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Growth of epitaxial (Sr, Ba)_{n+1}Ru_nO_{3n+1} films

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Abstract. We have grown epitaxial (Sr, Ba)_{n+1}Ru_nO_{3n+1} films, $n = 1, 2$ and ∞ , 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 Sr₂RuO₄ 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 Sr_{n+1}Ru_nO_{3n+1} Ruddlesden–Popper homologous series are unusual. The crystal structures of these compounds are shown in figure 1. The $n = 1$ member of this series, Sr₂RuO₄, 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, Sr₂RuO₄ is the only one which exhibits superconductivity without any 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 neighbouring ($n = 2$) compound, Sr₃Ru₂O₇, is ferromagnetic ($T_c = 104$ K) [5]. At the other end of the series ($n = \infty$) lies the ferromagnetic perovskite SrRuO₃ ($T_c = 160$ K) [6]. SrRuO₃ and Sr₃Ru₂O₇ are the only known ferromagnetic conductors among the 4d transition metal oxides [5, 6].

2. Experimental details

(Sr, Ba)_{n+1}Ru_nO_{3n+1} films, $n = 1, 2$ and ∞ , were grown by on-axis pulsed laser deposition (PLD) from targets with composition Sr₂RuO₄ (for $n = 1$ and $n = 2$), Sr_{1.6}Ba_{0.4}RuO₄ (for $n = 1$) and SrRuO₃ (for $n = \infty$). c -axis oriented (Sr, Ba)₂RuO₄ ($n = 1$) films were grown

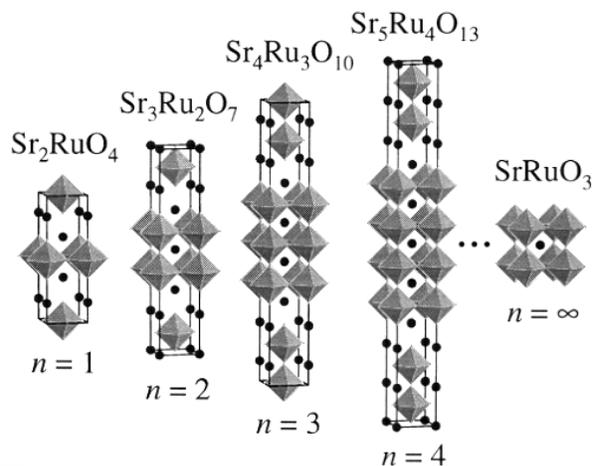


Figure 1. Crystal structures of the Sr_{n+1}Ru_nO_{3n+1} Ruddlesden–Popper homologous series.

on (100) LaAlO₃ [7], (110) NdGaO₃ and (100) SrTiO₃ substrates. a -axis oriented (Sr, Ba)₂RuO₄ ($n = 1$) films were grown on (100) LaSrGaO₄ and (100) LaSrAlO₄ substrates. The (100) LaSrGaO₄ and (100) LaSrAlO₄ substrates were grown by the Czochralski method as described elsewhere [8, 9]. c -axis oriented Sr₃Ru₂O₇ ($n = 2$) films were grown on (100) SrTiO₃ substrates. SrRuO₃ ($n = \infty$) films were grown on (100) SrTiO₃ and (100) LaAlO₃ [7] substrates. Optimal substrate temperatures and oxygen growth pressures depend on the n of the desired

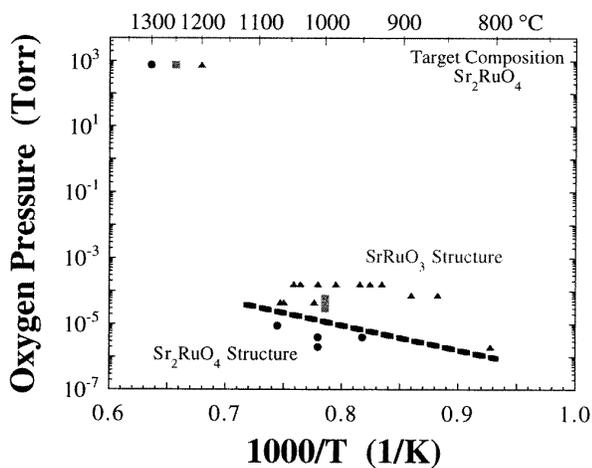


Figure 2. Pressure–temperature growth conditions yielding $n = 1$ (circles), $n = 2$ (squares) and $n = \infty$ (triangles) as the major phase from a target of composition Sr_2RuO_4 and PLD growth on an $\text{LaAlO}_3(100)$ substrate.

