MASTER

Time of flight ion scattering and recoiling spectroscopy : optimalization and first results

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Time Of Flight ion scattering and recoiling spectroscopy

Optimalization and first results.

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Summary

Several techniques are available for the analysis of surfaces. One of them is Low Energy Ion Scattering and Direct Recoil Spectroscopy (LEIS/DRS). LEIS/DRS uses a beam of low energy (0.5 - 7 keV) rare gas ions which interact with the surface. The energy loss of the scattered or recoil particles contains information about the elemental composition of the surface. The azimuthal distribution of these particles can be used to analyze the surface structure.

In this report, two LEIS apparatuses are used. The Energy and Angle Resolved Ion Scattering Spectrometer (EARISS) measures simultaneously, both the energy as well as the azimuthal distribution of backscattered ions. With the Time Of Flight ion scattering and recoiling spectrometer (TOF), forward scattered particles as well as recoiled surface atoms can be measured. For the analysis of the particles, the flight time from the sample to the detector, which is related to the energy, is determined. For this time of flight detection, a pulsed ion beam is required.

A new pulsing method was tried, which created ion pulses which were far too long to be used in the experiments. The old method, called "impuls sweeping", was optimized, which resulted in a beam of 2 keV Ne⁺ pulses with a FWHM of 54 ns. This pulse width is short enough for the TOF experiments. Other ions or energies can also be used.

With the EARISS and the TOF, the surface of a Cu₈₀Pd₁₅ (110)-p(2x1) crystal was analyzed. The EARISS measured a Pd concentration in the second layer of ~ 41 at.%) and a first layer concentration of < 14 at.%. Due to selective contamination of the Pd, the results varied. The data of the least contaminated surface was used for the calculation of the Pd concentration in the first and second layer.

The azimuthal distribution of the recoiled copper atoms and the backscattered ions, could be assigned to different crystal directions of the unreconstructed (110) surface. All these results are in reasonable agreement with previous measurements by other techniques on the Cu₈₀Pd₁₅ (110) sample.
Dankwoord

Als laatste wil ik mijn ouders en Jackeline bedanken voor de tijd en steun die ik heb gekregen om tot dit eindresultaat te komen.

Marc van de Grift

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1: I like to thank Steve Francis for his help with the Cu_{86}Pd_{15} measurements.
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6. The Cu_{85}Pd_{15} (110) surface
1. Introduction

In contemporary research, surface science is a subject of raised attention. Catalysis and semiconductor physics are two regions in which surface science plays an active role. In heterogeneous catalysis, surface science helps in understanding the reaction process and therefore in improving the capabilities of the catalyst.

In surface analysis, a wide range of surface sensitive techniques are used. Most techniques use a beam of particles (or photons) which interact with the sample. Analyzing the particles (or photons) coming from the surface, gives information about the sample surface. Every technique provides its own characteristic information. The combination of different techniques is, therefore, needed to make a complete description of the surface. Two examples of surface sensitive techniques are given below.

Low Energy Electron Diffraction (LEED), uses a beam of low energy electrons (≈ 100 eV). The diffraction of the electrons is displayed on a fluorescent screen, showing the surface structure in reciprocal space. X-ray Photoelectron Spectroscopy (XPS) is also an often used technique, which uses the emission of electrons by X-ray radiation. The energy of the electron depends on the binding energy of the atom from which it is emitted. By measuring the energy spectrum of the electrons coming from the sample, the composition of the surface can be determined. The information depth of LEED and XPS is a some atomic layers.

At the Eindhoven University of Technology, faculty of physics, the surface science group makes use of several surface sensitive techniques. The main one is Low Energy Ion Scattering (LEIS). LEIS uses a focused beam of low energy (0.5 - 10 keV) rare gas ions. The measured energy loss of a scattered particle depends on the mass of the surface atom with which it collided. Therefore, by measuring the energy distribution of the scattered particles, the element concentrations on the surface can be determined. A typical LEIS spectrum is shown in figure 1.1.

When only ions are detected, the high neutralisation probability of the rare gas ions makes LEIS extremely surface sensitive. The reason for this is, that
neutralization depends highly on the path length or the number of interactions of the ion with the surface atoms. The majority of the ion signal contains therefore single scattered ions from the first atomic layers.

When single crystals are used as a model for the real material, structural information about the surface can be obtained. This is done with the use of so-called shadowcones, which are created behind the atom. When an atom lies in the shadowcone of another atom, it cannot be detected. However, when the edge of the shadowcone falls on an atom, ions are focused on this atom and a maximum in the signal from this atom occurs. With this effect, it is possible to determine the positions of the atoms in the surface, by measuring the azimuthal distribution of the scattered ions.

In LEIS, scattered ions can be detected in two ways. With an electrostatic analyzer, only ions are measured. This results in an information depth of one or two atomic layers, due to the high neutralization probability. When also neutrals have to be detected, the time of flight method is often used. The flight time of a particle is simply related to its energy. With this method, surface sensitivity is obtained by placing the source at a grazing angle to the surface.

In the surface science group, the EARISS/TOF apparatus is used to analyze the surface with several surface sensitive techniques. The heart of it is the Energy and
Angle Resolved Ion Scattering Spectrometer (EARISS) itself. The EARISS makes a very efficient use of the scattered ions, by measuring at the same time the energy as well as the azimuthal distribution of the ions that are scattered by the surface over 145 degrees. Therefore, measurements can be done with very low ion doses, which causes very little damage to the surface. The scattering angle of 145 degrees is chosen for optimal mass separation. The azimuthal distribution of the scattered ions gives information on the crystal structure arising from blocking effects of the atoms. In this way, information about the relative positions of direct neighbour atoms can be obtained.

