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## Growth of Epitaxial $(\text{Sr,Ba})_{n+1}\text{Ru}_n\text{O}_{3n+1}$ Films

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**Abstract.** We have grown epitaxial  $(\text{Sr,Ba})_{n+1}\text{Ru}_n\text{O}_{3n+1}$  films,  $n = 1, 2$ , and  $\infty$ , by pulsed laser deposition (PLD) and controlled their orientation by choosing appropriate substrates. The growth conditions yielding phase-pure films have been mapped out. Resistivity versus temperature measurements show that both  $a$ -axis and  $c$ -axis films of  $\text{Sr}_2\text{RuO}_4$  are metallic, but not superconducting. The latter is probably due to the presence of low-level impurities that are difficult to avoid given the target preparation process involved in growing these films by PLD.

### 1. Introduction

The electronic and magnetic properties of the  $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$  Ruddlesden-Popper homologous series are unusual. The crystal structures of these compounds are shown in Fig. 1. The  $n = 1$  member of this series,  $\text{Sr}_2\text{RuO}_4$ , is the only known superconducting *layered* perovskite that is free of copper ( $T_c = 1.35$  K in bulk single crystals) [1-3]. This compound is believed to exhibit an unconventional  $p$ -wave pairing symmetry [4]. Among all known perovskites, layered or not,  $\text{Sr}_2\text{RuO}_4$  is the only one which exhibits superconductivity without any

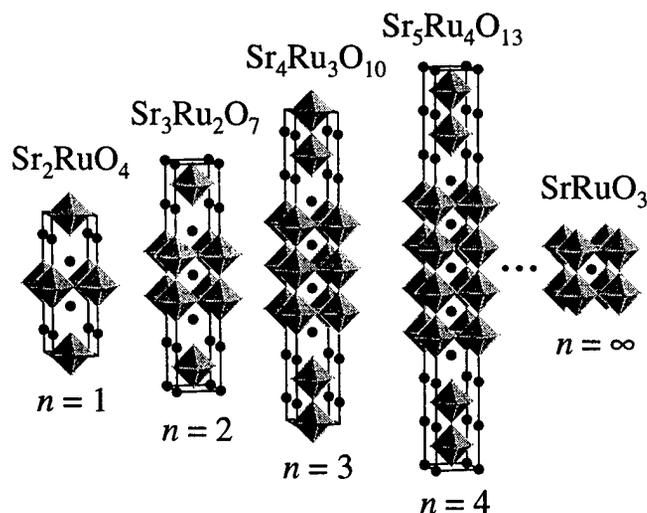


Figure 1. Crystal structures of the  $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$  Ruddlesden-Popper homologous series.

intentional doping. Superconductivity is only seen in very pure single crystals and not in polycrystalline samples. Even in single crystals, impurity levels of 400 ppm are sufficient to destroy superconductivity in this compound [3]. The neighboring ( $n = 2$ ) compound,  $\text{Sr}_3\text{Ru}_2\text{O}_7$ , is ferromagnetic ( $T_c = 104$  K) [5]. At the other end of the series ( $n = \infty$ ) lies the ferromagnetic perovskite  $\text{SrRuO}_3$  ( $T_c = 160$  K) [6].  $\text{SrRuO}_3$  and  $\text{Sr}_3\text{Ru}_2\text{O}_7$  are the only known ferromagnetic conductors among the  $4d$  transition metal oxides [5,6].

