Subsurface oxygen investigation on Rh(110) Crystal

Dissertation zur Erlangung des Grades eines Doktors der Naturwissenschaften

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Chapter 1

Introduction

Rhodium was first discovered in 1803/04 by the English doctor, physicist and chemist W.H.Wollaston. This element is occurring natively with other platinum metals as an ore in river beds of the Urals and in North and South America [1]. The annual world production of rhodium is a mere 7-8 tons, resulting the high current prices of 300$/g for powder and 1500Euro for oriented single crystals (ca. 10g by MaTeck).

The primary use of rhodium is reported as an alloying agent to harden platinum and palladium [2]. Such alloys are used for furnace windings, thermocouple elements, bushings for glass fiber production, electrodes for aircraft spark plugs, and laboratory crucibles. Furthermore, it is used as an electrical contact material because it has a low electrical resistance, a low and stable contact resistance, and is highly resistant to corrosion. Plated rhodium, produced by electroplating or evaporation, is exceptionally hard and is used for optical instruments due to its high reflectance, hardness and durability. Pure rhodium is used for mirrored surfaces in searchlights and as a plating finish for jewelry and silverware [2].

The most important aspect of rhodium in our case is that it is one of the six platinum group metals - iridium, osmium, palladium, platinum, rhodium and ruthenium, which have outstanding catalytic properties. In catalytic converters, platinum and rhodium catalyze [3, 4] more complete combustion of unburned fuel by converting diatomic oxygen ($O_2$) to monatomic free radical oxygen needed to convert carbon monoxide (CO) to carbon dioxide ($CO_2$). This reaction liberates a considerable amount of heat, which aids in the more complete combustion of hydrocarbon (HC) compounds in the fuel. At high temperatures, diatomic nitrogen ($N_2$) in the air-fuel mix can be cracked, leading to the formation of nitrogen oxides ($NO_x$), a major cause of smog pollution and a major ingredient in acid rain. Rhodium inhibits the cracking of $N_2$, and at the same time promotes the cracking of any $NO_x$ that may have formed, thus lowering the $NO_x$ emissions.

Practically used automobile converters work in a high temperature and pressure environment. Also, the catalyst consists of dispersed polycrystalline particles sup-
ported by other materials (e.g., ceramic pellet substrate). This differs considerably from basic research conditions in an ultra high vacuum (UHV) through so called pressure and material gaps. Recently surface science experimentalists tried to reduce this gap while working in high pressure and temperature conditions, and thereby observed that the catalytic behavior of these catalysts is influenced through the reaction conditions. At high pressure condition the catalytic property is changed with time, due to oxygen diffusion into the bulk and forming the subsurface (under the surface) oxygen species [5, 6]. Therefore, understanding the nature of the subsurface oxygen species is of fundamental importance for heterogenous catalysis.

The aim of this work is to study the generation of a subsurface oxygen state and its properties on the Rh(110) surface and thereby to contribute to the fundamental research.

In this work clean and oxygen covered Rh(110) surfaces with a special focus on the oxygen diffusion process into a subsurface region are studied. Due to previous studies on the rhodium crystal in our work group and the discovery of a new kind of subsurface oxygen species on the Rh(111) surface, the Rh(110) crystal was chosen for the following investigations. Furthermore, rhodium is an important catalyst in the decreasing of harmful substances in automobile exhaust gas and it has so far not been investigated if this high catalytical property is still present on the rhodium if the crystal contains subsurface oxygen species.

The thesis starts with a short description of used methods (chapter 2), which are outlined in the theoretical, experimental and analytical parts separately and subsequently. In following the experimental setups and the sample preparation methods (chapter 3) used in this work are described. The results from the present experiment are reported in chapters 4 and 5. The structure of the clean surfaces is addressed in section 4.1.

After the characterization of the clean Rh(110) with different methods, the adsorption states of oxygen on the surface were investigated by AES, STM and TDS methods. The experiments concerning particular oxygen chemisorption states can be found in section 4.2 separately. Generally, the chemisorption states on Rh(110) are well known, but it is a fundamental step before dealing further with the subsurface oxygen state. During the study also an unobserved partial oxygen induced structure was found.

Comparing the observed chemisorption states of oxygen with the results of other authors, the investigation of the subsurface oxygen state is begun as a next step. The results concerning this investigation are reported in section 5. Until now, this state on this surface had not been investigated.

Every chapter begins with a short summary of previous experimental work concerning the topic. In the following sections the results of the present work are reported and discussed. A conclusion including main points (chapter 6) closes this work.
Chapter 2

Basics of measuring methods

This chapter covers the experimental and theoretical basics of the measuring methods used throughout the work. The methods are already well established and have been described extensively before by many authors. Therefore only a brief introduction is given. For each method a short theoretical description following a practical part and models used for analyzing and interpreting the results are reported. More interested readers are referred to further literatures.

2.1 Thermal desorption spectroscopy (TDS)

Temperature Programmed Desorption (TPD) or Thermal Desorption Spectroscopy (TDS) is one of the most frequently employed techniques in surface science and catalysis. This method is used in this work as a main investigation method.

2.1.1 The basic principle of the TDS

In thermal desorption spectroscopy one investigates a binding of adsorbed particles through breaking the bond thermally and analyzing the desorbed particles. More precisely its main principle is: first exposing the sample surface to gas particles and reach thereby defined beginning adsorbate state; heating the sample with a rate \( \beta = dT/dt \) and at the same time detecting the desorbing gas particles by mass spectrometry. Any species adsorbed on a surface is bound to the surface with some specific amount of energy and desorbs at a rate determined by Bolzmann factor. Heating the surface will increase this desorption rate. And a study of temperature dependence of a desorption rate can lead to information of binding energy of adsorbate states. But it is often difficult for interpretation of obtained spectrum, specially if chemical (decomposing) reaction on the solid surface took place.

The main components of TPD method, adsorption and desorption processes are
briefly introduced in following.

**Adsorption**

The particle adsors on the surface if there is an attracting interaction. When the attraction defines by Van-der-Vaals force, then physisorption takes place and its binding energy is approximately below 50kJ/mol. When attraction is caused by ionic or complete covalent interaction then it forms a chemical bond and chemisorption occurs. The chemisorption process is an activated process, i.e. the formation of chemical bonding has an activation barrier to overcome. One common feature of chemisorption is the weakening of intramolecular bonds which often leads to dissociation of adsorbed molecule. An example of such activated dissociative chemisorption is oxygen adsorption on metal surfaces; oxygen molecule comes to surface and interacts with surface and then dissociates and adsorbs as an atomic oxygen.

The adsorption kinetic is controlled by a rate of adsorption \( R_{ads} \) of a molecule onto a surface, defined as a sticking coefficient times number of hitting of a molecule the surface per a time:

\[
R_{ads} = S \cdot \frac{P}{\sqrt{2\pi mk_B T}}
\]  

(2.1)

where \( m \) - the mass of particles, which hit the surface at partial pressure \( P(\text{[Nm}^{-2}\text{]}) \) and at temperature \( T(\text{[K]} \). The sticking coefficient \( S \) is defined as a property of the adsorbate/substrate system under consideration and it lies in the range of \( 0 < S < 1 \); this sticking coefficient depends not only on the geometrical structure of the substrate (step, edge, ...) but also on the existing coverage and temperature. Under these circumstances the equation can be written as following:

\[
R_{ads} = \frac{P}{\sqrt{2\pi mk_B T}} \cdot \sigma f(\theta) e^{-\frac{E_a}{RT}}
\]  

(2.2)

here \( \sigma \) is sticking probability; \( E_a \) - activation energy for adsorption; \( R \)- gas constant; \( k_B \)-Boltzmann constant; \( f(\theta) \) is a function of the existing surface coverage \((\theta = \frac{\text{number of ads. species}}{\text{number of surface ads. sites}}) \) of adsorbed species.

\( f(\theta) \) can be calculated only in simple cases for example for a non dissociative adsorption \( f(\theta) = (1 - \theta) \) (proportional to a number of empty places) and dissociative adsorption \( f(\theta) = (1 - \theta)^2 \) (it requires two adjacent empty places). Generally the activation energy for adsorption may itself be dependent upon the surface coverage, i.e. \( E_a = E(\theta) \).

In a experiment to estimate the surface coverage arising as a result of gas exposure one assumes \( R_{ads} = \frac{dN_{ads}}{dt} \) and \( N_{ads} \) could be obtained as:

\[
N_{ads} = \int_0^t S \cdot F \cdot dt \quad \Rightarrow \quad if \quad S = \text{const} \quad N_{ads} = S Ft
\]  

(2.3)
where $N_{ads}$ is the number of adsorbed species per unit area of surface, $F$ is gas flux, which is proportional to the gas pressure. The $S=\text{const}$ approximation is only valid for low coverage. For gas exposure is used the unit Langmiur, where $1\text{L}=10^{-6}\text{Torr}\cdot\text{s}=1.33\cdot10^{-6}\text{mbar}\cdot\text{s}$. From the linear proportionality of adsorbed molecule at low coverage to the exposing time one can estimate the sticking coefficient. For example, it is $\sim 0.9$ for an oxygen adsorption on the rhodium single crystal in contrast to $10^{-5}$ for oxygen on platinum.

**Desorption**

The desorption is a process whereby the binding of adsorbed species to the substrate would be broken and removed from the surface. This removing is a activated process and it succeeds by thermal, electron simulated, photo, ion impact, high electric field excitation. The desorption process is determined also by a desorption rate $R_{des} = -\frac{dN_{ads}}{dt}$, which is the number of desorbed particles from unit area per a unit period of time. From the reaction kinetic [7] the desorption rate is determined through its reaction rate constant ($k_{des}$) and coverage ($\theta$).

$$R_{des} = -k_{des} \cdot \theta^n \quad (2.4)$$

The reaction rate constant depends on the reaction temperature and this dependence is described by Arrhenius (eqn. 2.5) or Eyring (eqn. 2.6) equation.

$$k_{des}(T) = \nu_n \cdot e^{-\frac{E_{d,a}(\theta)}{RT}} \quad (2.5)$$

$$k_{des}(T) = \frac{k_B T}{h} \cdot e^{-\frac{\Delta G}{R T}} = \frac{k_B T}{h} \cdot e^{-\frac{\Delta S}{R T}} e^{-\frac{\Delta H}{R T}} \quad (2.6)$$

in which $\theta$ is the adsorbate coverage, $t$ the time, $n$ order of desorption, $\nu_n$ pre-exponential factor of $n^{th}$ order desorption, $E_{d,a}$ the activation energy of desorption (i.e. the energy required to lose the binding to the substrate), $R$ the gas constant, $h$ the Planck constant and $T$ the temperature. In Eyring equation $\Delta G$ (free activation enthalpy) can be separated in terms of $\Delta H$ (activation enthalpy) and $T\Delta S$, where $\Delta S$ is an activation entropy. These can be converted into the activation energy and pre-exponential factor respectively.

Using the Arrhenius form the desorption rate for $n^{th}$ order thermal desorption is written on by Polani-Wigner equation:

$$R_{des}(\theta) = -\frac{d\theta}{dt} = \nu_n(\theta) \cdot \theta^n \cdot e^{-\frac{E_{d,a}(\theta)}{RT}} \quad (2.7)$$

In thermal desorption experiment the temperature $T$ is increased with time $t$ linearly with a heating rate $dT/dt = \beta$. The desorption order can take following values:
• \( n = 0 \), the zeroth order desorption, the rate of desorption does not depend on the number of surface adsorbates.

• \( n = 1 \), the first order desorption, thus for molecular adsorbate, where the rate of desorption will depend linearly on the number of surface adsorbates available for desorption.

• \( n = 2 \), the second order desorption, thus if diatomic molecules adsorbed dissociatively and desorb re-associatively, then a requirement for desorption is that there are two suitable atoms adjacent to one another, the probability for which depends square of the surface adsorbed atomic concentration.

Through setting the desorption maximum condition \( \frac{dR_{\text{des}}}{dt} = 0 \) in equation 2.7 one gets the following one of the often used equation for determining the desorption parameters:

\[
\frac{E_{d,a}}{RT_m^2} = n \cdot \theta^{n-1} \cdot \nu_n \cdot \frac{\nu_n}{\beta} e^{-\frac{E_{d,a}}{RT_m}}
\]  

(2.8)

In general \( E_{d,a} \) and \( \nu_n \) are coverage dependent \( (E_{d,a}(\theta), \nu_n(\theta)) \), because of lateral interactions between adsorbate particles. This makes difficult to calculate the desorption parameters \( (E_{d,a}, \nu, n) \) from the TD experiment. Another often used form of desorption equation 2.7 is in following:

\[
-\frac{d\theta}{dT} = \frac{\nu_n(\theta)}{\beta} \cdot \theta^n \cdot e^{-\frac{E_{d,a}(\theta)}{RT}}
\]  

(2.9)

Using this equation 2.9 in Figure 6.1 are illustrated the dependencies of desorption behavior on its parameters. As it can easily be recognized that a strong binding of adsorbate can be caused in both first and second order desorption either by the high activation energy of desorption or by the small pre-exponential factor.

For further deep knowledge about adsorption and desorption processes the reader is refered to [8, 9, 10] and the references therein.

### 2.1.2 Experimental

The schema of simple TD experiment is in Figure 2.1.a presented. Its main components are controlled heating device and detector of desorbed gas particles (mass spectrometry). More about the experimental realization is elucidated in section 3.1.

Data obtained from this experiment contains intensity variation of each recorded mass as a function of time or temperature. Figure 2.1.b displays a typical TD spectrum, which is taken with a heating rate 10K/s from the Rh(110) crystal after exposing to 5L of oxygen.

The measured desorption signal is proportional to the desorption rate. And the desorption during the experiment causes a partial pressure change in the recipient.
Figure 2.1: a. The schematic view of TDS experiment, b. A typical TD spectrum 
\( p(T) \sim R_{\text{des}} \) of mass 32.

This partial pressure change is expressed by pressure balance equation, which contains pressure change, gain from desorption and loss through pumping:

\[
\frac{dp}{dt}_{\text{change}} = \frac{Ak_B T_g}{V} \frac{dn}{dt} - \frac{pS}{V}
\]  

(2.10)

in which \( p \) is partial pressure in chamber, \( k_B \) the Boltzmann constant, \( V \) the recipient volume, \( T_g \) the temperature of gas particle, \( n \) the number of desorbing particle per unit area, \( S \) the pumping velocity of the system.

In UHV performed experiments a condition \( \frac{dp}{dt} \ll \frac{pS}{V} \) keeps, so that the equation 2.10 could be simplified. In this case from the direct integration of the equation 2.10 one can get total number of desorbed particles like following:

\[
N_s(t_0) = N(t_{\text{end}}) = S \int_{t_0}^{t_{\text{end}}} p dt
\]  

(2.11)

Since determination of \( S \) is connected to large error, one assumes that in TD spectrum the area under the desorption curve is proportional to the total number of desorbed particle, and \( p(t) \) itself is proportional to the desorption rate at the moment.

This technique is only of interest when heating returns the “clean” surface.

2.1.3 TD spectra analysis procedures

There many analysis methods for determining the desorption parameters from TD spectra were developed. These methods differ considerably by required experimental data quantity. In some methods it needs only one TD spectrum or only one part of this, but in others it needs a set of measurements at different conditions. Here in table 2.1 most often reported methods are summarized and suitable references are given.
Table 2.1: Overview of TDS analyzing methods

<table>
<thead>
<tr>
<th>Methods</th>
<th>Principle</th>
<th>Condition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complete analysis</td>
<td>at every curve fixes a point of certain $\theta'$: $-\frac{E_d}{RT}$ as a slope of the plot: $\ln(R_{des})$ vs $\frac{1}{T}$ and from the intercept $n \ln \theta' + \ln \nu(\theta')$</td>
<td>required set of TD spectra with different initial coverages: $E_{d,a}(\theta')$, $\nu_{a}(\theta')$ calculated</td>
<td>[11]</td>
</tr>
<tr>
<td>Habenschaden-Küppers (HK) or leading edge analysis</td>
<td>in the region the variation of $T$, $\theta$ very small; $-\frac{E_d}{RT}$ as a slope of the plot: $\ln(R_{des})$ vs $\frac{1}{T}$ and from the intercept $n \ln \theta + \ln \nu(\theta, T)$</td>
<td>uses only low temperature side of TD spectrum (4%); $E_{d,a}(\theta)$, $\nu_{a}(\theta, T)$</td>
<td>[12]</td>
</tr>
<tr>
<td>&quot;Arrhenius&quot; plot</td>
<td>$-\frac{E_d}{RT}$ as a slope of the plot: $\ln(R_{des}/\theta^{\frac{n}{T}})$ vs $\frac{1}{T}$, from the intercept $\ln \nu$ and from the form $n$ is determined;</td>
<td>from different TD spectra with different initial coverages; $&lt; E_{d,a} &gt;$, $&lt; \nu &gt;$, $n$</td>
<td>[11]</td>
</tr>
<tr>
<td>Redhead’s peak maximum method</td>
<td>$E_d = RTm[ln(\frac{E_d}{\gamma})] - 3.64]$; $\nu$ is usually estimated as $10^{1.35-1}$ or if the $E_d$ is known: $\nu = \frac{E_d}{RTm^{2.695}e^{\frac{E_d}{RTm}}}$</td>
<td>from single TD spectrum peak maximum is required; one of the constant $E_{d,a}$ and $\nu_n$ can be calculated</td>
<td>[13]</td>
</tr>
<tr>
<td>Edwards peak width method</td>
<td>$E_{d,a}$ is polynomial of $T_m \pm \Delta W$</td>
<td>required from single spectrum the peak width and position; $\gamma = \frac{\Delta W}{T_m}$; constant $E_{d,a}$</td>
<td>[14]</td>
</tr>
<tr>
<td>Chan-Aris-Weinberg (CAW) method</td>
<td>for $n=1$: $E_{d,a} = RTm[-1 + (\gamma_{1/2}^2 + 5.832\gamma_{1/2})^{1/2}]$</td>
<td>from single spectrum peak maximum, peak half width and $3/4$ width are required; $\gamma_{1/2} = \frac{T_m}{W_1/2}$ and $\gamma_{3/4} = \frac{T_m}{W_{3/4}}$; $E_{d,a} \theta$, $\nu_{a}(\theta)$</td>
<td>[15]</td>
</tr>
<tr>
<td>Heating rate variations or Falconer Madix method</td>
<td>$-\frac{E_d}{RT}$ as a slope of plot: $\ln \frac{T_m}{\theta}$ vs $\frac{1}{T_m}$</td>
<td>$\beta$ set spectra with $\theta = const$; constant $E_{d,a}, \nu_{n}$</td>
<td>[16]</td>
</tr>
<tr>
<td>Thermal desorption spectra simulation</td>
<td>$E_{d,a}(\theta)=E_0-W \theta$; through varying the $E_0$ and $W$ find the fit curve of spectrum; $\ln \nu_{a}(\theta') = \frac{E_{d,a}(\theta)}{RTm} + c$</td>
<td>a single TD spectrum</td>
<td>[17]</td>
</tr>
<tr>
<td>Monte Carlo Simulation</td>
<td>adsorption heat for different adsorption places; $E_{d,a}(\theta), \nu_{a}(\theta, T)$</td>
<td>-</td>
<td>[18]</td>
</tr>
</tbody>
</table>
More detailed description about these methods can be read in references given on the table. A conclusion of most used methods is reported by Falconer and Schwarz [19].
Chapter 2. Basics of measuring methods

2.2 Low-energy electron diffraction (LEED)

The diffraction of low-energy electrons by single crystal surfaces was accidently discovered by Davisson and Gremer in 1927 [20]. Their results confirmed de Broglie’s postulate (1924) that the particles can be described by wave packets with a wave length \( \lambda = \frac{h}{mv} \) (m-mass, \( v \)-velocity) and therefore they should exhibit diffraction phenomena.

The interference intensity of slow electrons elastically scattered from the single crystal surface depends on direction and electron energy. The analysis from LEED is usually performed like following:

- determination of the interference maxima direction by inspection of the LEED pattern. Application of the simple geometric theory of diffraction then provides the unit cells of the periodic structure elements on the surface.

