

Deposition conditions and Crystallinity of Pyrochlore Iridates Thin Films

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1. Introduction

Strongly-correlated electron systems have been among the most important fields of research in modern condensed matter physics ever since the Mott insulators were discovered. Besides electron correlations, spin-orbit coupling (SOC), which is especially notable in $5d$ systems, is the key to bringing about nontrivial physics, such as topological materials. It has recently been realized that electron correlations, although weaker than in $3d$ systems, still play an important role in $5d$ transition metal oxides, making this class of materials advantageous for studying cooperative effects of electron correlations in the presence of strong SOC. As a high-profile example, pyrochlore iridates of the $R_2\text{Ir}_2\text{O}_7$ family, where R is a rare-earth element such as Y, Eu, Sm, Nd, or Pr, have been intensively studied. Pyrochlores are also famous for the 3-dimensional geometric frustration.

In particular, $\text{Pr}_2\text{Ir}_2\text{O}_7$ is the only member of the iridate pyrochlore series that remains metallic down to mK temperatures because the Pr ion has the largest ionic size among the rare earths that can be used to construct bulk pyrochlores. In this sense, $\text{La}_2\text{Ir}_2\text{O}_7$, due to the even larger ionic radius of La, is expected to be more exotic. Nonetheless, the large ionic radius makes $\text{La}_2\text{Ir}_2\text{O}_7$ unstable in bulk. Therefore, the only possible way to study this material is to synthesize in thin film form.

The electronic structure of $\text{Pr}_2\text{Ir}_2\text{O}_7$ is quite unusual. The bulk crystal shows quadratic band touching close to the Fermi level at the Γ point, which can be detected by the angle-resolved photoemission spectroscopy (ARPES). It is thus a Luttinger semimetal and a parent phase for diverse topological states that may appear by breaking different symmetries. For instance, a topological insulator phase can be induced by applying strain or Weyl nodes may appear if the time-reversal symmetry is broken by applying a magnetic field.

To observe significant electronic structure changes upon structural symmetry reduction, elastic strains on the order of 1% are required. This level of crystal deformation cannot be achieved in bulk crystal without fracturing. Moreover, an ARPES measurement is imperative for detecting the changes in the band structure change caused by lattice deformation. A high-quality stoichiometric crystal surface is therefore required. Thin films can fulfill the strain and stoichiometry requirements, but the only examples of iridate pyrochlore films so far have been synthesized by solid-phase epitaxy, which does not produce a stoichiometric surface and offers limited control over epitaxial strain.

2. Experiments

Iridate thin films were grown by Pulsed Laser Deposition (PLD) using a 248 nm KrF laser. Yttria-stabilized zirconia (YSZ) was selected as the substrate material because the YSZ lattice constant of 10.278 Å is only about 1.1% smaller than that of $\text{Pr}_2\text{Ir}_2\text{O}_7$ (10.394 Å). A commercial praseodymium oxide target and self-made mixed-oxide (Pr or La, Ir)Ox targets were made by Spark Plasma Sintering (SPS) in Kimura laboratory. The effect of the film growth temperature (700°C – 1000°C) and background pressure (0.01 mTorr – 50 mTorr) on the crystal structure was investigated by growing a set of samples and measuring symmetric out-of-plane X-ray diffraction (XRD) patterns with a laboratory Cu K_α x-ray source. The surface morphology of the films was studied by atomic force microscopy (AFM). Furthermore, instead of a pure oxygen gas environment, various oxygen-inert gas mixtures were used to control the kinetic energy of the atoms in the ablation plasma plume.

3. Results and Discussion

By annealing the YSZ substrates in air at 1250°C for 2 hours, a high-quality step-terrace surface was formed as shown in Figure 1.