## 2. Experimental

$(\text{Sr,Ba})_{n+1}\text{Ru}_n\text{O}_{3n+1}$  films,  $n = 1, 2$ , and  $\infty$ , were grown by on-axis pulsed laser deposition (PLD) from targets with composition  $\text{Sr}_2\text{RuO}_4$  (for  $n = 1$  and  $n = 2$ ),  $\text{Sr}_{1.6}\text{Ba}_{0.4}\text{RuO}_4$  (for  $n = 1$ ), and  $\text{SrRuO}_3$  (for  $n = \infty$ ).  $c$ -axis oriented  $(\text{Sr,Ba})_2\text{RuO}_4$  ( $n = 1$ ) films were grown on (100)  $\text{LaAlO}_3$  [7], (110)  $\text{NdGaO}_3$ , and (100)  $\text{SrTiO}_3$  substrates.  $a$ -axis oriented  $(\text{Sr,Ba})_2\text{RuO}_4$  ( $n = 1$ ) films were grown on (100)  $\text{LaSrGaO}_4$  and (100)  $\text{LaSrAlO}_4$  substrates. The (100)  $\text{LaSrGaO}_4$  and (100)  $\text{LaSrAlO}_4$  substrates were grown by the Czochralski method as described elsewhere [8,9].  $c$ -axis oriented  $\text{Sr}_3\text{Ru}_2\text{O}_7$  ( $n = 2$ ) films were grown on (100)  $\text{SrTiO}_3$  substrates.  $\text{SrRuO}_3$  ( $n = \infty$ ) films were grown on (100)  $\text{SrTiO}_3$  and (100)  $\text{LaAlO}_3$  [7] substrates. Optimal substrate temperatures and oxygen growth pressures depend on the  $n$  of the desired phase, as described below. A radiative heater allowed the substrates to be heated to temperatures as high as  $1090$  °C [10]. PLD was performed using a KrF excimer laser ( $\lambda = 248$  nm), a laser fluence of  $2\text{-}3$   $\text{J}/\text{cm}^2$ , and a pulse rate of  $2\text{-}40$  Hz. The  $n = 1$  and  $n = 2$  samples were cooled in vacuum after deposition, while the  $n = \infty$  films were cooled in  $0.5\text{-}1$  atmosphere of oxygen. The films were characterized using a Picker 4-circle x-ray diffractometer, a Nanoscope III scanning tunneling microscope (STM), and 4-point resistance versus temperature measurements.

## 3. Results and discussion

### 3.1 Growth conditions for $n = 1, 2$ , and $\infty$ $(\text{Sr,Ba})_{n+1}\text{Ru}_n\text{O}_{3n+1}$ films

A wide range of growth conditions were investigated for growth from a target with composition  $\text{Sr}_2\text{RuO}_4$  onto (100)  $\text{LaAlO}_3$  substrates in a pure oxygen ambient. The dominant phase present in the samples, as identified by 4-circle x-ray diffraction, is shown in Fig. 2 as a function of the background oxygen pressure and substrate temperature during growth. Experimentally, it is observed that the  $n = 1$  phase,  $\text{Sr}_2\text{RuO}_4$ , forms at low oxygen pressure and high temperature.  $\text{SrRuO}_3$  is observed at high oxygen pressure and low temperature. The  $n = 2$  compound,  $\text{Sr}_3\text{Ru}_2\text{O}_7$ , is observed in a very narrow intermediate range between the  $n = 1$  and  $n = \infty$  regions. Subsequent experiments in which argon was introduced in addition to oxygen to vary the total pressure confirm that it is the oxygen partial pressure that determines the phase stability. Note that the oxygen background pressure shown in Fig. 2 is a processing parameter, not the true oxygen pressure at the substrate. Due to the PLD process, the oxygen pressure is not constant and is not solely molecular oxygen. Also shown in Fig. 2 are conditions reported in the literature for the preparation of bulk  $n = 1$ ,  $n = 2$ , and  $n = \infty$   $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$  phases in air [11,12]. These bulk preparation conditions follow the same trend seen for the thin films. Further, when bulk  $\text{SrRuO}_3$  ( $n = \infty$ ) is heated to high temperatures ( $800\text{-}900$  °C) in nitrogen, it decomposes into  $\text{Sr}_2\text{RuO}_4$  ( $n = 1$ ) plus ruthenium metal [13].

