Andreev reflection and spin polarization of SrRuO$_3$ thin films on SrTiO$_3$ (111)

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Abstract. Epitaxial SrRuO$_3$ thin films with an extremely flat surface morphology suitable for the use in thin film heterostructures have been grown on SrTiO$_3$ (111) substrates. The transport spin polarization was measured by point contact spectroscopy for SrRuO$_3$ films on SrTiO$_3$ (111) and comparable samples on SrTiO$_3$ (001). The measured polarization for both types of samples is slightly smaller than previously measured by the same technique. Possible reasons for this difference are discussed.

1. Introduction
SrRuO$_3$ (SRO) is a metallic ($\rho \approx 200$ $\mu$Ωcm at room temperature) and ferromagnetic ($T_C = 160$K) oxide which has been attracting a lot of interest due to its potential use as electrode in oxide based electronic and spintronic devices. It is chemically extremely stable [1] and can be grown in heterostructures with other functional oxides, like superconductors [2,3,4], ferroelectrics [5], all oxide magnetic tunnel junctions [6] and spinel ferrites for spin filters [7,8]. SRO has an orthorhombic unit cell with $a = 5.553$ Å, $b = 5.567$ Å and $c = 7.845$ Å. The crystal structure derives from the cubic perovskite structure by distortion and a pseudocubic ($a_{pc} \approx 3.93$ Å) notation can be useful to describe SRO.

SRO can be grown in the pseudocubic (001)$_{pc}$ orientation on perovskite SrTiO$_3$ (001) (STO, $a = 3.905$ Å) and often vicinal cut substrates are used [9] to suppress the formation of a multidomain structure arising from the different growth modes that are possible due to the orthorhombic distortion of SRO (the pseudocubic (100)$_{pc}$, (010)$_{pc}$, (001)$_{pc}$ orientations are not equivalent) [10]. The properties of SRO grown on STO (001) have been extensively explored (see e.g. Ref. [9-11]).

However, for some applications SRO films in other orientations are more appropriate, e.g. for the use as bottom electrode in a spin filter structure with spinels as insulating ferrimagnetic tunnel barriers. Reason is that the spinel (001) surface is energetically unfavorable and therefore thin (001)-textured films are difficult to grow flat enough as needed for spin filters [12] on the most commonly used single crystalline perovskite (001) substrates [13]. Indeed, the growth of CFO on SRO buffered STO (001) was found to result in a very rough (rms roughness > 2nm) surface morphology [14]. In contrast, CFO (111) can be grown with flat surface (rms roughness < 0.3nm) on STO (111) with and without SRO buffer layers [7,8]. Using rf magnetron sputtering on STO (111) substrates, we have been able to obtain SRO films considerably more flat (rms roughness < 0.3nm) than previously reported [15]. These films can be used not only as bottom electrode for CFO based spin filters [7,8], but also in other situations, in which the pseudocubic (001)$_{pc}$ SRO surface is unfavorable.
For many of the possible applications of SRO thin films the transport spin polarization $P$ is a key quantity. $P$ is defined as:

$$P = \frac{I_\uparrow - I_\downarrow}{I_\uparrow + I_\downarrow} = \frac{N_\uparrow(E_F)v_{\uparrow}^n - N_\downarrow(E_F)v_{\downarrow}^n}{N_\uparrow(E_F)v_{\uparrow}^n + N_\downarrow(E_F)v_{\downarrow}^n}$$

(1)

with $n=1$ for ballistic transport. $N_{\uparrow\downarrow}(E_F)$ is the density of states at the Fermi level and $v_{\uparrow\downarrow}$ the Fermi velocity for the respective spin direction. In the case of SRO, it is believed that a negative transport polarization results mainly from differences in the Fermi velocities for spin up and spin down electrons rather than from the respective density of states, which is roughly equal [16,17].

The transport spin polarization of SRO films on STO (001) has been measured using planar tunnel junctions with magnetic [6] or superconducting counter electrode [1], yielding results of $P \approx 10\%$. In contrast, from point contact spectroscopy (PCS, explained in more detail below) a much higher polarization of $|P| = 50\%$ is inferred [17,18] (note that PCS is not sensitive to the sign of $P$). It has been proposed [1,17] that this discrepancy may be due to different decay length of surface states in the tunnel barrier, underlining that electrode properties can appear drastically changed when measuring through a tunnel barrier (like e.g. for epitaxial MgO/Fe).

In principle, the transport spin polarization $P$ as expressed in Equation 1 is dependent on the crystallographic direction through the Fermi velocity, which has to be taken into account. Therefore, for the new SRO films prepared on STO (111) an independent determination of $P$ is needed.