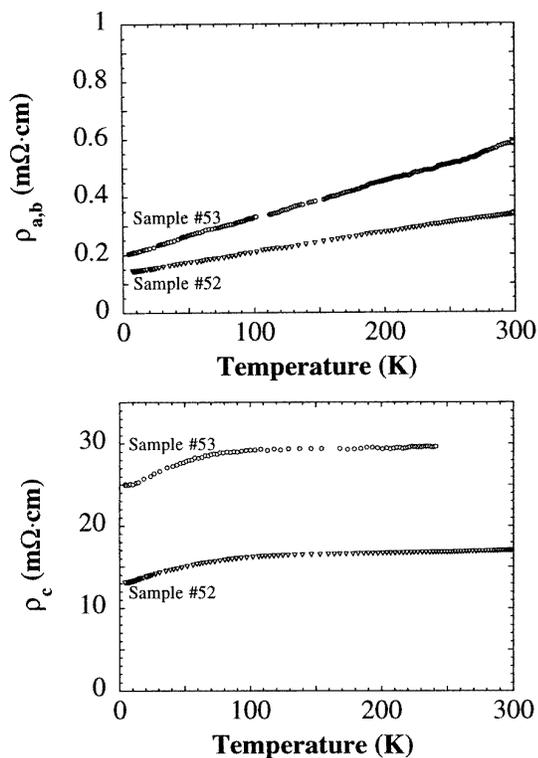


Figure 3. In-plane resistivity (top) and c -axis resistivity (bottom) of two $n = 1$ (Sr_2RuO_4) films grown on (100) LaSrAlO_4 .

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 $2\text{--}3$ J 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 four-circle x-ray diffractometer, a Nanoscope III scanning

tunnelling microscope (STM), and four-point resistance versus temperature measurements.

3. Results and discussion

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

A wide range of growth conditions were investigated for growth from a target with composition Sr_2RuO_4 onto (100) LaAlO_3 substrates in a pure oxygen ambient. The dominant phase present in the samples, as identified by four-circle x-ray diffraction, is shown in figure 2 as a function of the background oxygen pressure and substrate temperature during growth. Experimentally, it is observed that the $n = 1$ phase, Sr_2RuO_4 , forms at low oxygen pressure and high temperature. 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 figure 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 figure 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 SrRuO_3 ($n = \infty$) is heated to high temperatures ($800\text{--}900^\circ\text{C}$) in nitrogen, it decomposes into Sr_2RuO_4 ($n = 1$) plus ruthenium metal [13].

All of these phase stability data for the $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ phases, both those presented in figure 2 and those observed in bulk, are in accord with the crystal chemistry principle that the presence of more electropositive species in a compound favours a higher oxidation state of a transition metal [13]. Sr_2RuO_4 has more electropositive strontium than SrRuO_3 , and thus offers a stable environment for 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 SrRuO_3 as a function of pressure and temperature reveals regions of phase formation following the same trend as the data shown in figure 2, although the boundary lines are slightly shifted [14]. At sufficiently low background oxygen pressures, it is no longer possible to form the Sr_2RuO_4 ($n = 1$) phase by PLD. This boundary is not shown in figure 2.

3.2. Growth of c -axis and a -axis oriented Sr_2RuO_4 ($n = 1$) films

Single-phase epitaxial Sr_2RuO_4 films have been grown on the $\{100\}$ plane of the perovskite subcell of common perovskite substrates: LaAlO_3 , NdGaO_3 and SrTiO_3 .