- only a perfect instrument and an ideally periodic surface will yield diffracted intensity exactly in well-defined orientations. In all other cases the intensity will vary more or less smoothly with an angle near these preferred directions. Such "beam profiles" can be analyzed with a good approximation by applying the kinetic theory, which yields information for partial order.

- variation of primary electron energy yields intensity-voltage (I(V)) spectra

Only the first (simple) of these three analyzing methods is used in this work. In the following, the principle of LEED will be described briefly, for an in depth treatment of the subject the reader may refer to e.g. [21, 22].

2.2.1 Theoretical

In LEED experiment a monoenergetic electron beam impinges the sample surface and is diffracted by it (see left part of Figure 2.2). If the surface atoms are well ordered in the coherence zone of the beam, then diffraction patterns on the fluorescence screen of the LEED optic can be observed, which faces towards the sample. The geometry of this LEED pattern reflects the geometry of reciprocal image of the sample surface. And with the varying primary energy of electrons varies the intensity of spots, therefrom one can yield information about position and chemical nature (substrate or adsorbate) of the scattering atoms. Because of the low energy of electrons in this method only few atom layers contribute to the diffraction intensity, which makes this method very surface sensitive. The electrons used in LEED have energy of 20-500eV and wave-lengths \(^1\) of 0.05 – 0.03nm \(^2\).

\[ \lambda(A) = \sqrt{\frac{150.4}{E(eV)}} \]

\(^1\) in the region of atomic distance

\(^2\) in the region of atomic distance
In case of normal incidence of electron beam, there is very simple and special interdependence of several parameters in real and reciprocal space, which is visualized in the Ewald construction in Figure 2.2. Through the view port one observes the LEED patterns and can determine the distance between patterns $t$. Because the LEED pattern can be described in reciprocal space by Ewald sphere, there should be a valid similar triangles construction as illustrated on right graph. Therefrom the vectors of the surface unit cell can be determined via the following equation:

$$t \frac{R}{|k_0|} = |a_i^*| \Rightarrow a_i a_j^* = 2\pi \delta_{ij}$$

$$|a_i| = \frac{\lambda R}{t \sin(\theta(a,a_j))}$$

where $a_i$ are the lattice vectors of the surface unit cell, $a_i^*$ are corresponding reciprocal lattice vectors, $R$ is the radius of the LEED screen, $|k_0|$ is the k vector of the primary electrons ($k = \frac{2\pi}{\lambda}$), and $t$ is the separation of the diffracted beams on the screen. This equation can be used for rough estimation of unit cell vector lengths from the LEED pattern.

As can be seen from the figure, a higher primary energy ($k_0$) corresponds to bigger Ewald sphere. Consequently, more rods of the reciprocal space intersect the Ewald sphere, which means that more spots are visible on the screen. Since the direction of (0,0) spot stays constant through all energy, because of mirror reflex on the surface, the diffraction spots move from (0,0) spot away if decreasing the electron energy, and
move to the this spot if increasing the electron energy.

Because in the reality the surface structure is not ideal ordered and it contains defects, domains and steps, which make the diffraction patterns complicated. The complications are visible from an increased spot size or decreased contrast between the reflex maxima and surrounding background. A quality of the LEED pattern depends on a monochromaticity of the electron beam and the size of ordered region. Conventional electron beams have a coherence length of below 10nm, so that the LEED is sensitive to the order on length scales smaller than 10nm. The spot size is inversely proportional to the diameter of ordered region on the surface. The larger the ordered region, the sharper the spot in the LEED pattern. For illustration of the possible complications Figure 6.2 is presented.

As long as in this work the LEED pattern is used to determine only periodicity of the surface, more detail information about diffraction theory is not reported. More interested readers are referred to [9, 21] and references therein.

2.2.2 Experimental

In LEED experiment are required the source of focused slow electrons with normal incidence at the surface and detector (fluorescent screen) of the diffracted electrons. This is enabled as in Figure 2.3 illustrated. The electrons emit from the hot filament, collimated by lens system and leaves the drift tube. The electron beam with ∼1mm diameter reaches the sample. The scattered electrons from the surface travel to screen’s 1st grid straight because first grid and sample are both applied to ground. To grids 2 and 3 are applied (suppressor) a negative potential so that only elastically scattered electrons can pass. Grid 4 is grounded to reduce the influence of the screen voltage on the suppressor grids [23].

The pattern is viewed with a high resolution video camera from the back side of sample (in STM from the front side) and stored in a computer. From the reason that the earth magnetic field influences on the electron beam trajectory, one should compensate it so that the (0.0) reflex overlap with the beam origin.

Because of the irreversible alignment of sample manipulator and still not enough magnetic shielding the normal incidence condition can only approximated. But since no I(V) measurements are performed, this is of minor importance.

2.2.3 The analysis of LEED pattern

From the observed diffraction pattern, determined by reciprocal vector \( \mathbf{g} = h_1 \mathbf{a}_1^* + h_2 \mathbf{a}_2^* + h_3 \mathbf{a}_3^* \), one should estimate the structure of periodically arranged atoms in real space, which described by \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) unit vectors. The \( \mathbf{a}_1^* \), \( \mathbf{a}_2^* \) reciprocal lattice vectors are corresponding to \( \mathbf{a}_1 \), \( \mathbf{a}_2 \) vectors and \( \mathbf{a}_3^* \) is arbitrary vector perpendicular to them. Here \( h_1, h_2 \) are integer diffraction orders and \( h_3 \) is arbitrary.
If the diffraction maxima are from recurring spots with same distance, then it is possible to win information about surface periodicity. Generally one has a known single crystal so takes $\mathbf{a}_1$ and $\mathbf{a}_2$ unit vectors from the plane surface and calculate the reciprocal vectors $\mathbf{a}^*_1$, $\mathbf{a}^*_2$. If the observed spots have reciprocal vector ($\mathbf{g}$) for integer $h_1$ and $h_2$, then spots are from substrate and if they are not integer then spots are from overlayer structure.

The classification of the surface structures frequently follows a nomenclature proposed by Wood [25] based on X-ray crystallography. If $\mathbf{b}_i$ is the lattice vectors of overlayer structure, then in this nomenclature the ratios of the basis vectors $b_1/a_1$, $b_2/a_2$ and the angle of rotation $\theta$ between the two lattices are used for classification.

The surface unit cell can be primitive (p) or centered (c). In this nomenclature the shorter unit cell vector is notated with index 1 in real space. Wood’s nomenclature is simple but it can not describe all periodic surface structures, therefore there exists universal nomenclature so called matrix notation, which uses following relation:

$$\mathbf{b}_1 = m_{11}\mathbf{a}_1 + m_{12}\mathbf{a}_2 \quad \mathbf{b}_2 = m_{21}\mathbf{a}_1 + m_{22}\mathbf{a}_2$$

To exemplify this nomenclature it has been taken an overlayer structure shown in Figure 2.4. On the left side of the graph is drawn the substrate structure as a lattice (in this case (110) fcc lattice), and the atoms of overlayer structure are imaged by dark points. This overlayer structure is notated as c(2×6) in Wood’s nomenclature. In this case $\mathbf{a}$ and $\mathbf{b}$ vectors are parallel so the angle zero can be ignored. In a matrix notation it would be then $\begin{pmatrix} 1 & -1 \\ 3 & 3 \end{pmatrix}$. 
Figure 2.4: Model overlayer structure for illustration, created by LEEDPAT Programm [24]. Left real space, right reciprocal space image. Vectors $a_i$ and $b_i$ are basic vectors of substrate and overlayer structure’s respectively.

The surface structures in this work are described by Wood’s nomenclature.
2.3 Auger Electron Spectroscopy (AES)

The Auger electron spectroscopy is a standard method for analyzing the chemical nature of the sample. This method was the major importance in this work.

2.3.1 Mechanism of the Auger process

In the Auger process, it is a matter of an atom which has been ionized in one of the core states through X-rays or energetic electrons (usually 3-10keV). This atom may return to its electronic ground state via one of the following processes:

- **Photoemission**: an electron of an energetically higher level "jumps" into the core hole and thereby it emits the rest energy as a characteristic X-ray (see Figure 2.5a)

- **Auger effect**: the core hole is filled by an outer electron and the released energy is transmitted in a radiationless process to a second electron, which may then leave the atom with a characteristic kinetic energy (see Figure 2.5b)

![Figure 2.5: De-excitation processes of atomic core holes. a. Emission of X-ray radiation b. Emission of an Auger electron, $KL_1L_2$ and $L_1L_2M_1$ auger electrons](image)

Auger electrons are classified by referring to the energy levels involved in their production. The characteristic kinetic energy of auger electron is independent of the
primary beam energy and is determined only by binding energies of electrons in the shell. For example kinetic energy of $KL_1L_2$ and $L_1L_2M_1$ auger electrons are:

$$E_{KL_1L_2} = E_K - E_{L_1} - E_{L_2}$$

$$E_{L_1L_2M_1} = E_{L_1} - E_{L_2} - E_{M_1}$$ (2.14)

where, $E_K$, $E_{L_1}$, $E_{L_2}$ and $E_{M_1}$ are the binding energies of the electron in $K, L_1, L_2$ and $M_1$ shells respectively. From Figure 2.5 one can see the different characteristic auger transitions in a graphical demonstration.

2.3.2 Experimental

The essential parts of an Auger electron spectrometry are a source of primary excitation and a detector system.

The source of primary electrons is generally an electron gun with focusing and deflection electrodes was used, and the electrons had a high energies of 2KeV. Since in this process no need of electrons only with homogeneous energy, so energy filtering is not necessary. At the grazing incidence of the primary electrons (angle of $10^\circ - 15^\circ$), the electrons penetrate less into the bulk and therefore excite more particles from the surface.

In the TDS chamber for auger experiment is used a four-grid LEED system as a retarding field analyzer, the circuit is shown in Figure 2.6. Here the primary electron beam strikes the sample surface with an angle about $< 15^\circ$, and from the created secondary electrons only these electrons, which have higher kinetic energies than a $U_r$ repeller negative potential, can reach the collector. The collector is biased usually a few hundred volts positive to aid collection of slow electrons emerging from the grid section and inhibit secondary electron emission from the collector itself. To avoid local charging of phosphor on the collector the negative potential to repeller grids is varied continuously between $U_{max}$ and zero. The collector current ($i(U_r)$) as a function of the retarding potential ($U_r$) is given by:

$$i(U_r) \sim \int_{eU_r}^{\infty} N(E)dE$$ (2.15)

where $N(E)$ is the energy distribution of electrons emitted from the sample, assuming that secondary electrons created at the grids can be neglected. The energy distribution can be obtained by differentiation:

$$\frac{dI(U_r)}{dE} \sim N(E)$$ (2.16)

Many of the peaks in the $N(E)$ curve have a tail on the low energy side, so that in practice the position of a differentiated peak on the energy scale is more easily defined. This can be recognized from the Figure 2.7, where total and differentiated Auger electron spectrum from the clean Rh(110) crystal are presented.
Chapter 2. Basics of measuring methods

Figure 2.6: The circuit for recording AE spectra using a four-grid LEED system as a retarding field analyzer

Figure 2.7: Auger spectra from the clean Rh(110) surface. The energy distribution $N(E)$ and its first derivative $dN(E)/dE$ are presented
2.3.3 Auger spectra analysis

Qualitative analysis of Auger Electron spectra is easy, because the elements have peaks at specific energies. At first one should identify the major peaks referring to the standard spectra and label all peaks attribute to them. Residual not labelled peaks originates from the minor contamination.

But quantitative analysis is connected to difficulties e.g. inelastic scattering and backscattering effects. One relatively simple method is to use the major peak height of each element and relative sensitivities of Auger process to each element, which are available in reference tables [26]. According to this method the concentration ($C_X$) of a given element $X$ is:

$$C_X = \frac{I_X/S_X}{\sum_i (I_i/S_i)}$$  \hspace{1cm} (2.17)

The relative sensitivity of throughout the experiment used elements are given in table 6.1.

At this point it is worth to mention that the XPS (X-Ray Photoelectron Spectroscopy) is more sensible in the case of very small amount of impurity. Since it was not used as a main analyzing method, would not be introduced here. Nevertheless therefrom results are reported in further section. The interested readers into details are referred to [22, 27, 23, 26].
2.4 Scanning tunnelling microscopy

Scanning Tunnelling Microscopy (STM) technique is based on the quantum mechanical phenomena “tunnelling” and it was developed in the early eighties by nobel prize winners Binnig and Rohrer [28].

Using particle’s wavelike character in quantum mechanics one can calculate its nonzero probability for crossing a potential barrier. If one assumes the simplest rectangle barrier with a height $V_0$ and length $d$, then the crossing or tunnelling current should be:

$$I_t \sim e^{-2Kd} = e^{-\frac{\sqrt{8mV_0}}{\hbar}d}$$

From this formula one can see that the tunnelling current depends strongly on the length and height of the barrier. Specially it is very sensitive to the length e.g. only 1 Å change in $d$ leads to a change of order of magnitude in $I_t$.

In STM an electron tunnels because of applied voltage (barrier) between a sharpened metal tip and sample with a nanometer distance and this tunnelling current (a few nA) would be measured during scanning movement of the tip above the sample. The applied voltage between tip and sample allows to tune the barrier height. This method allows imaging of solid surfaces on the atomic scale. From the recording of the tunnelling current in this certain area, one becomes an image of sample surface topography. Under ideal circumstances, the individual atoms of a surface can be resolved and displayed. The schematical view of the STM is illustrated in Figure 2.9.

2.4.1 Tunnelling between metals

In our STM study were used a metal tip and metal sample. Therefore tunnelling between metals is reported here briefly. In this case tip and sample form a metal-insulator-metal junction in the STM configuration. If the tip and metals are brought so near, that they can interact with one another, then they would have equilibrium electronic state. It means the Fermi levels are equalized (thereby arises a potential difference in the vacuum region, which is determined by the difference of their work functions). When the bias voltage $V_{bias}$ between the electrodes is zero (s. Figure 2.8a), their Fermi levels stay equal and there is no tunnelling current between them (Figure 2.8.a). When $V_{bias}$ is positive (the tip is grounded), the energy levels of the sample are lowered by $eV_{bias}$ so that the electrons in the occupied levels of the tip (between $e_f$ and $e_f - eV_{bias}$) tunnel into unoccupied levels of the sample (Figure 2.8.b). When $V_{bias}$ is negative (the sample is grounded), the energy levels of the sample are raised by $eV_{bias}$ so that the electrons in occupied levels of the sample (between $e_f + eV_{bias}$ and $e_f$) tunnel into the unoccupied levels of the tip (Figure 2.8.c). The transmission probability of the tunnelling is the largest for the electron at the...
Fermi level of the negatively biased electrode and steadily decreases as the energy is lowered from that level (shown by the lengths of the arrows in Figure 2.8.b and c). In general, most of the tunneling electrons come from within 0.3eV of the Fermi level of the negatively charged electrode [29].

### 2.4.2 Theory of tunnelling

The calculation of the tunnelling current is problematic, because the exact wave functions of tip and sample are required. The actual atomic structure of tip is usually unknown and even if it is known, because of very low symmetry, an accurate wave function calculation of the tip is infeasible. Therefore it has been developed different models for the tip. One of the simplest and most practical model for the tip was developed by Tersoff and Hamman [30]. For the calculation of the tunneling current they used Bardeen’s transfer Hamiltonian approach [31]. In Bardeen’s perturbation treatment, the tunnelling between two metals through a barrier is described in terms of the overlap between their wave functions tails. In their theory, Tersoff and Hamman, assumed the tip as a mathematical point (an atom with an s-orbital) and neglected tip-sample interaction. In this case STM current $I_t$ is proportional to the local density of states (LDOS) of the sample at the position of the tip $r_t$,

$$I_t \sim \sum_i \int dk |\psi_i^s(r_t,k)|^2 \delta(e_s - e_f) \equiv \varrho(r_t, E_f)$$

(2.19)

where $\psi_i^s(r_t,k)$ is the $i^{th}$ electronic band orbital of the sample, and $e_s$ its band orbital energy.

The delta function insures that only the band orbitals of the sample at the Fermi level contribute to the LDOS. On metal surfaces the charge distribution at the Fermi level can further be approximated by total charge density [32], and therefore contours
of constant LDOS at $E_F$ resemble contours of constant total DOS, which is the topography [33]. Therefrom for a given sample surface, the brightness of the pattern in the STM image is related to the high density pattern of the $\rho(r, E_f)$ plot. It is worth to mention here that for non-metallic adsorbates on metal surfaces the contours of constant LDOS at Fermi level can differ significantly from the total charge distribution, and an interpretation of STM images as topographic maps is in those cases not appropriate.

Although the s-orbital model oversimplifies the electronic structure of the tip, the Tersoff-Hamman theory has been used successfully in interpreting the STM images of a large variety of organic and inorganic materials. From the viewpoint of Tersoff-Hamman theory, the STM images of an adsorbate/substrate system can be simulated in terms of the partial electron density plot $\rho_{d,e}$ calculated for the adsorbate/substrate system with the tip positioned above the adsorbate layer.

### 2.4.3 Experimental

For experimental realization the tip was mounted on a three piezoelectric tubes and applying a certain voltage to their electrodes it was possible to operate the tip movement in nanometer distance from the surface above a certain area with a very high accuracy (e.g. $\sim0.1\,\text{Å}$). The STM works in two different modes, namely:

- $I_t=\text{const}$, constant current mode. With help of feedback of piezos the tip movement is controlled in that way so the current stays always constant.
- $d=\text{const}$, constant height mode. Here the height would be held constant through changing the current

![Figure 2.9: Schematic presentation of scanning tunnelling microscopy](image)

Although the STM itself does not need vacuum to operate (it works in air as well as under liquids), ultrahigh vacuum is required to avoid contamination of the samples.
from the surrounding medium.

A problem in investigating metal surfaces is the fact that these surfaces appear very flat to an STM, i.e., the apparent height of individual atoms (corrugation) is 1/100 to 1/10 of an atomic diameter. Therefore the distance between the tip and the sample must be kept constant within 1/100 of an atomic diameter or better (approx. 0.002 nm) for resolving individual atoms. This demands not only very high rigidity of the STM itself, but the device must be also efficiently decoupled from environmental vibrations. For that reason the turbo and oil diffusion pumps during the measurement were put down.

Because the tunnelling current depends strongly on the gap distance between tip and substrate and local density of states of materials, the STM images display not only the geometric structure of the surface, but also illustrate the dependence on the electronic density of states of the sample, as well as on special tip-sample interaction mechanisms which are not fully understood yet.

STM images are usually displayed as gray scale images with protrusions shown white and depressions black. In this work the images were subtracted from the background and slightly smoothed by interpolation to the image size used for display. In a few cases image processing has been used for contrast enhancement to display both the atomic corrugation and a larger height range such as different layers of atoms. For further reviews concerning STM operation and theoretical aspects and examples refer to some of many sources dealing with these topics [34, 9, 27, 35, 36, 37, 38, 39].

![ STM images with annotations](image.png)

Figure 2.10: Illustrations for tip problematic. a. Changed tip during scanning, b. Double tip.
The STM tip preparation

It is very important for acquiring STM image with an atomic resolution to have a very sharp tip. In this experiment used STM tips were etched electrochemically and fixed on a special holder [27, 40]. After the transferring it into the vacuum chamber it is sputtered and annealed and at 500-600K. If the tip does not provide good images during the data acquisition, it is prepared often through nano preparation, which is applied voltage pulses up to 10V for ”crashing” the tip into the sample surface a few angstroms (Å). Such preparation does not supply ideal tip, therefore it includes several minitips that carry tunnelling current over different parts of the sample, so that the resulting image is a superposition of several scans (see Figure 2.10a). If the surface is quite rough, which is most often the case, then the closest minitip to the surface has more chance to carry main current. From this difficulty must be interpreted STM images very carefully, since they may not reflect the real sample topography. Usually for reasonably flat surfaces, such multiple tip effects can easily recognized, since step edges appear doubled (see Figure 2.10b) or tripled and step heights do not correspond to expected values. This has to be kept in mind when looking at STM images.
Chapter 3

Experimental setup

The experiments were carried out in two different Ultra High Vacuum (UHV) systems. The UHV was needed for ensuring a clean and controlled sample surface during the experiment and for application of some analyzing methods. The first system was used for thermal desorption spectroscopy and the second for scanning tunnelling microscopy experiments.

