exponents describing this behaviour are still under debate. A survey of the existing data on CaRuO$_3$ clearly shows that like most oxide films, the transport properties depend very strongly on the quality of the films [9–11] and till date there is no clear study of the effect of growth parameters on the structural, magnetic and transport properties of this material. Motivated by this observation we have studied the correlation between structural and electrical transport properties of CaRuO$_3$ thin films grown under different deposition conditions.

II. METHODS

Epitaxial thin films of CaRuO$_3$ (001) (CRO) were grown on single crystal SrTiO$_3$ (001) (STO) substrates by Pulsed Laser Deposition (PLD) technique using a KrF ($\lambda$ = 248 nm) laser. A stoichiometric target (20 mm diameter) of CaRuO$_3$ prepared using solid state reaction process was used as a target for the PLD. The as procured SrTiO$_3$ substrates were cleaned in trichloroethylene, acetone, isopropyl alcohol and finally nitrogen gas spray. The cleaned substrates were annealed in situ at 700°C for 1 hour in oxygen atmosphere before the deposition. The deposition conditions were: (i) 1.5 J/cm$^2$ fluence, (ii) frequency=5 Hz and (iii) 700°C substrate temperature. The only parameter varied during the growth was the oxygen partial pressure. Multiple films in each group were studied - in this letter we report the results on three representative films: S1 (0.15 mbar oxygen pressure), S2 (0.30 mbar oxygen pressure) and S3 (0.45 mbar oxygen pressure). The deposition rate in each case was 1.5 nm/min. Post-deposition, all the films were in-situ annealed at 500°C in 500 mbar oxygen pressure for 30 minutes. This is a commonly used method in the growth of many oxide thin films to improve their oxygen content [12–14]. Generally, in oxides thermogravimetric analysis shows that there is an oxygen intake between 450°C and 500°C. Hence the samples were annealed at 500°C to have the minimum oxygen deficiency. The thicknesses of the films as measured were 30±2 nm.

III. RESULTS

The structural properties of the three films were characterized using high resolution x-ray diffraction (HRXRD), Scanning electron microscope (SEM) and Atomic force microscope (AFM) measurements. In figure 1(a), we show the atomic structure of CaRuO$_3$ film and in figure 1(b), we show the 2θ x-ray diffraction pattern (XRD) for the three representative films. The measurements were done at room temperature in a Rigaku SmartLab using a source wavelength of 1.5418 Å. In all three cases the XRD peaks of the films and that of the substrate match well with published data [15]. From the measured peak positions, the lattice constants were eval-

*Electronic address: aveek@iisc.ac.in
were performed on different off specular planes to confirm the crystal structure of the films. It was observed that the generated stereographic projection has a good match with the crystal structure for all the three films. The slight shifts observed in the peak positions appeared because of strain. From these, we concluded that the strain in the films did not lead to significant structural changes.

So far we have established from XRD, SEM and AFM studies that the film S3 grown under the highest oxygen partial pressure has the best structural properties in terms of lattice structure, surface voids density and surface roughness. In order to correlate these structural characteristics with the transport properties of the films we studied the resistance, magneto resistance and resistance fluctuations of these films over an extensive temperature range from 295 K down to 245 mK. The resistance of the films were measured using a standard 4-probe ac lock-in technique. Linear electrical probes were defined by metalization (10 nm Cr/100 nm Au) through a metal mask. The measurements were performed in a cryogenic He-3 system.

The resistivity as a function of temperature for the three different films is shown in figure 5. Film S3 shows metallic behaviour (parametrized by $dR/dT > 0$) down to 0.245 K. In contrast S1 shows a metallic behaviour till 50 K before its resistivity begins to logarithmically increase with further decrease in temperature. For sample S2 the metallic behaviour persists down to about 2 K before it shows a small upturn in resistivity - the magnitude of the low temperature rise in resistivity for S2 being much smaller than that in S1. As expected, film S3 has the smallest room temperature resistivity and the largest residual resistivity ratio (RRR) as compared to S1 and S2 - it may be noted that the value of the room temperature resistivity for the films S3 is among the lowest reported till date [9, 10] attesting to the high quality of the film.

We have calculated the Ioffe-Regal parameter $k_F l_{mfp}$ to quantify the disorder level of three films by considering free electron approximation. The value of $k_F$ and $l_{mfp}$ are obtained from $k_F = \pi n$ and $l_{mfp} = v_F \tau$, where $v_F$ and $\tau$ are Fermi wave vector and mean time respectively [17] and $n$ is the number density taken from ref. [10]. The resistivity, charge carrier mean free path $l_{mfp}$ and the Ioffe-Regal parameter $k_F l_{mfp}$ for the three films at 300 K are tabulated in table I. The very low value of $k_F l_{mfp}$ measured in film S1 indicates the defective nature of the film and corroborates the conclusions reached from the structural studies.

