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Suppression of superconductivity by crystallographic defects in epitaxial Sr_2RuO_4 films

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Epitaxial Sr_2RuO_4 thin films grown by pulsed-laser deposition from high-purity (99.98%) Sr_2RuO_4 targets on (001) $LaAlO_3$ were found to be not superconducting down to 0.4 K. Structural disorder is believed to be responsible. A correlation was observed between higher resistivity ratios in electrical transport measurements and narrower x-ray diffraction rocking curve widths of the Sr_2RuO_4 films. High-resolution transmission electron microscopy revealed that the dominant structural defects, i.e., the defects leading to the observed variation in rocking curve widths in the films, are {011} planar defects, with a spacing comparable to the in-plane superconducting coherence length of Sr_2RuO_4. These results imply that minimizing structural disorder is the key remaining challenge to achieving superconducting Sr_2RuO_4 films. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1364659]

Sr_2RuO_4 is the only known Cu-free layered perovskite superconductor.[1] Recently, the issue of the pairing-state symmetry of Sr_2RuO_4 has attracted considerable attention.[2] Rice and Sigrist predicted that the pairing state of Sr_2RuO_4 is odd-parity, possibly p-wave,[3] and this possibility has received wide experimental support from nuclear magnetic resonance, muon spin relaxation, and tunneling measurements, among others.[2,4–6] Other relevant parameters of the Sr_2RuO_4 superconducting state, notably the superconducting energy gap, are still unknown, and thus the exact pairing state of Sr_2RuO_4 remains unresolved.

Phase-sensitive measurements similar to those carried out on high-T_c cuprates[7,8] would help to identify the superconducting pairing state, but are lacking for Sr_2RuO_4. To facilitate such experiments, an important step is the growth of superconducting epitaxial films. Although epitaxial Sr_2RuO_4 films have been prepared,[9–12] superconductivity has not been achieved in Sr_2RuO_4 films.

Both impurities and structural disorder can quench superconductivity in Sr_2RuO_4. For example, 300 ppm of aluminum impurity are sufficient to destroy superconductivity.[13] The suppression of superconductivity in Sr_2RuO_4 by structural disorder has been established using the same high-purity source materials and floating-zone (FZ) crystal growth method used to make Sr_2RuO_4 single crystals with the highest T_c reported.[14] A correlation of T_c with the residual resistivity (ρ_0), a measure of disorder in equivalent-purity crystals, was observed. Thus, in order to grow superconducting Sr_2RuO_4 films, it is important to minimize both impurities and structural disorder.

To date, there has been little characterization of structural defects in Sr_2RuO_4 single crystals and films. Consequently, the particular type of structural defects that suppress superconductivity in Sr_2RuO_4 is not established. Inoue *et al.* investigated the microstructure of FZ Sr_2RuO_4 single crystals by transmission electron microscopy (TEM) and electron microdiffraction. They observed striations in low-magnification bright-field images, and streaking in electron microdiffraction patterns indicative of planar faults, but these defects were not further characterized. No TEM study of the defects present in Sr_2RuO_4 films has been reported.

In this letter, we present the results of high-resolution TEM (HRTEM) imaging, electronic transport studies, and x-ray diffraction (XRD) analysis of high-purity, but nonsuperconducting, c-axis-oriented Sr_2RuO_4 films grown by pulsed-laser deposition (PLD). Although superconductivity was not found in the series of films grown, it appears that the transport properties of our films are dominated by disorder rather than by impurities.

All of the epitaxial Sr_2RuO_4 films reported have been synthesized by PLD.[9–12] Impurities introduced during traditional target preparation methods (i.e., from the grinding media) are of great concern considering the low concentration of impurities that can destroy superconductivity in Sr_2RuO_4. While such impurities have likely been sufficient to completely suppress superconductivity in prior epitaxial Sr_2RuO_4 films made by PLD, the high-purity Sr_2RuO_4 target used in the present work was made without the use of grinding media.[10] A lower-purity PLD target, fabricated by conventional solid-state grinding methods,[9] was also used for comparison.

