Growth of epitaxial *a*-axis and *c*-axis oriented Sr_2RuO_4 films

S. Madhavan and D. G. Schlom[a)]
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802-5005

A. Dabkowski and H. A. Dabkowska
Institute of Materials Research, McMaster University, Hamilton, Ontario L8S 4M1, Canada

Ying Liu
Department of Physics, The Pennsylvania State University, University Park, Pennsylvania 16802

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Epitaxial films of Sr_2RuO_4 have been grown *in situ* by pulsed laser deposition on (100) $LaAlO_3$ and (100) $LaSrGaO_4$ substrates. X-ray diffraction results show that the films are single domain and grow *c*-axis oriented on (100) $LaAlO_3$ and *a*-axis oriented on (100) $LaSrGaO_4$ substrates. X-ray ϕ scans indicate epitaxial alignment of the film and substrate in-plane axes in both cases. Resistivity versus temperature measurements reveal that the as-grown *c*-axis oriented films are semiconducting and the *a*-axis oriented films are metallic. © *1996 American Institute of Physics.* [S0003-6951(96)03504-1]

The compound Sr_2RuO_4 has been known for some time. It is the $n=1$ member of the Ruddlesden–Popper homologous series of the general formula $A_{n+1}B_nO_{3n+1}$ (A=Sr, B=Ru).[1,2] Interest in this compound was recently renewed due to its low resistivity and excellent lattice match with $YBa_2Cu_3O_{7-x}$.[3] These properties make it an attractive candidate for use as conductive electrodes or a normal metal barrier layer in device applications of high T_c superconducting films. Lichtenberg *et al.*[3] synthesized single crystals of this material and used it as a substrate for growing $YBa_2Cu_3O_{7-x}$. Further interest in this compound has been stimulated by the recent discovery of superconductivity in single crystals of Sr_2RuO_4 ($T_c=0.93$ K).[4]

Sr_2RuO_4 is the only known layered perovskite that is free of copper, and yet superconducting. In fact, it is isostructural with $(La_{1-x}Ba_x)_2CuO_4$, which was the compound in which high transition temperature (T_c) superconductivity was first discovered. By now, it is universally accepted that in order to understand the physics of high T_c superconductivity, one needs to understand the physics of CuO_2 planes found in all high T_c superconductors, and the effect of carrier doping by the charge reservoir layers adjacent to the CuO_2 planes. It has been emphasized recently that while Sr_2RuO_4 shares many common features with high T_c superconductors, important differences exist. In particular, the Cu^{2+} ($3d^9$) valence state in CuO_2 planes has spin $\frac{1}{2}$ but Ru^{4+} ($4d^4$) in RuO_2 planes has spin 1. This, together with the fact that Sr_2RuO_4 becomes superconducting without any extrinsic doping, suggests that mechanisms of superconductivity based on doping a 2D antiferromagnetic state of $\frac{1}{2}$ spins are not relevant for the occurrence of superconductivity in this compound. Furthermore, recent band calculations[5,6] indicated that the Sr_2RuO_4 may be a much less strongly correlated electron system than high T_c superconductors. This underscores the importance of a strongly correlated normal state in achieving high superconducting transition temperatures in layered perovskite oxides. This may provide useful insight for the search of superconductors with even higher T_c than those of known high T_c oxide superconductors.

Compared with high T_c superconductors, the properties of Sr_2RuO_4 are much less well characterized. For example, so far there have been no Hall measurements done on this material. As a result, its carrier density is not known. Other important superconducting properties such as upper critical field (H_{c2}) and the related Ginzburg–Landau coherence length (ξ), critical current density (J_c), the anisotropy of these quantities, and effects of any chemical substitutions are completely unknown. The absence of these experimental results is in part due to the technical difficulties involved in preparing high quality Sr_2RuO_4 samples. Polycrystalline samples of this phase are semiconducting.[4,7,8] Single crystals with sizes sufficiently large for determining superconducting and normal state properties are difficult to prepare. Hence, epitaxial films provide an attractive alternative for studying superconductivity in this material. In addition, epitaxial films would also pave the way for applications in superconducting electronics, e.g., use as a normal metal in superconductor–normal metal–superconductor (SNS) Josephson junctions. An all-perovskite oxide configuration has certain advantages in achieving high quality junctions. In this regard, it is important to emphasize that in addition to its high metallic conductivity, Sr_2RuO_4 is nonmagnetic (unlike $SrRuO_3$), a desirable feature for use in SNS junctions. To our knowledge, epitaxial films of this phase have not been grown before. Previous attempts at the growth of Sr_2RuO_4 films have been unsuccessful because the $SrRuO_3$ phase was more stable at the growth conditions employed.[9–11] In this letter, we report the growth and characterization of epitaxial Sr_2RuO_4 thin films on $LaAlO_3$ and $LaSrGaO_4$ substrates.