In the same vacuum chamber as the EARISS, the Time of Flight ion scattering and recoiling spectrometer (TOF) can be used for the analysis of the sample surface. The angle between the ion source and detector of the TOF is 35 degrees. With the TOF, ions as well as neutrals can be detected. With the backscattering of the EARISS, it is impossible to "see" atoms in the surface which have a lower mass than the mass of the ion. For elements with a slightly heavier mass than the ion, the detection efficiency is very low. The use of forward scattering and the detection of recoil particles with the TOF, makes it possible to look at the light elements on the surface, such as H, C, O and N. A disadvantage of forward scattering is the poor mass resolution for heavier elements. The combination of EARISS and TOF makes it possible to detect both light and heavy elements on the surface.

When the azimuthal dependence of different peaks in the TOF spectrum is measured, packing densities in different crystal directions can be determined. Also the angle of incidence can be varied, to obtain information about the interatomic distances and positions of adsorbed atoms.

The surface sensitivity of the TOF is obtained by the grazing angle of incidence. The TOF measures the flight time of the scattered and recoiled particles from the sample to the detector. This flight time is simply related to the energy of the particles. The energy of the scattered particle depends on the mass of the surface atom with which it collided and the energy of the recoil particle depends on the mass of the particle itself. A beam of ion pulses is required to measure the flight time. The generally used pulse width of the ion pulses in these kind of
experiments is between 50 and 100 ns. To make these pulses, a new pulsing method was tested, based on switching on and off the ionization process. This method could not produce pulses of the desired width, for fundamental reasons. Therefore, the old method was optimized, which uses the deflection of the ion beam by an electrical field.

With the EARISS and the TOF, measurements have been done on a Cu₈₆Pd₁₄ (110) single crystal. Cu and Pd are frequently used materials in catalysis. Therefore, it is interesting to investigate the catalytic activities of a CuPd alloy. To explain the reactions on the CuPd surface, it is necessary to look closer to the surface composition and structure. A single crystal is used as a model for the real catalyst surface. The azimuthal distribution of the TOF signal from different peaks in the CuPd spectrum is measured and compared to the EARISS measurements.

This report contains two main subjects.
The development and rejection of a new pulsing method and the optimization of the old method are described in chapter 4 and 5 respectively.
Measurements on the Cu₈₆Pd₁₄ (110) single crystal will be explained in chapter 6.
Chapter 2 contains the theory and some features of Low Energy Ion Scattering. A description of the set-up of the EARISS/TOF apparatus and in more detail the TOF, can be found in chapter 3.
Conclusions of the results in this report and remarks for the future are given in chapter 7.
2. **Low Energy Ion Scattering and Direct Recoil Spectroscopy (LEIS/DRS).**

### 2.1. Introduction

Low Energy Ion Scattering and Direct Recoil Spectroscopy (LEIS/DRS), is a surface sensitive technique, which uses low energy (0.5 - 7 keV) rare gas ions. The energy loss of the scattered particles is measured. This energy loss depends on the mass of the atom from which the ion was scattered. Therefore, a LEIS/DRS spectrum can be interpreted as a mass spectrum of the surface. In this chapter, the theory of LEIS/DRS is described and some features for surface structure analysis are explained.

### 2.2. Theory

#### 2.2.1 The binary collision model

To describe the interaction between the surface atoms and the incoming ions, an elastic, binary collision model is used. For LEIS/DRS, this model is valid, because the following conditions are fulfilled. Firstly, the deBroglie wavelength of the ions is much smaller than the lattice constant. This means that diffraction effects can be neglected and the trajectories of the ion and atom can be described in a classical way. Secondly, the interaction can be described with a screened Coulomb potential. This means that the collision can be considered to be elastically. Since the distance of closest approach is much smaller than the inter atomic distance and the screened Coulomb potential drops faster than 1/r, the collision can be assumed to be binary. During the collision, the surface atoms can be regarded as fixed, because the vibration time of the atoms is few orders of magnitude larger than the interaction time. For a schematic overview of the collision and the definitions, see figure 2.1.

By applying the laws of conservation of energy and momentum, it can be
calculated that the energy of the scattered particle $E_1^*$ is given by:

$$E_1^* = \left(\frac{\cos\theta \pm \sqrt{q^2 - \sin^2\theta}}{1 + q}\right)^2 E_1$$ (2.1)

and the energy of the recoil particle $E_2^*$:

$$E_2^* = \frac{4 \cdot q \cdot \cos^2\phi}{(1 + q)^2} E_1$$ (2.2)

where

$$q = \frac{m_2}{m_1}$$ (2.3)

Equation (2.1) is valid under the condition that $q > \sin \Theta$.

The total velocity after the collision should be positive so the - sign in equation (2.1) can only be used for $0^\circ < \Theta < 90^\circ$ and $q < 1$. For $90^\circ < \Theta < 180^\circ$ equation
(2.1) is restricted to \( q > 1 \).

Equation (2.2) is valid when \( 0° < \phi < 90° \), because also here the total velocity after collision should be positive.

When the ratio of \( E_1'/E_1 \) is plotted in a polar plot as a function of \( \Theta \) (figure 2.2), it is easy to see the different solutions of equation (2.1).