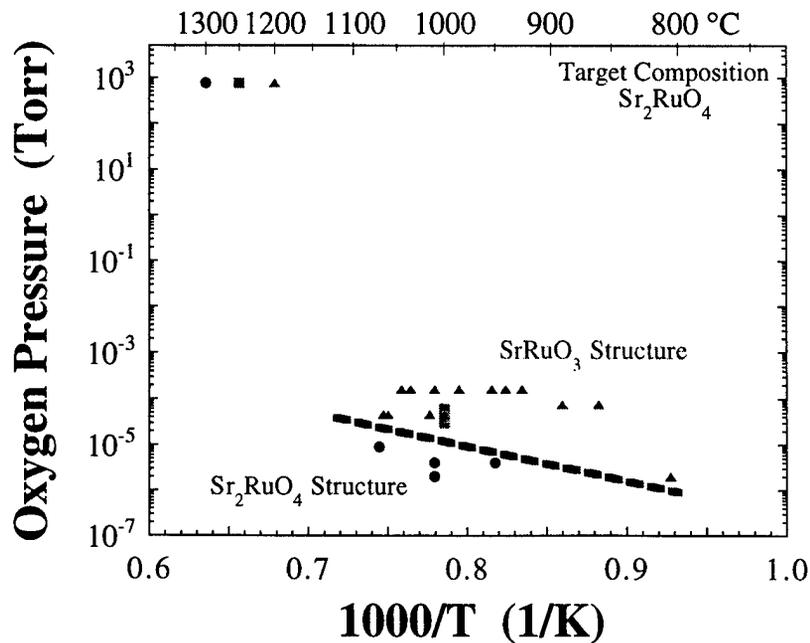


Figure 2. Pressure-temperature growth conditions yielding  $n = 1$  (circles),  $n = 2$  (squares), and  $n = \infty$  (triangles) as the major phase from a target of composition  $\text{Sr}_2\text{RuO}_4$  and PLD growth on a  $\text{LaAlO}_3(100)$  substrate.

All of this phase stability data for the  $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$  phases, both that presented in Fig. 2 and that observed in bulk, are in accord with the crystal chemistry principle that the presence of more electropositive species in a compound favors a higher oxidation state of a transition metal [13].  $\text{Sr}_2\text{RuO}_4$  has more electropositive strontium than  $\text{SrRuO}_3$ , and thus offers a stable environment for  $\text{Ru}^{4+}$  to lower oxygen partial pressures. The deviation of the extrapolated boundary dividing the  $n = 1$  and  $n = \infty$  phases in air versus by PLD is likely due in part to the presence of excited oxygen species in the PLD process. A similar study of the phases formed from targets with composition  $\text{Sr}_3\text{Ru}_2\text{O}_7$  and  $\text{SrRuO}_3$  as a function of pressure and temperature reveals regions of phase formation following the same trend as the data shown in Fig. 2, although the boundary lines are slightly shifted [14]. At sufficiently low background oxygen pressures, it is no longer possible to form the  $\text{Sr}_2\text{RuO}_4$  ( $n = 1$ ) phase by PLD. This boundary is not shown in Fig. 2.

### 3.2 Growth of $c$ -axis and $a$ -axis oriented $\text{Sr}_2\text{RuO}_4$ ( $n = 1$ ) films

Single-phase epitaxial  $\text{Sr}_2\text{RuO}_4$  films have been grown on the  $\{100\}$  plane of the perovskite subcell of common perovskite substrates:  $\text{LaAlO}_3$ ,  $\text{NdGaO}_3$ , and  $\text{SrTiO}_3$ . As expected from lattice matching considerations, the  $\text{Sr}_2\text{RuO}_4$  grows with its  $c$ -axis oriented normal to the  $\{100\}$  plane of the perovskite subcell of these substrates ( $c$ -axis oriented  $\text{Sr}_2\text{RuO}_4$  films) [15,16]. Single-domain  $a$ -axis  $\text{Sr}_2\text{RuO}_4$  films have been grown on  $(100)$   $\text{LaSrGaO}_4$  and  $(100)$   $\text{LaSrAlO}_4$  substrates [17]. These substrate materials are isostructural with  $\text{Sr}_2\text{RuO}_4$  and the growth of  $a$ -axis  $\text{Sr}_2\text{RuO}_4$  films is expected from lattice matching considerations.

