

Epitaxial Growth and Characterization of $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ Ruddlesden-Popper Series

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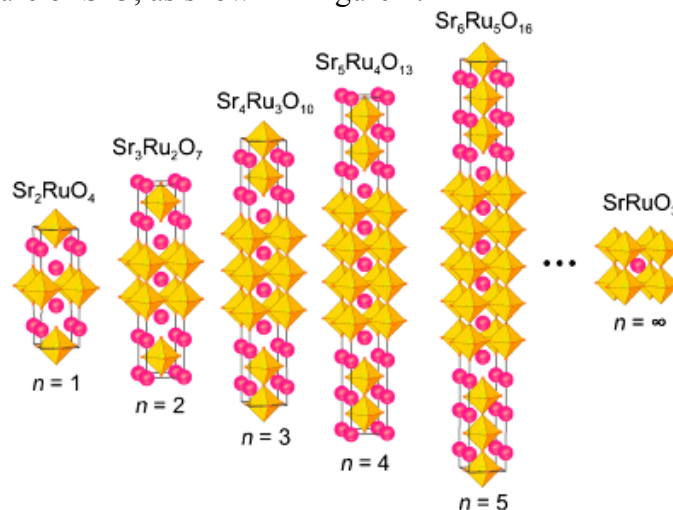
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Abstract

Although Sr_2RuO_4 and SrRuO_3 have been thoroughly investigated throughout the years, the Ruddlesden-Popper (RP) phases ($\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$) in between these end members still remain elusive.^{1,2,3} This is in part due to the volatility of growing thin films with ruthenium, but also due to the limited thermodynamic knowledge as to what narrow conditions these higher members of this series may grow in.^{4,5} Even so, when previous films have been grown with a shuttered layer-by-layer method, ruthenium vacancies have played a substantial role in limiting the transport properties.¹ This calls for growing in adsorption controlled flux, where supplying excess of the volatile species can help reduce defects and improve the film quality. The aim of this work is to use Sr_2RuO_4 and SrRuO_3 as building blocks for growing the higher n-member RP phases in an adsorption control regime to minimize the defects. We have shown that growing heterostructures of Sr_2RuO_4 and SrRuO_3 in non-adsorption control conditions leads to intergrowths in the RP phases, and that separately, quality of both the end members improve when grown in adsorption control. This work is ongoing, and the challenge ahead is making these heterostructures in adsorption control conditions.

Introduction

The Ruddlesden-Popper or RP phase of Strontium Ruthenate ($\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$, $n = 1, 2, 3, \dots$) refers to a structure where “n” is the number of perovskite layers sandwiched between a double rocksalt structure of SrO, as shown in Figure 1.^{1,2}

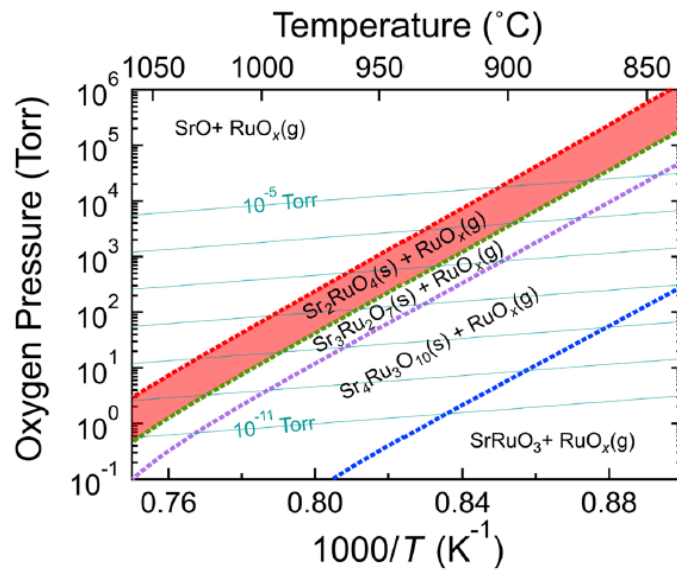


^{1,2}**Figure 1:** Ruddlesden-Popper phases $n = 1-5, \infty$

Just by increasing n or the amount of perovskite layers along the series, magnetization increases and the members of the series are found to shift from being paramagnets to ferromagnets. Also, interesting properties like metamagnetism and possible realization of magnetic monopoles are predicted for the intermediate members.¹

In the past, only one notable paper has shown the growth of first five members of this series using Molecular Beam Epitaxy (MBE) by a shuttered layer-by-layer growth where the flux is the same stoichiometric ratio of Ru/Sr as what the specific layer would normally want.¹ The crystallinity of the films grown by this method is good however, the problem with this method is that ruthenium is so volatile that Ru vacancies occur during the growth and reduce the transport properties of the films; due to increased scattering. The solution to this problem is to grow in adsorption controlled growth mode, where films are grown in excess Ru flux and Sr flux controls the deposition rate. The excess Ru flux reduces the amount of vacancies and can even help uncover properties in these films that are normally suppressed by impurities (i.e. superconductivity in Sr_2RuO_4).