The low temperature upturn observed in the resistivity of a metallic film can have two possible origins - (1) weak localization (WL) or (2) electron-electron interactions (EEI). When spin-orbit scattering and spin-spin scattering are negligible, both WL and EEI give a logarithmic divergence to the resistance at low temperatures:

$$\frac{R(T) - R(T_0)}{R(T)R(T_0)} \propto \ln \left( \frac{T}{T_0} \right)$$

The functional forms of the contributions from WL and EEI to the temperature dependence of resistance at zero-magnetic field being very similar, it is not possible to unambiguously

---

**Figure 1:** (a) The atomic structure of CaRuO$_3$ film. (b) Plot of 0-20 x-ray diffraction pattern of the three CaRuO$_3$ films. The inset shows the (002) x-ray diffraction peaks - the data have been shifted vertically for clarity.
establish from the resistivity data alone which of these processes dominate the electrical transport at low temperatures. However, it has been shown that the correction to the magnetoresistance at low magnetic fields from these two effects can be drastically different [18–20] and hence low field magnetoresistance (MR) measurements can be used to distinguish between the two mechanisms.

MR measurements were performed on all the three films at 245 mK in magnetic fields up to 8 T - the results are plotted in figure 6. For both S1 and S2 the MR are negative and hysteretic with a butterfly pattern characteristic of MR seen in ferromagnetic materials [21–23] with the area of the hysteresis loop much larger for S1 as compared to that in S2. This is consistent with the previous observations of ferromagnetism in tensile strained 30 nm films of CaRuO$_3$ grown on SrTiO$_3$ substrates [10]. The low field ($|B| < 0.35$ T) magnetoresistance $\sigma(B)$ data for these two films were fitted to the Hikami-Larkin-Nagaoka (HLN) equation [18]:

$$\sigma(B) - \sigma(0) = \frac{e^2}{2\pi^2\hbar} \left( \ln\left( \frac{B_\phi}{B} - \psi\left(\frac{1}{2} + \frac{B_\phi}{B}\right)\right) \right)$$

where $B_\phi$ is related to the phase coherence length $l_\phi$ as $B_\phi = \hbar/(4e^2l_\phi^2)$. From the measured value of $l_\phi$ we verify that for both the films $l_\phi > t$, where $t$ is the thickness of the film (see table 1). This justifies the use of the two-dimensional form of the equations for WL or EEI. It may be noted that EEI can also lead to MR, but only in much higher fields than are important in eqn. 2 [20], we can therefore ignore this contribution to the low-field MR. The MR of the film S3, on the other hand has the classic quadratic behavior over the entire magnetic field range, characteristic of a good non-magnetic metal.

The emergence of signatures of FM order in CaRuO$_3$ films having a high degree of tensile strain can be understood using the following reasoning: the magnetic order of CaRuO$_3$ differs from its isoelectronic dual SrRuO$_3$ only due to the difference in the amount of structural distortion [24]. It has been proposed [25] and subsequently experimentally demonstrated that modifying the Ru-O-Ru bond angle and orientation by either chemical substitution [26, 27] or tensile strain [10] can induce ferromagnetism in this material. The exact magnetic nature of CaRuO$_3$ films is debated [24, 28] - it has been suggested that the conflicting observations by different groups can be, at least to some degree, be explained by differences in the samples used for the studies [25]. Our measurements show conclusively that the ferromagnetic order seen in these materials depends critically on the level of tensile strain present in these films.

To understand further the effect of film microstructure on its transport properties we have measured low frequency resistance fluctuations (noise) in all three films using a digital signal processing (DSP) based ac 4-probe technique [29] (details of the measurement as well as data analysis techniques can be found in our previous publications [30–32]). This technique
allows simultaneous measurement of the background noise as well as the noise from the sample under study. The power spectral density (PSD) $S_R(f)$ of resistance fluctuations was evaluated from the measured time series of resistance fluctuations accumulated using a fast analog to digital conversion card (ADC). The PSD was seen to have a power law dependence on the spectral frequency $f$, $S_R(f) \propto f^{-\alpha}$ with the value of $\alpha$ very close to unity in all cases. In figure 9 we have plotted the values of $\alpha = -\left(\frac{\partial \ln S_R(f)}{\partial \ln f}\right)$ obtained from the slope of the PSD $S_R(f)$. In all three films $\alpha$ is seen to be almost independent of temperature down to 4 K.