The ~200-nm-thick Sr_2RuO_4 films were grown on (001) $LaAlO_3$ substrates at 1000 °C in a radiatively heated sample chamber[15] by PLD. A KrF excimer laser was used for growth with the following parameters: 10^4 pulses, 160 mJ/pulse, 2.7 J/cm^2 fluence, 2 Hz pulse rate, and a target-to-substrate distance of 7.5 cm. Background pressures

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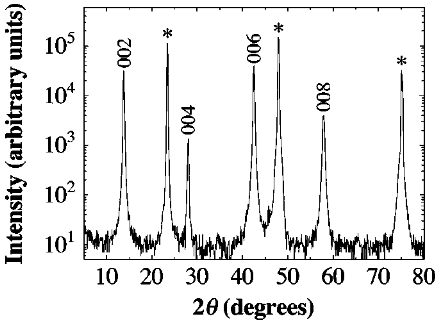

FIG. 1. θ–2θ x-ray diffraction scan of a high-purity PLD-grown Sr_2RuO_4 film. This 210-nm-thick film was grown in a background oxygen partial pressure of 3.5 μTorr. The substrate peaks are marked with an asterisk (*).

from 0.8 to 5.0 μTorr oxygen were maintained during growth and post-growth cooling.

Film thicknesses were computed from the number of laser pulses during film growth, calibrated by measuring the thickness of a representative film using TEM. The in-plane resistivity (ρ_{ab}) of the Sr_2RuO_4 films was measured as a function of temperature with a dip probe from 300 to 4.2 K, or to 0.4 K in a ^{3}He evaporation refrigerator, using the four-wire dc current bias method.

The θ–2θ XRD scan of a Sr_2RuO_4 film is shown in Fig. 1. Peaks in the θ-2θ scan are sharp, indicating that the film is single phase and is oriented with its c axis perpendicular to the plane of the substrate. The full width at half-maximum (FWHM) of the 006 peak is approximately 0.23° in the 2θ direction, and 0.33° in the ω direction. (Instrumental resolution is ~0.20°.) A ϕ-scan of the 103 Sr_2RuO_4 peak (not shown) indicated that the film is epitaxial with the ⟨100⟩ directions of the film aligned with the ⟨100⟩ directions of the pseudocubic perovskite subcell of the substrate. TEM examination (Fig. 2) revealed a well-ordered film with a sharp substrate interface. These structural characteristics are comparable to those of high-quality epitaxial films of cuprate superconductors.

All but one of the films on which electrical measurements were made showed metallic $\rho_{ab}(T)$ behavior, but crossed over to semiconducting behavior at low temperatures, a behavior which is not seen in Sr_2RuO_4 single crys-

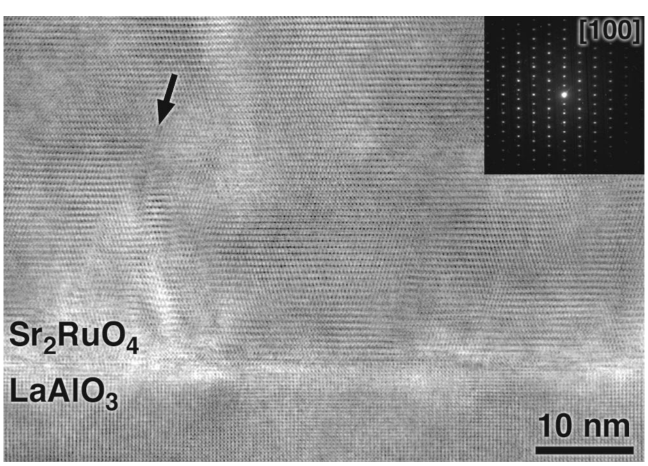

FIG. 2. A HRTEM image of the same high-purity c-axis Sr_2RuO_4 film whose XRD analysis is shown in Fig. 1. The inset shows a diffraction pattern of the Sr_2RuO_4 film viewed along the [100] Sr_2RuO_4 zone axis.