Thermodynamics of MBE, or TOMBE diagrams are an important tool to guide the growth of strontium ruthenate RP phases as for a given amount of excess Ru, the growth of each phase is a function of oxygen pressure and growth temperature, as shown below in Figure 2.^{4,5}



^{4,5}Figure 2: Thermodynamics of Molecular Beam Epitaxy (TOMBE)

For the intermediate RP phases there is not sufficient thermodynamic data to know the growth conditions and so a new method is required to synthesize the intermediate members. This method could be to grow the intermediate phases by mimicking their crystal structure by using the rocksalt layer from the Sr_2RuO_4 phase and the perovskite layer from the SrRuO_3 . In order to do this, there must be a precise shift during the same growth from the Sr_2RuO_4 and SrRuO_3 phases. If this is possible it relieves the need for thermodynamic data in these more complex RP phases and relies on the optimized growth of Sr_2RuO_4 and SrRuO_3 . In our previous work, we realized, by changing from one ratio of Ru/Sr to another and keeping the oxygen pressure and the growth temperature constant, the phase of strontium ruthenate shifts as well. Changing the phase by just changing the Ru/Sr ratio has speed advantages and it also helps increase the Sr_2RuO_4

thermodynamic growth window. So in this project, we show an attempt to synthesize intermediate n-members of the strontium ruthenate RP series by using the two end members through adsorption controlled MBE flux growths by just varying the Ru/Sr flux ratios.

Experimental

Molecular Beam Epitaxy was used to grow these films with a conventional effusion cell for Sr source and an electron-beam evaporator for heating the ruthenium source. Two strontium sources were employed to quickly switch between the Sr_2RuO_4 and SrRuO_3 phases by varying the ratio of Ru/Sr supplied to the sample. A SiC substrate heater was used to heat the sample and a thermocouple along with a pyrometer was used for an accurate substrate temperature control.

SrTiO_3 (001) (3.90 \AA) substrates were used due to their relative lattice match to Sr_2RuO_4 (3.86 \AA) and SrRuO_3 (3.94 \AA). X-Ray Diffraction $2\theta/\omega$ scans were used to characterize the phase and crystallinity of the films. If phase purity and narrow peaks were observed, low temperature 4-point probe measurements (dipper measurements) were used to attain a Residual Resistance Ratio (RRR) which helps give a quick idea of the defects present in the films. This was done by taking a ratio of room temperature 4-point resistance and low temperature 4-point resistance (4.3 K). For a general reference a film with a RRR greater than ~ 30 is a quality film.

Results and Discussion

The first thing that was investigated was to see if heterostructures of the Sr_2RuO_4 and SrRuO_3 phases could be used to realize the higher n-members of the series. A film for $n=5$ was attempted by alternating the Sr_2RuO_4 (1 layer) and SrRuO_3 (5 layers) in a stoichiometric flux controlled manner. It was found that indeed heterostructures of both phases could be used to get $n=5$ phase in a non-adsorption control regime, shown below in Figure 3. But the film was not phase pure and had $n=4$ impurities.

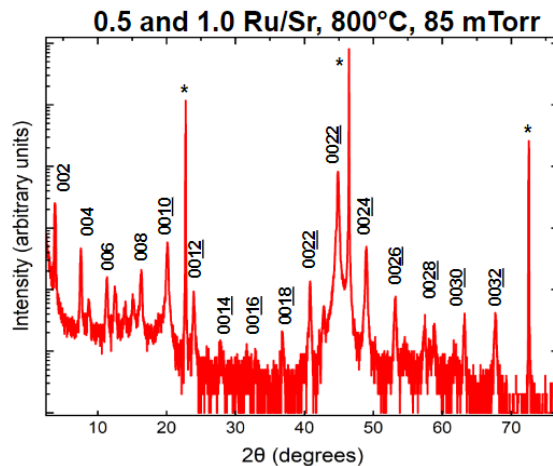


Figure 3: 22 repeats heterostructure of one Sr_2RuO_4 layer, five SrRuO_3 layers, and another Sr_2RuO_4 layer, growing the $n = 5 \text{ Sr}_6\text{Ru}_5\text{O}_{16}$ RP phase, indexed and compared to literature¹

This meant the next step was to find the ideal conditions where we can grow both Sr_2RuO_4 and SrRuO_3 in adsorption controlled manner. Growing too hot ($>900^\circ\text{C}$) favors Sr_2RuO_4 growth, but degrades SrRuO_3 as it favors growing at lower temperatures ($<750^\circ\text{C}$). It is difficult to say exactly what same temperature and oxygen pressure are the best to grow both these RP phases in adsorption control, however it seems that around 880°C at 85 mTorr (Baratron pressure) is a good middle ground between the two phases. And keeping these two parameters constant, the Ru/Sr ratio can be varied to grow Sr_2RuO_4 and SrRuO_3 . For our better samples we found going from ratio 0.7 to 2.0 seemed to give quality films of both phases as shown below in Figure 4.