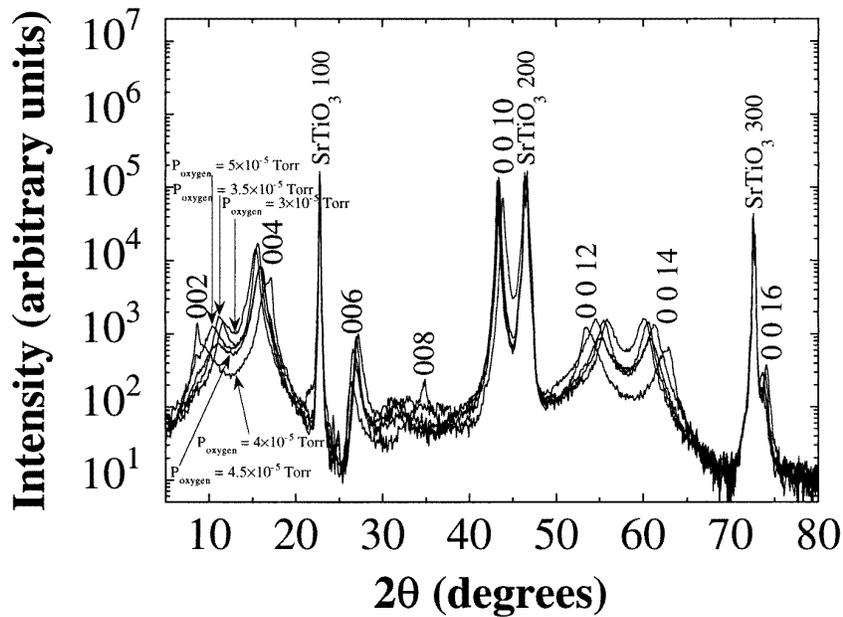


Figure 4. θ - 2θ x-ray diffraction scans for films grown from a stoichiometric Sr_2RuO_4 target on (100) SrTiO_3 substrates at substrate temperature of 1000°C at oxygen background pressures ranging from 3×10^{-5} Torr to 5×10^{-5} Torr. The $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($n = 2$) peaks are indexed.

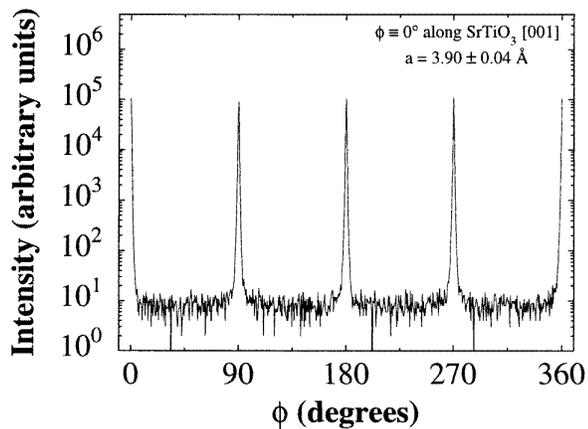


Figure 5. X-ray diffraction ϕ -scan of the 105 peak of a c -axis $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($n = 2$) film grown from a stoichiometric Sr_2RuO_4 target on (100) SrTiO_3 at a substrate temperature of 1000°C and an oxygen background pressure of 4×10^{-5} Torr.

As expected from lattice matching considerations, the Sr_2RuO_4 grows with its c -axis oriented normal to the $\{100\}$ plane of the perovskite subcell of these substrates (c -axis oriented Sr_2RuO_4 films) [15, 16]. Single-domain a -axis Sr_2RuO_4 films have been grown on (100) LaSrGaO_4 and (100) LaSrAlO_4 substrates [17]. These substrate materials are isostructural with Sr_2RuO_4 and the growth of a -axis Sr_2RuO_4 films is expected from lattice matching considerations.

Single-domain a -axis Sr_2RuO_4 films allow the film resistivity in the in-plane ($\rho_{a,b}$) versus out-of-plane (ρ_c) directions to be measured. This is shown in figure 3 for two different Sr_2RuO_4 films grown on (100) 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 behaviour), the magnitude of the drop is much less than in single crystals. Resistivity measurements down to 0.3 K show 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 $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($n = 2$) films

The $n = 2$ $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ phase, $\text{Sr}_3\text{Ru}_2\text{O}_7$, was grown by controlling the background pressure during growth to be between the $n = 1$ and $n = \infty$ regions (see figure 2). As is evident from the overlaid x-ray diffraction plots shown in figure 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 $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ 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 ϕ -scan of the 105 peak of a c -axis oriented $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($n = 2$) film, see figure 5, clearly shows that the $\text{Sr}_3\text{Ru}_2\text{O}_7$ film is epitaxial. The orientation 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) SrTiO_3 substrate is shown in figure 6. The surface steps are integral multiples of a half-unit cell (one formula