To compare the magnitude of noise seen in the three different films we used the frequency independent parameter $\alpha_V$ defined as:

$$\alpha_V = V f S_R(f) \left(\frac{R}{2}\right)^2$$  \hspace{1cm} (3)

where $V$ is the volume of the sample. In figure 7 we have plotted $\alpha_V$ as a function of temperature for the three different CaRuO$_3$ films. For metallic single component continuous films, resistance noise arises primarily from local fluctuations in the sheet resistance [33] and can be associated with the scattering of charge carriers by extrinsic defects or impurities. The noise in this case is known to scale as the residual resistivity ratio (RRR) of the film [33]. This is consistent with our observations that near room temperatures the noise in S1 is almost an order of magnitude larger than that of S3 with the noise magnitude of S2 lying in between these two values. The temperature dependence of noise in such systems can be attributed to thermally activated processes with a distribution of relaxation times $\tau_o$ [34]. The distribution $D(E_0)$ of the activation energies $E_0$ leading to these processes is related to the power spectral density of resistance fluctuations as [34–36]

$$D(E_0) \sim \frac{\omega S_V(\omega, T)}{k_B T}$$  \hspace{1cm} (4)

where $\omega = 2\pi f$, $E_0 = k_B T ln(2\pi f \tau_0)$ and $\tau_0$ is the attempt frequency of the activated process. Typical values of $\tau_0$ are of the order of $10^{-14}$ sec (of the order of an inverse phonon frequency) [34]. The values of $D(E_0)$ calculated using eqn. 4 are plotted in figure 8. The disorder-free nature of S3 is reflected in the much lower defect density levels present in it as compared to S1 or S2.

If the resistance fluctuations indeed arise due to the thermally activated fluctuations of local defects then the value of $\alpha$ can be extracted independently from the temperature depen-
Figure 4: Plot of the (a) Full width at half maximum of the (003) peak and (b) $c/b$ ratio for the three films S1, S2 and S3 versus oxygen pressure.

Figure 5: Resistivity of the three CaRuO$_3$ films as a function of temperature. The black solid line in (a) is the fit to the eqn. 1.

In Figure 9 we have plotted the values of $\alpha$ extracted from this model as a function of temperature for all three films. It can be seen that these values of $\alpha$ match very well with the values calculated from the frequency dependence of the power spectral density of resistance fluctuations, $\alpha = -(\partial \ln S_R(f) / \partial \ln f)$. This lends credence to the idea that the dominant source of resistance fluctuations in these materials are local scatterers.

IV. CONCLUSIONS

To conclude, we have carried out extensive structural and transport studies on three films of CaRuO$_3$ grown under different conditions. We find that when all other growth parameters are kept fixed, oxygen partial pressure affects very strongly the preferred orientation and surface roughness of the films. This in turn has profound implications on the magnetic ordering in this material - in the films having large disorder we observe signatures of ferromagnetic behaviour from characteristic hysteresis loops in the MR curves. For the best quality films on the other hand, the MR does not show any hysteresis. The electrical transport properties is strongly affected by the oxygen growth pressure as seen from the values of resistivity and the resistance fluctuations. We could verify that the re-

Figure 6: (a) and (b) show respectively the magnetoresistance (MR) of the films S1 and S2 measured at 245 mK. The dotted lines are the data for increasing magnetic field while the solid lines are the data for decreasing magnetic field. (c) Solid olive line shows the magnetoresistance (MR) of the film S3 measured at 245 mK. The data for increasing and decreasing magnetic field superpose on each other. The dotted line is a quadratic fit to the data.

Figure 7: Linear-log plot of $\alpha_V$ as a function of temperature for the three CaRuO$_3$ films. Note that the noise scales with the amount of disorder (quantified by the RRR) in the films.
Figure 8: Distribution of activation energies $D(E_0)$ of thermally activated processes calculated from the temperature dependence of the noise, plotted as a function of the activation energies for these processes.

Figure 9: Plots of the exponent $\alpha$ for the three films (a) S1, (b) S2 and (c) S3. Red filled triangles are the values extracted from the temperature dependence of the relative variance of resistance fluctuations using the Dutta-Horn model. The olive filled squares are the values extracted from frequency dependence of the power spectral density of resistance fluctuations, $\alpha = -\partial \ln S_R(f)/\partial \ln f$.

Acknowledgements

We acknowledge funding from Nanomission, Department of Science & Technology (DST) and HRDG, CSIR, Govt. of India.

[1] I. Mazin, D. J. Singh, Electronic structure and magnetism in Ru-based perovskites, Physical Review B 56 (5) (1997) 2556.
[2] G. Santi, T. Jarlborg, Calculation of the electronic structure and the magnetic properties of and, Journal of Physics: Condensed Matter 9 (44) (1997) 9563.
[3] J. Park, S.-J. Oh, J.-H. Park, D. Kim, C.-B. Eom, Electronic structure of epitaxial (Sr, Ca) RuO$_3$ films studied by photoluminescence and x-ray absorption spectroscopy, Physical Review B 69 (8) (2004) 085108.
[4] G. Cao, S. McCall, M. Shepard, J. Crow, R. Guertin, Thermal, magnetic, and transport properties of single-crystal Sr$_{1-x}$ Ca$_x$ RuO$_3$ (0 < x < 1.0), Physical Review B 56 (1) (1997) 321.
[5] S. Ruddlesden, P. Popper, New compounds of the k2ni4 type, Acta Crystallographica 10 (8) (1957) 538–539.