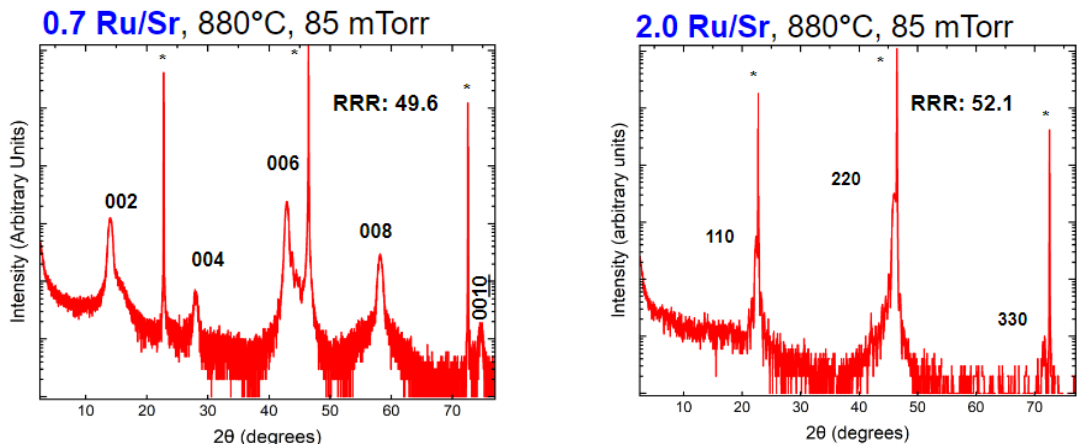


Figure 4: Sr_2RuO_4 shown on the left, SrRuO_3 shown on the right, both with RRR values above 30, which correlates to the reduction of scattering due to excess ruthenium

Later the substrate LSAT(001) was used to improve the Sr_2RuO_4 quality at these lower than ideal temperatures, since LSAT(001) is better lattice matched with Sr_2RuO_4 . As shown in Figure 5 this does increase Sr_2RuO_4 quality but work is still required for growing SrRuO_3 on LSAT(001) substrates at these higher temperatures:

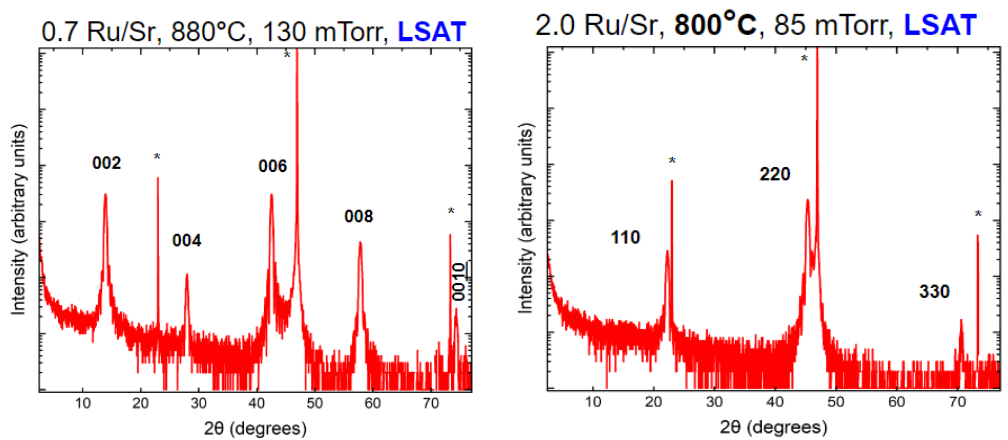


Figure 5: Sr_2RuO_4 shown on the left and quality improves, SrRuO_3 shown on the right however quality films the film growth was at 800°C instead of 880°C which requires further work

Conclusions

It is shown that the heterostructures of Sr_2RuO_4 and SrRuO_3 can be used in non-adsorption control conditions to realize higher n-members of the strontium ruthenate RP series. Since this can be used as a technique the next step is to find ideal growth conditions for the Sr_2RuO_4 and SrRuO_3 in adsorption controlled growth regime, where both grow at the same temperature and oxygen pressure and only the Ru/Sr ratio is varied. Samples around 880°C and 85 mTorr show promising results, however putting them together and moving into heterostructures maintaining consistent ruthenium flux during the growth brings its own challenges and further work needs to be done to achieve the goal.

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References

- ¹W. Tian, et al. Applied Physics Letters **90**, 022507 (2007)
- ²D. Schlom, et al. Journal of the American Ceramic Society, **91**; [8] 2429–2454 (2008)
- ³Y. Maeno, et al. Physics Today **54** (1), 42–47 (2001)
- ⁴H. Nair, et al. APL Materials **6**, 046101 (2018)
- ⁵H. Nair, et al. APL Materials **6**, 101108 (2018)