Fabrication of Pr$_2$Ir$_2$O$_7$ thin films and their electrical properties / Herstellung dünner Pr$_2$Ir$_2$O$_7$ Schichten und ihre elektrischen Eigenschaften

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Chapter 1

Introduction

Graphene, a well known compound of carbon, has extraordinary properties like a high conductivity and high stability in in-plane direction as well as a quantum spin Hall effect at room temperature [1, 2], making an application in field-effect transistors [3] or in frequency multipliers [4] possible. These fantastic properties have been investigated by Andre Geim and Konstantin Novoselov in 2004 [1] for which they got the Nobel prize in 2010. Since an industrial fabrication of graphene seems to be possible [5], it has attracted tremendous research interests in the field of physics, chemistry and material science. A great advantage would be to replace silicon as transistor material by graphene.

Unfortunately graphene has a two dimensional structure, which is composed of carbon atoms arranged in a hexagonal symmetry. So its properties like the high stability only occurs inside the layer.

The main reason for the properties of graphene is the special band structure exhibiting so called dirac-nodes. This is a point in the band structure where the conduction and the valence band touch each other. Theoretical models suggest that this structure is also possible in three dimensions [6]. Then they are called 3D Weyl-nodes. Materials with such a band structure are called Weyl semimetals and are expected to have exceptional properties like graphene, since Weyl-nodes are absolutely robust against pertubations. These systems have not been much investigated yet and up to now no Weyl semimetal was found. Iridates with pyrochlore structure are promising candidates for the realization of Weyl semimetal. Thus this thesis will focus on praseodymium iridate $\text{Pr}_2\text{Ir}_2\text{O}_7$.

Indeed, the praseodymium iridate $\text{Pr}_2\text{Ir}_2\text{O}_7$, i.e. a point of contact of the conduction and the valence band similar as for Weyl-nodes, however, with a quadratic dispersion, which might be modified by epitaxial strain in $\text{Pr}_2\text{Ir}_2\text{O}_7$ thin films. For the first time in literature, $\text{Pr}_2\text{Ir}_2\text{O}_7$ thin films are fabricated.

This thesis is divided in 5 chapters. The first chapter is the introduction with the motivation. The second chapter deals with the theory on Weyl-semimetals and describes the characteristics of the pyrochlore structured iridates. It also provides an overview of the properties of praseodymium iridate. In the next fabrication chapter, the influence of the main parameters (temperature, pressure, atmosphere) on
Chapter 1 Introduction

The growth process of thin films of Pr$_2$Ir$_2$O$_7$ is investigated to determine the optimum growth parameter. The thin films are analyzed using x-ray diffraction and atomic force microscopy. The fourth chapter discusses the electrical properties of the Pr$_2$Ir$_2$O$_7$ thin films and a comparison to literature values. The last chapter presents the conclusion of this work with a summary and an outlook for interesting future steps.
Chapter 2

Theory

Up to now only theoretical predictions of possible materials with Weyl-nodes exist. One possibility for the realization of such nodes are rare earth iridates with pyrochlore structure. In this family of materials, the praseodymium compound is exceptional, leading to remarkable physical properties, which are discussed in this chapter.

2.1 From 2D-Dirac-points to 3D-Weyl-points

Graphene is a famous material with fantastic properties like a high electrical conductivity and a high mechanical stability (see Ref. [7]). Mainly responsible for these physical properties are the 2D-Dirac-nodes, where the conduction and valence band touch each other (cf. Ref. [8]). There are six of them in the Brillouin-zone because of the hexagonal 2D honeycomb structure. Near these points the dispersion relation can be linearized Dirac-cones. For this reason electrons behave like massless and relativistic Dirac-particles and [9].

A theoretical description and calculation of these cones gives Young and coworkers by the effective Hamiltonian [10]:

$$H_{\text{eff,2D}} = \nu_F \cdot (k_x \sigma_x + k_y \sigma_y) ,$$

(2.1)

where $\nu_F$ is the Fermi velocity, $k = (k_x, k_y, k_z)$ is the reciprocal wave vector, and $\sigma_i$ ($i = x, y, z$) are the corresponding Pauli matrices. The Hamiltonian is invariant by an operation of the product of the time reversal operator and the parity operator. A consequence is an elimination of electron scattering at non-magnetic impurities resulting in a high conductivity (cf. Ref. [11]). Unfortunately this band structure is not very stable because it has one degree of freedom. $H_{\text{eff}}$ depends only on $k_x$ and $k_y$, and not on $k_z$ (cf. Eq. 2.1). A gap between the conduction and the valence band at the Dirac-cone can already occur by a small perturbation. Therefore, a band structure based on the three dimensional Bloch-Hamiltonian

$$H_{\text{eff,3D}} = \nu_F \cdot (k_x \sigma_x + k_y \sigma_y + k_z \sigma_z) ,$$

(2.2)

would solve the problem. Another advantage is that the corresponding material would be a bulk material and not a 2D-layer material like graphene. In 3D these
points are called Weyl-nodes and the corresponding material is a Weyl-semimetal (WSM). Weyl-nodes can only be generated in pairs with opposite chiralities corresponding to a positive or negative monopole charge [6]. They are very stable in case of external perturbations. Also Fermi arcs occur on the surface states of the Brillouin-zone of WSM, which is a consequence of the non-trivial bulk topology. For a more detailed discussion of Weyl-nodes see Ref. [6]. Now the question arise, how to create such a WSM.

For a strongly correlated system with finite spin-orbit coupling generic model Hamiltonian is given by [6]:

\[ H = H_t + H_\lambda + H_U \]

\[ = \sum_{i,j;\alpha\beta} t_{ij;\alpha\beta} c_{i\alpha}^\dagger c_{j\beta} + \text{h.c.} + \lambda \sum_i \mathbf{L}_i \cdot \mathbf{S}_i + U \sum_{i,\alpha} n_{i\alpha} (n_{i\alpha} - 1), \]

where \( c_{i\alpha} \) is the annihilation operator for an electron in orbital \( \alpha \) at site \( i \) and \( n_{i\alpha} = c_{i\alpha}^\dagger c_{i\alpha} \) is the corresponding occupation number, \( t \) is the hopping amplitude, \( \lambda \) is the strength of spin-orbital-coupling (SOC) and \( U \) is the Hubbard repulsion. Since this Hamiltonian is complicated, here are only discussed the main dependencies.

The strength of the SOC \( \lambda \) is proportional to \( Z^4 \), where \( Z \) is the proton number of the element. Therefore, a heavier element has a stronger SOC. The hopping amplitude \( t \) gives a quantification of the overlap of the orbitals in a compound. Thus when the overlap is larger, there is a higher hopping probability. The third term \( H_U \) depends on the Hubbard repulsion \( U \), which on the other hand mainly depends on the localization of the electrons. Especially for smaller angular momentums this term increases. A 3d-element \( (n = 3, l = 2) \) for example has a quite high \( U \) and small \( \lambda \) and result in a Mott-insulator (cf. Fig. 2.1(a)). The insulating effect hereby mainly comes from the high Coulomb repulsion of the neighboring atoms. By a transition to a 5d-element \( U \) decreases and \( \lambda \) strongly increases. This transition leads to the area of a Weyl-semimetal (cf. Fig. 2.1(a)).
2.1 From 2D-Dirac-points to 3D-Weyl-points

Figure 2.1: (a) A schematic “phase diagram” in terms of the relative strength of the Hubbard interaction $U/t$ and the SOC $\lambda/t$, based on equation (2.4). The positions of some different band structure forms are marked. The two lines divide the weak and strong correlation regions, and the weak and strong SOC regimes, thereby generating four quadrants [6]. For example low SOC and Hubbard repulsion lead to the area of simple metals. (b) A visualization of dirac-cones (from Ref. [12]). (c) A schematic description of two Weyl-no-des with different chirality in a Brillouin-zone. On the surface of the Brillouin-zone the Fermi-arcs are shown (from Ref. [6]).