![Figure 2.2: Polar plot of the energy ratio as a function of the scattering angle for different mass ratios \( q \). Intersections with \( \Theta = 35 \) are solutions for the TOF.](image)

Energy can be converted into time by the kinetic energy relation:

\[
E = \frac{1}{2} m \cdot v^2 = \frac{1}{2} m \cdot \left( \frac{l}{t} \right)^2
\]  

(2.4)

so over a fixed distance \( l \), the time of flight of a particle with energy \( E_i \) and mass \( m \) is:
This means that after the collision, the flight time over a distance \( l \) of the scattered particle is given by:

\[
t_i^* = \frac{l^*(1 + q)}{\cos \theta \pm \sqrt{q^2 - \sin^2 \theta}} \sqrt{\frac{m_1}{2E_1}}
\]  

(2.6)

and of the recoil particle:

\[
t_2^* = \frac{l^*(1 + q)}{\cos \phi} \sqrt{\frac{m_1}{8E_1}}
\]  

(2.7)

Since the scattering angle \( \Theta \) and the recoil angle \( \phi \) are fixed in the experiment, the energy or time spectrum can be interpreted as a mass spectrum.

### 2.2.2. Shadowing and blocking

The interaction between an atom and an ion is often described by the Thomas-Fermi potential, which is a screened Coulomb potential. For calculations, usually the Molière potential is used, which is an approximation of the Thomas-Fermi potential. The Molière potential is given by:

\[
V(r) = \frac{Z_1 Z_2 e^2}{4 \pi \varepsilon_0 \varepsilon_r r} \sum_{i=1}^{3} \alpha_i e^{-\frac{r_i}{a}}
\]  

(2.8)
with \( \alpha_i = (0.10; 0.53; 0.35) \) and \( \beta_i = (6.0; 1.2; 0.3) \). \( eZ_1 \) and \( eZ_2 \) are the nuclear charges of the ion and the target atom. \( r \) is the distance between ion and the atom and \( \alpha \) is known as the Thomas-Fermi screening length. For an ion-atom collision, the Thomas-Fermi screening length is given by:

\[
a = 0.885 \cdot a_0 \cdot Z_2^{-\frac{1}{3}}
\]  

(2.9)

with \( a_0 \) the Bohr radius (0.529 Å)

A cone is formed behind the atom, when ions with impact parameters \( s \) interact with the atom, see figure 2.3.

![Figure 2.3: A shadowcone is formed behind an atom.](image)

The radius \( R \) of this cone at distance \( l \) behind the atom is given in first approximation by [VEEN]:

\[
R = s + l \cdot \eta(s)
\]

(2.10)

Here the small angle approximation \( \eta = \tan(\eta) \) is used for the scattering angle \( \eta \). Also no recoil effect of the target atom is taken into account. LEIS/DRS is in the limit of this approximation. The edge of the shadowcone is the place where the density of the ions is the

- 9 -
largest. This can be calculated with:

\[
\frac{\partial R}{\partial s} = 0 \quad (2.11)
\]

or

\[
\frac{\partial \eta(s)}{\partial s} = -\frac{1}{l} \quad (2.12)
\]

and gives the shadowcone radius \( R \) at distance \( l \) behind the atom. For an unscreened Coulomb potential, the scattering angle determined by the impact parameter \( s \) is given by:

\[
\eta_c(s) = \frac{Z_1 \cdot Z_2 \cdot e^2}{4 \cdot \pi \cdot \varepsilon_0 \cdot E \cdot s} \quad (2.13)
\]

with \( E \) the initial energy of the ion. With the combination of equations (2.10), for (2.12) and (2.13), the following expression can be found for the radius of the shadowcone created by a Coulomb interaction:

\[
R_c = 2 \cdot \sqrt{\frac{Z_1 \cdot Z_2 \cdot e^2 \cdot l}{4 \cdot \pi \cdot \varepsilon_0 \cdot E}} \quad (2.14)
\]

For a Molière potential, the equations 2.10 and 2.11 can only be solved numerically, resulting in:

\[
R_M = \xi \cdot R_c \quad (2.15)
\]
where $\xi$ is the screening parameter.

In figure 2.4, $\xi$ is plotted as a function of $R_e/a$. This line can be described by the empirical formula [OEN]:

$$\xi = 0.924 - 0.182 \cdot \ln \left( \frac{R_e}{a} \right) + 0.0008 \cdot \left( \frac{R_e}{a} \right)$$  \hspace{1cm} (2.16)

for $4.5 \leq \frac{R_e}{a} \leq 100$ and :

$$\xi = 1.0 - 0.12 \cdot \left( \frac{R_e}{a} \right) + 0.01 \cdot \left( \frac{R_e}{a} \right)^2$$  \hspace{1cm} (2.17)

for $0 < \frac{R_e}{a} < 4.5$ .

For LEIS/DRS, is at the limit of this approximation, therefore, deviations occur at low energies and heavy ions.
When atoms are inside the shadowcone of another atom, they cannot have a collision with an ion from the initial direction. This effect is called shadowing. A similar effect occurs when an atom lies in the trajectory to the detector of another particle and stops it (see figure 2.5). This is called blocking.