Single-domain  $a$ -axis  $\text{Sr}_2\text{RuO}_4$  films allow the film resistivity in the in-plane ( $\rho_{ab}$ ) versus out of plane ( $\rho_c$ ) directions to be measured. This is shown in Fig. 3 for two different  $\text{Sr}_2\text{RuO}_4$  films grown on  $(100)$   $\text{LaSrAlO}_4$  substrates. Both films show similar features although they differ by about a factor of two in resistivity. The resistivity values at room temperature are comparable to those observed in single crystals [1,2,18]. However, although the films show a drop in resistivity with temperature (metallic behavior), the magnitude of the drop is much less than in single crystals. Resistivity measurements down to 0.3 K show

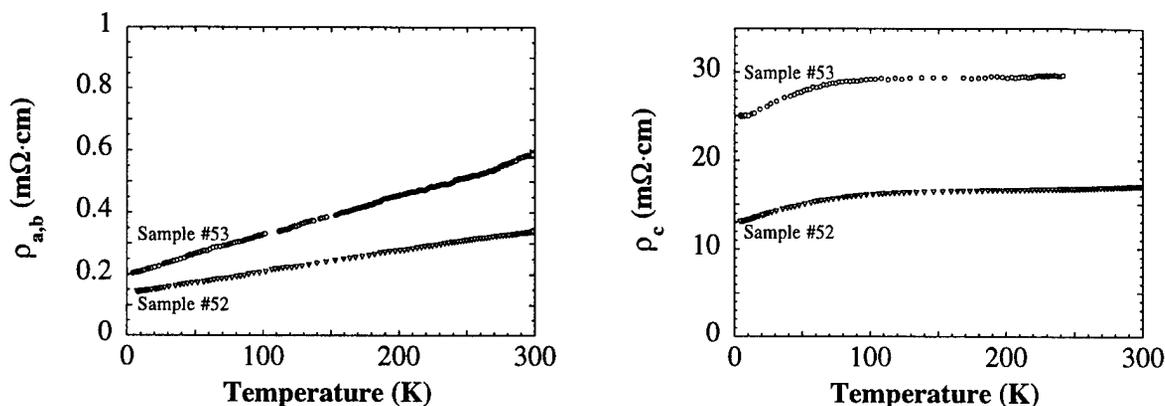


Figure 3. In-plane resistivity (left) and  $c$ -axis resistivity (right) of two  $n = 1$  ( $Sr_2RuO_4$ ) films grown on (100)  $LaSrAlO_4$ .

no evidence of superconductivity [19]. This is probably due to the presence of low-level impurities that are difficult to avoid with the ball-milling process used to make the PLD targets.

### 3.3 Growth of $c$ -axis oriented $Sr_3Ru_2O_7$ ( $n = 2$ ) films

The  $n = 2$   $Sr_{n+1}Ru_nO_{3n+1}$  phase,  $Sr_3Ru_2O_7$ , was grown by controlling the background pressure during growth to be between the  $n = 1$  and  $n = \infty$  regions (see Fig. 2). As is evident from the overlaid x-ray diffraction plots shown in Fig. 4, the structure forms in a very narrow region of background pressure. As the pressure is varied, the x-ray diffraction peaks shift and broaden, indicating the presence of syntactic intergrowths with other  $Sr_{n+1}Ru_nO_{3n+1}$  phases. Even under the optimal conditions that we have found to date, the peak widths of the  $n = 2$  phase are significantly more broad than those observed for the  $n = 1$  and  $n = \infty$  phases. The difficulty in synthesizing bulk samples of the  $n = 2$  phase free of intergrowths has been noted in the literature [20,21]. The  $\phi$ -scan of the 105 peak of a  $c$ -axis oriented  $Sr_3Ru_2O_7$  ( $n = 2$ ) film, see Fig. 5, clearly shows that the  $Sr_3Ru_2O_7$  film is epitaxial. The orientation