In Ref. [13] Ueda and coworkers present the pyrochlore structure as an promising material system to observe Weyl-nodes. Therefore in this work a pyrochlore structure with the 5$d$-element iridium is used, which are called pyrochlore iridates. The family of the iridates provides a large variation of properties. In particular a thermal phase transition and metal-to-insulator transition has been observed [6].
2.2 Iridates with pyrochlore structure

The pyrochlore structure has the elemental formula \( A^3_2 + B^{4+}_2 O^{2+}_7 \), where \( A \) is a rare earth element or yttrium and \( B \) is iridium in case of pyrochlore iridates. The crystal space group of pyrochlore is the \( Fd\bar{3}m \), which means it has a cubic symmetry. The unit cell is composed of two interpenetrating face centered cubic (fcc) cells with tetrahedra on \( A \)- and \( B \)-sites (see Fig. 2.2). The tetrahedra are surrounded by oxygen atoms, which reside on different sites leading to the formula \( A_2B_2O_6O \). The result is shown in Fig. 2.2. Each atom has a fixed place in the cell and can be described by the Wyckoff-positions listed in Tab. 2.1.

An important structural parameter is the oxygen \( x \)-parameter of the \( 48f \)-position.

<table>
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<th>Ion</th>
<th>Wyckoff positions</th>
<th>minimal coordinates</th>
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<td>( A^3+ )</td>
<td>16d</td>
<td>( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} )</td>
</tr>
<tr>
<td>( \text{Ir}^{4+} )</td>
<td>16c</td>
<td>0,0,0</td>
</tr>
<tr>
<td>( O^{2-} )</td>
<td>8b</td>
<td>( \frac{7}{8}, \frac{7}{8}, \frac{7}{8} )</td>
</tr>
<tr>
<td>( O'^{2-} )</td>
<td>48f</td>
<td>( \frac{1}{8}, \frac{1}{8} )</td>
</tr>
</tbody>
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Table 2.1: Wyckoff positions and coordinates of the ions in the pyrochlore structure of \( A_2\text{Ir}_2O_7 \) (from Ref. [14])

If \( x \) is equal to \( x_{\text{ideal}} = 0.3125 \) the oxygen ions form a perfect octahedron around each iridium tetrahedron [6]. If \( x \) is smaller (or larger) than \( x_{\text{ideal}} \), the oxygen octahedra are elongated (compressed). In experiments all pyrochlore iridates have trigonal compressed octahedra along the [111]-direction.

In [111]-direction, kagomé layers and triangular layers alternate as shown in Fig. 2.2(b) leading to preferred direction along [111].

All rare earth respectively lanthanide iridates except praseodymium iridate show a metal to insulator transition (MIT) at a certain temperature \( T_{\text{MIT}} \) (see Fig. 2.3(a)). The temperature of the MIT decreases to larger ionic radii of the lanthanides (see Fig. 2.3(b)). The area around neodymium (Nd) and praseodymium (Pr) seems to be very interesting because Fig. 2.3(b) suggests that inbetween these two compounds the MIT vanishes in a quantum critical point. However, recent theoretical calculations show that this quantum critical point at which \( T_{\text{MIT}} = 0 \text{K} \) is exactly at the Pr pyrochlore iridate (see dashed line in Fig. 2.3(b)), making \( \text{Pr}_2\text{Ir}_2O_7 \) very interesting.
2.3 Properties of praseodymium iridate Pr$_2$Ir$_2$O$_7$

The compound Pr$_2$Ir$_2$O$_7$ has many interesting properties. For example, Pr$_2$Ir$_2$O$_7$ exhibits an anomalous Hall-effect, which occurs at very low temperatures ($< 1.5$K) although no magnetic long-range order is present in Pr$_2$Ir$_2$O$_7$ down to 30mK [6]. Instead, novel freezing and non-Fermi liquid phenomena appear at low temperature. This and the anomalous Hall-effect without magnetic ordering leads to the proposal that praseodymium iridate is a realization of a chiral spin liquid, stemming from
a spin-ice type physics for the Pr moments, for example predominantly 2-in/2-out configurations on each tetrahedron (cf. Ref. [6]).

Pr$_2$Ir$_2$O$_7$ is a metal in contrast to all other rare earth iridates and does not show a MIT. Since it is a metal, its conductivity is high and increases to lower temperature [14]. The reason for this characteristics lays in the Fermi-nodes in the band structure, which is visualized in Fig. 2.3(c). At these points valence and conduction band touch each other but have a quadratic dispersion [6,14]. Thereby praseodymium iridate is not a candidate for a WSM, but otherwise by understanding its behaviour and the change of MIT between Nd and Pr, it can pave the way to find a WSM state.

The advantage of Pr$_2$Ir$_2$O$_7$ thin films is that the band structure especially at the Fermi-nodes can be changed by strain. Therefore, at the quantum critical point, illustrated in Fig. 2.3(d) a gap can occur by a perturbation as strain which would lead to a topological insulator. The other possibility would be an overlap of the bands which would lead to a metal. So this work will focus on the influence of strain on the band structure of Pr$_2$Ir$_2$O$_7$. 
2.3 Properties of praseodymium iridate $\text{Pr}_2\text{Ir}_2\text{O}_7$

![Diagram showing properties of praseodymium iridate $\text{Pr}_2\text{Ir}_2\text{O}_7$.]

Figure 2.3: (a) The resistivity of $\text{Ln}_2\text{Ir}_2\text{O}_7$ with $\text{Ln}$ as a rare earth in measurements by Gardner and coworkers [14]. (b) The metal to insulator transition (MIT) of rare earth iridates as a function of the ionic radius of each rare earth element. The interesting area is where the MIT strikes the 0K line. The quantum critical point is drawn at Pr (from Ref. [15]). (c) Quadratic band touching of Pr$_2$Ir$_2$O$_7$ called Fermi-nodes and marked with a circle (from Ref. [15]). (d) Band structure of a Fermi-node as a schematic sketch (from Ref. [15]).
Chapter 3

Fabrication of thin praseodymium iridate films

This chapter discusses the fabrication of thin films of praseodymium iridate (Pr$_2$Ir$_2$O$_7$) by pulsed laser deposition (PLD$^1$). The growth of this oxide depends on different parameters of which some, like the type of substrate, the substrate temperature, the atmosphere and pressure, are discussed in this chapter. The energy fluence of the excimer laser at the target is hereby set to $2 \, \text{J/cm}^2$. If nothing is specifically mentioned, the PLD process is composed of a total of 50,000 pulses, which are ordered in 200 packages each with 250 pulses, and a relaxation time of 10 seconds.