In this work, we report on the growth of SRO thin films in (111) orientation with extremely flat surfaces as required for heterostructures (spin filters). Using PCS, a transport spin polarization of $P \approx 42\%$ is determined by fitting experimental spectra with the extended Blonder-Tinkham-Klapwijk (BTK) model. Measurements on comparable SRO films grown on STO (001) yield the same $P$ within the experimental accuracy. This result is in agreement with some available band structure calculations [16], while appearing to be in contrast with another [19]. However, it turns out that the measured $P$ values of (111) and (001) SRO films are slightly smaller than previously measured by the same technique [17,18] and we discuss the possible reasons for this difference.

2. Sample preparation and characterization

SRO/STO films were grown by radiofrequency magnetron sputtering from a stoichiometric target. Previous to deposition, the single crystal substrates, (111) oriented STO, were annealed for one hour in the sputtering chamber, in high vacuum at 700 °C. The coatings were produced in a mixed Ar/O$_2$ atmosphere (in ratio 3:2), with a total pressure of 100 mTorr. An RF power of 15 W was supplied to the target, and the distance between the target and the substrate was fixed at 6 cm, resulting in a growth rate of $\approx 0.54$ nm/min. The typical deposition time was 50 min and the optimal substrate temperature during the growth was found to be 725 °C.

In Fig. 1a, X-ray diffraction (XRD) data taken on a 30nm thick SRO film on STO (111) is shown. SRO grows textured in pseudocubic (111)$_{pc}$ orientation on the STO (111) substrate. No impurity phases can be detected. Due to the orthorhombic distortion, the pseudocubic (111)$_{pc}$ can correspond to several, slightly different crystal directions, namely (011)$_o$ and(101)$_o$ of the orthorhombic structure. However, the differences between these orientations are so small that they cannot be resolved with standard XRD measurements. Importantly, the $d$(111)$= 2.31$ Å interplanar spacing deduced from the $\theta/2\theta$ scans X-ray scans indicate that the out-of-plane parameter of SRO, as a result of epitaxial strain, is slightly expanded compared to the expected position for bulk STO (vertical lines in inset of Fig. 1a).

The surface morphology of SRO films deposited on STO (111), as observed by atomic force microscopy (AFM), is extremely flat (Fig. 1b). For example, the rms roughness of the sample in Fig. 1b (18nm thick) is only 0.15nm.

In the left inset of Fig. 2a, the temperature dependent resistance $\rho(T)$ of a SRO film (30 nm thick) on STO (111) is shown. A kink at around $T_c \approx 100$ K signals the Curie temperature, which occurs at a
temperature lower than that of bulk samples ($T_C \approx 160$ K). The reduction of $T_C$ in SRO thin films has been attributed to strain [20] which indeed is observed in the XRD measurements. A certain degree of structural disorder is reflected in the relatively low residual resistance ratio $RRR \approx 1.8$, which however is among the best reported for SRO grown on STO (111) [21], and the value of $\rho(5 \text{ K}) \approx 200 \mu\Omega\text{cm}$ which is larger than that measured in state-of-the-art (001)SRO thin films [9].

3. **Point contact spectroscopy and Andreev reflection**

The process of Andreev reflection (AR) can occur at superconductor(SC)-metal(M) interfaces for bias voltages $V$ smaller than the superconducting energy gap $\Delta/e$. Under this condition, incoming electrons from the metal cannot enter the superconductor, unless becoming part of a Cooper pair. This requires that a second electron from the opposite spin density of states is transferred from the M to the SC, leaving a hole that is reflected in the metallic electrode. Since two electrons are transferred in this process, ideally the conductance of such contact doubles within the superconducting energy gap.
The AR process is partially suppressed when the metallic electrode is constituted of a magnetic material with a finite transport spin polarization $P$. This is most obvious in the case of a half metal where no electrons of the opposite spin direction are available and consequently no hole can be reflected. The degree by which the AR process is suppressed by $P$ is used in point contact spectroscopy (PCS) to infer the transport spin polarization of ferromagnetic thin films [22]. PCS consists of measuring the $dI/dV$ vs $V$ characteristics of a small Metal(Ferromagnet)-SC contact, e.g. formed by pressing a chemically etched thin wire tip on a sample.

The $dI/dV$ characteristics of point contacts can be described by the BTK (Blonder-Tinkham-Klapwijk) model and its extensions [23,24] for finite spin polarization $P$. Besides the transport spin polarization $P$, the model parameters are: the temperature $T$, the superconducting energy gap $\Delta$, the broadening of the energy gap expressed by $\Gamma$, and a dimensionless interface barrier $Z$. A barrier of $Z = 0$ corresponds to a fully transparent M@SC contact while for larger values $Z > 1$ the contact is in the M/I/SC tunneling regime. For materials with a non negligible resistance compared to the point contact, a serial resistance $R_s$ is introduced to account for the voltage drop in the sample [24].