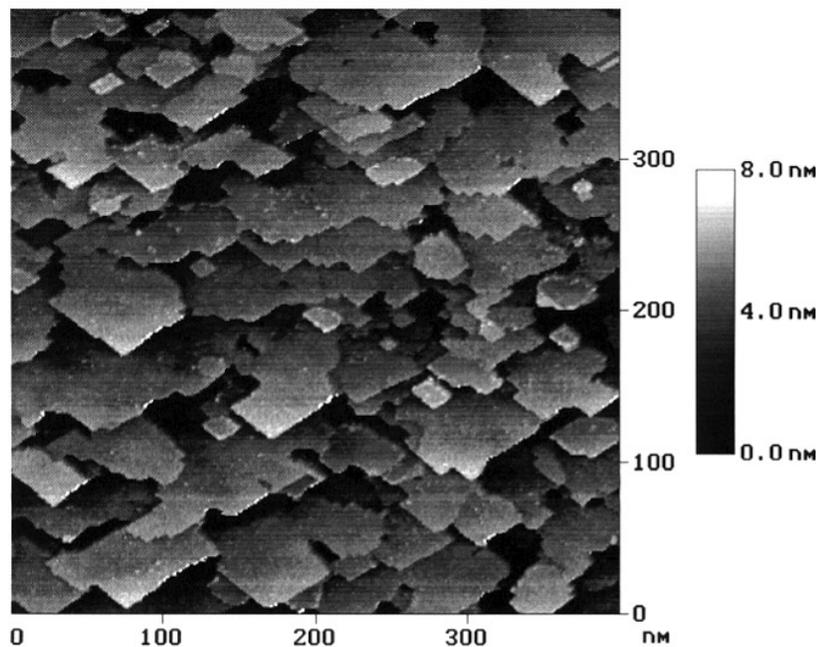


Figure 6. STM image of the surface of a c -axis oriented $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($n = 2$) film grown on (100) SrTiO_3 . The image edges are parallel to the $\langle 100 \rangle$ directions of the SrTiO_3 substrate and the $\text{Sr}_3\text{Ru}_2\text{O}_7$ film.

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° . 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.

4. Conclusions

Epitaxial $(\text{Sr}, \text{Ba})_{n+1}\text{Ru}_n\text{O}_{3n+1}$ films, $n = 1, 2$ and ∞ , 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 Sr_2RuO_4 films ($n = 1$) were grown on (100) LaAlO_3 , (110) NdGaO_3 and (100) SrTiO_3 substrates. Single-domain a -axis Sr_2RuO_4 epitaxial films were grown on (100) LaSrGaO_4 and (100) LaSrAlO_4 substrates. Resistivity versus temperature measurements show metallic conductivity for both a -axis and c -axis Sr_2RuO_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.

Acknowledgment

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References

- [1] Maeno Y, Hashimoto H, Yoshida K, Nishizaki S, Fujita T, Bednorz J G and Lichtenberg F 1994 *Nature* **372** 532–4
- [2] Maeno Y and Yoshida K 1996 *Czech. J. Phys.* **46** 3097–104
- [3] Maeno Y 1997 *1997 March Meeting Am. Phys. Soc.* (Kansas City, MO)
- [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** 1572–6
- [7] Pseudocubic indices. At the film growth temperature 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. Crystal Growth* **132** 205–8
- [9] Gloubokov A, Jablonski R, Ryba-Romanowski W, Sass J, Pajaczowska A, Uecker R and Reiche P 1995 *J. Crystal Growth* **147** 123–9
- [10] Clark J C, Maria J P, Hubbard K J and Schlom D G 1997 *Rev. Sci. Instrum.* **68** 2538–41
- [11] Itoh M, Shikano M and Shimura T 1995 *Phys. Rev. B* **51** 16432–5
- [12] Gardner J S, Balakrishnan G and Paul D McK 1995 *Physica C* **252** 303–7
- [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** 559–61
- [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** 2063–6
- [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 *Epitaxial Oxide Thin Films III* vol 474, ed D G Schlom *et al* (Pittsburgh, PA: Materials Research Society) pp 85–90

- [18] Lichtenberg F, Catana A, Mannhart J and Schlom D G 1992 *Appl. Phys. Lett.* **60** 1138–40
- [19] Liu Y, Mitchell J A, Madhavan S, Schlom D G, Dabkowski A and Dabkowska H A 1996 *Czech. J. Phys.* **46** 1113–14
- [20] Williams T, Lichtenberg F, Reller A and Bednorz G 1991 *Mater. Res. Bull.* **26** 763–70
- [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** 141–5