3.1 Yttrium stabilized zirconium oxide as substrate

Different factors are under consideration in the selection of a suitable substrate for the fabrication of Pr$_2$Ir$_2$O$_7$ thin films, including the lattice mismatch, and the thermal expansion coefficients. In this work yttrium stabilized zirconium oxide (Y:ZrO$_2$, YSZ), which has a fcc symmetry, is used. The main reason is the small lattice mismatch of YSZ and Pr$_2$Ir$_2$O$_7$. This is necessary for relative low epitaxial strain, and therefore low density of dislocations. The lattice constant of YSZ is $a_{\text{YSZ}} = 5.12 \, \text{Å}$ [16]. The polycrystalline Pr$_2$Ir$_2$O$_7$ powder, out of which the target was made, has a lattice constant of $a_{\text{poly}} = 10.427 \, \text{Å}$. However, the literature value of $a_{\text{single}} = 10.396 \, \text{Å}$ measured on a single crystal [14] is slightly lower. The difference might be caused by a different Ir-content in the samples. By comparing $a_{\text{YSZ}}$ and $a_{\text{poly}}$, the unit cell of Pr$_2$Ir$_2$O$_7$ will grow on four unit cells of YSZ, leading to a lattice mismatch of 1.8%. Another advantage in comparison to other substrates is that YSZ is purely diamagnetic. For magnetization measurements the substrate only produce a linear offset which is easy to add out.

These substrates are produced by the company “CrysTec” and have the dimensions $5 \times 5 \times 0.5 \, \text{mm}^3$. The difference to zirconium oxide ZrO$_2$ is that one Zr$^{4+}$ is substituted by a cell of yttrium oxide Y$_2$O$_3$. As shown in former experiments with neodymium

\footnote{PLD is described in the appendix A.1}
Chapter 3 Fabrication of thin praseodymium iridate films

iridate by M. Lammel [17] the preferred growth direction of pyrochlore iridates such as Nd$_2$Ir$_2$O$_7$ or Pr$_2$Ir$_2$O$_7$ is the [111]-direction. Therefore, (111)-oriented YSZ substrates are used throughout this thesis.

Prior to the growth process the back of the substrate is sputtered by a 180 nm platinum layer to ensure a uniform heat distribution of the heating laser during the PLD process.

3.2 Influence of oxygen as atmosphere

Since Pr$_2$Ir$_2$O$_7$ is an oxide, an oxygen atmosphere is used to avoid oxygen vacancies. The next two subsections deal with the fabrication of Pr$_2$Ir$_2$O$_7$ thin films in a pure oxygen atmosphere by varying the substrate temperature and the atmosphere pressure.

3.2.1 Variation of the substrate temperature

In this section the optimum growth temperature $T_S$ is determined. To this all parameters except the substrate temperature are fixed. Especially the pressure of oxygen is set at 25 µbar by a controllable valve. Now each sample is grown at a different temperature from 600°C to 800°C. After the growth process the samples are analyzed by x-ray-diffraction (XRD). Since there is a lattice mismatch of 1.8% in comparison to YSZ, the Pr$_2$Ir$_2$O$_7$ reflections of the thin film are expected at smaller 2Θ-angles compared to YSZ. Fig. 3.1(a) shows the 2Θ − ω-scans of the temperature series and confirm the expectation of the relative position of the thin film reflections. Additionally Laue-oscillations which are a sign for a coherent and crystalline growth can be observed. In this aspect the crystalline quality gets better for higher temperatures. At 600°C an impurity phase appears which is identified as an iridium oxide with a different valence of iridium. The dashed line shows the 2Θ-angle of Pr$_2$Ir$_2$O$_7$ with the assumption of no epitaxial strain. With the 2Θ-angle of the peak which is detected by fitting a Gauss trajectory, and the Bragg condition $2d_{hkl} \cdot \sin(\Theta) = n\lambda$, the smallest lattice plane distance $d_{hkl}$ is calculated, where $hkl$ are the Miller indices and $n$ is the order of the reflection. For a cubic symmetry the lattice constant is $a = \sqrt{h^2 + k^2 + l^2} \cdot d_{hkl}$. The thus obtained lattice constants as a function of the substrate temperature $T_S$ are shown in Fig. 3.1(b). It is obvious that the lattice constant becomes smaller with higher temperature. But they are still much larger than the expected lattice constant $a_{poly} \approx 10.4\,\text{Å}$. Therefore, a different praseodymium oxide might be crystallized with a different iridium content.

\[ ^2\text{XRD is described in the appendix A.2} \]
3.2 Influence of oxygen as atmosphere

Figure 3.1: (a) X-ray-diffraction (2Θ-ω-scans) of Pr$_2$Ir$_2$O$_7$ thin films fabricated at different substrate temperatures $T_S$ in a pure oxygen atmosphere. The magenta colored graph is the polycrystalline target material, which maximum intensity of the Pr$_2$Ir$_2$O$_7$ (222) reflection is marked with a gray dashed line. The high offset of the magenta colored graph is just caused by background. (b) The lattice constant $a$ for each substrate temperature $T_S$ with the assumption of a cubic symmetry. For comparison the polycrystalline lattice constant $a_{\text{polycrystalline}}$ and the lattice constant $a_{\text{single}}$ of a single crystal are drawn in the graph. (c) The intensity of rocking curves for different substrate temperatures as a function of $\Delta \omega$ whereas $\Delta \omega = \omega - \omega_{\text{peak}}$. $\omega_{\text{peak}}$ is the angle of the maximum intensity. (d) Full width at half maximum (FWHM) of the rocking curves in relation to the substrate temperature $T_S$.

Now the films are analyzed by their rocking curves. They are made by fixing the 2Θ-angle at the Pr$_2$Ir$_2$O$_7$ (222) reflections and changing the $\omega$-angle$^\text{c}$ For Fig. 3.1(c) the rocking curve are shifted by the angle of the maximum intensity $\omega_{\text{peak}}$. The main information of the rocking curve are the FWHM-values which are a rating for the

$^\text{c}$For further information see the appendix A.2
mosaicity and can be determined by a Gaussian fit. The smaller the FWHM-values the less is the mosaicity respectively the higher is the crystallinity. Fig. 3.1(d) shows that the FWHM-values at high temperature are getting smaller though they are well above 0.04°, which might be a good value. Therefore, the crystalline quality is worse. However, the rocking curve of the thin film fabricated at \(T_S = 750^\circ\) exhibits a second component with a lower FWHM value. Hence this temperature is chosen as best.

Figure 3.2: (a) X-ray reflectometry of \(\text{Pr}_2\text{Ir}_2\text{O}_7\) thin films produced at different substrate temperatures. (b) The thickness \(d\) and roughness \(r\) as a function of the substrate temperature. The values are derived by simulations of the reflectometry scans.