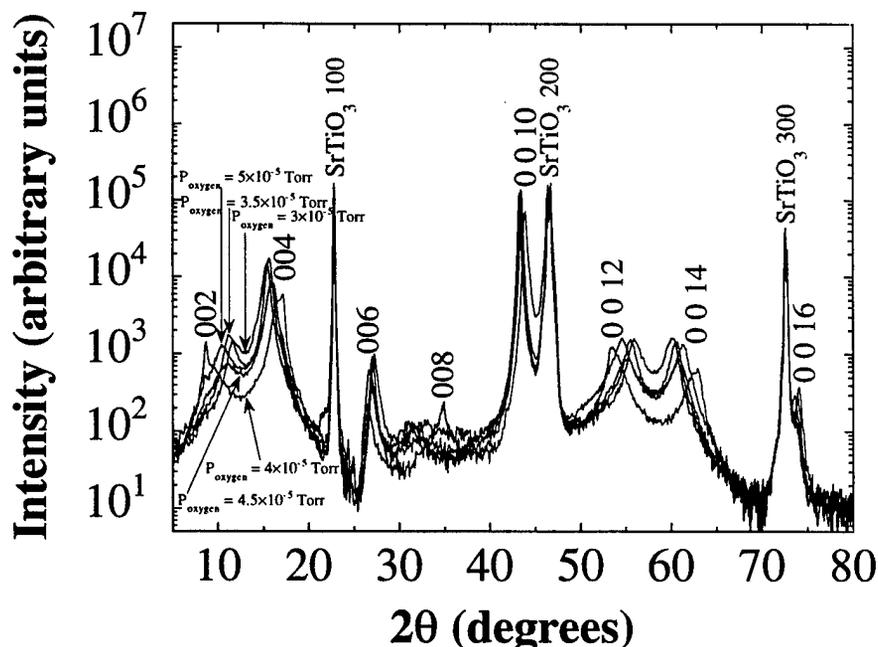


Figure 4.  $\theta$ - $2\theta$  x-ray diffraction scans for films grown from a stoichiometric  $Sr_2RuO_4$  target on (100)  $SrTiO_3$  substrates at substrate temperature of 1000 °C at oxygen background pressures ranging from  $3 \times 10^{-5}$  Torr to  $5 \times 10^{-5}$  Torr. The  $Sr_3Ru_2O_7$  ( $n = 2$ ) peaks are indexed.

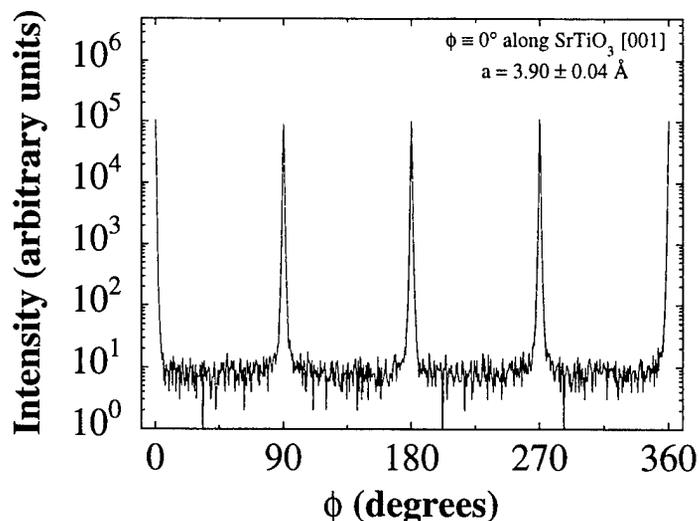


Figure 5. X-ray diffraction  $\phi$ -scan of the 105 peak of a  $c$ -axis  $\text{Sr}_3\text{Ru}_2\text{O}_7$  ( $n = 2$ ) film grown from a stoichiometric  $\text{Sr}_2\text{RuO}_4$  target on (100)  $\text{SrTiO}_3$  at a substrate temperature of 1000 °C and an oxygen background pressure of  $4 \times 10^{-5}$  Torr.

relationship is (001)  $\text{Sr}_3\text{Ru}_2\text{O}_7 \parallel$  (100)  $\text{SrTiO}_3$  and  $[100] \text{Sr}_3\text{Ru}_2\text{O}_7 \parallel [001] \text{SrTiO}_3$ .

The surface of a  $\text{Sr}_3\text{Ru}_2\text{O}_7$  ( $n = 2$ ) film grown on a (100)  $\text{SrTiO}_3$  substrate is shown in Fig. 6. The surface steps are integral multiples of a half-unit cell (one formula unit). The surface morphology revealed by STM is highly dependent on the misorientation of the substrate. The image shown is for a film grown on a substrate misoriented by  $0.5^\circ$ . The surface is stepped in the direction of the misorientation, indicating that the growth occurs by step-propagation. The  $\text{Sr}_3\text{Ru}_2\text{O}_7$  is faceted in-plane along  $\langle 110 \rangle$ -type directions.