In this chapter experimental setups of the chambers are briefly and successively introduced in two separate sections. The principal background of used single equipments is given in further subsections. At the end of every section a short commentary on standard sample preparation procedures are reported.

3.1 Thermal desorption spectroscopy chamber

For the performance of the Thermal Desorption Spectroscopy (TDS) experiments it was available all-metal UHV chamber of Varian. In Figure 3.2a and b. are presented a photo and a schematic view of this TDS-UHV system. In 60L chamber the UHV was generated by oil diffusion pump(1), turbo-molecular pump(2) combined with ion getter pump(3) and titan sublimation pump(4), and final heating the chamber to 400K for \( \geq 20 \) hours. The obtained UHV had a base pressure of \( \leq 5 \cdot 10^{-10} \) Torr, was measured by cold-cathode ionization gauge. The main components of the residual gas are hydrogen (masse 2), water (masse 18) and carbon monooxide (masse 28), and this can be seen
from a mass spectrometer(9) recording of in Figure 3.1. The water content in chamber is increased because of alternative using of hydrogen and oxygen gases.

Figure 3.2: a. A Photo of the TDS chamber b. A schematical view of the TDS chamber. LEED/AES optics is hidden behind the recipient.

Gas inlet/ dosage

For inlet the different gases into the chamber were available two different ways: the first, directly from the gas chamber(6) by opening the variable leak valve \(^1\) of a certain gas bottle; the second, through the homemade nozzle(7), which is for not much worsening the base pressure during the exposure. Its schema is drawn in Figure 3.3 in detail. These both enabled a constant partial pressure in the chamber.

All exposure data are given in unit Langmiur (L), where \(1L=1\cdot10^{-6}\text{Torr} \cdot \text{s}\). The necessary gases for the sample preparation and the experiment were oxygen \((O_2, \text{purity } 4.8)\), argon \((Ar; \text{ purity } 5.0)\), hydrogen \((H_2; \text{ purity } 5.0)\) and all from the firma Messer Griesheim in 12Bar gas cans.

\(^1\)minimum leak rate of \(10^{-10}\text{Torr} \cdot \text{s}\), working pressure from atmospheric to \(10^{-11}\text{Torr}\)
3.1.1 Measuring devices

The investigating sample was mounted in the center of this UHV recipient on a manipulator with four moving freedoms, namely in x, y, z movable and around z turnable. At the side flanges of the chamber were installed the devices: QMS(9), sputter canon(10), electron canon and LEED/AES optics. In Figure 3.4 the cut of the recipient through a sample plane is illustrated to give a topology representation of the measuring devices and the sample. In following short principal descriptions of the devices (which not introduced in section 2) are given separately.

![Figure 3.4: The imaginary cut of the recipient through the sample plane](image)

Quadruple mass spectrometry

The main measuring device in the TDS chamber was a Quadruple Mass Spectrometer (QMS) of Balzers, which had a homemade cup for detecting only the signal from the sample. The QMS-112 of Balzers GmBH consists of ion source, rod system, ion detector and housing with montage flange. A schematical drawing of QMS-112 is in Figure 3.5a displayed. The ion source consists of emitting glow (cathode) and electron collector (anode). The electron emission leads to ionizing through electron strike the molecules of analyzing gas mix. In dependence of specific arrangement of electrodes and screen it lets the ions channel into the rod system. The rod system consists of four cylindrical and accurate grind rod electrodes, whose adjustment is the decisive factor for irreproachable and reproducible mass separation. At the rod system during operation is applied a changeable high frequency voltage and this proportionally overlays direct voltage. The vibration property of ion in this resulting electrical field affect
so that in dependence of amplitude of vibration only thus ions with certain mass and charge can reach the detector, the rest would be out filtered. The ions appear in detector in a form of electrical current, which can be measured with the help of secondary electron amplifier.

![Diagram of QMS](image)

Figure 3.5: a. Schematical drawing of the QMS after [41], b. The schema of the QMS coating.

The QMS in this recipient has provided an extra cone formed coating for avoiding to measure disturbing beside signals from an environment. The cone end foraminates opening with a 3.7mm diameter (see Figure 3.5b). During the measurement the sample will be positioned directly in front of the opening in distance of \( \sim 3 \text{mm} \). To avoid stagnation in the coating of QMS, it is pumped differentially by the turbo molecular pump (see Figure 3.2 (9)).

**LEED/AES optics**

**LEED** For recording of LEED pattern a four-Grid-LEED/AES optic of Varian (see Figure 2.2), Panasonic TV camera and M.Hoheisel "LEED” software (version 1.5) were available. Its functionality is described in section 2.2.

**AES**

Grazing flow of electrons with 2KeV energy were used as primary electrons. For controlling if the electrons meet the sample, the so called sample current was measured and at the same time observed the illumination of the LEED screen. It should be optimized at high sample current and best screen illuminating. The single components used for the retarding field AES (see Figure 2.6) are:

- electron gun, Varian
• CMA collector, Varian 981-2601
• Counter XR 2206,
• Log in Amplifier Dynatrac-3191a, Ithaco
• RC-generator, Grundig

The functionality can be read in section 2.3.

3.1.2 The sample and sample preparation

Two different Rh(110) crystal were used through out the experiment. The first one is inherited by precursors and the second one was bought from GmBH Mateck. The sample discs had an orientation accuracy of 1° and <0.3°, a diameter of 8mm and 10mm, and a thickness of 1mm respectively. Both contained four symmetrically positioned holes with a diameter of 0.22mm at the edge just to be hung by tungsten wires as is explained in following.

Sample holding

The sample has been mounted at the manipulator via two tungsten wires with a diameter of 0.2mm (partly 0.18mm) as presented in Figure 3.6. The tungsten wires were fixed onto the molybdenum rods, which were plugged to the holes of a copper block. The copper block and molybdenum rods were isolated (electrically and thermally) by sapphire tubes. For heating the sample the molybdenum rods (resp. tungsten wires) were connected to electrical feedthroughs, and supplied electricity. The copper block was mounted to the double tube nitrogen cooling rod of manipulator. Through this the sample can be cooled down to 150K temperature. The Ni-NiCr (Nickel-Alumel) thermoelement was fixed on the back side of the sample and measured the sample temperature with a 0.03K precision. These thermoelements had outside the chamber a reference point (with temperature of ice water: 0°C) and this signal was amplified at first 100 times by homemade amplifier and then sent to A/D modifier.

The sample heating occurs via a direct applying current through tungsten wires at the same time measuring the sample temperature with thermoelements. As a power source was available a direct voltage equipment, which was controlled by a home
made "tds" programm. This programm enabled a heating with a constant rate and also keeping the temperature constant at the same time recording of desorption spectra.

**Sample preparation in TDS chamber**

The preparation of rhodium crystal has been reported in many works. The first step is sputtering the crystal at room temperature by Ar\(^+\) ions (5·10\(^{-5}\)Torr Ar base pressure) with energy of 1KeV at a 5 – 6\(\mu\)A sample current. The defects formed thereby were healed up by annealing at 1000K-1100K for ca. 10 minutes and the crystal was flashed for several seconds through electron bombarding to 1400K. The carbon contamination was removed through oxygen treatment. This can be done in following two ways. The first, expose the sample with oxygen and take the thermal desorption spectra (TD spectra) to 1400K. It would be repeated until the sample shows no CO desorption (or very small) in TD spectrum. This procedure can take months. The second, heating the sample from 500K to 1200K in oxygen atmosphere (10\(^{-8}\)Torr oxygen partial pressure). It would be repeated long enough and excluding heating in vacuum to 1400K. This preparation method has a shortening influence at a life time of heating wires, therefore is seldom used.

The best way to check the sample cleanness is taking a TD spectrum from the oxygen covered surface. If the sample is not clean and plane enough, in TD spectra do not form nice separated single peaks, like in spectra [42, 43], but grows a shoulder instead single peak and peak position change obviously. This can be seen in Figure 3.7a, the oxygen TD spectrum from the clean surface is drawn by compact line and from not clean enough surface with dashed line. The CO desorption spectrum on the top left graph signifies a small amount of residual carbon. About the clean surface in detail is reported in section 4.

### 3.2 Scanning tunnelling microscopy chamber

The UHV system for STM measurement consists of three separate chambers (fast entry, preparation, and analysis chamber) which are sealed from each other by full metal gate valves. In Figure 3.8 the photo of this system is represented.

The UHV in the preparation chamber (~5litr) was created same as in TDS chamber by standard pumps and in the chamber a base pressure of \(\leq5\cdot10^{-10}\) Torr was obtained. This preparation chamber was equipped with ion gun, gas inlet valves, which connected through narrow tubes to the gas chamber with bottles of argon, hydrogen, oxygen and carbon mono oxide, and a manipulator with a heating filament (heatable to \(\geq1150\text{K}\)) and nickel-alumel thermoelement.\(^2\)

The analysis chamber is pumped through the turbo pump of preparation chamber until

\(^2\)the sample temperature is assumed to be same as the manipulator temperature
Figure 3.7: Oxygen TD spectra from clean and not enough clean Rh(110) surface are presented with compact and dashed line respectively.

Figure 3.8: The photo of the STM-UHV system. The preparation and fast entry chambers are hidden behind the STM chamber.
the pressure reaches the getter pump working range then it has pumped with its own ion getter pump and titan sublimation pump. The base pressure of \( \leq 5 \cdot 10^{-11} \) Torr enabled staying the sample for several days uncontaminated. This main chamber was equipped with STM, LEED, AES with half sphere analyzer, heatable manipulator and mass spectrometry for residual gas analysis.

The STM was a commercial Omicron STM-1, which uses the tripod scanner setup. Its the biggest scan region is 400nm \( \times \) 400nm and scan rate is low. The acquisition of one image usually requires about 30-60s. Detailed explanation about its functionality is in section 2.4.

### 3.2.1 Sample preparation in STM chamber

In STM chamber was used nearly the same sample preparation method as in the TDS chamber. Only difference is that the sample cleanliness is checked by STM except LEED and AES. Because a new Rh(110) crystal was bought for STM measurements, the cleaning procedure of a new sample was observed continuously. This is reported in following.

After the transferring the sample into the UHV chamber was taken an AE spectrum, marked with a in Figure 3.9. It shows the production induced main contaminations of Sulfur (S), Carbon monooxide (CO) and a little Boron (B).

![Figure 3.9: The AE spectra: a. from new bought Rh(110) crystal after transferring into the chamber, b. after the first 20min sputtering, c. after following oxygen treatment](image-url)

These contaminations are nearly not any more present after the first 20min long sput-
tering, which is recognizable from the AE spectrum marked with b. After the first oxygen treatment acquired AE spectrum (marked with c) shows only rhodium peaks. Further sputtering, annealing and oxygen treatment cycles do not bring much difference in AES and LEED, because of their sensitivity limit. To become clean enough surface for STM measurements it needed many cycles of cleaning procedure and it took in our case two months.

During the sample cleaning procedure implanted argon bubbles were observed as shown in Figure 3.10. These have averagely 50-100 Å cross-section and ~0.6 Å protrusion, which agree well with results by Varga [44] et al. Argon bubbles are caused by sputtering and because of following low temperature annealing at 830K they are not healed up. It is to consider, that a high annealing temperature (≥ 1000 K) should be avoided after sputtering because of carbon segregation from bulk to surface. But in contrast to that to remove the implanted argon bubbles it requires annealing at least at 1000K. Therefore is made a compromise and used 1000K for the annealing in our experiments.

![Figure 3.10: The imaging of of implanted argon bubbles and its corresponding line profiles. The crystal was annealed after sputtering at 830K for an hour.](image)

Annealing caused traces of segregated carbon contaminants may be removed through heating the sample after oxygen exposure. Final short sputtering and annealing is required, since the highest available temperature is 1200K, and still some oxygen remain on the sample.
Chapter 4

Clean and oxygen covered Rh(110) surface

As mentioned previously the experiments were performed on two different Rh(110) crystals. These are rough and smooth crystal, respectively. The first crystal was polished during the experiment, so that in this work the results from three different crystals are reported. Therefore, results are notated as from the rough, smooth and polished crystals respectively. The surface roughness plays an important role in the subsurface state generation process and this will be reported in detail in chapter 5.

The section 4.1 deals with the main properties of a clean surface from a preliminary study. Next, the oxygen adsorption states are discussed in 4.2. An overview of previous studies is given at the beginning of every section.

4.1 Clean Rhodium (110) surface

As a usual routine in surface study, it is necessary to produce a clean surface and to employ the investigation methods to this surface before beginning with the main investigation.

4.1.1 General remarks and previous results

The geometrical structure

As a single crystal the rhodium forms a face centered cubic (fcc) lattice (see Figure 4.1a). Its space group is A1 in Pearson’s symbol or Fm$\bar{3}$m Hermann-Mauguin-System. The fcc structure is completely defined by the lattice constant $a_0$, which is
3.81 Å for rhodium at room temperature. For an unrelaxed Rh(110) the interatomic distance in [100] direction is 3.81 Å, in [110] direction 2.69 Å and the layer distance in [110] 1.35 Å. For graphical illustration a hard-sphere model of the Rh(110) surface is represented in Figure 4.1b.

A clean Rh(110) surface is unreconstructed and therefore shows a (1×1) LEED pattern in contrast to Au(110) and Pt (110) surfaces, which show a (1×2) missing row reconstruction. This difference is explained by the smaller number of surface stress ratio for the Rh(110) \( \frac{\text{stress}_{[100]}}{\text{stress}_{[110]}} \) compared to Au and Pt crystals according to Baroni et al. [45]. From the ab initio calculation of Eichler et al. [46] the Rh(110) is the least closely packed and the most corrugated low index surface. This surface shows an inward relaxation on the first layer and outward relaxation on the second layer (see Table 6).

This inward relaxation is caused by increased bond strength with the decreasing coordination number. Indeed the increased strength of the surface bonds leads to a reduced nearest-neighbor distance for the surface atoms. According to the law of strength dependency on the square root of next-neighbor number\(^2\), the bond strength of the Rh(110) surface atom increases by 41% [46].

The origin of the increased bond strength has been discussed in several models. In the Pettifor model [47], because of the non equilibrium repulsive \( sp \) and attractive \( d \) electron (see Figure 4.2a) interactions at the surface of transition metals, \( sp \) electrons ”spill out” into a vacuum; therefore the increased strength of \( d \) electron bonds leads to an inward relaxation. In the Finnis and Heine model[48], which is based on Smoluchowski smoothing [49], the electron density on the rough surface will relax

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\(^1\)Each atom in fcc has 12 nearest neighbors (nn), and the distance is for rhodium \( a_{nn} = \frac{a_0}{\sqrt{2}} = 2.69 \text{ Å}.\)

\(^2\)F\(\sim\sqrt{nn}\)
automatically in order to minimize density gradients and to reduce the kinetic energy of electrons; this charge redistribution leads to an inward force for the surface atoms. Using the latter model it has been determined that the charge redistribution on the Rh(110) surface allows a bonding character between the first and second layers and antibonding character between second and third layers. This relaxation has been confirmed in many other studies as represented in Table 6.

The electronic structure

The periodic arrangement of atoms in a crystal causes an overlap of the outer electron states. This results a formation of broad bands out of states in crystal, which can be graphically visualized by plotting the Density Of electron States (DOS) (number of electrons with energy in a certain dE region) via its energy and direction. If the DOS is summarized by all directions one gets a total density of states for certain energy range dE.

In transition metals the conduction band is dominated by the overlap of $d$-orbitals of single atoms. So for a rhodium crystal the valence band is dominated by $4d$ bands, which can be easily recognized from the plot of calculated total DOS versus energy [50] in Figure 4.2a. The electronic band structure of the surface differs from that of the bulk [46], which caused by unsaturated bonds of surface atoms. This can be seen easily from the Figure 4.2c.

Experimentally, using X-ray Photoelectron Spectroscopy (XPS) and Ultraviolet Photoelectron Spectroscopy (UPS) techniques, one can determine the total DOS (also direction dependent local DOS). In Figure 4.2b the valence band spectra, corresponding to total DOS, from present XPS and UPS measurements are shown. Because of used small excitation energy (40.8eV) the UPS is very surface sensitive. Therefore the UPS valence spectrum agrees well with the calculated surface DOS in graph c. Here, the spectrum contains two peaks, one at the Fermi edge and the another broad peak at around 2.5eV. Because of high excitation photon energy of 1486.6eV in XPS, the penetration depth is higher. The XPS valence spectrum exhibits a reasonable agreement with the calculated DOS, showing three features at matching energies with the peaks in the calculation.

4.1.2 Results of the present work

An overview and local STM images of the clean smooth crystal are shown in Figure 4.3a and b, respectively. Although the crystal was annealed for a long period of time, point defects (missing atoms) are still observable in the overview image (marked

\textsuperscript{not necessarily periodic but merely because atoms come closer}
Figure 4.2: (a.) Total DOS of the Rh(110) crystal, after [50]. The conduction band is dominated by the contribution of d-orbitals rather than sp. (b.) Valence band spectra of Rh(110) surface from XPS and UPS measurements. (c.) Total DOS projected into surface, subsurface and bulk layers, after [46].
with circles). No clear explanation about their favorability exists. The atomically resolved STM image in Figure 4.3b illustrates the surface structure very well. It ensures from the line profiles on the right side of the graph, that the atomic distances average in the [100] direction to 3.71 Å (97% of 3.81 Å) and in the [1\bar{1}0] direction to 2.69 Å (99% of 2.69 Å). These are in reasonable agreement with the expected values (see Figure 4.1b). The contrast change in the STM image is due to a tip change, an uncontrollable problem in STM scanning.

Although the used sample has an orientation accuracy of <0.1°, regions can be found where steps are accumulated. Figure 4.4 shows an overview topography image of such a region. As can be seen from the graph, the steps are not only in main directions [1\bar{1}0] and [100] but also in [1\bar{1}1], [1\bar{1}1] directions. The line profiles provide the value for single step height of (1.33±0.04) Å, which reasonably corresponds to inter-layer spacing reduced by ∼9.8%. Further, it gives values of (2.54±0.04) Å for double steps and of 4.3 Å for triple steps, which largely deviate from the expected values. This shows the limitations of STM for quantitative estimation of such large distances, but the values still provide qualitative estimation for steps.

The STM images of the rough (inherited) crystal (presented in Figure 4.5) showed smaller terraces and an increased step density in comparison to smooth topography of a new crystal. The polished fist crystal contained narrower flat terraces and more steps (not shown here).

The LEED pattern, recorded with 90eV electron energy, is displayed in Figure 4.6a. It implies the structural cleanliness of the surface. The main spot (0,0) is hidden behind the sample, the pattern is taken with the back view LEED. The chemical composition of the surface can be recognized from the comparison of the recorded AE spectrum and the reference AE spectrum [51] in Figure 4.6b. Both spectra are calibrated at the Rh_{305} main peak height. Up to a small Auger peak around 275 eV, these spectra resemble each other, which is due to the sample chemical cleanliness. The peak at 275 eV is assumed to be a small carbon contamination at that time of STM measuring, but from an ex-situ XPS measurement it has been determined as a Ruthenium contamination of 1.5% (see Figure 4.7), which is identified explicitly through its 3d double-peak structure. This is a production conditioned contamination.

### 4.2 Oxygen adsorption on Rh(110)

Since the oxygen chemisorption on the surface is a pre-requisite state for the subsurface oxygen, the investigation started with oxygen adsorption structures. During this study additional new features regarding oxygen adsorption process were discovered.

The adsorption process of oxygen on the Rh(110) surface is quite complex, nevertheless well studied. Different adsorption states exist with different bindings depend-
Figure 4.3: (a.) The overview STM image of a clean smooth crystal, 250×250Å². The circles indicate defect sites, (b.) The atomically resolved STM image, 50×50Å². The unit cell and relevant main directions are indicated. The line profiles are illustrated on the right. The scanning parameters are: $V_b$=-0.8V, $J$=0.7nA.
Figure 4.4: The overview STM image from a stepped local place on a smooth Rh(110) surface, 150×150Å². $U_b = 0.8V, I = 0.8nA$.

