

論文の内容の要旨

論文題目 Growing Iridium Oxide Thin Films by Pulsed Laser Deposition
(パルスレーザー堆積法によるイリジウム酸化物薄膜の作製)

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Introduction

Iridium oxides have recently attracted theoretical and experimental interest due to the possibility of exploring electronic systems with strong spin-orbit coupling. The large spin-orbit splitting is especially interesting in the Ir^{4+} ion with a $5d^5$ electronic configuration. The d levels split due to a crystal field into partly occupied, triply-degenerate t_{2g} levels and unoccupied e_g levels that are located several eV higher in energy. The physical properties of Ir^{4+} oxides are dominated by a further spin-orbit splitting of the t_{2g} levels into $J_{\text{eff}}=3/2$ and $J_{\text{eff}}=1/2$ states. Since the $J_{\text{eff}}=3/2$ levels are fully occupied and only a single electron occupies the $J_{\text{eff}}=1/2$ level, the Ir^{4+} ion behaves as a simple $1/2$ spin, despite having a large number of valence electrons.

The initial motivation for this thesis work came from the prediction of interesting low-temperature spin states and the appearance of possible topologically protected surface states in the pyrochlore $\text{Pr}_2\text{Ir}_2\text{O}_7$ phase. Detailed electronic structure studies by angle-resolved photoelectron spectroscopy require strain-controlled thin films with atomically well-defined surfaces. However, growing iridate thin films is complicated by the thermodynamics of iridium oxidation, which requires high oxygen activity, as is common for all noble metals, but can easily lead to the formation of volatile IrO_3 species. For these reasons, iridium tends to either segregate as a metal or evaporate in the form of IrO_3 , changing the effective stoichiometry of a thin film.

In my work, I therefore started by studying the formation and stability of the simplest Ir^{4+} oxide, IrO_2 . Besides the interest in Ir oxidation kinetics in a vacuum process, IrO_2 is an interesting oxide on its own as an electrocatalyst, as a highly metallic electrode material, and as a possible spin detector material. The pulsed laser deposition (PLD) process parameter window where phase-pure IrO_2 thin films can be obtained was determined. Several mechanisms that can lead to film stoichiometry changes were considered and experimental work was carried out on the plasma plume kinetic energy moderation by changing the ambient gas mixtures. This technique was used to attempt the growth of the $\text{Pr}_2\text{Ir}_2\text{O}_7$ phase. The formation of the pyrochlore phase was confirmed by x-ray diffraction analysis.

PLD growth of IrO₂ films

PLD with a KrF laser ($\lambda=248$ nm) operating at 5 Hz was used for fabricating the IrO₂ films. The laser fluence was 0.9 J/cm². The films were grown at various temperatures and oxygen background pressures on TiO₂(110) substrates. The ablation target was an IrO₂ pellet. A summary of the types of films obtained in the PLD process is shown in Fig. 1. In general, better crystallinity of thin films would be expected when films are grown at high temperature, but as shown by the mapping results, polycrystalline Ir metal films were obtained at low oxygen pressure and no film growth occurred at high pressure. The reduction of iridium to metallic state at high temperature was expected, but the loss of film growth at higher oxygen background pressures was unexpected since bulk IrO₂ is stable at atmospheric pressure up to about 1100 °C. It is likely that the loss of film growth occurred due to the formation of volatile IrO₃ due to the high kinetic energy of the ionized species in the ablation plume. The kinetic energy of the plume was determined by time-of-flight plume current measurement with an electrode inserted in the PLD chamber at the sample position.

Although the film oxygen stoichiometry is mostly controlled by the ambient oxygen pressure, oxygen is also obtained from the ablation target. Visual inspection of the target surface showed that the normally black IrO₂ surface became metallic gray after the growth of a single sample, indicating that the target surface tends to be reduced to Ir metal during ablation. The target surface was therefore re-polished after each sample growth experiment to obtain repeatable growth conditions, but there is a possibility that the ablation plume composition changes during the initial growth stage.

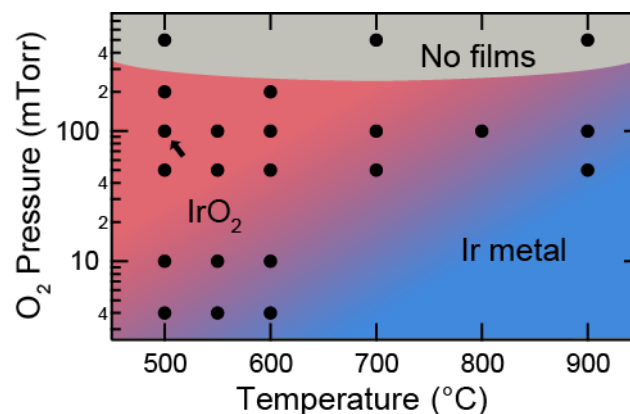


Fig. 1. Growth parameter phase diagram for IrO₂ films grown by PLD. Each circle represents a film sample. The point marked with an arrow corresponds to the optimal growth conditions that resulted in the highest IrO₂ film crystallinity.

IrO₂ film characteristics

The surface morphology of the IrO₂ films was analyzed by atomic force microscope (AFM). Even under optimal growth conditions of 100 mTorr and 500°C, multigrain surface morphologies were obtained. Although large grains were observed on the surface, the top surface of each individual grain appeared to be very flat, which is consistent with IrO₂ films grown on TiO₂(110) maintaining the tetragonal rutile structure. The strain state of the films was analyzed by CuK α x-ray diffraction (XRD). Conventional symmetric diffraction measurements showed that the IrO₂(220) peak was at 57.88°, which is close to the expected bulk position of 57.94° ($d = 1.59 \text{ \AA}$). This means that the films grown at optimal conditions were fully relaxed on the TiO₂(110) substrate. Reciprocal space mapping was performed along the [001] and [1-10] directions, but showed no presence of strained IrO₂ component, which means that the strain relaxation occurred at the film-substrate interface.