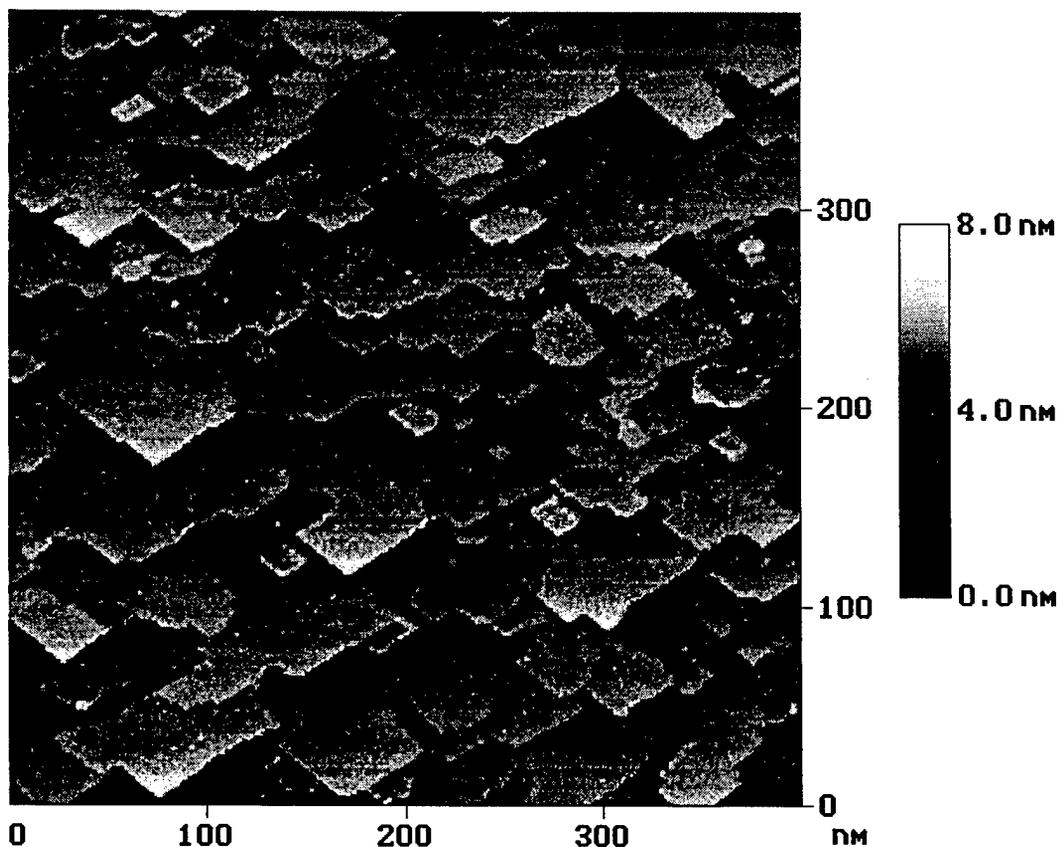


Figure 6. STM image of the surface of a  $c$ -axis oriented  $\text{Sr}_3\text{Ru}_2\text{O}_7$  ( $n = 2$ ) film grown on (100)  $\text{SrTiO}_3$ . The image edges are parallel to the  $\langle 100 \rangle$  directions of the  $\text{SrTiO}_3$  substrate and the  $\text{Sr}_3\text{Ru}_2\text{O}_7$  film.