Figure 4.5: STM topography images from the rough Rh(110) crystal.
Figure 4.6: (a.) (1×1) LEED pattern from a clean smooth Rh(110) surface, electron energy 90eV, (b.) Differentiated AE spectrum from a clean surface (below) compared with a reference AE spectrum (above), after [51].

Figure 4.7: The XP spectrum from the clean surface, measured in Katowice, Poland. The surface shows no other contamination except Ruthenium.
ing on the exposed amount of oxygen.

4.2.1 Previous results

Molecular oxygen adsorption

It has been reported that the oxygen on the rhodium surface does not form a molecular adsorption state because of its high reactivity [52], but it dissociates into atomic states. The recent Density Functional Theory (DFT) calculation [53] concluded that molecularly chemisorbed species exist on the rhodium surface and are quite stable with respect to the free molecule, although the barrier between the molecularly chemisorbed and dissociated states is found to be low enough to give the molecular state a very short lifetime. However there is a suggestion, that the atomic oxygen makes the surface less active for dissociation, so that the molecular oxygen becomes more stable. The molecular oxygen state has been very rarely observed on the Rh(110) surface but it was nevertheless reported in the TPD [54] and HREELS [55] works. It has been concluded that molecular oxygen species bind peroxy-like, which means the O-O bonded oxygen lies flat on the surface and each oxygen atom is bonded to rhodium atoms lying beneath it. In our work we did not observe this molecular state, supposedly because of high adsorption temperature.

Atomic oxygen adsorption

The atomic adsorption of oxygen on the Rh(110) surface was well investigated in numerous works [42, 43, 52, 56] and references therein. Different adsorption states and adsorbate-induced surface reconstructions, caused by coverage dependent interaction of the rhodium surface and oxygen adsorbates, are well known. At low adsorption temperature the surface reconstruction does not occur, but at high temperature (at 500K already) different kind of reconstructions occur involving the diffusive movement of surface atoms.

In the earlier work of Schwarz [42] and Falkenberg et. al. [43] five oxygen adsorption peaks were identified in the thermal desorption spectrum labelled $\beta_1 - \beta_5$ (see Figure 4.8a). In the results by Comelli et al. [52] only $\beta_3$ and $\beta_2$ peaks and additional molecular oxygen state at 170K were reported. Comelli et al. [52] reinterpreted the TPD data, summarizing from LEED, TDS [42, 43] and STM [57, 56] experiments on the O/Rh(110), as being due to known ordered oxygen phases $(2\times2)pgO$, $(2\times6)O$ and $(2\times8)O$.

Recently, Vessely et al. [58] reported a new strained $(10\times2)O$ high coverage oxygen structure on the Rh(110) surface from the study with XPS, LEED and STM. In this structure the oxygen atom exhibits a binding energy of 529.75eV, which is smaller than the energy of 530.25eV of the oxygen atom in the $(2\times2)pgO$ structure.
This difference interprets their adsorption site difference.

In the tight binding model calculation by Stokbro and Baroni [50] it was described that the oxygen interaction with the rhodium atoms takes place in two steps. First the O 2p orbital interacts with the Rh 5s and Rh 5p valence orbitals and then the resulting renormalized O 2p orbital interacts with the Rh 4d valence orbital. These bonding states have more O 2p character and there is a charge transfer from the Rh 4d orbitals into the O 2p orbitals.

4.2.2 Results of the present study

The results of the oxygen TPD experiments from the first crystal are illustrated in Figure 4.8b. In the inset the coverage versus time of exposure is presented, which implies its Langmiur (saturating) character. Comparing these results with the reference spectra by Schwarz [42] in graph a., one can recognize that here not only $\beta_2 - \beta_4$ peaks were observed, but also a new small $\gamma$ peak, which belongs to the "subsurface" oxygen. The reason of indistinctive observation of single peaks $\beta_1$ and $\beta_3$ is the subsurface oxygen impurity, which will be discussed in detail in chapter 5. Each peak and shoulder in TDS identifies one stable structure, namely:

\[
\begin{align*}
\beta_5 & \rightarrow (2 \times 3) pO, \\
\beta_4 & \rightarrow (2 \times 2) pgO, \\
\beta_3 & \rightarrow c(2 \times 6) O, \\
\beta_2 & \rightarrow c(2 \times 8) O, \\
\beta_1 & \rightarrow c(2 \times 10) O \text{ or } (10 \times 2)O \text{ structure (not yet known)}
\end{align*}
\]

For the $\beta_1$ peak the exact LEED pattern is not clearly known. Because of recent observations of a $(10 \times 2)O$ [58, 59] very high coverage structure in STM, one can assign this to the $\beta_1$ peak. The c$(2 \times 10)$O structure denomination appeared so far only as an assumption that such a coverage can exist theoretically as following the c$(2 \times 8)$O structure.

$(2 \times 2) pgO/Rh(110)$

The $\beta_4$ desorption peak is caused by the $(2 \times 2)pg$ oxygen adsorption structure, which contains the most strongly bounded oxygen atoms to the substrate. This structure can be separated very easily from the other structures, by heating to 1050K, and is therefore used in many experiments as a calibration. It corresponds to a 0.25ML-0.5ML oxygen coverage, depending on the exposed oxygen amount. The oxygen atoms at this coverage force the surface to a $(1 \times 2)$ reconstruction, they are coordinated to three rhodium atoms, one from the second layer and two from the first layer, and sit in a
Figure 4.8: TPD spectra from an oxygen covered Rh(110) surface (a.) Reference spectra by Schwarz [42], (b.) Present result from the rough crystal
zig-zag form along the [1\(\bar{1}\)0] rhodium rows as is demonstrated in hard-sphere model (see Figure 4.9b). This geometry is confirmed by many studies including LEED I-V [60] and LDA calculation [50]. Concerning this LDA calculation, the formation of \((1\times2)\) substrate reconstruction costs only 0.2eV/atom energy. Experimentally the surface reconstruction takes place only if the surface temperature is above 450K.

![STM image](image1.png)

![Ball model](image2.png)

![LEED pattern](image3.png)

![LEED model](image4.png)

**Figure 4.9:** (a.) A STM image of a \((1\times2)\) reconstructed Rh(110) substrate and zig-zag ordered oxygen atoms, \(90\times90\text{Å}^2\), \(U_b=-0.8V\); \(I_t=0.8mA\), (b.) A hard-sphere model corresponds to the STM image as an illustration, (c.) Respective LEED pattern, recorded after the STM measurement with 90eV electron energy, (d.) The model of LEED pattern was created by the LEEDPATH program [24].

In the STM chamber this structure was produced on the smooth Rh(110) surface through exposure of 5L oxygen at 570K surface temperature. Therefrom results are in Figure 4.9a presented. It is very easy to recognize the \((1\times2)\) substrate reconstruction
and the zig-zag formed adsorbate induced depressions in the STM image (see Figure 4.9a). The oxygen atoms appear dark in the STM because of their non-metallic character and lower DOS near the Fermi level. For clarifying, some oxygen positions in the image are marked by black circles. The unit cell superstructures are outlined as well in the STM image and the ball model.

The analysis of STM images gives the distance in the [100] direction as \((7.3\pm0.2)\,\text{Å}\), which deviates 4% from \(2\times3.8\,\text{Å}\), and a step height of \((1.37\pm0.06)\,\text{Å}\) (with a deviation of 0.7% from 1.36Å). The atomic distance of oxygen atoms seems to be in the \([1\bar{1}0]\) direction \((5.57\pm0.1)\,\text{Å}\) (3% of deviation from \(2\times2.7\,\text{Å}\)). These discrepancies can be attributed to the thermal drift while measuring at room temperature as in [57]. Although the change in the step compared to a clean surface seems to be real, the surface relaxation drops down with the oxygen coverage. The corrugation of troughs along \([1\bar{1}0]\) direction is determined as \((0.66\pm0.12)\,\text{Å}\), which is smaller than the reported value of \((0.82\pm0.1)\,\text{Å}\) in [57]. Furthermore one can see a domain wall in the STM image, which is marked by an ellipse, as well as a missing rhodium atom point defect pointed to by an arrow. In Figure 4.9b and c the LEED pattern, taken at 90eV electron energy, and its model from LEEDPATH [24] simulation program are presented respectively. Good quality of the LEED pattern reflects nice periodicity of surface atoms in both \([1\bar{1}0]\) and \([100]\) directions. Geometrical knowledge of the \((2\times2)\text{pgO}\) structure is roughly completed by symmetry determination by LEED (in this case \((2\times2)\text{pg}\)) and the adsorption position determination by STM (3 fold coordinated). The AE spectrum in Figure 4.10 was subsequently recorded to measure the relative amount of adsorbed oxygen. The Rh\(_{446}\) peak has an intensity comparable to the oxygen O\(_{514}\) peak, and this oxygen amount (0.89% of Rh\(_{305}\) peak) corresponds to a 50% oxygen coverage.
In the TDS chamber this oxygen structure was produced on the rough Rh(110) crystal by exposing the sample to 1.5L of oxygen at 573K (see Figure 4.11a). In the TD spectrum it is indicated as a desorption peak ($\beta_4$) at 1130K, which shows at low coverage 2$^{nd}$ order desorption behavior. The peak contains a hardly isolated $\beta_5$ shoulder and a total peak width amounts to 195K. The respective LEED pattern, displayed on the right graph b., visualizes a nice periodicity of the structure. But the edge spots of the LEED pattern show deformation, which is caused by a not sufficient magnetic shielding against the earth magnetic field.

By analyzing the TD spectrum, one can determine the activation energy of the adsorption state and the pre-exponential factor, which correspond to the binding energy and vibration frequency of adsorbed atom, respectively. In table 4.1 the results from different calculation methods (see section 2.1) are shown. In the Redhead’s method (RPMA) for 1$^{st}$ order desorption the pre-exponential factor ($\nu$) was assumed to be $10^{13}$s$^{-1}$. According to Chan-Aris-Weinberg (CAW) method both

Figure 4.11: (a.) A TD spectrum (black dotted curve) from (2×2)pgO covered rough Rh(110) surface; Parameterized fitting corresponding to the Polani equation with n=2 (compact black line); more in text. (b.) Before desorption experiment recorded LEED pattern, 54eV.

Figure 4.12: The calculated activation energy and pre-exponential factor for (2×2)pgO structure using Arrhenius plot.
Chapter 4. Clean and oxygen covered Rh(110) surface

50

Table 4.1: The calculated desorption parameters using different methods for (2 × 2)pgO structure. More in the text.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>EPWM</th>
<th>RPMM</th>
<th>CAW-II (w1/2)</th>
<th>CAW-II (w3/4)</th>
<th>Sim II ord.</th>
<th>Arr.</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_d,a (kJ/mol)</td>
<td>32.2</td>
<td>291 280 [42]</td>
<td>174</td>
<td>267</td>
<td>196.5</td>
<td>150</td>
</tr>
<tr>
<td>ν</td>
<td>-</td>
<td>3.2·10^{13}</td>
<td>3.2·10^7 [cm^{-2}s^{-1}]</td>
<td>2.5·10^7 [cm^2s^{-1}]</td>
<td>3.5·10^8 [cm^2s^{-1}]</td>
<td>3.1·10^8 [cm^2s^{-1}]</td>
</tr>
</tbody>
</table>

parameters using 1/2 and 3/4 peak width for 2nd order desorption are calculated. These are labelled in the table as CAW-II with w1/2 and w3/4, respectively. SIM II is an abbreviation for parameterized simple simulations of the Polani equation 2.7 for the 2nd order β4 desorption (see Figure 4.11(a)).

Using TD spectra (not shown) with 0.1L to 1L oxygen exposures an Arrhenius plot (see Figure 4.12) was drawn.

The simulated total curve, where not only main β4 peak taken into account but also shoulders β3 and β5 and peak γ, shows quite good reproducibility for the experimental curve. For choosing the adequate parameters was the value of pre-exponential factor important because it defines the peak width as it can be seen from Figure 6.1. And also a ratio of total desorbed particle (area under desorption curve) for single peaks is responsible. In this case we estimated that the area under β5 + β4 curves corresponds to 0.5ML. Therefore it follows that the area under β5 curve is 0.17ML. These limitations resulted adequate values for desorption parameters as it can be seen from simulation graph. From the values listed in the table 4.1 one can observe that the activation energies and the pre-exponential factor are comparable in methods used 2nd order desorption. But still they have quantitatively different results. The activation energy from Edward’s method is too small and from Redhead’s method is too large. At this point it is to mention that except simulation method all other methods considered the total peak as only β4 desorption peak. There a larger number for peak width is used, which leads to wrong results. To make the simulation result comparable, we have simulated the curve for an only one peak, too. It has resulted 170kJ/mol and 1.26·10^7 cm^2s^{-1} values. These agree well with the results from CAW-II (w1/2) and Arr.

But it is to remember again that these approximation methods are only used to give an estimation.

From the above reported STM and TDS results (in Figure 4.9 and Figure 4.11), it is easy to recognize that different amount of oxygen exposures are needed to produce the same structure in different chambers. This can be explained by the fact that in the TDS chamber the sample was cleaned from the carbon contamination not only on the
surface but also in the bulk. In contrast to this, the crystal in the STM chamber was cleaned only on the surface. So during the annealing after oxygen exposure carbon diffuses from the bulk to the surface and desorbs as a carbon monoxide and only the residual oxygen produces the surface structure.

Although many authors believe that the surface reconstruction is caused by geometrical displacement of rhodium atoms, there is a mind that it is caused by oxygen induced electronic changes on the surface [61]. The definite answer can be obtained from the following hydrogen reduction experiment on an oxygen covered surface. Hydrogen will react catalytically on the Rh(110), forming water which will then desorb leaving a clean reconstructed surface. In this experiment: to produce only saturated $(2 \times 2)_{pgO}$ structure the crystal was exposed to 3L of oxygen and annealed at 1050K; while the adsorbate structure was controlled with LEED, the oxygen was reduced at 430K heating in $8 \cdot 10^{-8}$Torr partial hydrogen pressure for some minutes. One could effectively observe with LEED that the $(2 \times 2)_{pg}$ LEED pattern (see Figure 4.13a) changed to the $(1 \times 2)$ pattern (see Figure 4.13b). After this reduction experiment the TD spectrum was recorded to check if the oxygen was removed completely. The TD spectrum in Figure 4.13c shows a small amount of oxygen desorption at 530K and 1100K after 1 min titration. It is exclusive that the peak at 530K can be caused by the molecular oxygen desorption, where molecular oxygen desorbs under 300K [54]. Also it can not be assigned to atomic oxygen desorption. Therefore, we assume that this stems from the holding wire. Because of its non catalytic property the oxygen on the wire is not reduced. A residual small desorption peak at 1100K signifies the incomplete reduction process. From further reduction experiments with different lengths it has been ascertained that 2 min is a sufficient time for the complete reduction at this partial pressure.

The remaining of the $(1 \times 2)$ LEED pattern after this reduction experiment con-

![Figure 4.13](image)

Figure 4.13: (a.) The LEED pattern of $(2 \times 2)_{pgO}$ structure, performed at 60eV, (b.) LEED pattern of $(1 \times 2)$ surface reconstruction, performed at 57eV, (c.) Oxygen TD spectrum after the hydrogen reduction. From the adsorbed oxygen a very small part is remained.
firms the real missing row character of dark stripes in the STM image. This rules out a suggestion by C.Q. Sun [61] that the depressed stripes in the STM image are caused by the deformation of electron clouds of rhodium rows through oxygen atoms. In the hydrogen reduction experiment, controlled with STM by Africh [59], the surface reconstruction was definitely recognizable.

\((2\times3)p\text{O/Rh}(110)\)

During the recording the STM images from the \((2\times2)\text{pgO}\) prepared surface, thick white stripes were observed (see Figure 4.14), which do not belong to this structure. For these stripes two possible reconstruction models can be proposed. The first is that the stripes are an image of a \((1\times3)\) added-row oxygen-induced rhodium reconstruction, as illustrated in Figure 4.9b with light balls on the left corner of the hard-sphere model. From the line profile of the STM image (see Figure 4.14) one can see that these stripes have a protrusion of \((0.37\pm0.1)\,\text{Å}\) relative to the \((1\times2)\) reconstructed rows. Ideally, an added row reconstruction should have a protrusion of \(1.36\,\text{Å}\), which corresponds to the one step height. The number obtained from the line profile is considerably smaller than the step height. This makes the proposal of the added-row model unlikely. The second alternative is that these thick stripes belong to a \((1\times3)\) missing row rhodium reconstruction. Precisely, two unreconstructed rhodium \([\text{110}]\) rows and the third row is missing. Along these missing rows oxygen atoms sit possibly in a zig-zag way. It is consequential that the oxygen-free rhodium rows would be imaged lighter in the STM concerning that the oxygen covered surface shows a higher work function in PEEM [62, 62, 63, 64].

Such kind of structure on the Rh(110) has not been reported before from STM study. This corresponds to lower oxygen coverage than \((2\times2)\text{pgO}\). Considering the last proposed model and its low coverage nature, it can be assigned to a \((2\times3)\text{O}\) structure. According to the STM image this structure builds at terraces as well as at edges. Analyzing the line profiles provides a distance in \([100]\) direction between the \((1\times3)\) reconstructed rows of \((10.77\pm0.4)\,\text{Å}\), which is well consistent with the \(3\times3.8\,\text{Å}=11.4\,\text{Å}\). Due to the short range periodicity of this \((2\times3)\text{O}\) structure there is no sign of it in the LEED pattern (see Figure 4.9c).

To check whether this low coverage structure exists as a single stable structure, the sample was exposed to only 0.5L of oxygen. In the STM image (see Figure 4.15) the homogenous \((1\times3)\) substrate reconstruction was expected. Instead, one still observed mixed \((2\times3)\text{O}\) and \((2\times2)\text{pgO}\) structures in the presence of unreconstructed rhodium terraces.

In the results of Falkenberg [43] at an oxygen exposure below 0.4L such a
Figure 4.14: An overview STM image of mixed (1×2) and (1×3) reconstructed substrate, 30nm ×30nm

Figure 4.15: An STM image of mixed (2×2)pgO, p(2×3)O and (1×1)Rh terraces at low coverage, 500Å×500Å.
p(2×3) LEED pattern on the Rh(110) with a weak spot intensity has been observed. This state was indicated in the TD spectrum as a \( \beta_5 \) shoulder. In other words this structure does not build a single desorption peak. Considering this and our observation it can be concluded that this (2×3) structure does not exist homogenously as a stable structure.

Although Falkenberg has observed the primitive LEED pattern of the p(2×3) superstructure, and also no oxygen induced zig-zag arrangement is recognizable in the STM image in Figure 4.14 (these indicate an primitive arrangement), it is difficult to conclude about the exact adsorption arrangement of oxygen atoms. If the supercell is primitive, then the question arises why it should deviate from the stable oxygen zig-zag arrangement. But it can be assumed that at this coverage the interaction of oxygen atoms in [110] direction is stronger than in [100] direction, so that no energy minimizing zig-zag arrangement in another direction is necessary. The calculation using Cluster-Variation (CVM) and Monte Carlo (MC) methods by Rosengren et. al. [65] demonstrated also a low-coverage (2×3) adsorbate induced reconstruction on the (110) fcc metals, which supports our proposal. R.Rosei et.al. [66] have observed short ranged domains with the (2×3)O arrangement at a 170K of surface temperature on not reconstructed Rh(110) surface with the STM. This is a partial confirmation of stability of the (2×3)O ordering. In our case the surface is additionally reconstructed because the surface temperature allows it. As it can be seen in Figure 4.11a the desorption parameters can be estimated as 201kJ/mol and 3.5·10⁸cm²s⁻¹ respectively. These parameters are very similar to the parameters of (2×2)pgO structure, so that they can easily change from one to another.

c(2×6)O/Rh(110)

The next higher coverage, stable oxygen structure on the Rh(110) is c(2×6)O (0.5 < \( \theta \) < 0.75), which has been studied by different authors by various methods including the STM [58].