When the edge of a shadowcone is focused on another atom, an enhancement of the signal occurs, because the density on the edge of the shadowcone is maximal. This is known as focusing. These effects can be used to investigate surface...
2.3. Surface structure analysis

When an ion hits the surface at the right impact parameter, it is possible to get not only single but also multiple scattering. Especially when a small angle of incidence is used, this effect becomes important. When a double collision is treated as a combination of two single collisions, the total energy after the collision can be calculated by applying equation (2.1) two times. The total energy loss for a multiple collision is lower than with a single collision. To calculate the energy loss, due to multiple scattering from atoms which are aligned in a row, computer simulations have been done on scattering from a 1 dimensional atom chain model [FEIJEN]. In figure 2.6 the relation between the energies of the scattered ions as a function of the scattering angle is plotted for different angles of incidence.

![Figure 2.6](image)

Figure 2.6 : The energy of scattered ions from a 1 dimensional row of atoms as a function of $\Theta$, for different angles of incidence ($\psi$). The dashed line is the ideal single collision, calculated with equation 2.1. [NIEHUS]

For a particular value of $\Theta$, two solutions are possible, resulting in two peaks in the spectrum. These two peaks are often called quasi single and quasi double collisions (the index $qs$ and $qd$ are used e.g. Cu$_{qs}$).

With the TOF, shadowcone calculations are used for the interpretation of the
measurements. For structural analysis, the TOF can be used in different modes:

A) Looking at scattered particles, while varying angle of incidence, $\alpha$:
When the angle of incidence is varied, an enhancement of scattered-ion signal is measured when the edge of the shadowcone falls on the next atom. With this critical angle $\alpha_c$ and the dimensions of the shadowcone, the distance between the two atoms can be calculated, see figure 2.7.

![Diagram](image)

**Figure 2.7**: Example of the dependence of the TOF signal as a function of angle of incidence. [RABALAI][S]

B) Looking at scattered particles as a function of the azimuthal angle $\delta$:
When specular reflection (angle of incidence = exit angle) is used, at certain azimuthal angles $\delta$, a maximum appears when atoms are close together, because the atoms lay in each others shadowcones. In the non-specular mode, a minimum occurs. Using this maxima or minima, it is possible to determine the packing densities in these crystallographic directions, see figure 2.8.

C) Looking at the recoil signal as a function of the angle of incidence $\alpha$:
This works the same as mode A, but now the recoil signal is measured. In this mode, it is possible to determine the position of an adsorbate atom on the surface in a specific direction.
**Figure 2.8**: Azimuthal variation of the scattered-ion signal from a Ni(110) sample. [RABALAIS]

D) Looking at the recoil signal as a function of the azimuthal angle $\delta$:

Here it is possible to determine packing densities of the adsorbate atoms.
3. Experimental set-up

3.1. Introduction

The EARISS/TOF apparatus is built for the analysis of surface structures. It contains several surface sensitive techniques. The different parts of the EARISS/TOF apparatus are shown in figures 3.1 and 3.2.

![Diagram of EARISS/TOF apparatus](image)

**Figure 3.1**: Front view of the EARISS/TOF apparatus.

The sample is in the center of the vacuum chamber. The position of the sample can be changed with a computer controlled Panmure Instruments LTD manipulator, which has six degrees of freedom.

The analyzer and ion source of the Energy and Angle Resolved Ion Scattering Spectrometer (EARISS) are placed above the sample. The EARISS is described further on.
The ion source of the Time Of Flight ion scattering and recoiling spectrometer (TOF) is mounted at a grazing angle of 20 degrees. The TOF measurements are done with a pulsed beam of low energy rare gas ions. Information about the surface is obtained by measuring the flight time of the particles coming from the surface.

With the in-line channeltron detector, direct measurements of the shape of the ion pulse can be done and a flight tube with a channelplate detector is used for the actual time of flight measurements. The angle between ion source and detector for the TOF is 35 degrees.

The Low Energy Electron Diffraction (LEED) apparatus (VG RVL900) is available for checking the surface structure and crystal orientation. With Auger Electron Spectroscopy (AES) the element concentrations, especially of contaminants can be determined. The AES part is not yet implemented.

There is a sputter gun for sample cleaning and a filament is placed under the sample holder for heating the sample by radiation. A storage room for samples is available in the system which can keep up to 7 samples. A transfer system can be used for transporting samples from the storage chamber to the manipulator.
The whole system is under UHV. Every part is connected with a turbo pump and has its own ion getter and Ti-sublimation pump. The background pressures in the central chamber and the LEED/AUGER part are approximately $5 \times 10^{-10}$ mbar.

3.2. EARISS

The Energy and Angle Resolved Ion Scattering Spectrometer (EARISS) consists of a rare gas ion source which is directed perpendicular to the sample surface. The analyzer detects only ions which are scattered over an angle of $145 \pm 1.7$ degrees. A picture of the EARISS analyzer is shown in figure 3.3. Low energy ions from the surface are more deflected by the analyzer plates than ions with a higher energy. The azimuthal distribution of the ions is not changed. This results in a two dimensional image, containing both the energy as well as the azimuthal information. The azimuthal range of the detector is 320 degrees, for technical reasons. With the zoom lens (accelerator / decelerator) an energy range can be selected. The width of the energy range is 12% of the pass energy. The radial and azimuthal information is stored into a two dimensional multi channel analyzer (MCA). The data can be analyzed on a HP workstation.
The time of flight ion scattering and recoiling spectrometer (TOF) consists of an ion source with focusing and deflection elements, which is adapted to produce a pulsed beam of rare gas ions. The time between the moment that the pulse is generated and when a particle is detected is measured. This flight time is simply related to the energy of the particle. By using equations (2.3) and (2.4), the mass of the recoil particle or the mass of the surface atom from which an ion is
scattered can be calculated. For good resolution, the width of the ion pulse has to be small enough. Most TOF apparatuses nowadays use a pulse width between 50 and 100 ns. The creation of the pulsed beam is described in chapters 4 and 5. In both cases, a source, which produces a continuous ion beam, is adapted to produce the ion pulses. Figure 3.4 shows a schematic view of the TOF ion source.