Sr_2RuO_4 has a tetragonal structure of the K_2NiF_4 type ($a=3.87$ Å and $c=12.74$ Å).[1,2] $LaAlO_3$ (pseudocubic perovskite with lattice constant $a=3.79$ Å)[12] and $LaSrGaO_4$ (tetragonal structure with lattice constants $a=3.84$ Å and $c=12.68$ Å)[13] were chosen as substrates based on their lattice parameters. The $LaSrGaO_4$ substrates were grown by the

a)Electronic mail: schlom@ems.psu.edu

Czochralski method as described elsewhere.[13] The good *a*-axis lattice match of Sr_2RuO_4 with $LaAlO_3$ encourages growth of films with their *c* axis oriented perpendicular to the substrate (*c*-axis oriented films) and the ⟨100⟩ Sr_2RuO_4 axes aligned with the ⟨100⟩ axes of the substrate. On the other hand, since both the *a* and *c* axes of Sr_2RuO_4 and $LaSrGaO_4$ are well matched, *a*-axis oriented films can be expected to grow on (100) $LaSrGaO_4$ substrates. The *a*-axis geometry is optimal for measuring the anisotropy of superconducting properties and would also be desirable for making sandwich-type Josephson junctions with *a*-axis $YBa_2Cu_3O_{7-x}$, due to the longer coherence length along the *a* axis of $YBa_2Cu_3O_{7-x}$ than along its *c* axis. The growth of *a*-axis oriented $YBa_2Cu_3O_{7-x}$ films on (100) $LaSrGaO_4$ has been demonstrated.[14–16]

A Sr_2RuO_4 target for thin film deposition was fabricated by solid state processing methods. Stoichiometric proportions of $SrCO_3$ (Alfa Aesar, 99%) and RuO_2 (Alfa Aesar, 99.9%) powders were weighed out and ballmilled in isopropanol for 24 h. The ground powder was dried and then calcined at 1000 °C for 24 h in air. After regrinding, the powder was pressed into a disk of 2.5 cm diameter with a uniaxial press (10 MPa). This pellet was then further densified by pressing in a cold isostatic press (275 MPa). The pressed pellet was sintered in an Al_2O_3 crucible at 1350 °C for 24 h in air. X-ray diffraction analysis indicated that the target was a single-phase polycrystalline Sr_2RuO_y.

The films were grown *in situ* by pulsed laser deposition (PLD) using a KrF excimer laser (248 nm, Lambda Physik EMG103MSC) on single crystal (100) $LaAlO_3$ [indexed based on the pseudocubic perovskite subcell, or equivalently (012) of the rhombohedral unit cell][12] and (100) $LaSrGaO_4$ substrates. Deposition was done using an on-axis geometry, with the substrate placed normal to the ablated plume. The substrate was placed at a distance of 7.5 cm from the target and was radiatively heated. Oxygen pressures of 1–2 mTorr, substrate temperatures of 950–1050 °C, pulse energies of 90–130 mJ, and laser energy densities of 3–4 J/cm^2 were the deposition conditions used. The films discussed here were 1500–2500 Å thick. After growth, the films were cooled down to room temperature in vacuum. Films grown at significantly lower temperatures and higher oxygen pressures contained mainly $SrRuO_3$, consistent with previous observations.[10,11]