At this oxygen coverage the rhodium atoms are forced to a (1×3) missing row reconstruction, where every third [110] row in [100] direction on the surface is missing. The oxygen atoms sit three-fold coordinated along the rhodium rows in a zig-zag way as shown in the hard-sphere (see Figure 4.16b) model structure. Experimentally, the c(2×6)O structure was established through a 45L oxygen exposure and subsequent annealing at 650K. From the amplified STM image in Figure 4.16a it is very easy to realize the zig-zag arrangement as well as along the rhodium rows and also along the troughs. For illustration the oxygen adsorption sites on the STM image are marked with dark spots, and the cells outlined. Adjacent zig-zag structured rows in the unit cell are in phase, but the on adjacent double stripes in antiphase, as illustrated in the model graph. Looking comparatively at both lines on the topography and model images, one can recognize the above described arrangement clearly. This interpretation
disagrees with the statement by Dhanak [67, 57] and Bowker [56] that the zig-zag structures are not present along troughs but rather between the rhodium rows and that these zig-zags on adjacent rows are in antiphase. Nevertheless it corresponds to the reinterpretation by Comelli et al. [52].

The line profile analysis provides values of (1.3±0.2) Å for the step height and

Figure 4.16: In the STM chamber the c(2×6)O structure was produced on the smooth Rh(110) through 45L oxygen exposure at 570K and subsequent annealing at 650K. (a.) An STM image of the (1×3) reconstructed rhodium substrate and zigzag ordered oxygen atoms along [1\bar{1}0] row, 750 Å×750 Å (b.) Hard sphere model of the STM image (c.) The LEED pattern recorded after STM imaging, 90eV (d.) A model of LEED c(2×6) superstructure on fcc(110) surface, using LEEDPATH software [24]

(11.2±0.2) Å for the distance in [100] direction. These values are reasonable consistent with the expected numbers (1.36 Å, 11.4 Å respectively). The measured corru-
gation along the [100] direction amounts to \((0.68 \pm 0.03) \AA\) and agrees with previous results \([67]\).

Another interesting observation has been made through measuring the line profiles of the \((2\times2)\)pgO structured stripes and comparing them to \(c(2\times6)\)O terraces, whereby the stripes exhibit a \(\sim 0.6\)\AA\ depression. This again confirms the statement mentioned above that an increasing coverage weakens the inward relaxation of the first rhodium layer, because of saturation of the bindings of rhodium atoms through the oxygen chemisorption.

The STM image presented in Figure 4.16a shows no long-range periodicity of oxygen atoms in the [1\(\overline{1}\)0] direction. This is also reflected in the LEED pattern in Figure 4.16c, where the spots in \(2\times\) periodicity along [1\(\overline{1}\)0] direction are indistinguishable. For illustration of ideal ordered \(c(2\times6)\)O structure the model LEED pattern is shown in Figure 4.16d. The Auger spectrum, presented in Figure 4.17, proves its oxygen induced nature through a remarkable amount of oxygen signal. The percent quantity, written on the graph, identifies its higher coverage.

![Figures showing STM and LEED patterns](image)

Figure 4.17: The respective overview AE spectrum (left panel) of the \(c(2\times6)\)O structured surface and the magnified oxygen region of it (right panel). It is recorded after STM and LEED experiments.

In the TDS chamber this structure was established through exposing the sample to 6L of oxygen at 573K. In the TPD spectrum this state is referred to the \(\beta_3\) peak as shown in Figure 4.18a. Although this is a molecular desorption of atomic oxygen adsorbates, it behaves like a 1\(^{\text{st}}\) order desorption, and the peak maximum remains at 940K independent on the oxygen coverage. This structure changes to the \((2\times2)\)pgO structure through annealing at a temperature above 1000K. The single sharp peak in the TPD and the LEED pattern (Figure 4.18b, taken at 90eV energy) signifies its good
quality.

Most analyzing methods of TDS are performed only for a single desorption peak.

As the spectrum contains multi desorption peaks, \( \beta_3, \beta_4, \beta_5 \) and \( \gamma \), it becomes now difficult to determine the desorption parameters. Nevertheless the methods using peak height and width can be applied. The thus extracted results are presented in table 4.2. In the simulation only the parameters for \( \beta_3 \) peak are varied and for remaining \( \beta_4 \) and \( \beta_5 \) peaks the best fit parameters are taken from the previous result in table 4.1. The present fitting result is illustrated in Figure 4.18a. Through its independency of the peak position on the coverage, the \( c(2 \times 6)O \) desorption peak shows experimentally the 1\(^{st}\) order character, even it is a recombinative desorption. But it seems in this case that the role of diffusion and recombination frequencies are not determining in the desorption pre-exponential factor.

Comparing the results from different methods one can recognize easily that the pre-exponential factor in the simulation differs by 4. order of magnitude from the assumed \( \nu \) of \( 10^{13}s^{-1} \) in 1\(^{st}\) order desorption. But in our parameterized simulation if this value were used then the activation energy would have been higher than for the lower coverage, which will be absurd. The results for the activation energy deviate also in considerable manner, but it is to remember that the calculated values in table 4.2 is only an estimation.

The hydrogen reduction experiment was performed for this structure, too. Here, the sample was exposed to 5L of oxygen and annealed at 800K to separate only this structure, and the quality was confirmed with LEED (see Figure 4.19a). Afterwards the sample was heated to 430K in a \( 8 \cdot 10^{-8} \) Torr hydrogen atmosphere, and the structure was controlled at the same time with LEED (see Figure 4.19b). As in the previous case, the TD spectrum is recorded after reduction. It shows no oxygen desorption.

Figure 4.18: a. TDS simulation of \( c(2 \times 6)O \) structure after Polani 2.7 equation. b. The LEED pattern was recorded before TPD.
Chapter 4. Clean and oxygen covered Rh(110) surface

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Methods</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>RPMM</td>
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<tr>
<td>Activation energy, $E_d$ (kJ/mol)</td>
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</tr>
<tr>
<td>Pre-exponential factor, $\nu$</td>
<td>$10^{13}$ s$^{-1}$</td>
</tr>
</tbody>
</table>

Table 4.2: Calculation of desorption parameters for the c(2×6)O structure.

either at 530K or at higher temperatures (see Figure 4.19c). Thus, the absence of the oxygen desorption at 530K in contrast to Figure 4.13 can be explained that the manipulator stayed cool during this experiment because of liquid nitrogen cooling and therefore the desorption from the wire did not contribute to the spectrum. These results of the reduction experiment also confirm the geometrical rearrangement of substrate reconstruction.

![LEED patterns](image)

(a) before reduction  (b) after reduction  (c) TD spectrum

Figure 4.19: a. LEED pattern of c(2×6)O superstructure performed at 57eV, b. LEED pattern of (1×3) substrate reconstruction at 82eV, c. Oxygen TD spectrum after hydrogen titration.

**c(2×8)O/Rh(110)**

The next stable high coverage oxygen induced structure on the Rh(110) surface is c(2×8)O (0.75 < $\theta$ ≤ 0.8). This structure is also commonly known and easily reproducible. Adsorbed oxygen at this coverage forces the surface to a (1×4) reconstruction. In our experiment this structure was established through exposing the sample to 50L of oxygen followed by annealing at 570K. The STM image of the c(2×8)O covered surface and its hard-sphere structure model are shown in Figure 4.20a and b, respectively. From the STM image it is easy to recognize the substrate (1×4) missing
row reconstruction in [100] direction and the zig-zag arrangement of oxygen atoms along the [1\bar{1}0] rhodium rows. The nice periodicity is also to observe from the STM image and from the LEED pattern (Figure 4.20c). For illustration, the model LEED pattern of the c(2×8) superstructure on a fcc(110) surface is presented in Figure 4.20d. The line profile analysis provides values for the step height, (1.3±0.3)Å, the distance in [100] direction, (14.7±0.2)Å, distance in [1\bar{1}0] direction between zig-zags, (5.5±0.2)Å, and the corrugation, (0.7±0.13)Å. The step height and the reconstruction distance are smaller than the expected value of 1.36Å and 4×3.81=15.24Å respectively. But the distance in [1\bar{1}0] direction agrees quite well with expected 5.4Å, and the corrugation is comparable as in the previous case. It should be mentioned that the resolution of STM images increases with increasing oxygen coverage. This is due to the contribution of the non metallic oxygen atoms to the electronic structure.

From the STM image one can observe not only the c(2×8)O structure, but also (1×2) reconstructed non zig-zag formed rows in [100] direction at the edges of terraces. This is in agreement with the results by Dhanak [67, 57] and Bowker [56]. It has been marked there as a (1×2)O structure. But since the (10×2)O structure on the Rh(110) was reported by Vesseli [58], where this high coverage was achieved by an oxygen exposure at 170K, it is clear that the (1×2)O structure is only part of the (10×2)O structure (see Figure 4.22).

From our STM image one can see with the naked eye the 2× periodicity in [100] direction. But in [1\bar{1}0] direction the 10× periodicity is irregular, which is caused by the room temperature oxygen exposure. Nevertheless, the line profile analysis (not shown) has indicated such the 10× partial periodicity. From our observation the concentration of (10×2) structured areas had an increasing tendency even at room temperature with further additional oxygen exposure.

In addition to the (10×2)O structure one can observe areas in the STM image with (1×5) and (1×6) substrate reconstructions, which are attributed to c(2×10)O and c(2×12)O structures respectively. These areas are marked on the amplified STM image with arrows. These are also high oxygen coverage structures, but the (10×2)O structure seems to be energetically more favorable because of its frequent occurrence.

The AE spectrum taken after STM measurements is shown in Figure 4.21. This contains nearly no Rh\textsubscript{449} signal but an increased oxygen signal. The comparison of \(I_{O\textsubscript{515}}/I_{Rh\textsubscript{305}}\) value, indicated on the left graphic, to previous coverages illustrates this clearly. The decrease of \(I_{Rh\textsubscript{446}}/I_{O\textsubscript{515}}\) value confirms again the statement, that the origin of the Rh\textsubscript{446} signal is the first layer of adsorbate free rhodium atoms.

In the TD spectrum the desorption of oxygen atoms from c(2×8)O structure is identified as a \(\beta_2\) peak. In Figure 4.23 is displayed an oxygen desorption spectrum from with 15L oxygen exposed surface. A perfect c(2×8)O ordering of oxygen atoms can be reached through annealing the surface at 600K-650K after the exposure. To give an estimation about the desorption parameters the above reported methods are used again for this coverage. Therefrom results are in table 4.3 listed. In the parameterized simulation only parameters for \(\beta_2\) peak is varied, and the present result is shown.
Figure 4.20: The c(2×8) structure on the smooth Rh(110) (a.) STM image of (1×4) reconstructed substrate and zigzag ordered oxygen atoms along unreconstructed rows, 300×300Å². (b.) Hard sphere model of this STM data. (c.) Corresponding LEED picture, recorded after STM data. (d.) LEED model for the c(2×8) superstructure
Figure 4.21: The AE spectrum, recorded after STM and LEED measurements in previous picture.

Figure 4.22: At 170K exist (10×2)O structure on Rh(110), after [58]. Left panel: (a.)-(d.) model presentation. In (a.) (2×2)pgO structure, (b.) at further low temperature exposure partially (1×2) arrangement, (c.) partially ordered (10×2), (d.) complete ordered (10×2). Right panel: STM Image.
in Figure 4.23. This describes the experimental curve quite well. An attempting to use 2nd order desorption for $\beta_2$ and $\beta_3$ peaks is failed for this coverage. Because of quite symmetrical shape of 2nd order desorption curve, no two curves were possible to create such separate maximums.

An important observation from the simulation is that the area under the $\beta_2$ and $\beta_3$ desorption is higher than the area under $\beta_4$ and $\beta_5$ desorption, which relates to the 0.5ML. This result would then wrongly mean that the surface coverage in this case is above 1ML. Because it is to exclude, one can explain this associating with the surface roughness. On the rough surface the (2×2)pgO structure can not be saturated so the area under $\beta_4$ and $\beta_5$ desorption does not correspond to 0.5ML.

The hydrogen reduction experiment was also performed for this coverage. In this experiment the sample was exposed to 15L of oxygen and annealed at 650K and subsequently reduced with hydrogen under the same condition as in previous case. Only the (1×4) substrate reconstruction was left after the reduction (see Figure 4.24), which illustrates the oxygen induced geometrical rearrangement of rhodium overlayer atoms.

4.3 Influence of Ru on oxygen adsorption on the Rh(110)

During the STM scanning some "strange" and unexpected structures were observed. These were marked on the STM images in previous sections with circles (see Figure 4.16a, Figure 4.20a). For the interpretation of these structures the ex-situ XPS measurements contributed very useful information about the sample. Therefore the XPS results will be introduced at the beginning. Thereafter the results from the STM will be presented.

4.3.1 Results from XPS

As mentioned above, ex-situ XPS measurements were performed after the STM measurements. As a result a ruthenium contamination with an amount of ~1.5% has been determined by the Ru3d double peak in the smooth crystal (see Figure 4.7). Furthermore it was observed that during the oxygen exposure, the shape and width of the ruthenium double peak changed. In the experiment 10L, 30L, 45L and 60L of oxygen exposures and subsequent annealing at 573K were used. To remove the adsorbed oxygen and thereby separate the expected subsurface oxygen the sample was annealed to 873K and 973K, respectively. After each preparation a survey spectrum was taken, and finally multiplex spectra of rhodium, ruthenium and carbon, oxygen (1s and AE) regions(see Figure 4.25) were recorded respectively.

Observing the rhodium 3d signal on the top left graph one can see that this signal does not change in position and form before and after oxygen preparation. The only
Figure 4.23: The TD spectrum from c(2×8)O/Rh(110) surface. Using Polani equation 2.7 the desorption peaks are with chosen value redrawn.

Table 4.3: Calculation desorption parameters for the c(2×6)O structure.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Methods</th>
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<td>RPMM</td>
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<tr>
<td>$E_d$(kJ/mol)</td>
<td>222</td>
</tr>
<tr>
<td>$\nu$(s$^{-1}$)</td>
<td>$10^{13}$</td>
</tr>
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</table>

Figure 4.24: (a.) The LEED pattern of the c(2×8)O structure, performed at 82eV. (b.) LEED pattern of the (1×4) substrate reconstruction, at 83eV after the reduction. (c.) Oxygen TD spectrum after the hydrogen titration. No oxygen desorption is detected.
Chapter 4. Clean and oxygen covered Rh(110) surface

<table>
<thead>
<tr>
<th></th>
<th>Rh3d&lt;sub&gt;3/2&lt;/sub&gt;</th>
<th>Ru3d&lt;sub&gt;3/2&lt;/sub&gt;</th>
<th>RuO&lt;sub&gt;2&lt;/sub&gt;</th>
<th>RuO&lt;sub&gt;3&lt;/sub&gt;</th>
<th>C1s (ref)</th>
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<td>E, eV</td>
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<td>282.3-282.7</td>
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<td>530</td>
<td>1223</td>
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<td>Δ, eV</td>
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<td>4.17</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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Table 4.4: Binding energies after [51].

discrepancy is a small broadening of the peaks at the low binding energy sites after annealing at 873-973K. This can be explained through an increasing number of defect sites or increased single ad-atom concentration on the rhodium first layer, which are caused by the high mobility of rhodium atoms at elevated temperature.

In contrast to this aspect the ruthenium 3d main peak changes obviously in form and width, which illustrates its oxidation and de-oxidation (see lower left panel). Precisely, after the oxygen exposure the Ru-3d double peaks developed a shoulder structure because of a Ru-O chemical shift, which disappeared after annealing at 873K. At low oxygen coverage the O-signal disappeared completely at 873K annealing temperature but for higher coverage a heating to 973K was needed. Although these temperatures would be normally not high enough for complete oxygen desorption, the oxygen was removed completely. This could have been caused by an interaction of adsorbed oxygen with a residual gas in the vacuum chamber. The residual gas pressure in the XPS chamber was 3·10<sup>-9</sup>Torr, which is not a good UHV condition. The loss of oxygen signal was already noticeable after staying more than 30min in this vacuum.

By the way the comparison of the intensities of AES and XPS oxygen signals draw attention to the fact that AES is less sensitive to the surface species at low coverage.

To separate the overlapping of ruthenium and carbon peaks from each other, this region was fitted using the Multipak software. The results are presented in Figure 4.26. At first the Rh3d region was fitted to obtain adequate parameters for metal peak asymmetry, tail length and other parameters. These parameters were used for further fittings of other regions. The spectrum in Figure 4.26a. stems from the sample after sputtering and annealing. Therefore, in addition to the ruthenium signal it should contain a carbon signal, caused by segregation from the bulk. The first ruthenium peak is observed at 280.1eV as in the reference [51] (see table 4.4). From the fit of the superposed second ruthenium and carbon region, a peak has been identified at 283.92eV, which is lower than the expected reference value of 285eV for carbon. This peak disappears after the oxygen preparation (graph b.) as would be expected for a carbon contamination. For that reason this is assigned to the carbon signal. The peak at 280.81eV can be assigned to RuO<sub>2</sub>, which has a chemical shift of 0.5eV.
Figure 4.25: XPS high energy resolved multiplex spectra taken from the smooth Rh(110) crystal. Here, top left: Rhodium 3d; bottom left: Ruthenium 3d and carbon 1s; and top right: Oxygen 1s regions; bottom right: Oxygen Auger regions are displayed respectively.
Chapter 4. Clean and oxygen covered Rh(110) surface

Figure 4.26: Fitting of Ru and C regions with Miltipak Software. (a.) after annealing the sample. Carbon signal could stem from the bulk segregated impurity and also from an adsorbed CO. (b.) after oxygen preparation.

4.3.2 Results from STM

As mentioned already, during the investigation of oxygen structures with STM some plateaus with different structures were observed. From the demonstrated XPS results this can be assigned to the ruthenium and ruthenium oxide structure. In the following demonstrated experiment, the sample was exposed to hundreds Langmuir of oxygen and then annealed to 1100K. This preparation was repeated three times. The results are presented in Figure 4.27a. and b. In the overview image (a.) one can easily recognize a plateau with a completely different arrangement. Because of the partial quasi-hexagonal arrangement of atoms (see panel (b)) and a rutile-like mapping (amplified right top image on a.), this plateau can be identified as a ruthenium contamination-induced structure. The quasi-hexagonal ordering is attributed to the ruthenium hcp structure. From the line profile analysis (EF and JK in graph b.) one obtains $(5.47 \pm 0.1)\text{Å}$ and $(5.04 \pm 0.07)\text{Å}$ average basis vectors with ca. $120^\circ$ temporary angle. For the ruthenium hcp bulk structure is expected the basic vectors with a length of $2.7\text{Å}$ and a temporary angle of $120^\circ$. Comparing and using these values a model of ruthenium atoms on rhodium lattice is made as shown on the top left corner in Figure 4.27a. To the ruthenium structure can be assigned a $(2 \times 2)$ arrangement of atoms. The incommensurability of ruthenium hcp lattice with the rhodium bulk fcc structure causes the quasi-hexagonal ordering.

It has been reported by Böttcher et.al [68] from the ruthenium oxidation study, that an oxygen induced $(2 \times 2)$ LEED pattern was observable until annealing at 1150K. Considering this result we attribute to the observed plateau a partial $(2 \times 2)$O/Ru structure. Around this well arranged quasi-hexagonal regions, randomly arranged atoms are present, which partially have a quasi-hexagonal as well as rectangular arranged neigh-
bors. The AB and CD line profiles in Figure 4.27b give the average distances of 
(5.61±0.18) Å and (8.7±0.1) Å. Analyzing these values one can realize easily that these 
arrangements are defect constructions of in model shown structure.