Figure 3.4: Schematic view of the TOF ion source.

The ions are created in the ionization part at the left, which has a cylindrical symmetry. A high current flows through the filaments and creates electrons. Since the filaments are put at a lower voltage than the grid, the electrons are accelerated towards the grid. The grid has a transparency of approximately 90%, so most electrons fly through it. The rare gas which is inside the grid will be ionized, because the electrons have an energy which is higher than the ionization potential of the gas atoms. The electron density has a maximum at the center of the grid. This creates a potential well, which holds the ions. To create an optimal ionization, the field inside the ionization part must be cylindrical. This means that the potential of the shell has to be lower than the filament voltage. The voltage on the extraction plate, which is combined with the first focus lens, pulls the ions out of the ionization chamber. The whole part which is described above is at a high voltage, \( V_{prin} \), compared with the elements to the right of the first focus lens. So after the ions are extracted, they are immediately accelerated. The created ion beam, is focused and directed onto the sample with four lenses and deflection plates. There is also a Wien type mass filter, which is a combination of a magnetic and an electric field. Two apertures are placed in
the beam, for the ion chopper described in chapter 5. The ion current can be measured at two different places with two grids\textsuperscript{14}.

To detect the particles, two types of detectors are used. Firstly, a channeltron is placed directly in the beam line. A channeltron consists of a copper cup with a curled tube. The inside of the tube is coated with a material with a high electron emission coefficient. When a particle hits the cup of the channeltron, it creates some electrons. Because there is a voltage applied over the channeltron, these electrons are accelerated to the inside and every time they collide with the wall, they create more and more electrons. This effect forms a little charge pulse, which can be measured, see figure 3.5.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{channeltron_diagram.png}
\caption{Schematic view of a channeltron.}
\end{figure}

The other detector is mounted at the end of the flight tube. It consists of two channelplates with a collector plate at the end. A channelplate is a glass plate with a lot of small channels through it. The inside of the channels is coated with a material with a high electron emission coefficient. Once a particle hits the first channelplate, electrons are created and accelerated to the second channelplate, because there is a voltage applied. Meanwhile they create more and more electrons and form an electron cloud, which eventually hits the collector plate. With a pre-
amplifier, these pulses are immediately amplified to minimize the effect of noise during transport.

The scheme of the detection electronics is shown in figure 3.6.

![Figure 3.6: Scheme of the detection electronics for the TOF.](image)

The pulse generator rules the whole detection. It starts the ion pulse and triggers the time to amplitude converter (TAC) via a delay. The pre-amplifier signal is amplified again, before it reaches the single channel analyzer, which gives a well defined stop signal for the TAC. The TAC gives an output voltage which is proportional to the time between the start and stop pulse. Therefore the output voltage is linear with the flight time of the particle.

An AD converter translates this voltage to a digital word, which is stored into a
multi channel analyzer (MCA) with 4096 channels. The MCA programme S100 (Canberra) runs on an Olivetti PC and is used to measure the data.
4. First pulsing method: Pulsing the ionization process.

4.1. Introduction

Pulsing an ion beam is usually done with deflection plates and an aperture. (see chapter 5). Some [SUL1] however tried a different method and succeeded to make a low-energy time of flight ion scattering and recoiling spectrometer with reasonable resolution. What we want to achieve is an ion pulse length of about 50 ns, at a frequency of 5 to 20 kHz for 1 to 7 keV He, Ne, or Ar ions. The group mentioned in reference [SUL1] claimed that they developed a pulsed ion source which produced ion pulses with a width of a few nanoseconds [SUL2]. The creation of ion pulses is done, in this case, by switching on and off the ionization process. This is further described in the set-up section.

4.2. Experimental set-up

The set-up of the TOF ion source is already explained in chapter 3. To pulse this ion source a pulse of 130 Volts is applied between the filaments and the grid. When the voltage is low, the electrons going from the filaments to the grid don't have enough energy to ionize the gas atoms inside the grid. When the voltage is high enough to ionize the gas inside the grid, ions are created which follow the same way to the target as in the continuous situation, as described in chapter 3. The electric scheme of the pulsed source is shown in figure 4.1. The electrical pulse is made with a pulse generator (AVTECH AVL-AV-1-C-P-FOICA) with the following specifications: 0 to 130 Volt pulse height, 2 to 50 ns width and a frequency of 0 to 20 kHz. The rise time is smaller than 1 ns and the fall time is smaller than 2 ns. The shape of the ion pulses can be measured with the in-line channeltron detector. This pulsing method has several advantages in comparison with the deflection method, which is described in chapter 5. Firstly, no extra apertures are needed, which results in a higher output current of the source. The method doesn't need extra space for deflection, so the ion source can be made shorter. Another advantage is that this method makes a pulse of which the width
is independent of the mass and energy of the ion and therefore can be easily operated. The optimization of the source was done in the continuous situation, because in the pulsed mode the average ion current is some orders of magnitude lower. At 10 kHz and a 100 ns ion pulse, the ion current is 1000 times lower. This means that the current on the second grid drops from 3 nA to 3 pA, which is below the detection limit of the Ampère meter used here.