A 4-circle x-ray diffractometer, using Cu $K\alpha$ radiation and a graphite monochromator, was used to characterize the films. A θ–2θ scan of a Sr_2RuO_4 film on $LaAlO_3$ showed that the film is predominantly *c*-axis oriented with a *c*-axis length of 12.70±0.01 Å [see Fig. 1(a)]. The full width at half-maximum (FWHM) of the 006 peak in the θ–2θ scan was 0.5°. The rocking curve FWHM of the 006 Sr_2RuO_4 peak was 0.4°. Figure 1(b) shows a ϕ scan of the 103 Sr_2RuO_4 reflection with sharp peaks (FWHM of 1°) at ϕ=0°, 90°, 180°, and 270°, clearly indicating that the film is single domain with the ⟨100⟩ directions of the film being aligned with the ⟨100⟩ directions of the substrate. From the position of the 103 Sr_2RuO_4 peak, the in-plane lattice parameter was calculated to be 3.90±0.05 Å.

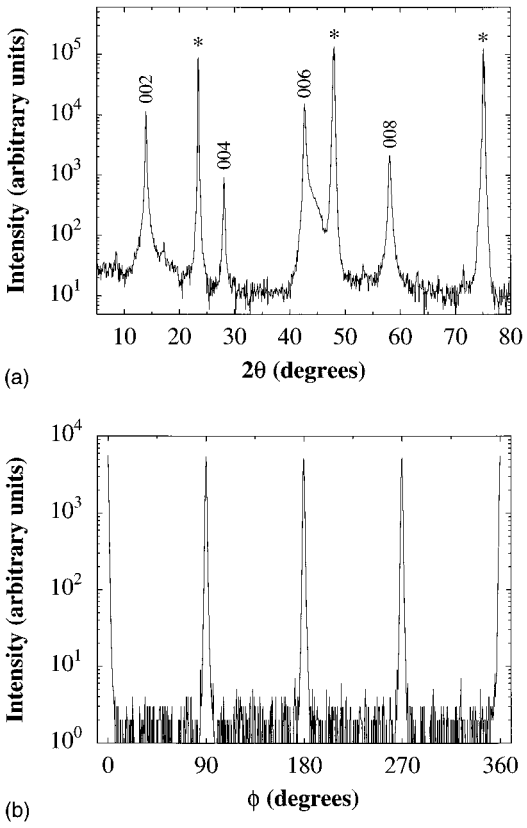

FIG. 1. (a) θ–2θ x-ray diffraction scan of a 2000 Å thick *c*-axis oriented Sr_2RuO_4 film on a (100) $LaAlO_3$ substrate. The substrate peaks are marked (*). (b) X-ray ϕ scan of the Sr_2RuO_4 103 reflection. ϕ=0 is along the substrate [001] direction.

The Sr_2RuO_4 films grown on (100) $LaSrGaO_4$ were *a*-axis oriented with an *a*-axis length of 3.90±0.01 Å [see Fig. 2(a)]. Figure 2(b) shows a ϕ scan of the 305 Sr_2RuO_4 peak. The 305 peak was chosen for the ϕ scan, as the resolution of our 4-circle diffractometer is sufficient to distinguish between Sr_2RuO_4 and $LaSrGaO_4$ at this reflection and to determine the in-plane orientation of the *c* axis. The sharp peaks seen at ϕ=0° and 180° indicate that the films are single domain with the in-plane epitaxial arrangement of Sr_2RuO_4[001] ∥ $LaSrGaO_4$[001]. From the position of the 305 peak, the *c*-axis length was calculated to be 12.72 ±0.17 Å. The rocking curve FWHM of the 200 Sr_2RuO_4 peak was 0.5°. The FWHM widths in θ–2θ and ϕ were 0.3° and 1°, respectively.

Resistivity measurements of both *a*-axis and *c*-axis oriented films were made using a 4-point probe. The film thickness was determined using a profilometer. Gold contacts were sputtered onto the films. The resistivity of the films were measured as a function of temperature, from room temperature to 4.2 K. Figure 3 shows the resistivity versus temperature of an *a*-axis oriented Sr_2RuO_4 thin film grown on a $LaSrGaO_4$ substrate. The measurement current was 1 μA. It exhibits metallic resistivity of a magnitude intermediate between that measured along the *a* axis and *c* axis of Sr_2RuO_4 single crystals.[3,4] The macroscopic direction of current transport was not along the *a* or *c* axis, but rather in between them (the sample was too small to conveniently