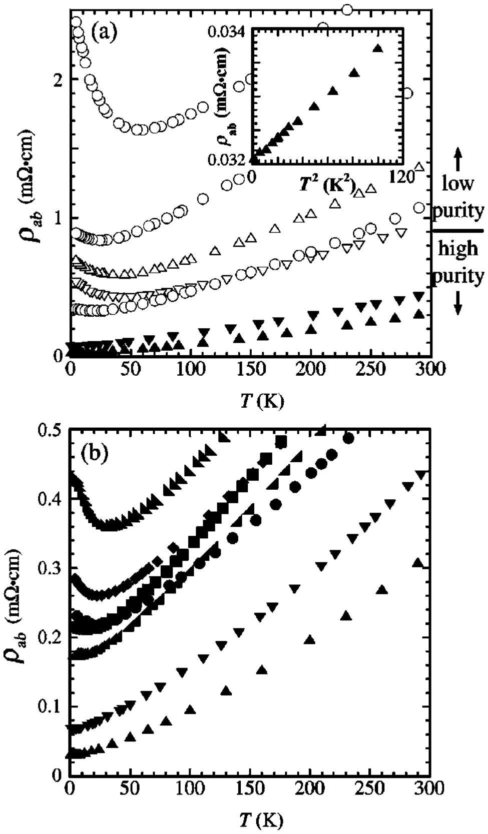

FIG. 3. Resistivity versus temperature plots for seven high-purity (filled symbols) and five low-purity (hollow symbols) Sr_2RuO_4 films grown by PLD at oxygen partial pressures from 0.8 to 5.0 μTorr. As all of the high-purity samples have lower resistivities than the low-purity samples, only two of the high-purity samples are shown in (a) to allow comparison yet avoid an overlap of data points. The vertical scale in (b) is expanded by a factor of five compared to (a). Triangles indicate two pairs of high- and low-purity films grown under oxygen partial pressures of 3.0 μTorr (▲△) and 2.5 μTorr (▼▽), and show the effect of impurities on resistivity in Sr_2RuO_4. The solid squares correspond to the same film characterized in Figs. 1 and 2. One film remained metallic down to 0.4 K, exhibiting a T^2 temperature dependence below 15 K, as shown in the inset in (a).

tals. Figure 3 shows the temperature dependence of the in-plane resistivity for several Sr_2RuO_4 films grown from high-purity (filled symbols) and low-purity (hollow symbols) targets at oxygen partial pressures from 0.3 to 3.5 μTorr.[16] Films grown from the low-purity target exhibited semiconductor-type $\rho_{ab}(T)$ behavior at low temperature due to impurities. The fully metallic film exhibited a T^2 temperature dependence below 15 K, shown in the inset in Fig. 3. This behavior is also seen in the in-plane conduction of superconducting single-crystalline Sr_2RuO_4.

None of our Sr_2RuO_4 films, however, showed signs of superconductivity. The fully metallic film had a residual resistivity of $\rho_{ab,0}=32\ \mu\Omega\,cm$, while the maximum residual resistivity for observing superconductivity in Sr_2RuO_4 is about 1 $\mu\Omega\,cm$.[13] Likewise, the fully metallic film had a resistivity ratio $[\rho_{ab}(300\ K)/\rho_{ab,\min}]\approx 10$, while the resistivity ratios of superconducting Sr_2RuO_4 single crystals are at least 120.[13] The films grown from the high-purity target clearly are superior to the films grown under similar conditions from the low-purity target. Given the qualitative similarity in $\rho_{ab}(T)$ of the high-purity films to that of the low-purity films, impurities may not be the only factor destroying superconductivity in these films.