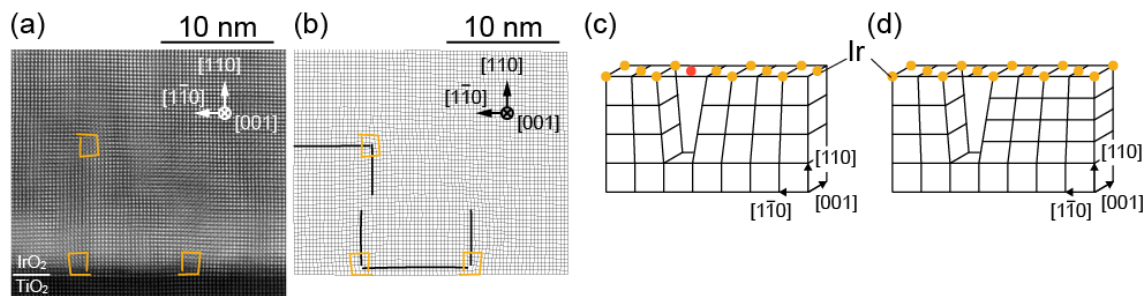


Fig. 2. (a) STEM image of the dislocation structure of an IrO₂ film. Three dislocation cores are marked in the image. (b) A schematic diagram of the same STEM image area, showing that each [110] direction dislocation column is accompanied by an added row along the [110] direction. (c) A dislocation column model. Ir atoms are shown in yellow, the position of the first atom of an adatom column is shown in red. The red atom does not fit the rutile structure. (d) The misfit column can be accommodated if an additional lattice row is added on one side of the dislocation.

A high-resolution scanning transmission electron microscopy (STEM) image in Fig. 2(a) shows the details of the strain relaxation at the film - substrate interface along the [110] direction. An added crystal row can be seen in the middle of the imaging area. The position of the added rows and columns can be more easily seen in the schematic lattice diagram in Fig. 2(b). It is clear that an adatom [110] direction column and a [1 $\bar{1}$ 0] row always nucleate at the same point in the lattice. The reason for this particular dislocation structure can be understood by considering the rutile structure, illustrated in Figs. 2(c,d). If a single vertical adatom column is added in a crystal along the [110] direction, an adatom cannot be added into the rutile structure. However, if the number of lattice rows differs in the [110] direction by one on either side of the dislocation, a continuous lattice can form, as shown in Fig. 2(d). The -2.1% in-plane

misfit relaxation along the $[1\bar{1}0]$ of the IrO_2 film on the TiO_2 substrate surface thus leads to large out-of-plane disorder.

The low-temperature resistivity behavior of the films was measured for various film thicknesses and oxygen annealing treatments. All films were metallic, but the low temperature resistivity saturated below 100 K. This saturation behavior does not follow the bulk behavior [1]. The residual resistance ratio (RRR) of an as-deposited film grown at 500°C and 100 mTorr was about 3.2, which is similar to other published reports on IrO_2 films grown by PLD [2] and by molecular beam epitaxy [3]. It appears that at low temperatures the film resistivity is limited by the grain boundaries in the film, and is thus related to the peculiar misfit strain relaxation mechanism of the rutile lattice. The transport behavior was not significantly affected by varying the film thickness or performing oxygen annealing. This indicates that the increased residual resistivity is related to the stacking fault structures at the grain boundaries.

PLD growth of $\text{Pr}_2\text{Ir}_2\text{O}_7$ films

The conclusion from the IrO_2 film growth studies was that the film morphology and stoichiometry can be affected by three mechanisms: Iridium oxidation kinetics, target surface composition changes, and resputtering of the film surface. Since it is known that the pyrochlore iridate thin films cannot normally be grown by PLD, an attempt was made to moderate the kinetic energy of the ablation plume by growing films in an Oxygen – Xenon gas mixture. Growing $\text{Pr}_2\text{Ir}_2\text{O}_7$ films in a heavy gas ambient decreases the kinetic energy of the iridium atoms through gas-phase collisions, reducing the iridium loss caused by resputtering. Moderate ambient gas buffering did indeed prove successful, with XRD analysis of nominal $\text{Pr}_2\text{Ir}_2\text{O}_7$ films showing clear pyrochlore structure diffraction peaks. AFM images of $\text{Pr}_2\text{Ir}_2\text{O}_7$ film surfaces grown in the mixing gas showed flat triangle terraces and steps with about 0.3 nm height, which corresponds to the lattice plane distance of $\text{Pr}_2\text{Ir}_2\text{O}_7$ along $[111]$ direction.

Conclusion

I aimed to grow pyrochlore $\text{Pr}_2\text{Ir}_2\text{O}_7$ thin films by PLD, starting with a study of the simplest iridium oxide, IrO_2 . The growth window of IrO_2 was identified and I found that the film contains grain boundaries that originate from strain relaxation. $\text{Pr}_2\text{Ir}_2\text{O}_7$ films were grown by PLD in an oxygen—xenon gas mixture to moderate the kinetic energy of iridium in the ablation plume. Iridium loss could thus be eliminated and pyrochlore films were obtained.

[1] W. D. Ryden and A. W. Lawson, Phys. Rev. B **1**, 1494 (1970).

[2] W. J. Kim *et al.*, Phys. Rev. B **93**, 045104 (2016).

[3] M. Uchida *et al.*, Phys. Rev. B **91**, 241119R (2015).