4.3. Measurements / Results

Using the set-up described above, no pulse could be created for fundamental reasons explained further on. To investigate the rise and fall time of the ion pulse, a pulse generator was used which could make 100 V pulses of 100 ns up to 1 ms width (HP214A). When a pulse width of 180 μs and a frequency of 250 Hz was applied to the grid, an ion pulse could be measured in the channeltron detector. This ion pulse is shown in figure 4.2.
Figure 4.2: Pulse measured in the channeltron.

The rise time is 50 μs and the fall time is 15 μs. These large rise and fall times can be explained by looking closer at the ionization process. The acceleration of the electrons, the creation of the potential well and the ionization of the rare gas atoms, takes only a few nanoseconds. To pull the ions out, an extraction plate is placed in front of the ionization chamber at a lower potential than the grid. The extraction voltage creates an electric field inside the grid. To simplify the calculations, a constant electric field is assumed inside the grid. In figure 4.3, the assumed potential inside the grid is plotted.

The electric field inside the grid is constant and has the value:

\[ E = \frac{V_{\text{extr}}}{l_{\text{grid}}} \tag{4.1} \]

where \( V_{\text{extr}} \) is the voltage on the extraction plate (\( V_{\text{grid}} = 0 \) V) and \( l_{\text{grid}} \) is the distance from the grid to the extraction plate in the beam direction (z-axis).
Figure 4.3: Model for the potential inside the grid.

This means that when the ion has mass $m_{\text{ion}}$, the acceleration in the $z$ direction is:

$$a = \frac{e}{m_{\text{ion}}} \cdot \frac{V_{\text{extr}}}{l_{\text{grid}}} \quad (4.2)$$

The time for the ion to travel from one side of the grid to the extraction plate, over the distance $l_{\text{grid}}$ is given by:

$$t_{\text{extr}} = \sqrt{\frac{2 \cdot l_{\text{grid}}}{a}} = \sqrt{\frac{2 \cdot m_{\text{ion}} \cdot l_{\text{grid}}^2}{e \cdot V_{\text{extr}}}} \quad (4.3)$$

For $l_{\text{grid}} = 5.44$ cm, $V_{\text{extr}} = 300$ V and neon ions, $t_{\text{extr}} = 2.02$ μs.

This extraction time determines the rise time of the ion pulse.

The rise time obtained with this simple calculation is far too long. To make a shorter rise time, a smaller grid has to be used or the extraction voltage should be increased. The first possibility requires a totally different source and increasing the extraction voltage introduces an extra energy spread in the ion beam.

When the real situation is considered, the field inside the grid is not constant and
much lower. The grid acts like a Faraday cage and therefore the field penetration is not optimal. This means that initially, there is even a lower force acting on the ions. So in the real situation, the ions start much slower than calculated before, which results in a larger rise time. So \( t_{\text{rise}} > 2.02 \ \mu s \). The measured rise time of the ion pulse confirms these calculations. The fact that the fall time is shorter than the rise time, can be explained by the creation of the potential well inside the grid. When the pulse ends and the voltage drops to zero, the potential well disappears in a few nanoseconds, because the electrons are not pulled in the grid any more. The ions which were held together inside the potential well, now spread out over the ion source. This results in a fast decrease of the ion current. This means a smaller fall time compared to the rise time, of the ion pulse. The source which is used by the group from reference [SUL1], is much smaller. The grid length is only 5 mm, this means that the rise time drops with a factor of 10, so \( t_{\text{rise}} > 180 \ \text{ns} \). This appeared in practice to be the smallest pulse, which could be made.

With the ion source of the TOF, the pulse width of the ion pulses created by this method is too large for our experiments.
5. Second pulsing method: chopping the ion beam

5.1. Experimental set-up

A commonly used pulsing method is electrical chopping. In figure 5.1 the chopper for the Time of Flight ion scattering and recoiling spectrometer is shown. The so-called "impulse sweeping method" [FOWLER] is used.

\[
\begin{align*}
11 & = 20 \text{ mm} \\
12 & = 465.5 \text{ mm} \\
d & = 10 \text{ mm} \\
S_b & = 2 \text{ mm} \\
S & = 2 \text{ mm or 1 mm}
\end{align*}
\]

Figure 5.1: TOF chopper. [HEIER]

Two deflection plates, A and B (number 8 in figure 3.4) and two slits, D_1 and D_2 (numbers 18 and 19 in figure 3.4) are placed in the beam. The first slit is used for limiting the diameter of the ion beam. When no voltage is applied to the deflection plates, the ions fly through the first and second slit. When the voltages \(V_A\) (\(>0\)) and \(V_B\) (\(<0\)) are applied to the deflection plates, the ions are deflected and blocked by the second slit.

When the voltage on the deflection plates is pulsed, a chopped beam is created. The ideal electrical pulse shape is shown in figure 5.2.

During time \(\tau\), there is no electrical field between the deflection plates. The ions which were between the plates when the voltage dropped or rose, have only felt a field during part of their flight time between the plates and are less bent to the
negative side. This means that the ion pulse which is created, can be divided into three parts, see figure 5.3.