Figure 2 shows the phase change with the increase of oxygen pressure during film growth at 1000°C. The dashed line in Figure 2 indicates the expected pyrochlore phase position on the left-hand side of the YSZ substrate peak. The peaks at lower angles belong to different praseodymium oxides. Higher substrate temperatures and low oxygen pressures are appropriate for the formation of the pyrochlore phase, but may also result in the generation of a segregated iridium metal phase. Several unknown peaks appear in the XRD result, which are considered to be various nonstoichiometric praseodymium oxides, the relative contributions of which depend on the oxygen pressure, for instance, the PrO_x peak near the 25° position.

For better understanding of these phases, a series of films were grown from a pure Pr_2O_3 target as shown in Fig. 3, which precisely match the several unknown phases and phase change in Figure 2. Moreover, it appears that the valence of praseodymium can easily change with the oxygen pressure, which may be a key factor in the formation of the pyrochlore phase.

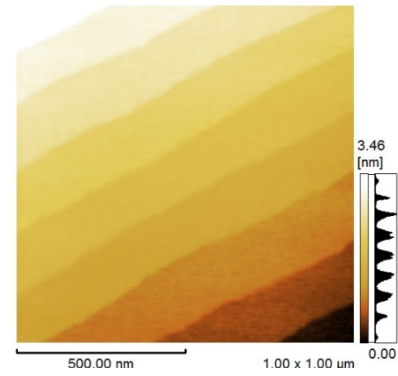


Fig. 1 YSZ substrate after annealing

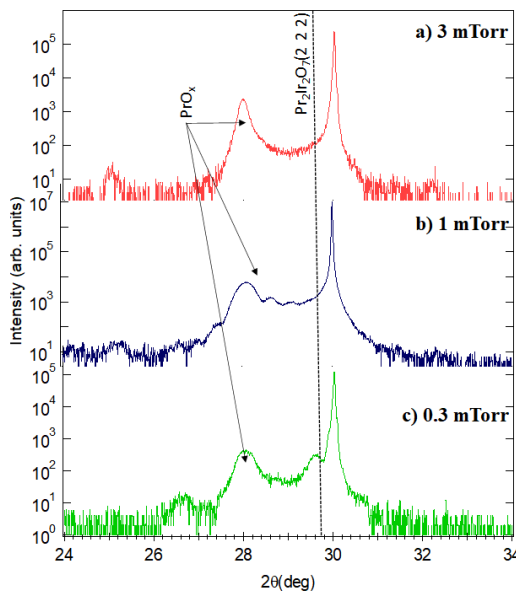


Fig. 2 XRD 2θ-θ scans of $\text{Pr}_2\text{Ir}_2\text{O}_7$ films grown at different PO_2 at 1000°C.

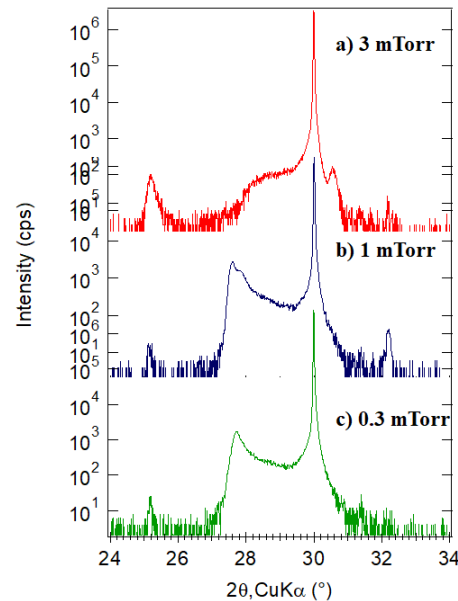


Fig. 3 XRD 2θ-θ scans of Praseodymium Oxides grown at different PO_2 at 1000°C.

There is only a very narrow process window for the pyrochlore phase to form due to the presence of volatile Ir oxides. If the oxygen pressure is too high or too low, either a pure metal phase will segregate or Ir forms IrO_3 , which sublimates rapidly. For eradicating the impact of the iridium metal phase, an inert gas mixture was used to reduce possible resputtering effects of the film surface. The results indicate that inert gas can effectively reduce iridium metal segregation.