The X-ray reflectometries are shown in Fig. 3.2. With the aid of these reflectometries the thickness \(d\), the roughness \(r\) and the density \(D\) of the film can be determined. The thickness is reciprocally proportional to the distance of the oscillations (see Fig. 3.2(a)). From a simulation of the reflectometries with the program “LEPTOS” the thickness und the roughness can be derived. The thickness and the roughness of the films decrease continuously with increasing substrate temperature. If the thickness exceeds a critical value, the thin film does not grow in a layer-by-layer mode but in a island mode resulting in tilted planes with a high mosaicity. The reflectometry also provides information regarding the density of the film. In this case the density is in a range of about \((7.8 \pm 0.1) \text{ g cm}^{-3}\). For \(\text{Pr}_2\text{Ir}_2\text{O}_7\) a density of around \(\rho_{Pr} = 9.202 \text{ g cm}^{-3}\) would be expected. That is a further hint that these films exhibit not the correct \(\text{Pr}_2\text{Ir}_2\text{O}_7\) phase. In Fig. 3.3 two films are compared to a simulation each with the expected density of \(\text{Pr}_2\text{Ir}_2\text{O}_7\) \(\rho_{Pr}\) and with the fitted density. Since it is still a fairly large gap, this can not be explained by a random error.
3.2 Influence of oxygen as atmosphere

Figure 3.3: (a) Reflectometry of a thin film grown at 600°C with a simulation using a density of \( \rho_{\text{fit}} = 7.736 \text{ g/cm}^3 \) and a simulation with the expected density of \( \text{Pr}_2\text{Ir}_2\text{O}_7 \). Especially the area between 0.5° and 1.0° changes with density. (b) Reflectometry of a thin film grown at 750°C with a simulation using \( \rho_{\text{fit}} = 7.763 \text{ g/cm}^3 \) and a simulation using the expected density \( \rho_{\text{Pr}} \).

To summarise the 2Θ-ω-scans reveal an impurity phase for substrate temperatures lower than 700°C. Furthermore, a higher roughness of the thin films is expected for \( T_S < 700°C \). From the rocking curves a second component with a high crystalline quality is visible for the thin film fabricated at \( T_S = 750°C \). Therefore, the optimum growth temperature in oxygen is set to 750°C.

3.2.2 Variation of the oxygen pressure

After investigating the influence of the substrate temperature \( T_S \), the oxygen pressure of the growth process is varied. Therefore, the temperature is hold constant at 750°C and the pressure is varied from 0.5 μbar to 50 μbar. The quality of the films are again analyzed with x-ray diffraction.

The 2Θ-ω-scans reveal a great difference on the thin film reflection at different \( p_{O_2} \) (Fig. 3.4(a)). This implies the influence of pressure on the phase. At high pressures, an impurity phase at 2Θ ≈ 28.1° is present. At lower pressure \( p_{O_2} < 1.0 \text{ μbar} \), for the first time, the Pr\(_2\)Ir\(_2\)O\(_7\) phase appears. At 0.5 μbar even distinctive Laue oscillations are visible, proving a coherent growth with a well crystallinity. The calculation of the lattice constant \( a \) is again made in assuming a cubic symmetry (see chapter 3.2.1). The obtained lattice constants \( a \) are shown in Fig. 3.4(b) as a function of \( p_{O_2} \). The lattice constant decreases strongly at lower oxygen pressure and gets close to the expected polycrystal lattice constant \( a_{\text{poly}} = 10.427 \text{ Å} \). However, the values are still larger than the lattice constant of the polycrystalline target \( a_{\text{poly}} \). The difference might be cause by oxygen vacancies or a finite epitaxial strain due to the
different lattice constants of Pr$_2$Ir$_2$O$_7$ and YSZ substrate. At higher pressures the determination of the lattice constant has a larger error because the determination of the film peak has a higher uncertainty.

Figure 3.4: (a) X-ray diffraction (2θ−ω-scans) carried out using Pr$_2$Ir$_2$O$_7$ thin films fabricated at different oxygen pressure but with fixed substrate temperature $T_s$. The magenta colored curve shows the polycrystalline Pr$_2$Ir$_2$O$_7$. The dashed gray line marks expected 2θ-angle of the Pr$_2$Ir$_2$O$_7$ (222) reflection. (b) Lattice constant in relation to the oxygen pressure $p_{O_2}$. The dashed lines show the lattice constant for a polycrystalline material and the literature value. (c) Rocking curves of Pr$_2$Ir$_2$O$_7$ thin films fabricated at different $p_{O_2}$. They are again shifted by $\omega_{\text{peak}}$ for better visibility. (d) FWHM values for each rocking curve in relation to $p_{O_2}$. For rocking curves with two components a large FWHM (black framed square) and a low FWHM value (black filled square).

The rocking curves, again carried out around the 2θ-angle of the Pr$_2$Ir$_2$O$_7$ (222)-reflection, are illustrated in Fig. 3.4(c). They are again shifted by $\omega_{\text{peak}}$ for better
3.2 Influence of oxygen as atmosphere

visibility. Two components are visible for $p_{O_2} < 25 \mu\text{bar}$. One with a low FWHM value and therefore with a good crystalline quality and another one with a high value. Both FWHM values are shown in Fig. 3.4(d). Obviously, the component with the high mosaicity decreases with decreasing the oxygen pressure. Therefore, the crystalline quality of the Pr$_2$Ir$_2$O$_7$ thin films increases for $p_{O_2} < 1 \mu\text{bar}$.

The X-ray reflectometries are shown in Fig. 3.5(a). It can be observed that the thickness increases to higher pressure. This is unusual because at higher pressure the scattering of the particles is larger. So they have less energy and velocity. The analysis with the program “LEPTOS” reveals the thickness and the roughness as illustrated in Fig. 3.5(b). For the roughness no clear trend is identifiable. However, the dependence of the thickness and the roughness on the oxygen pressure $p_{O_2}$ clearly changes for $p_{O_2} < 1 \mu\text{bar}$. This is the pressure range where the Pr$_2$Ir$_2$O$_7$ phase appears.

![Figure 3.5: (a) X-ray reflectometry of Pr$_2$Ir$_2$O$_7$ thin films fabricated at different oxygen pressures $p_{O_2}$. (b) The thickness $d$ and roughness $r$ shown as a function of $p_{O_2}$. The values are derived from the reflectometry scans.](image)

To conclude the results of the X-ray diffraction reveals the emergence of the desired Pr$_2$Ir$_2$O$_7$ phase for oxygen pressures lower than 1 $\mu\text{bar}$. However, in the $2\Theta-\omega$-scans an impurity phase at $2\Theta \approx 27.5^\circ$ is still discernible for all pressure values. Therefore, in the next step the atmosphere is changed from a pure oxygen atmosphere to an argon atmosphere.

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3.3 Influence of argon atmosphere

Since parasitic phases are present while fabricating Pr$_2$Ir$_2$O$_7$ thin films in a pure oxygen atmosphere, in the next step the growth in a combination of argon and oxygen as well as in a pure argon atmosphere will be analyzed in this chapter.

3.3.1 Determination of the ideal growth pressure

This section analyzes the optimum pressure in argon atmosphere. For this the substrate temperature is kept constant at 750°C, which is the optimal substrate temperature for the fabrication in a pure oxygen atmosphere. One film is made in an atmosphere composed of 99% Ar and 1% O$_2$ at a pressure of 0.5 µbar. The other three films are fabricated at 0.5 µbar, 1.0 µbar and 25 µbar in a pure argon atmosphere.

The films again are analyzed with x-ray diffraction. The 2Θ-ω-scans (see Fig. 3.6(a)) reveal only reflections from the Pr$_2$Ir$_2$O$_7$ phase and no indication of an impurity phase was found. Laue oscillations proof a coherent growth and high crystalline quality for the thin films fabricated in pure argon atmosphere. These oscillations are most pronounced for the growth at $p_{Ar} = 25$ µbar. In Fig. 3.6(b) the lattice constant of the film as function of pressure is displaced. The calculation is based on the Pr$_2$Ir$_2$O$_7$ (222) reflection of the 2Θ - ω-scan. The lattice constant is now close to the lattice constant of the polycrystalline material. The difference is only about 0.07 Å which corresponds to approx. 0.7%. This might again be caused by a finite epitaxial strain as well as oxygen vacancies or iridium loss.