In region II, none of the ions have felt any field during their stay between the plates. The width of region II is thus related to the electrical pulse width $\tau$ and the ion energy $E_i$ and mass $m_i$, by the following expression:
The ions in regions I and III have only partly felt a field. Therefore, some of them are able to go through the second slit. The widths of these regions are given by [HEIER]:

\[ t_{\text{II}} = \tau - l_1 \cdot \sqrt{\frac{m_i}{2E_i}} \]  
(5.1)

This expression is only valid for an ideal plate capacitor. The total width of the ion pulse, \( t_{\text{pulse}} = t_1 + t_{\text{II}} + t_{\text{III}} \), is given in table 5.1 for different ions and different energies.

<table>
<thead>
<tr>
<th>Ion</th>
<th>( \tau ) (ns)</th>
<th>( E_i ) (keV)</th>
<th>( t_{\text{II}} ) (ns)</th>
<th>( t_{\text{pulse}} ) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>100</td>
<td>3</td>
<td>47</td>
<td>55</td>
</tr>
<tr>
<td>Ne</td>
<td>200</td>
<td>1</td>
<td>96</td>
<td>106</td>
</tr>
<tr>
<td>Ne</td>
<td>200</td>
<td>2</td>
<td>56</td>
<td>71</td>
</tr>
<tr>
<td>Ne</td>
<td>200</td>
<td>3</td>
<td>82</td>
<td>100</td>
</tr>
<tr>
<td>Ar</td>
<td>300</td>
<td>1.5</td>
<td>65</td>
<td>83</td>
</tr>
</tbody>
</table>

Table 5.1: Calculated pulse widths for different energies and ions. With \( V_{AB} = 120 \) V.

The widths of regions I and III depend on the applied voltage \( V_{AB} \). \( V_{AB} \) has to be so large, that the widths of regions I and III are small compared to the width of region II.

A disadvantage of a high \( V_{AB} \) is that the energy spread of the ion pulse in parts
I and III is larger. Particles in parts I and III, can have a different energy than the particles in part II, because the particles only partly felt a field. When no divergence is assumed, the energy spread can be estimated with [LEENEN]:

\[ \Delta E = \frac{1}{2} e \cdot V_{AB} \cdot S_b \]

With

\[ \Delta t = \frac{1}{2} (\frac{\Delta E}{E}) \cdot t \]

the energy spread can be translated into a time spread.

Equation (5.3) is again only valid for an ideal plate capacitor.

The electrical pulse is created with a self-build pulse generator, shown in figure 5.4 [HEIER].

The heart of it is an avalanche transistor, which can hold a high voltage (here 150 Volts), between collector and emitter. When the base is triggered, the transistor collapses and becomes conducting. At that time, a reflection at the collector occurs. The height of this reflection is determined by the value of \( R_d \) and determines the voltage step at the emitter. The reflection travels through the triax cable to the resistors \( R_c \). These have a high resistance and act like an open end. The reflection travels back as a negative step. This creates the end of the pulse. After this, the transistor closes and loads to the starting situation. The resistor \( R_d \) determines the pulse height. The length of the triax cables determines the pulse width. Two pairs of triax cables are available. A 10 meter and a 20 meter set, which can make pulses of 100 ns and 200 ns. For a pulse of 300 ns, triax cable connectors were build, to connect the 100 ns and the 200 ns cables. Other lengths can also be made. Voltages \( V_{p1} \), \( V_{p2} \), \( V_{n1} \) and \( V_{n2} \) are adjusted so, that the pulse drops or rises to 0 volts. If \( R_d \) equals the characteristic impedance of the triax cable, no extra reflections occur. When \( R_d \) is higher than this characteristic impedance, a larger
reflection occurs, but also multiple reflections are created.

5.2. Measurements / Results

Three values for $R_d$ have been tried, which result in the pulses shown in figure 5.5. The pulses are measured with two high impedance probes (10 MΩ, 14 pF) with 10 times attenuation and an oscilloscope, directly on the feedthroughs to the deflection plates. The voltage difference at $t = 0$ determines the rise time and the voltage difference at $t = 200$ ns determines the fall time of the ion pulse. $R_d = 82$ Ω makes the largest step at $t = 200$ ns. Therefore this resistance is chosen for the pulse generator. To test the chopper, 2 keV neon ions were used. The time of flight of these ions through the deflection plates is 144 ns. When the triax cables of 200 ns are used, the ion pulse width should be between 56 ns and 71 ns, see table 5.1.
Figure 5.5: Pulses on the chopper plates for three values for $R_d$. The solid line is $R_d = 50$ Ω, the long-dashed line is $R_d = 82$ Ω and the small-dashed line is $R_d = 220$ Ω.

The pulse was measured with the channeltron. The results are shown in figure 5.6.

The full width at half maximum of the ion pulse is 54 ns, with a rise and fall time of 40 ns and 30 ns. For our TOF measurements, this pulse is small enough. For the measurements on the copper-palladium single crystal (chapter 6), 1.5 keV Ar ions are chosen to be able to separate the copper and palladium single scattering peak. For these ions, the flight time between the plates is 235 ns, so an electrical pulse width of 300 ns was used. According to table 5.1, the ion pulse width for 1.5 keV argon ions, should be between 65 ns and 83 ns. A picture of the measured pulse is shown in figure 5.7.

The full width at half maximum of the measured ion pulse is 140 ns.
The broadening of the 1.5 keV Ar ion pulse, can be explained by the energy spread caused by the chopper. With this high ion mass and low energy, the velocity of the ions is low. This causes a larger time spread in the ion pulse. When equation (5.3) is applied to this situation, the energy spread for a voltage $V_{AB} = 120$ V, is $12$ eV, which is $0.8\%$ of the initial energy. This means a time spread of $0.4\%$ according to equation (5.4). The time of flight from the chopper to the channeltron is $11.5$ us, so the absolute time spread is $46$ ns, which is comparable to the initial pulse width. The ion source itself has an energy spread of $0.5\%$, which enhances the broadening even more. Due to the divergence of the ion beam, observed by [HEIER], equation 5.4 is no longer a good approximation and a larger energy spread is created, causing a broader pulse.