As our ex-situ XPS measurements have shown, the ruthenium atoms oxidize 
partially after oxygen exposure. Analyzing the STM images has confirmed this oxida-
tion too. Namely, at the top edge of the ruthenium plateau the RuO$_2$ structure can 
be identified through its rutile like mapping. From the line profiles (not shown) the 
average distance between RuO$_2$ rows (5.53±0.18) Å is determined. Taking note on the 
similarity of this value and an above mentioned value of (5.61±0.18) Å (CD profile in 
Figure 4.27b), one can suppose that the random arrangement is a pre-state of oxide 
building. The rutile structure on a Ru(0001) was previously observed by Over et.al. 
[69] with unit cell dimensions of 6.47Å×3.00Å, which differ significantly from our 
measured numbers. But in our case it is to consider that the small ruthenium terrace is

Figure 4.27: STM topography image of the smooth Rh(110) surface after annealing of 
the oxygen covered surface to 1100K. (a.) The surface contains ruthenium and ruthen-
ium oxide mixed terraces additionally, 500×500Å$^2$. The ruthenium oxide region is 
displayed in a magnification on the left top. (b.) The magnified image of the ruthenium 
plateau (200×200Å$^2$) and its corresponding line profiles.
strongly influenced by the rhodium lattice. That the rutile arranged rows are situated in the [1\10] direction of rhodium surface, identifies the overlapping of one of the main directions of both lattices. Along this direction the Ruthenium atoms are not atomically resolved, therefore the atomic distance is not determined.

The TDS experiments, which were performed ex-situ after XPS measurements, confirmed again the oxidizing of ruthenium after the above mentioned preparation. The ruthenium oxide structure has been identified in TDS through a desorption peak at 1200K (see Figure 5.21). This corresponds to the result from the investigation of oxygen on the Ruthenium surface by Böttcher [68]. In his experiment the ruthenium oxide structure formed at annealing above 800K in oxygen atmosphere. Although the surface was not annealed in oxygen atmosphere in our case, the ruthenium oxide structure was developed. This can be explained by oxygen atoms diffusing on the rhodium surface, which has higher binding energy than on the ruthenium therefore not desorbed yet. These atoms act as an oxygen source for ruthenium small terraces. On edges of ruthenium terraces the oxygen could bind with ruthenium and forms an more stable oxide structure.

To check if the ruthenium oxide formation is caused by very slow annealing (1K/s), were performed in the TDS chamber experiments with a different heating rates (2K/s, 5K/s, 7K/s and 10K/s). The results in Figure 5.21 suggest an independency on the heating rate of the ruthenium oxide formation but dependency on the final annealing temperature. It forms only if the surface is heated first to 1100K, where the residual oxygen on the rhodium surface at this temperature acts as an oxygen source and this temperature is high enough to grow an oxide structure. A TD spectrum recorded to 1420K without 1100K pre-heating shows no ruthenium oxide induced desorption, because oxygen atoms on the rhodium surface desorbs directly from the surface so that for forming the ruthenium oxide structure no enough time was left.

Another ruthenium induced structure is shown in Figure 4.28a. The image has been recorded from the sample, which was exposed to 50L oxygen and annealed to 600K. After this preparation there should be no ruthenium oxide structure, instead the terraces should be covered by oxygen ((1\times1)O/Ru). The STM image has unwanted been scanned with a double tip, so that every terrace is imaged twice. In the magnified region in Figure 4.28a one can easily observe the hexagonal arrangement (the angle between), which illustrates its ruthenium-induced nature. From the line profiles one obtains average distances alone the AB line of 4.54\pm0.1\AA, and along the CD line of 4.87\pm0.1\AA. These values are smaller than the lattice vectors of the quasi-hexagonal structure imaged in Figure 4.27b and seem to be related to the bulk rhodium lattice vectors in the way of c(2\times2), where the distance amounts to 4.66\AA. Böttcher et.al. [68] has reported the (1\times1)O/Ru structure changes to c(2\times2)O/Ru because of a loss of oxygen. In this respect this structure can be assigned to c(2\times2)O/Ru, but the lattice vectors deviate recognizably from the ruthenium lattice vectors. Therefore the statement is only a speculation.

After annealing this surface (see Figure 4.28a) above 1000K, the sample topography changes as shown in Figure 4.28b. According to the results in Figure 4.27 and due
Figure 4.28: STM topographies after annealing of the fully oxygen covered surface to (a.) 600K (b.) above 1000K. In (a.) the oxygen covered rhodium surface coexists with oxygen covered ruthenium domains. In (b.) oxygen free rhodium surface with a partly \((1 \times 2)\) structured ruthenium terraces. (c.) Corresponding ball models of STM images.
to the preparation similarity, the present image should contain ruthenium oxide terraces. Instead of observing the ruthenium rutile-like mappings on the STM image, it contains another kind of differently structured plateaus, which are developed as well at step edges and also on terraces. One recognizes at first sight a quasi-hexagonal arrangement in this structure, and thus identifies its ruthenium induced character. From the line profiles the average distances along the AB line of $4.06\pm0.15\text{	extdegree}$, the CD line $5.27\pm0.06\text{	extdegree}$, and the EF line $4.71\pm0.24\text{	extdegree}$ (not shown) can be extracted. The angle between the CD and EF profiles amounts to $117^\circ$. To make it easier to understand the structure, dark spots are placed on the depression positions of the STM image. The arrangement of dark spots looks zig-zag along [110] row, and they are placed off phase in neighbor strokes. The strokes contains quite random by three or four [110] rows. Inside the strokes the distance of rows in [100] direction (AB profile) seems to be a little higher than the $3.8\text{	extdegree}$ of rhodium lattice, which puts down again to the lattice incommensurability of both elements. The distance of spots from the CD profile agrees well with $2\times2.7\text{	extdegree}$ of the rhodium and ruthenium lattices. For illustration of the STM images their corresponding ball models are presented in Figure 4.28c. Supposing that ruthenium atoms are quasi-hexagonally arranged on the rhodium lattice forming a $(1\times2)$ structure. While it differs from the ruthenium oxide rutile arrangement, the rhodium surface showed no regular oxygen structure (see Figure 5.12), the oxygen atoms seem to be already desorbed.
Chapter 5

Subsurface oxygen state on Rh(110)

5.1 General remarks

A subsurface region is a very surface near area, which begins just under the first atomic layer. If surface adatoms migrate into the subsurface region and sit on interstitial sites, they are situated in so called subsurface state. The occupation of subsurface sites is connected with a distortion of the host lattice, therefore it takes place only if there enough energy is available. The Figure 5.1 [9] illustrates the subsurface (impurity) atom and its influence on the lattice graphically. A formation of this state succeeds in different ways:

- during the catalytic processes on transition metals (e.g. oxidation) takes place a high mobility of adsorbed and metal atoms and this allows the diffusion of adsorbates under the first layer [70, 71, 63, 72, 73, 74, 75, 76, 62, 77, 78];

- annealing the fully oxygen covered surface to a temperature, just below the oxygen desorption, causes a migration of oxygen adatoms into the subsurface region [79, 80, 6];

- exposing the sample at an increased surface temperature to adsorbate gas makes possible a penetration of adatoms into the deep lying layers [81, 82, 83];

The subsurface state is generally very rarely studied in metal surfaces but in contrast the subsurface doping atoms on semi-conductor surfaces are more familiar.
Chapter 5. Subsurface oxygen state on Rh(110)  

Methods

<table>
<thead>
<tr>
<th>Methods</th>
<th>Descriptions</th>
<th>Systems and References</th>
</tr>
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</table>
| TDS     | through a significant different desorption character of subsurface species from the adatoms | O/Rh(110)[80]  
          |               | O/Rh(111)[79]  
          |               | O/Pd(111)[84]  
          |               | O/Ru(0001)[85, 82, 83] |
| HEELS   | the vibration frequencies differ in different sites | O/Rh(111) [86] |
| SCLS(XPS) | distinguishable through different binding energies | O/Pd(111)[84]  
          |               | O/Ag(100)[71, 70]  
          |               | O/Ag(111)[87] |
| XPD     | through subsurface species caused forward scattering should be observable | O/Rh(111) [88] |
| PEEM    | distinguishable through its significant work function difference | H₂ + O₂/Rh(111) [62]  
          |               | NO + H₂/Rh(111)[62]  
          |               | NO + H₂/Rh(110) [63]  
          |               | H₂ + O₂/sputtered Rh(110) [64]  
          |               | other transition metal surfaces[63, 72, 73, 74, 75, 76, 77, 78] |
| ISS     | through depth profiling analysis can be distinguished between the surface and subsurface species | O/Ag(111)[87] |
| DFT     | through checking the favorability of different sites with different coverages finding out the right position | O/Rh(111)[89]  
          |               | O/Tr. metal [90] |

Table 5.1: The methods applied up to date to the investigations of the subsurface species.

Nevertheless diffusions of oxygen and hydrogen into the subsurface region on transition metal surfaces were reported in time and again, but detailed information about their true nature is rather poor. Furthermore, not all existing results are comparable and some of them contradict each other completely. This more in detail is introduced in section 5.1.1.

The reason why this state so poor investigated is that only few surface science techniques exist, which can be applied to the investigation of the subsurface state. It is also difficult to distinguish this state from the surface state. Here in table 5.1 are listed the methods, which were applied to the investigations of subsurface state and explained briefly their main characteristics.

By summarizing the up to date works, one can ascribe the following properties to the subsurface state:

- it desorbs at a higher temperature than the chemisorption state [43, 79, 80],
- in contrast to this, its binding energy is lower than that of the surface state [91, 92] and it desorbs at a lower temperature [93, 83],
- because of its existence in a region near to the surface, it could be removed completely through a short sputtering [71],
depending on its amount, it has an obvious influence on the chemisorption states [91, 92, 88],
• because of its spatial isolation in the subsurface region, it does not react with adsorbed reacting gas atoms [79, 80, 82],
• in partial agreement to this, the reactivity of this state is lower than of the surface state [62].
• the subsurface species can influence (even worse) the catalytic reactivity of the surface [5, 85, 6]

To contribute for clarification of this state our study has been concentrated on the subsurface oxygen state in the Rh(110) crystal. It is appropriate to find out whether or not these properties appear on our investigating subsurface oxygen state.

In the following sections the results from our TDS and STM investigations on the subsurface oxygen state in rough and smooth Rh(110) crystals are subsequently introduced. The rough crystal was inherited from previous experimentalists [80]. Since it has been used before, the cleaning procedure on this surface was shorter. The sample was clean afterwards, not only on the surface but also in the bulk. This surface showed an oxygen assimilation behavior in the subsurface region. More detail can be read at the beginning of the section 5.2.1.

This oxygen assimilation property might be caused by macroscopical scratches, that occurred on the surface. This can be assumed due to the investigations of Huang [77] and Waterhouse et.al. [94], where the scratches caused an increased oxygen dissolution. From this reason the scratches were removed by polishing. The TDS experiments were again performed on this polished surface to check if the attained properties regarding subsurface oxygen are reproducible. The results will be introduced in the last part of the section the 5.2.1.

The smooth crystal was new bought. The main purpose of using a new crystal was to observe the subsurface oxygen generation process from the beginning and continuously on the smooth crystal. In the section 5.2.2 the results will be discussed in detail.

At the very beginning the current state of research is briefly summarized.

5.1.1 Previous results

The subsurface oxygen state has been investigated in the past with TDS by Arndt (on Rh(110)) [80] and Paals (on Rh(111)) [79]. The existence of a high temperature oxygen desorption peak at \( \sim 1400K \), which is attributed to the subsurface oxygen state, was reported. Such high temperature oxygen desorption on the Rh(110) surface was also mentioned by Falkenberg [43]. According to Arndt and Paals this oxygen species reacted above 800K with deuterium gas by diffusing to the surface in contrast to the chemisorbed oxygen, which reacted below 600K and formed a \( D_2O \) and desorbed.
The filling of the subsurface region with oxygen was made possible through the annealing of a fully oxygen covered surface at 800K. By the duration of the annealing process is determined the amount of the filling. Contradicting this the results of Scheffler et.al. describes that the high temperature desorption peak, which assumed to be as a subsurface oxygen desorption, does not belong to the oxygen atoms under the surface instead is due to the oxygen atoms adsorbed at undercoordinated surface atoms. In this study the binding of oxygen on the Ag(111) surface with preexisting vacancies was stronger and it increased further with the increasing vacancy concentration [95].

The subsurface state on Rh(111) has been investigated by Peterlinz with He scattering and TDS [92]. They realized that the oxygen is bounded on the surface more strongly (by 18kJ/mol) than the oxygen in the subsurface sites, which is contradictory to the previously suggested high desorption nature.

In the oxidation experiments of Rh(111) surface at a high temperature and pressure condition Somorjai et.al. [96] and Logan et.al. [97] have observed a Rh$_2$O$_3$ surface oxide growth with LEED, AES and TDS techniques. The oxidized surface showed $(8\times8)$O LEED pattern and the O KLL Auger line was shifted to lower energies by 6eV. According to them the dissolution of oxygen should have taken place before the epitaxial growth of oxide.

With XPD (X-ray Photoelectron Diffraction), Wider [88] has illustrated that through an extended exposure of oxygen at 470K a certain fraction of adsorbed oxygen species occupy the interstitial octahedral sites, located just underneath the fcc adsorption sites. These subsurface oxygen atoms force the adsorbed oxygens to switch from fcc sites to hcp sites above the octahedral site (hcp/octa -subsurface/surface oxygen configuration). Gandulgia-Pirovano [89] has shown in his DFT (Density Functional Theory) calculations that this hcp/octa combination could be possible as a metastable state, but the most favorable one is the fcc/tetra-I configuration. The calculation has demonstrated that the oxygen chemisorption is more favorable due to the large local expansion of the metal lattice, caused by occupation of subsurface sites, but it becomes favorable above a certain critical oxygen coverage. This corresponds with previous results [80, 79] that oxygen penetration occurs only if the surface is covered almost fully with oxygen.

In the investigations of the $H_2 + O_2 \rightarrow H_2O$ reaction on catalytical Rh(111) [62] as well as $NO + H_2 \rightarrow N_2 + H_2O$ reaction on Rh(111)[62, 63] and on sputtered Rh(110)[64] surfaces with PEEM (Photo Electron Emission Microscopy) low work function (WF) areas have been observed. The low WF areas had an enhanced brightness in PEEM and were observed under reaction conditions through two colliding reaction fronts after a very large dose of oxygen preparation ($> 10^{6}$L at 770K). These areas were supposed to attribute to subsurface oxygen species. It is based on the argument that the oxygen sits underneath the surface plane and exhibits a reverse dipole moment therefore shows a low WF area in PEEM.

In the case of the excitable $NO + H_2$ reaction, Schaak et.al. [62] have observed

$^{11}$ Torr O$_2$ at 973K
reaction pulsus instead of fronts. This subsurface oxygen (low WF area) was removed through hydrogen or carbon monoxide reduction, but its reactivity was lower\(^2\). Confirming these results, a three variable model simulation using Langmuir-Hinshelwood (LH) mechanism by Imbihl et. al reproduced the formation of low WF areas [62, 63]. It has been reported on Pd(100) that low WF areas are created on surface defects easier than on the perfect surface [77].

The formation of the subsurface oxygen on Pd(111) surfaces was studied with TDS, XPS, LEED, HREELS (High Resolution Electron Emission Los Spectroscopy) [84]. The subsurface oxygen was distinguished from the surface state in XPS and HREELS spectra through its higher binding energy and lower vibration frequency respectively. In their experiment the oxygen diffusion into the subsurface region occurred only at an elevated temperature of 523K. This state is not affected by the presence of CO adsorbate.

On the Ag(001) surface the subsurface oxygen species were formed during the CO oxidation process [71]. The binding energy of this species was (>530.5eV) higher than of surface oxygen (SuperESCA XPS) too.

### 5.2 Results of the present experiment

#### 5.2.1 Results from the rough Rh(110) crystal

The surface quality was examined via recording the TD spectra from the oxygen covered surface and comparing them to the known Schwarz spectra [42], shown in Figure 4.8a. This procedure produced an unexpected result. Precisely, the recorded TD spectra in Figure 5.2a are very different from the expected one. These arrays of spectra contain only two peaks instead of 5 peaks at high coverage, and the desorption temperature is also higher than the expected values. LEED patterns from the clean and oxygen covered surface were still normal and adequate, aside from some high underground noise \(^3\). Presuming the sample surface was rough, the crystal was annealed at 1100K extra long before the oxygen exposure. The form of the TD spectra did not change very much through this annealing, but single shoulder structures were obtained as shown in Figure 5.2b. The top left presented CO desorption curves illustrate the cleanliness of the surface from carbon. The recognizable CO desorption at 409K is caused by residual gas and small contamination of used oxygen gas bottle. The basic pressure in chamber after the exposure amounted to 8\(\cdot\)10\(^{-10}\)Torr. This growing of single structures in oxygen TD spectra signifies that the surface became smoother through

\(^2\)At \(P_{H_2}=9\cdot10^{-8}\text{mbar and } T_p=480\text{K condition subsurface species were removed after 3min in contrast to surface oxygen species after 2min.}\)

\(^3\)because at that time the AES was out of work no information about the chemical content of the surface was obtainable.
annealing but not flat enough to form the whole separate single structures. Normally Tamann’s temperature of 1100K is high enough to anneal the surface after sputtering, but it seems to be not high enough to smooth this kind of roughness. It is arising now questions:

what is the reason of this unexpected roughness? Does the sample contain any contamination?

In order to answer this question, the surface chemical content has been examined with AES. AE spectra were performed step by step after different preparations. The results are presented in Figure 5.3 (a.-d.). All spectra are normalized at the height of the Rh\textsubscript{305} peak. As expected, the AE spectrum (a.) from the oxygen covered surface contains a remarkable amount of oxygen. But surprisingly the AE spectrum (b.), recorded after the TDS experiment, contains a noticeable amount of residual oxygen signal, which identifies its contamination with oxygen. This contamination was removed through short sputtering of the surface and can be seen in (c.) the AE spectrum, which contains only rhodium signals.

Considering the results in the previous chapter, that the most strongly bounded adsorbed oxygen atom desorbs completely below the temperature of 1300K, which is lower than the TDS recorded temperature of 1400K, it can be assumed that this residual oxygen is not a surface oxygen species. In other words the surface is left contaminated after the TDS recording with some amount of oxygen, which can be assigned to the subsurface oxygen. This species makes the surface rough so that not all single structures can be performed on it.

Annealing at high (>1400K) temperature for a long time (>10min) has cleaned the sample surface from the subsurface oxygen contamination and the surface roughness was annealed as shown in (d) spectrum. However such a high temperature was reachable at that time only by electron impact heating, which is used only once for less than 2min to avoid a warming of surroundings through the thermal radiation and a worsening of the residual gas pressure, and therefore had to be repeated several times.

Besides this observation, the rhodium auger peak at \( \sim 449\)eV\textsuperscript{5} seems to be a good sensor for the surface cleanness as mentioned in the previous case. It disappears completely in the case of an oxygen covered surface (b) and appears again if the surface is free from adsorbed oxygen but not free from subsurface oxygen.

The removal of this subsurface oxygen species through short (<5min) sputtering or annealing at high temperature (longer) signifies its placing in the near-surface region and it corresponds with the subsurface state property mentioned at the beginning [71]. Furthermore, from the previous TD spectra (Figure 5.2b) it could be realized, that this subsurface oxygen has influence on the desorption maximum temperature of chemisorbed oxygen states (\(T_m\)), which is consistent with results of other authors [91, 92, 88]. This change (in our case an increase) of \(T_m\) might be explained by the

\textsuperscript{4}using the heating filament for this high temperature was avoided in order not to break off the wire

\textsuperscript{5}valence band sensitive N\textsubscript{I1}N\textsubscript{I} V Auger transfer
Chapter 5. Subsurface oxygen state on Rh(110)

(a) Without annealing

Figure 5.2: (a.) TD spectra from the subsurface oxygen contaminated rough Rh(110) surface. The desorption peaks of adsorbed oxygen are observed at higher temperatures, namely at 1000K and 1330K. (b.) After previous TDS recording the surface was annealed for 10min at 1100K. Thereafter taken oxygen desorption spectra are shown. The top left displayed CO desorption spectrum serves for the examination of carbon contamination.

(b) Extra annealed
subsurface oxygen induced adsorption site change as was reported on Rh(111) [88]. On the other hand, because of lateral repulsive interaction with the subsurface oxygen the binding of the chemisorbed oxygen atoms should become weaker.

After finding out what contamination the surface was exposed to and how to remove it, the cleanness of the surface was verified again for sure with traditional TDS recordings. The surface cleanness and smoothness are satisfactory as shown in Figure 4.8b.