Similar to the growth of Pr$_2$Ir$_2$O$_7$ thin films in pure oxygen the rocking curves of the Pr$_2$Ir$_2$O$_7$ thin films fabricated at low pressures in Ar atmosphere (see Fig. 3.6(c)) reveal two components. One with a small FWHM indicating a good crystalline quality and another with a high FWHM value. However, the Pr$_2$Ir$_2$O$_7$ thin film fabricated at $p_{Ar} = 25$ µbar has the smallest component with the high FWHM value. A possible way to quantify this is the ratio of the area under a curve between each component of the Gaussian fit. The sample fabricated at $p_{Ar} = 25$ µbar has the best ratio $\frac{A_p}{A_b} = 0.53$.

The rocking curve of the thin film fabricated at 1 µbar has a plateau lateral of the central peak. This might be caused by an ordered network of dislocations causing satellite peaks [18].
3.3 Influence of argon atmosphere

The reflectometries of this pressure series are shown in Fig. 3.7(a). The Pr$_2$Ir$_2$O$_7$ thin film fabricated in an atmosphere composed of argon and oxygen exhibits high roughness because the intensity decreases faster at low 2θ-angle. Further information on the thickness and roughness can be found in Fig. 3.7(b). The roughness of the Pr$_2$Ir$_2$O$_7$ grown in pure argon atmosphere is very similar. But the thickness
differ a lot. While the Pr$_2$Ir$_2$O$_7$ thin film fabricated at 1.0 µbar is very thick, the 0.5 µbar and 25 µbar film are 20 nm thinner. This is unusual and should be confirmed by an additional Pr$_2$Ir$_2$O$_7$ thin film fabricated at 0.5 µbar.

Figure 3.7: (a) Reflectometries of Pr$_2$Ir$_2$O$_7$ thin films fabricated at different argon pressures $p_{Ar}$. The green color marks the graph of the film grown at an atmosphere composed of argon and oxygen. (b) The thickness $d$ and roughness $r$ shown as a function of $p_{Ar}$. The values are derived from the reflectometry scans.

Viewing the simulations of the reflectometries in Fig. 3.8 shows again difference of the density of the films to $\rho_{Pr}$ but not as large as in section 3.2.1. The density here is around $\rho = 8.0 \frac{g}{cm^3}$. However, the difference to the density of Pr$_2$Ir$_2$O$_7$ is still large. Fig. 3.8 shows a large difference between the two simulations in the area between 0.5° and 1.0°.

To conclude, the optimum growth pressure is 25 µbar in pure argon. The rocking curve of this Pr$_2$Ir$_2$O$_7$ thin film show a small component with a high FWHM. The 2Θ – ω-scan reveals Laue oscillations, which proof a coherent growth and thus good crystalline quality.
3.4 Conclusion of the best growth parameters

As discussed in the previous sections, the optimum parameters are a substrate temperature of \( T_S = 750^\circ C \) and an argon pressure \( p_{Ar} = 25 \, \mu \text{bar} \). The optimum substrate temperature is taken from the growth series in pure oxygen. The films grown in pure argon with a total of 50000 pulses have an average thickness of 42 nm. The growth rate is therefore with a frequency of \( f = 10 \text{Hz} \) \( \lambda = 8.5 \, \text{pm/s} \).

Since the films have a relative small thickness \( \text{Pr}_2\text{Ir}_2\text{O}_7 \) films with three times more of the pulses are fabricated to get bulk-like thin films with no epitaxial strain. In addition a measurable resistance by a larger cross-section area might be achieved. But surely a three times thicker film can not be expected because the growth rate might not be linear. However, a constant growth rate is assumed in first approximation since the thickness of these thin films could not be measured by X-ray reflectometry.

For the examination of the surface topography of the \( \text{Pr}_2\text{Ir}_2\text{O}_7 \) films an atomic force microscopy (AFM\(^3\)) image performed, which are shown in Fig. 3.9. The images show a very flat and plain surface. The roughness in this scanned \( 5 \times 5 \, \mu \text{m}^2 \) area given by the AFM data is 0.47 nm. Therefore this value is in the same order of magnitude of all other films grown in pure argon. The average value is \( \bar{r}_{\text{rms,Ar}} = 0.46 \, \text{nm} \).

\(^3\)AFM is described in the appendix A.4
Chapter 3 Fabrication of thin praseodymium iridate films

Therefore, it is a verification of the values got by the XRD-measurements (see section 3.3.1).

![Figure 3.9](image.png)

Figure 3.9: (a), (b) Surface morphology of a Pr$_2$Ir$_2$O$_7$ thin film.

One observation which runs through the whole fabrication chapter is that the lattice constant $a_{\text{film}}$ is not equal to $a_{\text{poly}}$ or $a_{\text{single}}$. As already discussed a loss of iridium or praseodymium could be a reason for that.

Another possible reason could be oxygen vacancies or epitaxial strain. To get a value and a quantitative classification for the strain, reciprocal space maps (RSM) are made. One RSM is carried out around the symmetric (111)-reflex and the other around the (315)-reflex of the YSZ-substrate. The maps are shown in Fig. 3.10. The values of the scattering vector $q_{\text{HHH}}$ and $q_{\text{H0H}}$ are given in reciprocal lattice units relative to the YSZ-substrate. The substrate in the upper left corner in Fig. 3.10(a) has a very high intensity while the film reflex down right has a low intensity but is clearly decernable from the background. The orange line in Fig. 3.10(a) is the relaxation line of the Pr$_2$Ir$_2$O$_7$ thin film on YSZ. The right end, marked with an orange point, is the position of the film reflex in case of a Pr$_2$Ir$_2$O$_7$ thin film with no epitaxial strain. There the lattice constant is $a_{\text{film}} = a_{\text{poly}} = 10.427$ Å. Due to the cubic structure the two in-plane (here $[\bar{1}01]$-direction) and the out-of-plane (here $[111]$-direction) lattice constants are the same. The other left end is the position of a completely strained film. Now the two in-plane lattice constants adjust to the ones of the substrate and so it applies $a_{i,\text{film}} = 2 \cdot a_{\text{YSZ}}$. The out-of-plane lattice constant $a_{o,\text{film}}$ has to be calculated which can be done by different ways:

In the totally relaxed case there is $a_{\text{film}} = a_{\text{poly}} = 10.427$ Å. Therefore, the lattice constant of the polycrystalline material and of the Pr$_2$Ir$_2$O$_7$ thin film are equal. The

---

4 For further information see the appendix A.2.
position in the RSM can be determined by the relation:

\[
\begin{align*}
    \frac{q_{404,\text{film}}}{q_{202,\text{YSZ}}} &= \frac{d_{\text{YSZ}}}{d_{\text{film}}} = 2 \cdot \frac{a_{\text{YSZ}}}{a_{\text{film}}}, \\
    \frac{q_{222,\text{film}}}{q_{111,\text{YSZ}}} &= \frac{d_{\text{YSZ}}}{d_{\text{film}}} = 2 \cdot \frac{a_{\text{YSZ}}}{a_{\text{film}}}. 
\end{align*}
\] (3.1)

Thus, the scattering vector of the Pr$_2$Ir$_2$O$_7$ film can be calculated in relation to the scattering vector of the YSZ-substrate.