Compared with Pr, the valence of La is relatively stable +3 in most cases. Therefore, it may be easier to fabricate a $\text{La}_2\text{Ir}_2\text{O}_7$ thin film. The experiment results have verified the stability of La's valence; however, further research is required to understand Ir clustering during $\text{La}_2\text{Ir}_2\text{O}_7$ growth.

Metal segregation during film growth is a kinetic process, influenced by the ablation pulse rate. Even when the laser pulse rate was 10 Hz, an iridium metal peak with high intensity still appeared in

XRD, which indicates that the clustering speed of iridium is much higher than the usual estimates for oxide surface diffusion and leads to phase separation. On the other hand, the Ir metal peak intensity drops gradually with the decrease of frequency as shown in Fig. 4. This is strong evidence that evaporation of iridium happens on the film surface if the growth rate is very low. This behavior matches the results of a recent calculation, which showed that the [111] facet of iridium has the highest oxidation rate. Moreover, experiments with interval pulsed laser deposition reveal that a certain number of pulses is required to ensure the stability of iridium clusters even at very high deposition rates. An unstable iridium metal phase is expected to be reactive to rare-earth elements.

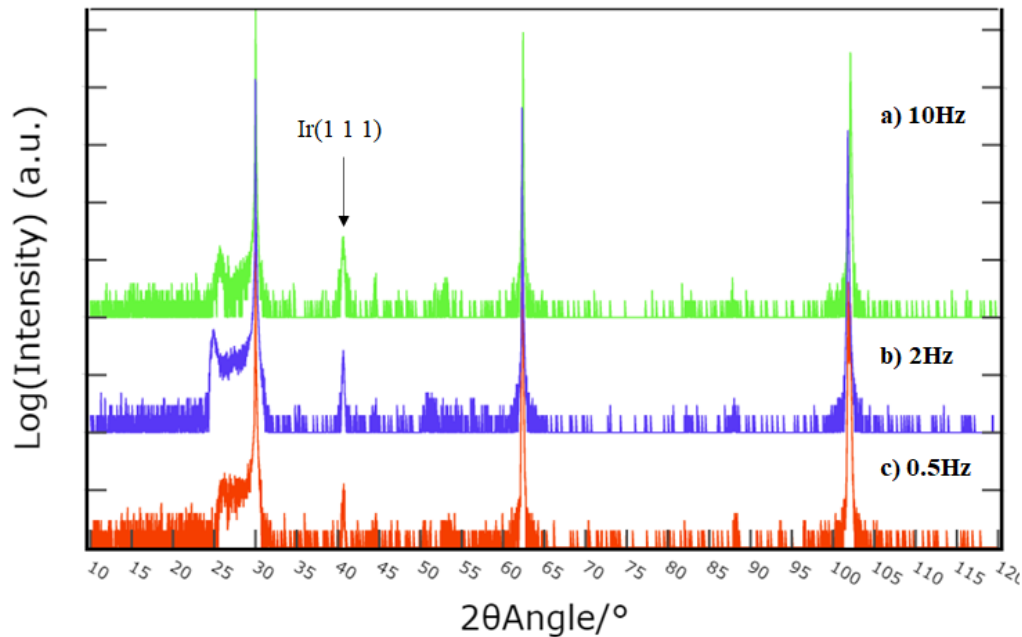


Fig. 4 XRD 2θ scans of the Ir metal peak with different intensity in different laser frequencies. Temperature = 900°C, oxygen pressure = 10mTorr.

4. Conclusion

In this work, the control of the A-site ion valence was found to be crucial for the formation of the pyrochlore phase, which is extremely sensitive to the oxygen partial pressure in the case of Pr. Additionally, in contrast to the naïve conjecture that the difficulty of growing pyrochlore iridate is caused by the volatility of iridium, the research of iridium behavior indicates that clustering is the biggest obstacle in this experiment, which is also possible for other 2-dimensional iridate materials when grown along the [1 1 1] direction. Moreover, it appears to be possible for unstable iridium cluster to form at certain growth conditions, which may be the key to achieving direct PLD growth of stoichiometric pyrochlore iridate films.

References

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Presentation

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