#### 4. Conclusions

Epitaxial  $(\text{Sr,Ba})_{n+1}\text{Ru}_n\text{O}_{3n+1}$  films,  $n = 1, 2,$  and  $\infty$ , have been grown by pulsed laser deposition (PLD). The growth conditions yielding phase-pure films have been mapped out. The oxygen pressure / substrate temperature region in which each of these phases form is consistent with the crystal-chemical principle that structures containing more electropositive species (lower  $n$  phases) are stable to lower pressures. The film orientation was controlled by choosing appropriate substrates. Single-domain  $c$ -axis  $\text{Sr}_2\text{RuO}_4$  films ( $n = 1$ ) were grown on (100)  $\text{LaAlO}_3$ , (110)  $\text{NdGaO}_3$ , and (100)  $\text{SrTiO}_3$  substrates. Single-domain  $a$ -axis  $\text{Sr}_2\text{RuO}_4$  epitaxial films were grown on (100)  $\text{LaSrGaO}_4$  and (100)  $\text{LaSrAlO}_4$  substrates. Resistivity versus temperature measurements show metallic conductivity for both  $a$ -axis and  $c$ -axis  $\text{Sr}_2\text{RuO}_4$  films, but no superconductivity. The absence of superconductivity is probably due to the presence of low-level impurities that are difficult to avoid given the target preparation process involved in growing these films by PLD.

#### 5. Acknowledgements

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#### 6. References

- [1] Maeno Y, Hashimoto H, Yoshida K, Nishizaki S, Fujita T, Bednorz J G, and Lichtenberg F 1994 *Nature* **372** 532-534
- [2] Maeno Y and Yoshida K 1996 *Czech. J. Phys.* **46** 3097-3104
- [3] Maeno Y 1997 presented at the 1997 March Meeting of the American Physical Society in Kansas City, MO (unpublished)
- [4] Rice T M and Sigrist M 1995 *J. Phys.: Condens. Matter* **7** L643-L648
- [5] Cao G, McCall S, and Crow J E 1997 *Phys. Rev B* **55** R672-R675
- [6] Callaghan A, Moeller C W, and Ward R 1966 *Inorg. Chem.* **5** 1572-1576
- [7] Pseudocubic indices. At the film growth temperature  $\text{LaAlO}_3$  is cubic. However, on cooling to room temperature it transforms to rhombohedral. The substrate orientation is (012) for the rhombohedral axes.
- [8] Dabkowski A, Dabkowska H A, and Greedan J E 1993 *J. Cryst. Growth* **132** 205-208
- [9] Gloubokov A, Jablonski R, Ryba-Romanowski W, Sass J, Pajaczkowska A, Uecker R., and Reiche P 1995 *J. Cryst. Growth* **147** 123-129
- [10] Clark J C, Maria J P, Hubbard K J, and Schlom D G, to be published in *Rev. Sci. Instrum.*
- [11] Itoh M, Shikano M, and Shimura T 1995 *Phys. Rev. B* **51** 16432-16435
- [12] Gardner J S, Balakrishnan G, and Paul D McK 1995 *Physica C* **252** 303-307
- [13] Cava R J 1997 personal communication
- [14] Madhavan S and Schlom D G unpublished
- [15] Madhavan S, Schlom D G, Dabkowski A, Dabkowska H A, and Liu Y 1996 *Appl. Phys. Lett.* **68** 559-561
- [16] Madhavan S, Liu Y, Schlom D G, Dabkowski A, Dabkowska H A, Suzuki Y, Takeuchi I, Trajanovic Z, and Sharma R P 1997 *IEEE Trans. Appl. Supercond.* **7** 2063-2066.
- [17] Schlom D G, Merritt B A, Madhavan S, Liu Y, Hawley M E, Brown G W, Dabkowski A, Dabkowska H A, Uecker R, and Reiche P 1997 in: *Epitaxial Oxide Thin Films III* edited by Schlom D G, Eom C B, Hawley M E, Foster C M, and Speck J S, Vol. 474 (Pittsburgh: Materials Research Society)
- [18] Lichtenberg F, Catana A, Mannhart J, and Schlom D G 1992 *Appl. Phys. Lett.* **60** 1138-1140
- [19] Liu Y, Mitchell J A, Madhavan S, Schlom D G, Dabkowski A, and Dabkowska H A 1996 *Czech. J. Phys.* **46** 1113-1114.
- [20] Williams T, Lichtenberg F, Reller A, and Bednorz G 1991 *Mat. Res. Bull.* **26** 763-770
- [21] Cava R J, Zandbergen H W, Krajewski J J, Peck W F Jr., Batlogg B, Carter S, Fleming R M, Zhou O, and Rupp L W Jr 1995 *J. Solid State Chem.* **116** 141-145

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