As explained above in a completely strained case the in-plane lattice constants are predetermined by the substrate $a_{i,\text{film}} = 2 \cdot a_{\text{YSZ}} = 10.24\,\text{Å}$. The out-of-plane lattice constant can be calculated in two ways. One way is by presuming a constant volume of the unit cell: $V_{\text{cell}} = a_{\text{poly}}^3 = 2^2 \cdot a_{\text{film}} \cdot a_{o,\text{film}}$. In this case an out-of-plane lattice constant of $a_{o,\text{film}} = 10.81\,\text{Å}$ is calculated which is much larger than $a_{\text{poly}}$.

Furthermore, the $2\Theta - \omega$-scans in section 3.3.1 reveal an average lattice constant of $a_{o,XRD} = 10.47\,\text{Å}$ of the Pr$_2$Ir$_2$O$_7$. This shows that the assumption of a constant volume of the unit cell might be too simple.

The second approximation is to calculate the out-of-plane strain using elastic constants. For this there has to be made a coordinate transformation of the strain tensor because normally its components are defined for the [100], [010], [001] directions. For the calculation it is referred to Ref. [19]. By this the component of the strain tensor $\epsilon'_3$ in [111]-direction is given by:

\[
\epsilon'_3 = -\left(\frac{c_{11} + 2c_{12} - 2c_{44}}{c_{11} + 2c_{12} + 4c_{44}}\right) \cdot \left(\epsilon'_1 + \epsilon'_2\right),
\] (3.3)

where $c_{ij}$ are the components of the elastic shiftness matrix. The components $\epsilon'_1$ and $\epsilon'_2$ in in-plane direction are given by the lattice mismatch:

\[
\epsilon'_1 = \epsilon'_2 = 0.018 = \frac{\Delta l}{l} = \frac{a_{\text{poly}} - 2a_{\text{YSZ}}}{a_{\text{poly}}},
\] (3.4)

With Eq. (3.4) and Eq. (3.3) the out-of-plane component of the strain tensor can be calculated. However, the elastic constants for Pr$_2$Ir$_2$O$_7$ are not known in the literature. Therefore, the elastic constants of a similar compound, for example a titanate ($X_2\text{Ti}_2\text{O}_7$, where $X$ is another element like for example yttrium) is used for the calculation. The titanates equally have a pyrochlore structure and they assume they probably have similar elastic constants to praseodymium iridate. With an average value of the elastic constants of some titanates, which are taken from Ref. [20] ($c_{11} = 3.447$, $c_{12} = 1.109$ and $c_{44} = 0.956$), the out-of-plane strain is calculated to

\[
\epsilon'_3 = -0.014 = \frac{\Delta l}{l} = \frac{a_{\text{poly}} - a_{\text{film}}}{a_{\text{poly}}}.
\] (3.5)
Chapter 3 Fabrication of thin praseodymium iridate films

This leads to a lattice constant in [111]-direction to \( a_{\text{film}} = 10.279 \text{Å} \). With the aid of \( a_{\text{film}} \) and Eq. (3.1) the position of the completely strained film in the RSM can be calculated.

![Figure 3.10](image)

Figure 3.10: (a) Reciprocal space map (RSM) of a 36.4nm thick film of Pr\(_2\)Ir\(_2\)O\(_7\) around the (135) YSZ-reflex. The dashed lines denote the maximums of the substrate reflection \( (q_{111} = 3.0 \text{rlu} \text{ and } q_{100} = -2.0 \text{rlu}) \) and of the film reflection \( (q_{111} = 2.955 \text{rlu} \text{ and } q_{100} = -1.891 \text{rlu}) \). The orange line marks the relaxation line between a fully relaxed thin film \( (q_{111} = 2.946 \text{rlu} \text{ and } q_{100} = -1.965 \text{rlu}) \) and a fully strained one \( (q_{111} = 2.988 \text{rlu} \text{ and } q_{100} = -2.000 \text{rlu}) \). (b) RSM around the (111) YSZ-reflex of the same sample. The dashed lines again mark the maximums of the substrate \( (q_{111} = 1.000 \text{rlu} \text{ and } q_{100} = 0.000 \text{rlu}) \) and film reflection \( (q_{111} = 0.983 \text{rlu} \text{ and } q_{100} = -7.8 \cdot 10^{-5} \text{rlu}) \). Laue oscillations are marked by red arrows.

If the difference between the measured lattice constants of the Pr\(_2\)Ir\(_2\)O\(_7\) thin films fabricated in argon atmosphere (see Fig. 3.6) is caused only by epitaxial strain, the film reflex should lay on the above mentioned relaxation line between the two extreme points of a fully relaxed and completely strained thin film. However, Fig. 3.10(a) reveals that the film reflection largely deviates from the relaxation line. Thus, there must be another reason for the larger lattice constant compared to the polycrystalline material.

For the film reflection in Fig. 3.10(a) a distance of the lattice planes \( d_{006, \text{film}} = 0.100 \text{Å} \) in [111]-direction can be calculated, which leads to a lattice constant of \( a_{\text{film}} = 10.396 \text{Å} \) assuming a cubic symmetry. This is exactly the lattice constant of the literature value. In this and the following calculations the tilt of the lattice planes between substrate and film is disregarded because the tilt with \( \Delta \Theta = 0.35^\circ \) to the left is very small. This tilt is derived from the RSM-measurement of the symmetrical [111]-reflection shown in Fig. 3.10(b). In in-plane direction the distance
of the lattice planes is $d_{404, \text{film}} = 0.191 \frac{1}{\text{mm}}$ which would give a lattice constant of $a_{\text{i, film}} = 10.830 \text{Å}$. In comparison to the lattice constant got by the $2\Theta - \omega$-scans in the previous section, one recognizes that they do not agree with each other. The most likely reason is that the unit cells are not cubic which is declared by comparing $a_{\text{i, film}}$ and $a_{\text{o, film}}$. But in all calculations in this work a cubic symmetry is assumed. If the volume of the cell of the measured lattice constants is calculated and compared to the volume of the polycrystalline material

$$V_{\text{film}} = a_{\text{i, film}}^2 \cdot a_{\text{o, film}} = 1.219 \text{nm}^3 > 1.134 \text{nm}^3 = a_{\text{poly}} = V_{\text{poly}},$$  \hspace{1cm} (3.6)

one can see that the volume of the unit cell in the film is larger. This might be an indication of non-stoichiometric effects like oxygen vacancies or iridium loss.

In conclusion, $\text{Pr}_2\text{Ir}_2\text{O}_7$ thin films with high crystalline quality and low surface roughness are fabricated in pure argon atmosphere. By using an oxygen atmosphere the fabrication of single-phase $\text{Pr}_2\text{Ir}_2\text{O}_7$ thin films could not be achieved using different substrate temperatures as well as various oxygen pressures. This is in contrast to $\text{Nd}_2\text{Ir}_2\text{O}_7$ thin films. These thin films exhibit the best crystalline quality, if they are fabricated in a pure oxygen atmosphere [17]. However, reciprocal space maps and the (135)-reflection of the YSZ substrate suggest a volume of the unit cells of the $\text{Pr}_2\text{Ir}_2\text{O}_7$ thin films compared to the polycrystalline material, which might be an indication of non-stoichiometric effects like oxygen vacancies or iridium loss.
Chapter 4

Electric characteristics of Pr$_2$Ir$_2$O$_7$ thin films

As described in chapter 2 Pr$_2$Ir$_2$O$_7$ shall be metallic with no metal to insulator transition like the other pyrochlore iridates RE$_2$Ir$_2$O$_7$. Therefore, the electrical conductivity of the Pr$_2$Ir$_2$O$_7$ thin films are investigated.