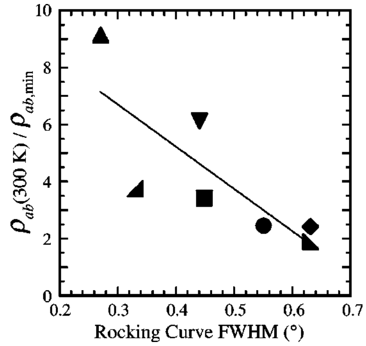

FIG. 4. The resistivity ratios $[\rho_{ab}(300\,K)/\rho_{ab,\min}]$ of the high-purity films shown in Fig. 3, plotted vs the rocking curve FWHM of the 006 peak. High-purity, but crystallographically less-perfect, films exhibit lower resistivity ratios. Symbols correspond to those in Fig. 3.

The degree of crystalline imperfection also affects the resistivity of Sr_2RuO_4 films. In Fig. 4, the resistivity ratios of the high-purity Sr_2RuO_4 films are plotted versus the FWHMs of the rocking curve widths of the 006 Sr_2RuO_4 peak, a measure of the ''flatness'' of the RuO_2 planes where in-plane transport takes place. The resistivity ratio is an indication of the level of quenched disorder in these films (including impurity effects) and characterizes the film's quality as a metal. Although there is significant scatter in the plot, the correlation between the resistivity ratio and the 006 FWHM is apparent. More defective films exhibit lower resistivity ratios. This strong correlation was only observed for the high-purity films: a regime where lattice imperfection effects dominate in limiting in-plane resistivity.

Although the crystalline perfection of these Sr_2RuO_4 films is comparable to superconducting films of the high-T_c cuprates, the much longer superconducting coherence length of Sr_2RuO_4 and its unusual pairing symmetry make Sr_2RuO_4 more sensitive to defects. These epitaxial films do have defects. Planar defects are indicated by arrows in Figs. 2 and 5. Note that the spacing between these planar defects is *not* significantly greater than the in-plane superconducting coherence length of Sr_2RuO_4, $\xi_{ab}(0)\approx 66$ nm.[17] These planar defects, known as crystallographic shear defects, are inclined by 73° from the (001) Sr_2RuO_4 plane, which corresponds to the {011} Sr_2RuO_4 plane. In all images covering a sufficiently large area, at least one such defect was observed over any $a-b$ plane interval of 66 nm. And, since any lattice defect can be a pair-breaker, these planar defects that disrupt the RuO_2 planes are likely responsible for the suppression of superconductivity in these high-purity Sr_2RuO_4 films.

Other factors could be responsible for the suppression of superconductivity in these epitaxial films, including off-stoichiometry or interdiffusion from the $LaAlO_3$ substrate at the high deposition temperatures used. These factors, however, should be the same for films grown from low- or high-purity Sr_2RuO_4 targets on $LaAlO_3$ substrates, since the same growth conditions were used, and they would not explain the correlation seen in Fig. 4.

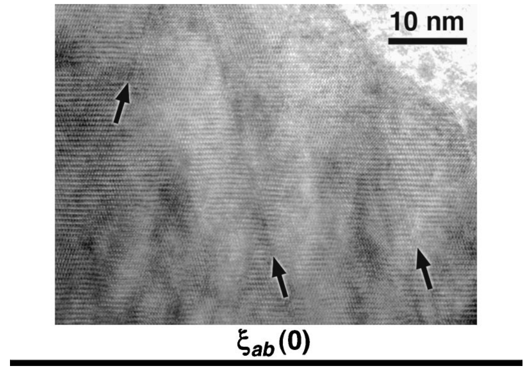

FIG. 5. A [100] TEM image of a different region of the same Sr_2RuO_4 film shown in Fig. 2. A high density of planar defects, some indicated by arrows, is observed in this region of the film. Re-examination of all images of the Sr_2RuO_4 film revealed at least one of these defects (e.g., the arrowed region in Fig. 2) over any interval of the in-plane superconducting coherence length, $\xi_{ab}(0)$, of Sr_2RuO_4, indicating that they are present in a density sufficient to quench superconductivity in the films. The magnitude of $\xi_{ab}(0)$ is indicated by the scale bar.

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