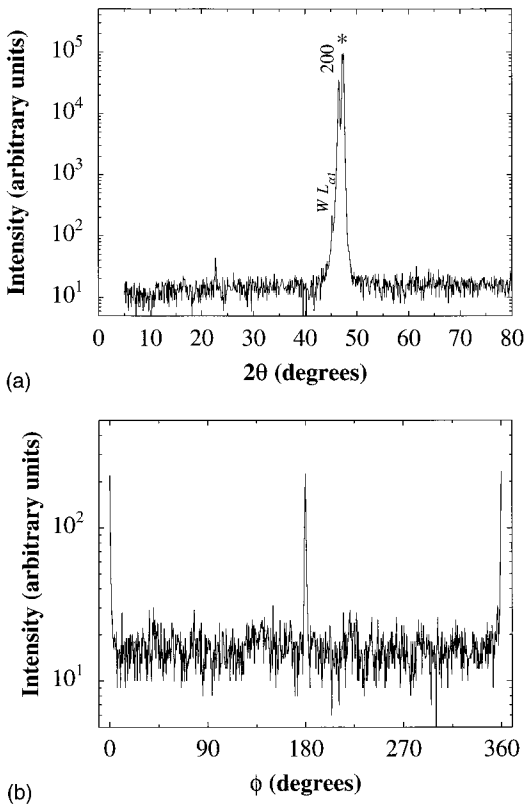

FIG. 2. (a) θ–2θ x-ray scan of a 1700 Å thick *a*-axis oriented Sr_2RuO_4 film on a (100) $LaSrGaO_4$ substrate. The $LaSrGaO_4$ peaks are marked (*). (b) X-ray ϕ scan of the Sr_2RuO_4 305 reflection. ϕ=0 is along the substrate [001] direction.

measure the anisotropy in the film resistivity along these axes).

Resistivity versus temperature measurements of *c*-axis oriented Sr_2RuO_4 films grown on $LaAlO_3$ indicated higher resistivities (20 mΩ cm at room temperature) and semiconducting behavior at low temperatures. A minimum in the resistivity occurred in the range 70–160 K, depending on growth conditions. The mechanism for the observed semiconducting behavior is unclear at the present time. We note that $SrRuO_3$ films grown from a stoichiometric $SrRuO_3$ target at low pressures (e.g., 20 mTorr) also exhibit higher resistivity and semiconducting transport behavior in contrast to $SrRuO_3$ films grown at higher pressure.[17] More detailed transport measurements down to lower temperatures in both zero and finite magnetic fields are currently underway.

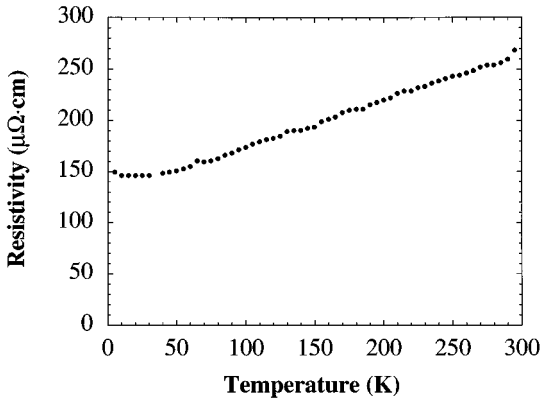

FIG. 3. Resistivity vs temperature for a 2200 Å thick *a*-axis oriented Sr_2RuO_4 film on a (100) $LaSrGaO_4$ substrate.

In conclusion, *a*-axis and *c*-axis oriented epitaxial films of Sr_2RuO_4 films have been prepared using PLD. X-ray diffraction scans showed that the films are single domain with excellent epitaxial in-plane alignment. Electrical transport measurements indicate that the *a*-axis oriented films are metallic while the *c*-axis oriented ones are semiconducting. Measurements to lower temperatures are needed to see if these films ultimately become superconducting. The successful preparation of epitaxial Sr_2RuO_4 films will likely provide new opportunities in studying superconducting and normal state properties of this interesting material. It may also help the effort of fabricating high quality oxide superconductor SNS junctions.

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