4.1 Preparation of the samples for electrical measurements

At first the fabricated Pr$_2$Ir$_2$O$_7$ samples are cut into pieces of approximately 2.5 x 2.5 mm$^2$, which represents a quarter of the sample. The reason for this is that more measurements with this sample are possible. Then they get cleaned and sputtered with gold using a shadow mask to define electrical contacts. The Au layer has a thickness of about 200 nm. The result of this process is shown in Fig. 4.1. The stripe not sputtered by gold has a width of $l_{ss} = 480 \mu$m. These samples now can be either measured at a probing module with a multimeter or alternatively stuck on a chip carrier to contact with bond wires. With the second opportunity it is also possible to do a resistivity versus temperature ($\rho(T)$) measurement in the cryostat.

A second possibility is to structure the samples by optical lithography$^5$. This with gold sputtered (thickness is about 80 nm) IDT-structure$^6$ is shown in Fig. 4.2. These are also contacted with bond wires because the structure is too small for the probing module. As you can see in the figure, the structure is each bonded with two contacts. A simple resistivity measurement can check whether the contacts are placed firmly. For the resistivity measurements, these samples are stuck on chip carriers.

$^5$Patterning by optical lithography is explained in the appendix A.3
$^6$IDT: interdigital transducer.
4.2 Electrical conductivity measurement with a simple stripe structure

The resistance of the samples with the simple stripe structure as shown in Fig. 4.1 is measured initially at the probing module. For this a voltage \( V \) is applied and the related current \( I \) is measured. The resistance is calculated by:

\[
R = \frac{V}{I}
\]  

assuming an ohmic dependence. The measurements were carried out at room temperature with four different voltages (100V, 200V, 300V, 400V). To get a comparable expression, the resistivity

\[
\rho = R \cdot \frac{A}{l} = \frac{V}{I} \cdot \frac{d \cdot b}{l}
\]  

is calculated, whereas \( d \) is the thickness, \( b \) the width of the sample and \( l_{ss} \) is the distance of the gold contacts. \( d \) and \( b \) are depending on the particular sample dimensions while \( l_{ss} \) is equal to 480 µm (cf. Fig. 4.1(a)). The results of the specific resistance are plotted in Fig. 3.10 in relation to the growth pressure.

As obvious from Fig. 4.1(b), the resistivity varies from \( 0.5 \cdot 10^4 \Omega \text{cm} \) to \( 1000 \cdot 10^4 \Omega \text{cm} \), depending on the specific sample used for the measurement. However, no clear trend is observable. For example, there are two samples which are grown at 25 µbar in argon, one with a normal thickness (50000 pulses and marked with “thin”)
4.3 Electrical conductivity measurements with the use of IDT-structures

and one which is three times thicker (150000 pulses and marked with “thick”). The normal sample has an enormous high resistivity while the thick one has a relative small value. Probably this is an error in measurement possibly induced by a bad or insufficient contact between test prod and the gold layer. The resistivity values are more than six orders of magnitude larger than the literature value of bulk samples, which is around \(2 \times 10^{-2} \text{\Omega cm}\) [14]. This high resistivity value indicates an insulator rather than a conductive metal.

Furthermore, the electrical current \(I\) is in the area of 0.1nA up to a maximum value of 200nA at 400V and therefore at the measuring limit of the used instrument. Thus, in the next step, a IDT-structure is used to improve the resistivity measurement.

4.3 Electrical conductivity measurements with the use of IDT-structures

Since the resistivity measurements performed with a simple stripe structure exceeds the limit of the used measuring instrument, resistivity measurements using a IDT-structure are discussed in this chapter. For this the Pr\(_2\)Ir\(_2\)O\(_7\) films are measured in a cryostat performing resistivity versus temperature \(\rho(T)\) measurements. The measured \(\rho(T)\) curves are shown in Fig. 4.2. As obvious from Fig. 4.2(b), the resistivity value is strongly dependent on the used measuring structure. The resistivity values derived from the measurements are more than three orders of magnitude larger than the corresponding measurement with the simple stripe structure. A possible reason could be that caused by a high voltage \((V_{\text{SS}} = 100\text{V})\) at the stripe structured film creepage currents or flashover arise in contrast to the IDT-structured film at which only a voltage of \(V_{\text{IDT}} = 20\text{V}\) is applied. But a comparison of the electric fields make a flashover at the IDT-structure more likely:

\[
E_{\text{IDT}} = \frac{V_{\text{IDT}}}{l_{\text{IDT}}} = \frac{20\text{ V}}{3.4\text{ \mu m}} > \frac{400\text{ V}}{480\text{ \mu m}} = \frac{V_{\text{SS}}}{l_{\text{SS}}} = E_{\text{SS}}
\]

Therefore, this can be excluded. Still remains the possibility of creepage currents in the measuring equipment itself.

Furthermore, by using a IDT-structure the resistivity of the Pr\(_2\)Ir\(_2\)O\(_7\) thin films is even higher in the order of \(10^9\text{\Omega cm}\). Therefore, these films are insulating. Moreover, they barely show a temperature dependency as it is the case for polycrystalline Pr\(_2\)Ir\(_2\)O\(_7\) bulk material as shown in Fig. 4.2(c) and (d). This might be again caused by non-stoichiometric effects like iridium loss or oxygen vacancies.
4.4 Conclusion about the electrical characteristics of \( \text{Pr}_2\text{Ir}_2\text{O}_7 \)

The resistivity of the \( \text{Pr}_2\text{Ir}_2\text{O}_7 \) thin films is measured by two different methods. First, a simple stripe structure is used to determine the resistivity. However, in these measurements the current value does not exceed 200nA at a voltage of \( V = 400 \text{ V} \) due to the high resistivity of the \( \text{Pr}_2\text{Ir}_2\text{O}_7 \) thin film. Therefore, creepage currents might influence the measurement. Second, an IDT-
4.4 Conclusion about the electrical characteristics of Pr\textsubscript{2}Ir\textsubscript{2}O\textsubscript{7}

structure in combination with a current amplifier is used. In these measurements the resistivity of the Pr\textsubscript{2}Ir\textsubscript{2}O\textsubscript{7} thin film is of the order of 10\textsuperscript{9} Ωcm and therefore more than eleven orders of the magnitude larger than the corresponding value for polycrystalline Pr\textsubscript{2}Ir\textsubscript{2}O\textsubscript{7} bulk material. At the moment, this behaviour is unclear. One possibility might be non-stoichiometric effects like iridium loss or oxygen vacancies. In conclusion the praseodymium films are not electrical conductive and have no metallic characteristics as a decreasing resistivity to lower temperature. Further experiments like XPS have to be made to reveal the stoichiometry in Pr\textsubscript{2}Ir\textsubscript{2}O\textsubscript{7} thin films. Then concrete conclusions can be drawn whether the characteristics of the bulk material change to thin films.
Chapter 5
Summary and outlook

In this bachelor thesis, for the first time in literature, the fabrication of Pr$_2$Ir$_2$O$_7$ thin films and its electrical properties have been investigated in detail. The thin films were fabricated by pulsed laser deposition (PLD).