From the results of the previous experiment it can be established, that the oxygen penetration process into the subsurface region takes place during the TDS recording process. Then, as a next step, one can determine how much oxygen diffuses into the subsurface region at every TDS recording. The aspect of saturation of this state is also interesting. In order to observe a gradual oxygen filling into the subsurface region, the following experiments were performed.
The extra cleaned surface was exposed to 1.5L, 6L, 12L and 15L oxygen and TD spectra were recorded respectively (drawn by compact lines in Figure 5.4). After every TDS recording the sample was exposed again to the same amount of oxygen without any extra cleaning and the experiment was repeated two times. Resulting spectra are plotted with dashed and pointed lines respectively in the graphics. It is easy to observe for all coverages that the intensity of $\gamma$-peak at 1400K raises with the increasing TDS recording number, which illustrates a raised residual oxygen content in the subsurface region. Furthermore the low temperature single peaks disappear and at the same time high temperature peak shifts to the low temperature side. The decrease of the area under the desorption curve implies the subsurface oxygen induced surface roughening procedure, where on the rough surface a smooth place available for the adsorption has shrunk.

The results of this experiment enable us to determine the subsurface oxygen state properties, so that the observed subsurface oxygen ($\gamma$ peak) has a higher desorp-
Figure 5.4: Four different oxygen exposures, as marked on the graphs, were used. The TD spectra on single graphs differs only through the content of subsurface oxygen on the crystal. The compact drawn spectra are taken from at least, the dashed and pointed spectra are from more and at most subsurface oxygen contaminated surfaces.
tion temperature (stronger binding) and a strengthening influence on the binding of the adsorbed oxygen state to the substrate.

As it was recognizable from the previous graph in Figure 5.4, after three TDS recordings the subsurface oxygen content is not so big as it was observed in Figure 5.2a. Therefore, to show that the drastic change of TD spectra is caused only through the filling up of oxygen in the subsurface region, TDS recording have been repeated so many times that the content of oxygen in the subsurface region becomes high enough and comparable with the previous result. To accelerate the filling up procedure not only high oxygen exposure (50L) was used, but also occasional heating at 800K in oxygen atmosphere. To give a quantitative number, it is worth to mention that TDS recordings repeated 15 times were still not enough.

The final result is shown in Figure 5.5 and it agrees very well with the Figure 5.2. This confirms the prediction that the change of the desorption spectrum is caused only by the oxygen contamination procedure in the subsurface region. On the top left part presented CO desorption spectra still serve for a verification of sample cleanliness from carbon. The importance of this point will be discussed more in detail in section 5.2.2.

Analyzing the TD spectrum from full subsurface oxygen contaminated surface, one can easily recognize the disappearance of the $\gamma$ peak (in Figure 5.5 and Figure 5.2). A reasonable explanation for this disappearance of the subsurface oxygen desorption peak is, that there are different kinds of subsurface places available (in 2$^{nd}$ and 3$^{rd}$ layers) and at this saturated coverage of subsurface oxygen the strongly bounded oxygen in these sites would desorb at higher temperatures (e.g. $\gamma_1$, $\gamma_2$). In other words complete desorption requires further heating at higher temperatures.

A summary of these results is demonstrated in the following model in Figure 5.6. The adsorbed oxygen atoms on the surface, which recombine by diffusing with another oxygen atom, cause the $\beta_{1,\ldots,5}$ desorption peaks. In contrast to that the $\gamma$ peak is caused by the recombination process of two oxygen atoms, the one from the subsurface region the other diffusing on the surface. If further heating was possible, one could observe the peaks $\gamma_{1,2,\ldots}$, which would be caused by recombination of two subsurface
oxygen atoms from different layers diffusing into the surface.

![Diagram of desorption process](image)

Figure 5.6: A model for the desorption process of surface and subsurface oxygen species.

**Further results after polishing**

The above demonstrated results on the one hand caused us hesitation, because the O/Rh(110) system has been investigated before by many authors and no one has reported such a strong subsurface oxygen contamination in the crystal. In addition, the used crystal contained some macroscopically observable scratches on the surface. Therefore it was to consider that this crystal shows enhanced oxygen diffusion into the subsurface region since the scratches might have played a role of source for diffusion and influenced the desorption data. For that reason the scratches were removed through polishing and finally the quality of the new polished surface was checked using LEED and TDS. The results (not shown here) have confirmed not only its (110) character and much more important is that on this surface the above concluded predictions about the subsurface state were reproducible.

As mentioned before, two different chambers were used and the preparation conditions in the chambers were different. In the STM chamber for the preparation (results will be discussed in the next part) the temperature of 1100K was at most and a heating rate of only 1K/s was available because of technical limits. In order to check if this difference in the preparation caused any new behavior in the TD spectra, this preparation on a new polished surface was used in the TDS chamber too. In Figure 5.7 differentiated AE spectra are presented, which were taken from the polished rhodium crystal after different preparations, namely after annealing the oxygen covered surface to 1100K with a heating rate of 1K/s \(^6\) (compact line) and after TDS recording to 1420K (dashed line). Both spectra are normalized at the Rh\(_{305}\) signal height. The oxygen signal intensity in the AE spectrum, recorded after the TDS, was decreased but

\(^6\)the main preparation used in STM chamber
still some residual oxygen signal is present, which can be attributed to the remaining subsurface oxygen species. On the bottom right, the oxygen region of AES is magnified illustrated. One can observe that the signal positions are the same in both cases and do not differ significantly in form. On the top right of the graph the TD spectrum, recorded after the preparation of 1100K, is presented. This spectrum shows just a high temperature desorption between 1200K and 1400K.

This observed desorption of strongly bounded oxygen identifies only some residual oxygen species. Since no hydrogen titration experiment has been performed on the remaining oxygen, it is difficult to conclude exactly that the residual oxygen originates from the subsurface region. However we assumed this as a subsurface oxygen species according to the characters of very high temperature desorption and influence on the chemisorption state (not shown) as reported in previous part.

Present results from XPS

The ex-situ XPS measurements were performed on the polished crystal to distinguish the subsurface oxygen state from the surface oxygen state. In this attempt was succeeded to observe oxygen species with two different binding energies. Here, it has
been used different amount of oxygen exposures at different conditions. In Figure 5.8
the high resolution XPS spectra of the Rh3p3/2 and O1s regions, performed after dif-
ferent preparation conditions, are shown. The a. spectrum is taken after >30L oxygen
exposure, and was expected to observe high coverage oxygen chemisorption state. The
intensity of oxygen signal is quite small to compare to the f. spectrum, which was taken
in another ex-situ chamber from the smooth crystal after the oxygen saturation. This
is confirming again the roughness of this surface, which is already mentioned from the
STM experiments in section 4.1. The polished crystal contained narrower terraces so
that the total smooth region for oxygen chemisorption is smaller. Although the inten-
sity of oxygen signals in a. and f. curve differ, their positions are same, which is
consistent with their same nature, namely chemisorbed oxygen.

To check if the oxygen signal would increase in intensity, further high oxygen ex-
posures were used (b. and c. spectra). The oxygen state was satisfied. The c. spectrum
was taken after the oxygen preparation at 600°C heating, which enables the oxygen
diffusion into the subsurface region. The shift of oxygen peak maximum from 529eV
to 530eV, signifies the generation of subsurface oxygen state. In further d. experiment
the sample was prepared at 914°C in oxygen atmosphere, which corresponded to 150L
oxygen exposure. The d. spectrum confirms also the shift of oxygen peak to the higher
binding energies. The next hydrogen reduction experiment clarifies clearly the origin
of the oxygen signal at 530eV in the subsurface region. In e. spectrum, after the hy-
drogen reduction, only the subsurface oxygen signal is present. This is an important
completion of the assumption, discussed in previous section, and proves clearly the
existence of the residual oxygen not on the surface.

As mentioned it before XPD (X-ray Photoelectron Diffraction) was used to de-
termine the positions of the subsurface oxygen atoms in the Rh(111) surface [88]. We
have tried to perform similar experiment on the Rh(110) using XPD equipment with
unmonochromased Aluminium X-ray source. Unfortunately it did not succeed and
reasons for that are:

1. the intensity of oxygen 1s signal is low and it overlaps partly with Rh3p signal
made the observation of the O 1s backscattering pattern impossible
2. the sample holder contained molybdenum ring around the sample, which oxi-
dized during the oxygen treatment. This oxygen signal was much stronger than
the residual subsurface oxygen signal in the rhodium crystal.

Therefore as a next step it should be used a synchrotron light source with a very local
(∼ millimeter) beam, high resolution and variable wavelength.

5.2.2 Results from the smooth Rh(110) crystal

On this smooth surface were tried to detect subsurface oxygen species with STM.
Therefore it is important to introduce first the actual state of STM investigation about
Figure 5.8: High resolved XPS spectra of Rh3p3/2 and O1s regions from the polished Rh(110) surface at various oxygen coverage. The coverages and respective conditions are given in right angle on the graph.
Previous results from the STM according to the subsurface species

The STM is not an adequate method for the investigation of subsurface species because STM images reflect electronic structures of surfaces in the vacuum region where the influence of the outermost layers is dominant. Therefore the subsurface structures are usually not observed by STM. However, the Moiré patterns\(^7\) on metals and at low temperatures the subsurface dopant induced hillock structures\(^8\) on semiconductors were observed. This is the evidence for the influence of subsurface structures in STM images.

Kabayashi [98] has illustrated in the work "Mechanism of subsurface imaging in STM" theoretically how the subsurface impurities on semiconductors can be imaged in STM. In his numerical calculation the different behaviors of an atomic-scale waves (originating from an atom) and nano-scale waves (originating from a defect and impurity) were taken into account. The result was that the nano-scale waves were propagating to the surface without decaying and can be detected by the tip. Depending on the depth of the subsurface impurity it has been imaged in STM from corrugation with dark fringes to depression with light fringes.

Furthermore, on metal surfaces (Al(111), Cu(111) and Cu(001)) the image of implanted subsurface argon gas bubbles were observed by STM in Varga group [44]. The standing waves caused by argon bubbles played a main role in the imaging. The argon implantation took place during the sample preparation with sputtering and it was not detectable in AES. The appearance of argon bubbles has depended strongly on the tunnelling voltage. At low voltages fringes surrounding the bubbles were appeared (see Figure 5.9).

Results of the present STM study

The subsurface argon gas bubbles were observed in our case during the preparation procedure too. This is reported already in section 3.2.1. Since no tunnelling voltage dependent measurements have been done, the fringes around the bubbles can not be seen. Nevertheless, the lateral size of several nanometers and the corrugation height of several dozen picometers these argon bubbles were in good agreement with the above mentioned result of Varga [44].

In this experiment we attempted to view the subsurface oxygen atoms by STM. To prepare a subsurface oxygen-contented surface, the fully oxygen covered surface was heated to 1100K with a heating rate of ~1K/s and kept at this temperature for >10 minutes. From the previous TDS experiments it is clear that the temperature of

\(^7\) a superposition of outermost and second layer atomic structures
\(^8\) attributed to Friedel oscillations
1100K is not high enough to allow all oxygen species to desorb from the surface because the desorption maximum of the most strongly bonded oxygen on Rh(110) lies at 1150K (see Figure 4.11a). But long holding heating at 1100K seemed to be sufficient for complete desorption, because on the surface no familiar adsorption structure was left. Repeating the preparation is assumed to increase the assimilation of oxygen in the subsurface region. The results from the surface, prepared in this manner, are presented in Figure 5.10a. In (a.) a big overview image and in (b.) a local area are displayed respectively.

It is easy to recognize from the STM image that these topographies differ much from the images of the oxygen covered and clean surfaces as reported in previous chapter 4. Here “buckle and dark fringe” structures are present. These are optically very similar to the STM imaging of subsurface semiconductor dopants. Therefore the name of hillock-like structure is undertaken in this work for the “buckle and dark fringe” structures. Because the sample was prepared especially so that it could contain subsurfaces oxygen species, we have assumed that these are the imaging of subsurface oxygen species in STM.

In any case the AE spectrum recorded after this STM measurement still shows a small amount of oxygen signal (see Figure 5.11). This can be interpreted as its oxygen induced character. However it is typical that small amounts of subsurface species in AE can not be detected even if it is observable in STM [44].

More detailed information about this hillock-like structure can be given from a very local STM image and its line profiles, shown in Figure 5.12a. and b. respectively.
Figure 5.10: The surface topography after repeated oxygen preparation, namely, $3 \times$ (240L oxygen exposure followed by annealing at 1100K for 8min).
The line profile marked with 1 belongs to the hillock-like structure. Quantitatively the buckle shows $\sim0.6\,\text{Å}$ protrusion and the ring $\sim0.5\,\text{Å}$ depression. It is easy to recognize that this line profile strongly resembles the line profile of the subsurface Argon bubble (see Figure 5.9), namely both are seen as a buckle with a dark ring (depression). This definitely observable similarity of the hillock-like structure allows to speculate again these as the image of the subsurface oxygen species.

It is important to mention at this point that this hillock-like structure was always reproducible after above introduced preparation. This reproducibility identifies that the structuring in this way is a stable phenomena.

To check if the annealing temperature causes this structuring, the surface was prepared again at a lower temperature of 1000K. Surprisingly this temperature also causes the hillock-like structure as shown in Figure 5.13a and that is contradictory to the results from the TDS. There is no zig-zag ordered (2×2)pgO structure. Instead, hillock-like structures and “dark grubs” are observable. The AE spectrum (in c.) recorded after the STM contains a still recognizable oxygen signal, that is why it is attributed to oxygen. The ”dark grubs” seem to be missing rhodium atoms, and its line profile (not presented) shows $\sim0.5\,\text{Å}$ depression. This value is well comparable with the in Figure 5.12b. shown missing atom defect site profile (marked as 3). Further, it can not be left out that the missing rows are closed by hillock-like structures or in other words that hillock-like structures are established at most expanded places. Considering the lateral expansion of lattice due to a subsurface oxygen atom, it can be expected that the subsurface oxygen atoms form rather at defects or such expanded places. The line profiles of hillock-like structures showed a $\sim0.5\,\text{Å}$ protrusion.

\[9\text{in TDS chamber the annealing at 1000K was used to separate only the (2×2)pgO structure}\]
Figure 5.12: (a) The STM image, 12×12nm $U_b = -0.8V$ $I = 0.8nA$ (b) The line profiles of buckle and defect sites.
To the qualitative difference regarding the 1000K preparation in STM and TDS chambers can be speculated following two explanations. First, the temperature in the STM chamber is measured quantitatively wrong, strictly speaking there dominates a higher temperature because the most strongly bonded adsorbed oxygen species were already disappeared at 1000K. But this is unlikely because from previous experiment we know how bright the rhodium lights if it reaches e.g. 1200K. And on the other hand the temperature measuring is having an error of 200K is unbelievable. Second proposal is that the temperature is measured quantitatively right and the lost of adsorbed oxygen caused by segregated carbon atoms, which oxidize and desorb as explained in sample preparation procedure. This is more likely basing on the results from TDS chamber on this smooth crystal. There the sample showed high CO desorption besides the oxygen desorption (see section 5.2.2). Knowing the disappearing reason of oxygen atoms one can make a statement that the residual small amount of oxygen on the rhodium establishes a hillock-like structure, which resembles well the subsurface structures imaged with STM. But amongst other such a structure has been also observed from the low coverage adsorbed oxygen on the Al(100) [99] during the STM scanning at below 50K. Since no hydrogen reduction experiment has been done their whereabouts either on- or under the surface can not be clearly determined.

Furthermore we are interested if this structure would exist still after further heating. The sample state shown in Figure 5.13a was annealed additionally at 1050K. Its STM topography and the Auger spectrum are presented in Figure 5.13b and d respectively. Instead of hillock-like structures increased defect sites as ”dark holes” are observed and the oxygen signal in the AE spectrum differs hardly from the noise. If the residual oxygen atoms were placed on the surface they could have been reacted with segregated carbon as already discussed. But if they were placed under the surface through additional heating the oxygen atoms could have diffused into the deep bulk. According to the facts from the TDS experiment, the diffusion of the subsurface oxygen into the surface requires an high activation energy and therefore it desorbs only at a very high temperature above 1400K. Because this temperature was not reachable with our setups, the subsurface oxygen species is diffused to the bulk instead of desorbing. We assume that tracks of diffusion are still observable as defects on the surface. As it has been reported in semiconductor dopant STM scanning, that different kinds of subsurface structures exist [100], we can suppose that the hillock-like structure can be associated with subsurface oxygen atoms just under the surface and ”dark hole” structures with deep lying oxygen atoms.

Present TDS study

The formation of subsurface oxygen

The sample used in the STM experiment was mounted in the TDS chamber to check if the results from the rough crystal are reproducible with this crystal. As usual
Figure 5.13: The sample has been exposed to 100L oxygen and subsequently annealed at 1000K. (a.) STM topograph; (c.) AE spectrum recorded after STM. The sample was annealed further at 1050K; (b.) STM topograph; (d.) AE spectrum, recorded after STM.
start the TD spectra from the oxygen covered surface were recorded just to compare
with the reference spectra and thereby to check the sample cleanness. Figure 5.14
shows some of the subsequently acquired TD spectra of mass 32 and 28. The oxygen
desorption curve is drawn with a compact line, while the carbon monoxide desorption
curves are presented by a dashed lines. From the top left graph to the bottom right
the acquiring number of TD spectrum increases.
Although the obtained oxygen desorption spectra have very good agreement with the
reference spectra from the beginning (top left Figure 5.14), at the same time there is
a huge amount of carbon monoxide desorption observable. This signalizes a lot of
carbon segregation and from the successively recorded oxygen desorption spectra one
can see that the total amount of carbon segregation has no influence on the oxygen des-
orption procedure. Because the oxygen desorption peaks are observed at the expected
position and the form. The only recognizable difference in these TD spectra is that
the dominating desorption of mass 28 (CO) slowly decreases in intensity and in width
with an increasing spectrum acquiring number, while the oxygen desorption intensity
increases. It is very likely that the peak width identifies the thickness of layers, where
carbon atoms were segregating. At the beginning not only near surface regions and but
also bulk layers are not carbon free. From near surface layers carbon atoms segregate
to the surface easier and react there with oxygen atoms and desorb as CO molecules at
a lower temperature. And from the deeper lying layers segregating carbon causes CO
desorption at correspondingly higher temperature.
On the first graph the oxygen signal is more than 5 times weaker than the CO signal,
but on the last graph the oxygen desorption is much more dominant. Between these
single graphs a dozen of TDS recordings were performed. This indicates how slow the
releasing of the carbon contamination occurs.
An important finding from this experiment is that the small γ subsurface oxy-
gen desorption peak at 1400K becomes observable with decreasing carbon monoxide
desorption. By controlling the desorption of these two masses we could confirm the
previous statement [79, 80] that the oxygen dissolution into the subsurface region could
succeed only if no more carbon segregation is present.
Even low index rhodium surfaces have been investigated by numerous authors,
[96, 42, 43] and the references therein, with the same method (TDS), there very few
observations of the subsurface oxygen state exist. Instead, one can find in literature
a warning to avoid annealing at high temperatures because of excessive carbon seg-
regation. Concerning this and our result, we suppose that the scientist either did not
use carbon free clean samples or did not apply high enough desorption temperature,
therefore could not observe the subsurface oxygen state.

The TD experiment at various preparation temperatures
To distinguish the subsurface oxygen species from the chemisorbed species Leisen-

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10The desorption of carbon monoxide is an indication of bulk carbon segregation (carbon contamination) into the surface, which reacts with adsorbed oxygen and desorbs as a CO
Figure 5.14: The TD spectra of mass 32 and 28 from the smooth Rh(110) plane crystal at different oxygen coverages.
berger et. al. [84] have suggested a preparation temperature above the maximum desorption temperature of the chemisorbed oxygen. To prove if this prediction is valid in our case, TD experiments at various preparation temperature ($T_p$) from 570K to 1200K ranges were performed, while the oxygen exposure kept constant at 10L (see Figure 5.15). One can see on the graph a shifting of the leading edge to higher temperatures and thereby the apparent maximum at $1114K^{11}$ stays without displacement until $T_p=1000K$. Above $T_p \approx 1050K$, the peak maximum shifts to a higher temperature as well. This identifies that the most strongly bounded adsorption structure, $(2 \times 2)pgO$, can not be performed at these higher temperatures because of its instability. According to this only much stronger bounded oxygen species, namely the subsurface oxygen or a pre-rhodium oxide phase, can be produced. On the top right graph the area under the desorption curve (total adsorbed oxygen) is plotted against the preparation temperature (Figure 5.15). The decreasing sticking coefficient with increasing preparation temperature can be seen.