To determine the transport spin polarization of SRO films on STO (111), we have performed PCS measurements in a variable temperature (1.5–300 K) cryostat. The point contacts were formed by

![Figure 2](image-url)

Fig. 2: Differential conductance $dI/dV$ normalized to values at high bias voltages, measured for a) SRO in pseudocubic (111) orientation and b) SRO in pseudocubic (001) orientation. In the right insets the best fit $\chi^2$ as function of $P_{\text{trial}}$ is shown. Left inset in a) $\rho(T)$ of a 30nm thick SRO film on STO (111).
pushing a chemically etched Nb tip on the sample surface with the probe thermalized in 4He gas. A piezo motor and scan tube were used to vary the distance and the position between tip and sample. The current-voltage (I-V) characteristics were measured by a conventional four probe method and a lock-in technique was used to measure the differential conductance dI/dV spectra as function of the applied voltage directly.

In Fig. 2a an experimental spectra recorded on SRO (111)$_{pc}$ is shown, normalized to the conductance value at high voltages. The best fit (line), obtained with the parameters given in the figure, yields a spin polarization of P ≈ 42%. Although the point contact is expected to be in the diffusive regime (estimated contact radius $r_c \approx 20$ nm using Wexler’s formula [25] and ρ(5 K) ≈ 200 μΩcm ), for simplicity ballistic formulas were used, as it has been shown that the error translates into Z instead of P [24]. As a possible interplay of the different parameters is not easy to control, it was proposed [26] to perform an optimization process in which for each fixed $P_{\text{trial}}$ the best fit in ($\Delta$, $\Gamma$ and Z) is calculated. The resulting $\chi^2$ values present a minimum at the correct spin polarization. In the right inset of Fig. 2a, the calculated $\chi^2$ values for the spectra of Fig. 2a are shown. There is a clear minimum around P ≈ 42%, in agreement with the best fit of the data.

Although in a similar range, the value of P ≈ 42% for the SRO films grown on STO (111) is somewhat reduced compared to previously reported values P ≈ 53% [17,18] for high purity SRO samples grown on vicinal SRO (001). In principle, this difference could be either due to an anisotropy of the transport spin polarization P or a reduction of P in the present samples as an effect of structural disorder and/or strain. To check for these two possibilities, PCS was also performed on equivalent samples grown on SRO (100), with an RRR ≈ 2 (Fig. 2b). The best fit is obtained for P = 45% and again the value of P is confirmed by the $\chi^2$ analysis in the inset. We thus conclude that our (111) and (001) SRO samples lead to similar spin polarization values: P(111) ≈ 42% and P(001) ≈ 45%.

Before discussing on the implications of this isotropic spin polarization, it is worth to comment on origin of the dissimilarity of the corresponding measured spectra (Figs. 2a and 2b). Some insight can be gained from an analysis of the other fit parameters. It is observed that the most remarkable changes refer to the value of the superconducting energy gap; the superconducting gap of the spectra in Fig. 2b ($\Delta \approx 1.09$ eV) is clearly reduced (in agreement with the experimental observation of a reduced $T_c$ of the Nb tip) compared to that of Fig. 2a ($\Delta \approx 1.45$ eV) and that of bulk Nb, and also considerably more smeared out (Γ). Although the reason for this reduction (tip degradation, a proximity effect of the magnetic SRO, stronger in (001) direction) cannot be decided on the basis of the present data, the reduction of $\Delta$ and increase of $\Gamma$ explains the different shapes of the spectra in Figs. 2a and 2b.

We turn now to the major question addressed in this manuscript, that close similarity of the experimental values of P(111) ≈ P(001). This finding gives support to available band structure calculations [16] predicting an isotropic spin-dependent Fermi velocity, while contradicting other theoretical calculations [19] indicating a substantial anisotropies in the Fermi surface and Fermi velocities. Our data do not support such scenario. However, since the residual resistivity ratio of our films is RRR ≈ 2 thus implying substantial scattering in the point contact area. To what extent these scattering events could average the spin-dependent Fermi velocity angular distribution and thus produce a more isotropic spin polarization of SRO cannot be addressed on the basis of present measurements. On the other hand, our data for P(111) ≈ P(001) ≈ 42-45 % are comparable but definitely smaller than that reported by Nadgorny et al [17] (P(001) ≈ 53 %); it can not be excluded that the above mentioned scattering mechanism could be at the origin of the observed relatively lower spin polarization.

4. Conclusions

In conclusion, flat epitaxial SRO thin films have been grown by rf magnetron sputtering on STO (111) oriented substrates. The transport spin polarization was measured by PCS and found to be P ≈ 42%. The finding of a very similar value of P ≈ 45% for SRO (001) films supports available band structure calculations predicting an isotropic transport spin polarization.
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