In order to determine the optimal growth parameters temperature and pressure series in different atmospheres were performed. By x-ray diffraction and atomic force microscopy the optimal substrate temperature and the optimal growth pressure was found to be $T_S = 750^\circ$C and $p_{Ar} = 25\mu$bar, respectively. Furthermore, it was observed that the quality of the Pr$_2$Ir$_2$O$_7$ thin films depend strongly on the atmosphere used in the PLD process. While for a pure oxygen atmosphere no single-phase Pr$_2$Ir$_2$O$_7$ thin films was obtained, in an argon atmosphere the fabrication of Pr$_2$Ir$_2$O$_7$ thin films with a high crystalline quality could be achieved.

The electrical transport measurements show no electrical conductivity of the Pr$_2$Ir$_2$O$_7$ thin films. With a resistivity in the order of $10^9\Omega cm$ these films are insulating with no metallic behaviour although the bulk material of Pr$_2$Ir$_2$O$_7$ is metallic and has a low resistivity of $10^{-2}\Omega cm$. This might be explained by non-stoichiometric effects like an iridium loss due to its high volatility. First XPS-measurements suggest an iridium loss in the Pr$_2$Ir$_2$O$_7$ thin films, but further experiments have to be carried out.

An extraordinary discovery, which not has been expected, is that the Pr$_2$Ir$_2$O$_7$ thin films are not chemically stable in air. Fig. 5.1 shows how the film structure changes. A guess is that the Pr$_2$Ir$_2$O$_7$ film reacts with the oxygen in the air forming a praseodymium oxide. This just shows how sensitive Pr$_2$Ir$_2$O$_7$ thin films are. This could already have been seen at the sensitive growth parameters. But this short stability of the Pr$_2$Ir$_2$O$_7$ phase needs to be investigated in further experiments.

Further experiments are necessary whether Pr$_2$Ir$_2$O$_7$ thin films change their properties by the strain or by other reasons like iridium loss.
Figure 5.1: (a) Microscope image of an Pr$_2$Ir$_2$O$_7$ thin film directly after the PLD process. The area on the lower right only the YSZ substrate is visible, since the substrate is masked during the PLD process by the sample holder in this area. (b) Microscope image of the same film after one month.
Appendix A

Experimental methods

In this first section of the appendix the experimental methods, which are used in this thesis, are shortly described. In particular, it includes the pulsed laser deposition (PLD), the x-ray diffraction (XRD), electrical measurements in a liquid $^4$He-cryostat and the atomic force microscope (AFM).

A.1 PLD- pulsed laser deposition

To produce thin films of praseodymium iridate in this work the method of pulsed laser deposition is used. In the following the functionality is described in more detail (see Fig. A.1). At the beginning the substrate is put into the PLD-chamber and is heated by an infrared laser to the required temperature. In the next step the beam of the excimer laser is focused on the polycrystalline target which has the right stoichiometric ratio. This happens by a lens system. Because of the high energy density at the target, this gets ionized. With this a plasma occurs. The plasma propagates to the substrate.

The RHEED-system (reflection high energy electron diffraction), which is used to
observe the growth of the crystal already during the growing process, is not used in this work. For further information to the PLD and RHEED system it is referred to Refs. [21, 22].

A.2 XRD- x-ray diffraction

Figure A.2: (a) Description of the incidence angle $\omega$ and its relation to the $2\Theta$-angle. (b) A visualization of the angles $\omega$, $\chi$ and $\phi$ and how they change the orientation of the sample.

The x-ray diffraction is used for the structural examination for the samples in this work. The irradiated light is diffracted at the crystal and then the detector measures the intensity addicted to the angle. In this case the irradiated light is radiation of the Cu K$_{\alpha 1}$ spectral peak with a wavelength of $\lambda = 1.5418$ Å which is achieved by a monochromator and a Goebel mirror. To get a maximum intensity the Bragg condition must be satisfied:

$$2d_{hkl} \cdot \sin \Theta = n\lambda. \quad (A.1)$$

Here $d_{hkl}$ is the distance of the lattice planes of the crystal, $\Theta$ is the angle of incidence of the x-rays relative to the out-of-plane direction and $n$ is the diffraction order of the maximum. For the examination in this work $2\Theta - \omega$-scans, rocking curves and reflectometries are used.

At the $2\Theta - \omega$-scan the observed crystal is scanned with a fixed ratio between $2\Theta$ and $\omega$ in out-of-plane direction. By this one will get the so called symmetrical reflexes. They only give information about the distance of lattice planes in out-of-plane direction. If the distance of lattice planes in in-plane direction is searched, an asymmetrical reflex by a RSM is necessary.

In a RSM (reciprocal space map) several line-scans in out-of-plane and in-plane direction around the asymmetrical reflex are made. The RSM gives information about the thin film whether it is relaxed or strained.
In the rocking curve the $2\Theta$-angle and the position of the detector is fixed and the $\omega$-angle is changed. The FWHM value gives information about crystalline quality. With the reflectometry the thickness and roughness of the samples can be determined. This includes $2\Theta - \omega$-scan from $2\Theta = 0.5^\circ$ to $2\Theta = 5^\circ$ whereby the radiation is reflected at the surface of the thin film and at the boundary layer between thin film and substrate.

For more detailed information it is referred to Refs. [21, 22, 23]. At the determination of the lattice constant with the aid of the $2\Theta - \omega$-scans the systematical errors have to be considered. For this the calculated values of the lattice constant are extrapolated by the Nelson-Riley-method to $2\Theta = 180^\circ$. So the error is proportional to

$$\frac{\cos^2\Theta}{\sin\Theta} + \frac{\cos^2\Theta}{\Theta}$$

(see Refs. [24, 25] for more information).

### A.3 Optical lithography

All processes to the optical lithography are taken place in the clean room with exclusion of ultraviolet (UV) light. Since in this work only the lift-off-process is used, just this process is described. In the beginning the sample is cleaned in the ultrasonic bad with acetone and isopropanol. Following this cleaning process the photoresist is spinned on the film by putting the sample on a centrifuge. Then the sample is prebaked 70s at $110^\circ$C.

In the next step the mask with the desired structure (here IDT-structure) is placed on the film, using a mask aligner. The structure is built up of a metal layer which is impenetrable for UV light. The mask and sample is exposed ca. 5s with UV light which corresponds an energy of 36 mJ. Now the sample is rebaked 30s at $120^\circ$C and then is lighted with UV light again with an energy of at least 200 mJ. At last the sample is developed 30s and the process in the clean room is finished. On the surface of the film now is photoresist everywhere, only the form of the structure is spared out.

On the whole surface of the film a 100nm thick gold layer is now sputtered. The gold which lays on the photoresist gets removed (→ lift-off) by cleaning the sample in acetone, whereby only this gold layer remains which is located directly on the film. So at last only the structure in form of gold is on the surface.
A.4 AFM- atomic force microscopy

For determining the surface roughness of a sample the atomic force microscopy can be used. By this method a quantitative value of the roughness is determined and also a picture of the topography is made.

In the process the sample is gauged by a cantilever (cf. Fig. A.3). This needle is sensitive to the surface potential and is attracted or rejected depending on the distance to the surface. The movement of the cantilever is transferred by a laser beam on a photodiode. To determine the movement of the needle very precisely, it is placed on a piezo element which regulates the height of the cantilever so that the signal of the laser at the photodiode does not change. This height regulation can be used to create a surface profile. For more detailed descriptions of the functionality and the setting see Ref. [26].
Appendix B

Samples and parameters

The fabricated samples and their growth parameters are summarized in this chapter.
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Bibliography


Appendix B Bibliography


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