The important observation from this experiment is again the subsurface oxygen peak at 1400K, which is always present and slowly increases in intensity with increasing preparation temperature. This is reasonable if one assumes that through preparing at high temperature the vibration amplitudes of rhodium atoms become bigger, and this accelerates the diffusion of oxygen atoms into the subsurface region. On the other hand, because of successively repeated oxygen exposure, the influence of vacuum chamber wall increases, which could lead to a general signal increase at glowing sample temperature. Therefore it is important to check if the increase in desorption intensity stems from the sample or is caused by the repeated (long continuing) oxygen treatments. As mentioned before, the gas nozzle in the chamber was available in order to not worsen the residual gas pressure. Using this gas nozzle kept the residual gas pressure during the experiment better than an order of magnitude. The same TD experiments were performed at the sample temperature of 700K, 900K and 1050K, and the sample was exposed to oxygen for 2 min with the nozzle. This corresponds to $\geq 18L$ exposure. One can observe from Figure 5.16 a slow increase of oxygen desorption intensity at 1400K with increasing preparation temperature, which reasonably confirms the previous result without a gas nozzle.

Using AES one can ascertain whether this 1400K oxygen desorption originates from the sample. In Figure 5.17 shown results the sample was annealed to 1420K and the thereafter taken AE spectrum drawn with a compact line (black). This spectrum is from the clean surface, so it should not contain any oxygen signal; but, there is still small amount of oxygen. In following the sample was exposed to 10L oxygen and was recorded an AE spectrum, which drawn with a dashed line (red). Finally the sample was annealed to 1300K to let desorb the adsorbed oxygen and to separate the subsurface oxygen and then the AE spectrum, marked with a (blue) square, was taken. The graph illustrates the origin of the residual oxygen after annealing at 1300K in the crystal. This residual oxygen causes the subsurface oxygen desorption at 1400K (not

\[11\] most strong bounded oxygen desorption temperature
Figure 5.15: The preparation temperature dependent TD spectra. The sample temperature is varied between 570K-1200K, while the oxygen exposure kept constant at 10L. On the top left and right layers are corresponding CO desorption and areas under O\textsubscript{2} desorption curves via T\textsubscript{p} presented.
Figure 5.16: The TD spectra at varied (700K (black), 900K(red) and 1050K(green))
sample temperatures. For the oxygen exposure (≥18L) the gas nozzle is used.

shown).

The TD experiment on a roughened surface

From the previous results one can easily recognize that the desorption intensity of
subsurface oxygen species is still quite low compared to the results of the previous
samples. Therefore the question arises, how one can increase this intensity. Is it true,
that the oxygen diffuses into the subsurface region easier on a rough surface? If yes,
through sputtering roughened surface would contain more subsurface oxygen species
than from the sample prepared at extended temperature?

To find answers to these questions the following experiments were performed. First
the experiment at extended sample temperature was completed for comparison. To
eliminate the influence of surroundings the gas nozzle was used for oxygen exposure.
The crystal was exposed at 700K and 800K to 390L oxygen and at 900K to 150L.
Visually the results in Figure 5.18 are consistent with previous results in Figure 5.15
and Figure 5.16.

For the next preparation, the surface was sputtered for 2min and 3min and thereafter
exposed to 60L. \(^{12}\) Thereafter recorded TD spectra are plotted at the bottom of the
graph in Figure 5.18 and marked with d. and e. respectively. The presentation of TD
spectra from extended preparation temperature and from roughened surface on top of
the others enables quantitative comparisons to be made. The decrease of the total area
under the TD spectrum from roughened surface can be explained through the shrink-

\(^{12}\) oxygen partial pressure of \(P_{O_2} = 5 \times 10^{-7}\)Torr was used
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Figure 5.17: AE spectra recorded after different sample preparations. From the clean sample (drawn with a black compact line), after oxygen exposure (red dashed line), after annealing at 1300K (square marked blue line), after hydrogen reduction the oxygen covered sample (star marked green line).

The characterization of surface and subsurface oxygen species by means of their reactivity is discussed. The H₂/H₂O conversion process is used here as a simple measure of reactivity. From the previous section we know that chemisorbed oxygen would be removed through hydrogen reduction. First the oxygen adsorption structure is created through 10L oxygen exposure at the sample temperature of 570K (a, b and d) and at 1300K (c).

---

13Heating the sample at 430K in H₂ atmosphere with the partial pressure of 2 x 10⁻⁷ Torr
Figure 5.18: The oxygen TD spectra from the roughened surface. The surface has been roughened by 2min (compact, e.) and 3min (dashed, d.) sputtering. For quantitative comparing the TD spectra from different preparation temperature experiments (700K (green, c.), 800K (blue, b.) and 900K (cyan, a.) in oxygen atmosphere with a partial pressure of $P_{O_2} = 5 \times 10^{-7}$Torr) are put together.
400K (c) respectively. Thereafter the sample were annealed at certain temperature to fill the subsurface region (more detail in next part) and finally the hydrogen reduction experiments were performed to remove only the surface oxygen species. Subsequently were recorded TD spectra of mass 32, 18, 28 and in Figure 5.19 is only presented the oxygen desorption spectra. One can observe the desorption of residual oxygen only at 1400K in all spectra, which explicitly implies its strong bounding character in comparison to surface oxygen species. The unreactive nature with hydrogen illustrates its existence in the subsurface region.

Furthermore, the AE spectrum plotted with star marked line in Figure 5.17, taken after hydrogen reduction confirms the origin of this residual oxygen in the crystal too. The amount of the oxygen species remaining after the annealing at 1300K and after the hydrogen reduction seem to be the same in the AE spectra, which signifies their common origin.

**Annealing temperature dependency**

In the previous reactivity experiment different annealing temperatures were used and the results will be discussed here in detail. One can see in Figure 5.19 the TD spectra performed after the hydrogen reduction experiment. These spectra differ only in preparation temperature after oxygen exposure as given on the graph. Basing on the the fact that at 400K there is no great thermal motion of rhodium atoms \(^{14}\), the oxygen atoms can not diffuse into the subsurface region and therefore no subsurface oxygen desorption is expectable at 1400K. But from the spectrum b. one can still observe some small amount of oxygen desorption, which assumingly originates from the remaining subsurface oxygen after the previous preparation. The exposure at 573K (in a.) admits the motion of rhodium atoms \(^{15}\), so the oxygen can diffuse into the subsurface region. Considering the result on Rh(111) \([79]\) the oxygen diffusion increases through annealing at 800K (just below the desorption temperature) and especially the duration of annealing should play a major role. This preparation is used partly in c and d for 1min and 2min respectively.

On the top left corner in Figure 5.19 the whole oxygen content under the desorption curve is shown. One can easily see the agreement with the assumption, that with the increasing annealing temperature the oxygen diffusion increases. But the increase is quite small to compare to in \([79]\).

Basically it is possible to increase the annealing temperature further, but then the surface would begin to loose oxygen through desorption. As it has been determined theoretically \([89, 90]\) the oxygen diffusion into the subsurface region is only favorable if the surface is saturated with the adsorbed oxygen. Concerning this, the loss of oxygen will prohibit the diffusion into the subsurface region.

\(^{14}\) in previous section the rhodium reconstruction is remained after the oxygen reduction experiment

\(^{15}\) takes place the oxygen induced surface reconstruction
Chapter 5. Subsurface oxygen state on Rh(110)

Figure 5.19: Oxygen desorption spectra from different amounts of subsurface oxygen-rich surfaces. In all cases the sample was prepared with 10L oxygen at: (a.) at 573K, no following annealing, (b.) at 400K, no annealing, (c.) at 573K, following annealing at 800K for 1min, (d.) at 573K, annealing at 800K for 2min. Thereafter surface oxygen species were removed through hydrogen treatment at 430K as described previously. Subsequently recorded TD spectra show only desorption of subsurface oxygen species.
Determination of the desorption parameters

The desorption of subsurface oxygen atoms is not complete and the observed desorption is only one part. Thus makes difficult to apply the TDS analyzing methods. Nevertheless the Falconer-Madix method is applicable because it uses only left flank of the spectrum. In this method have been required different isotherm desorption spectra with same initial coverage. At first the the surface was exposed to 30L oxygen at 570K surface temperature. Then the crystal was annealed at 1300K to let to remain only the subsurface oxygen species. And finally the isotherm oxygen desorption spectra were taken. To empty the subsurface state completely the target temperature was hold so long that no more oxygen desorption were present. On the other hand it is to take into account that the longer the holding of such high temperature the more probable is an influence of surrounding desorption. As it can be seen from the bottom graph in Figure 5.20 the duration of temperature holding was not long enough to let to desorb all subsurface oxygen species. The right flank of the curves have not a same height. For two different coverage, marked with different colors on the curves, the desorption parameters are determined (see Figure 5.20). We have used this pre-exponential factor in the simulation graph in Figure 4.11. One can see that the activation energy of 467 kJ/mol for $\gamma$ is not far different from the above determined values on the graph, and these are in well agreement with the reported values of 490kJ/mol and $2 \cdot 10^{17} \text{cm}^{-2}\text{s}^{-1}$ [79] for $\gamma$ on Rh(111).

The comparison of TDS and STM studies

The supposed subsurface species from TDS and STM studies should be discussed at the same time to ascertain that one deals with the same species. But because (as above mentioned before) the preparation conditions were different, a direct comparison is not possible. To make it comparable, the same preparation conditions were used in the TDS chamber for the smooth crystal as well. As in the STM chamber a very low heating rate was used, here arises the question, whether the heating rate plays any role for the generation of subsurface oxygen species or not. To check this aspect, experiments at various heating rates were performed. Here the sample was exposed to oxygen and heated at a rate of 1K/s to 1100K. The heating rate is low, therefore the desorption intensity is weak and chemisorption peak positions are shifted to lower temperatures (see Figure 5.21a). Subsequently a TD spectrum with a rate of 10K/s (to make it comparable with TDS results) to 1420K was recorded to measure the amount of residual oxygen species (see Figure 5.21b). From the TD spectra on the right of the graph it is easy to recognize two desorption peaks at $\sim$1200K and 1400K. The peak at 1400K was present before in other spectra, and it is assumed to be the subsurface oxygen desorption peak. In contrast, the peak at $\sim$1200K was not clearly observable before. To test if this oxygen desorption comes from the subsurface region, the hydrogen reduction ex-

\[16\] was the highest available temperature in the STM recipient
Figure 5.20: Desorption parameters obtained using Falconer-Madix method

- $E_a = 408\,kJ$
- $\nu = 1.5 \times 10^{17}$

- $E_a = 432\,kJ$
- $\nu = 1.5 \times 10^{17}$
periment was performed. The thereafter attained TD spectrum (marked with a line and star (yellow) on the right graph) shows the disappearance of the peak at 1200K. This identifies its existence on the surface in contrast to the remaining oxygen at 1400K. The new surface oxygen structure is assigned to the ruthenium oxide and is reported in detail in section 4.3. The experiments with different heating rates, namely 2K/s (b), 5K/s (c), 7K/s (d) and 10K/s (e) were performed. The results are independent of the heating rate and are reproducible.

Figure 5.21: The $O_2$ TD spectra recorded to 1100K (left) at varied heating rates after constant 30L oxygen exposure at 573K surface temperature. The oxygen partial pressure of $5 \times 10^{-7}$Torr is used. The spectra are marked with different letters respectively their rates. On the right side are shown the finally performed desorption spectra to 1400K (rights) with a rate of 10K/s. The curve k. is taken after the hydrogen reduction of at 1100K annealed surface.

Further AES measurements are performed to find out if these oxygen states differ in their binding energy. It is easy to recognize from Figure 5.22a that the binding energy of oxygen in CO is higher than the energy of chemisorbed oxygen. This confirms the non-dissociating molecular adsorption of CO because of its high binding character.
Figure 5.22: (a.) The oxygen regions of the AE spectra taken after different oxygen preparations. The preparations are listed on the graph in a right angle. The rhodium region can be seen on the bottom graph. (b.) An another contradictory results to (a.) after similar preparation.
But for the residual subsurface oxygen the binding energy seems to be lower than by the adsorbed oxygen. This is contradictory to the TD results, where the subsurface oxygen species desorbs at higher temperatures and through that, illustrates its stronger binding character.

To approve the Auger results the measurement was performed at another coverage (see Figure 5.22b). The above reported statement is not confirmed. Hence no accurate information was attainable from the Auger measurement about their binding energy.
Chapter 6

Summary

In the present work the surface and subsurface oxygen species on the rough and smooth Rh(110) surfaces were studied with TDS, LEED, AES, XPS and STM. The difference in the surface roughness was clear not only from the STM surface topographies but also from the TDS, where the single desorption peaks form only if the surface is smooth, and from the XPS, where the oxygen intensity at saturated coverage on the rough surface was lower than on the smooth one.

The quite well known surface oxygen phases are investigated for their reproducibility and also for the checking the surface quality. Therefrom results are given in chapter 4 in detail. At the beginning of the chapter about clean surface is introduced and as following the adsorbate induced single structures, $\text{(2} \times 2)\text{pO}$, $\text{(2} \times 3)\text{pO}$, $\text{c(2} \times 6)\text{O}$, $\text{c(2} \times 8)\text{O}$, are reported separately. In our STM a partial $\text{(2} \times 3)\text{pO}$ structure has been observed as first. The existence of such structure has been reported in earlier LEED work of Falkenberg [43]. But in our experiment this low coverage oxygen structure did not form homogenously, so that it could not be imaged in LEED. But this metastable structure is real from the fact that in oxygen TDS an $\beta_5$ shoulder is always present.

On the oxygen adsorption structures the hydrogen reduction experiments were done. During the controlling the oxygen covered surface $\text{(2} \times 2)\text{pO}$, $\text{c(2} \times 6)\text{O}$, $\text{c(2} \times 8)\text{O}$) with LEED the sample is heated at below 450K in $2\cdot10^{-7}$Torr hydrogen atmosphere. The LEED patterns are changed directly to the reconstructed $\text{(1} \times 2)\text{Rh}$, $\text{(1} \times 3)\text{Rh}$, $\text{(1} \times 4)\text{Rh}$ rhodium LEED patterns. This experiment was important to find out the confident pressure-temperature relation for the removal of surface oxygen species.

It turned out from the XPS that the smooth crystal contained ca. 1.5% of ruthenium contamination, which could clearly be determined through its Ru 3d double peak. The influence of this contamination was observable as well as from the STM and the TDS results. Interestingly the ruthenium atoms are always formed quasi-hexagonal arranged islands in the STM images. Annealing the oxygen covered smooth surface at above 1000K caused the ruthenium islands to oxidize. This feature was confirmed from TDS and XPS measurements. Considering these the ruthenium in Ru/Rh alloys
would oxidize at ultra high vacuum condition, not as typical at high pressure oxygen atmosphere. More in detail is given at the end of the chapter 4.

In transition metal surfaces the forming of subsurface oxygen is interesting because of an expected influence of it on their catalytic properties and this knowledge will be of technical importance for catalytic industries. Therefore, generation behaviors of subsurface oxygen species on the rough and smooth surfaces were studied and the results are subsequently described in chapter 5.

On the rough surface a recognizable amount of oxygen desorption peak at around 1400K, which is assumed to the subsurface oxygen species, observed. Its amount has increased with the further oxygen preparation. At the same time because of increased subsurface oxygen content in the sample the form of oxygen TD spectrum was changing. Considering these changes has been proposed an model that the desorption peak around 1400K is caused by recombination of subsurface oxygen atoms and on surface oxygen atoms. Further recombination and desorption of subsurface oxygen atoms will be observed at much higher temperature so that with our setups can not be observed. These species were only possible to be removed completely through short sputtering.

On the smooth surface the subsurface oxygen desorption is only observed after the complete removal of carbon impurities. The subsurface oxygen species is identified through its high temperature desorption nature in the TDS. Through sputtering caused roughness did not increase the subsurface oxygen amount on this smooth surface.

The reactive nature of oxygen atoms with hydrogen on the rhodium were used for affirming the staying of subsurface oxygen atoms under the surface. Both on the rough and smooth surfaces the subsurface oxygen species showed no reaction with adsorbed hydrogen, because of their lateral apart. The XPS spectrum from the rough crystal provided higher binding energy for the subsurface oxygen, which intensifies the speculation their existence under the surface.

The rough surface contained more subsurface oxygen than the smooth one. This can be explained through its high step density, which contributes to the extended diffusion.

In the STM study the smooth sample, prepared so that it contains subsurface oxygen, showed "hillock-like” structure. This is supposed to be the imaging of subsurface oxygen atoms.
Bibliography


[100] M. van der Wielen, H. van Kempen. Study of imperfections near the cleaved GaAs(110) surface by low-temperature scanning tunneling microscopy. *Promotion*.

Appendix

Figure 6.1: Dependency of desorption spectra on the different parameters of desorption. The curves are drawn after equation 2.9. At each graph only one parameter is varied and the rest are kept constant. Left array of graphs belongs to 1st order desorption and the second array to 2nd order desorption. Beginning from the first row of graphs the coverage, the activation energy, the pre-exponential factor and the heating rate have been varied respectively.
<table>
<thead>
<tr>
<th>Major Auger peaks</th>
<th>MNN Rh$_{302}$</th>
<th>KLL O$_{503}$</th>
<th>KLL C$_{271}$</th>
<th>MNN Ru$_{273}$</th>
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</thead>
<tbody>
<tr>
<td>Relative sensitivity, $S_x$</td>
<td>0.7</td>
<td>0.5</td>
<td>0.2</td>
<td>0.5</td>
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Table 6.1: Relative Auger sensitivity of used elements after [26]

<table>
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<tr>
<th>Method</th>
<th>$\Delta d_{12} [%]$</th>
<th>$\Delta d_{23} [%]$</th>
<th>$\Delta d_{34} [%]$</th>
<th>W [eV]</th>
<th>Reference</th>
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</thead>
<tbody>
<tr>
<td>Ab. Initio LDOS</td>
<td>-10.5</td>
<td>4.4</td>
<td>-1.6</td>
<td>-</td>
<td>[45]</td>
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<tr>
<td>Ab. Initio LDOS</td>
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<td>2.6</td>
<td>0.8</td>
<td>-</td>
<td>[46]</td>
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<tr>
<td>LDA</td>
<td>-9.9</td>
<td>2</td>
<td>-</td>
<td>4.94</td>
<td>[101]</td>
</tr>
<tr>
<td>GGA</td>
<td>-9.2</td>
<td>2.1</td>
<td>-</td>
<td>4.59</td>
<td>[101]</td>
</tr>
<tr>
<td>Ul.PP</td>
<td>-9.7</td>
<td>3.6</td>
<td>-2.2</td>
<td>5.14</td>
<td>[50]</td>
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<tr>
<td>LEED I-V</td>
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<td>2.22</td>
<td>-</td>
<td>-</td>
<td>[60]</td>
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Table 6.2: The relaxation data for the clean Rh(110) crystal
<table>
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<th>LEED Profile</th>
<th>Shape of the surface</th>
<th>Description</th>
</tr>
</thead>
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<td>. .</td>
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<td><img src="image" alt="Surface" /></td>
<td>regular steps</td>
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<tr>
<td><img src="image" alt="Spot" /></td>
<td><img src="image" alt="Profile" /></td>
<td><img src="image" alt="Surface" /></td>
<td>random steps</td>
</tr>
<tr>
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<td><img src="image" alt="Surface" /></td>
<td>regular size or regular distance islands</td>
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<tr>
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<td>random size and distance islands</td>
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Figure 6.2: The information can be extracted from LEED spots.
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