For the measurements on the copper palladium crystal (chapter 6), the width of
the ion pulse is small enough, because the widths of the peaks in the spectrum are determined by the interaction with the surface.

Figure 5.7: Pulse of 1.5 keV Ar ions, measured in the channeltron.
6.1. Introduction

In catalysis, platinum, palladium, copper, nickel and silver are frequently used materials. Binary alloys, such as Cu$_x$Pd$_{1-x}$, are of recent interest. These alloys can have a totally different catalytic reactivity than their component elements. The main use of the CuPd alloy is the oxidation of CO and the dehydrogenation and cracking of hydrocarbons. The reaction processes are given below.

1) oxidation of CO:

$$\text{CO}_{(g)} + \frac{1}{2}\text{O}_{2(g)} \rightarrow \text{CO}_{(ad)} + \text{O}_{(ad)} \rightarrow \text{CO}_{2(g)}$$ \hfill (6.1)

2) dehydrogenation and decomposition of HCOOH:

A) adsorption of acid on the surface:

$$\text{HCOOH} \rightarrow \text{HCOO}_{(ad)} + \text{H}_{(ad)}$$ \hfill (6.2)

$$2\cdot\text{H}_{(ad)} \rightarrow \text{H}_{2(g)}$$ \hfill (6.3)

B) decomposition of adsorbate:

$$\text{HCOO}_{(ad)} \rightarrow \text{CO}_{2(g)} + \text{H}_{(ad)}$$ \hfill (6.4)

$$2\cdot\text{H}_{(ad)} \rightarrow \text{H}_{2(g)}$$ \hfill (6.5)

and much slower:

$$\text{HCOO}_{(ad)} + \text{H}_{(ad)} \rightarrow \text{HCOOH}$$ \hfill (6.6)
The reaction rates and the temperature dependence of the decomposition of HCOOH are known for a pure Cu (110) surface. A small amount of palladium in the copper can change these reaction parameters. Therefore, a Cu\textsubscript{85}Pd\textsubscript{15} (110) sample was analyzed with various techniques.

With Temperature Programmed Desorption (TPD), the decomposition of HCOOH on the Cu\textsubscript{85}Pd\textsubscript{15} sample was analyzed, by measuring the amount of CO\textsubscript{2} coming from the surface as a function of the temperature. The results are compared with the reaction on the Cu (110) sample. The desorption of HCOOH on Cu\textsubscript{85}Pd\textsubscript{15} appears at a lower temperature, 475 K instead of 490 K with the Cu sample. Also the activation energy of the decomposition is significantly lower with the Cu\textsubscript{85}Pd\textsubscript{15} sample, resulting in a higher decomposition rate than with the Cu (110) sample.

[NEWTON]

To understand the reactions at the surface, determination of the structure and composition of the first atomic layers of the Cu\textsubscript{85}Pd\textsubscript{15} sample is needed. Therefore, several surface sensitive techniques are combined to analyze the surface. Cu\textsubscript{85}Pd\textsubscript{15} has an fcc structure. A picture of the fcc (110) surface is shown in figure 6.1.

![Figure 6.1: The fcc (110) surface.](image)

With Low Energy Electron Diffraction (LEED) the transition from a (1x1) LEED
pattern after cold sputtering with Ar ions, to a p(2x1) pattern after annealing above 600 K was analyzed. [HOLMES] The (2x1) pattern is an indication for an ordering of the surface. The unit cell of this super structure is a factor of 2 larger in the [110] direction. The results of these measurements are shown in figure 6.2.

![Figure 6.2: Change in intensities of the LEED (2x1) spot (D), the background (A) and the spot intensity after background substraction (o) as a function of the anneal temperature. Measurements were done at room temperature. [B3]](image.png)

With LEED experiments, the lattice constant was measured: \( a = 3.86 \text{ Å} \). [BARNES] The interlayer spacings between the first and the second, \( d_{12} \), and between the second and the third layer, \( d_{23} \), were determined to be \( 1.24 \pm 0.04 \text{ Å} \) and \( 1.29 \pm 0.04 \text{ Å} \) respectively. With the Average T-matrix Approximation (ATA) several models for the layer compositions have been tested to explain the LEED results. First, the origin of the p(2x1) structure, arising after annealing above 600 K, was explained to originate from an ordered 50% Cu and 50% Pd structure in the second layer. The possibilities of a 50% Pd (2x1) top layer or an ordered (2x1) deeper layer were ruled out by the LEED measurements. The palladium concentrations of the first and third layer were found to be \( 30 \pm 15 \text{%} \).
at.% and 0 + 15 at.%, respectively. [BARNES] The value of 30 at.% Pd in the first layer was rejected by several other techniques. [NEWTON, HOLMES] In the (2x1) situation, Angle Resolved X-ray Photoelectron Spectroscopy (ARXPS) measurements showed a copper enriched first layer and a palladium enriched second layer. Temperature Programmed Desorption (TPD) measured a similar HCOOH decomposition activity for the Cu$_{86}$Pd$_{15}$ sample as for the pure Cu crystal. [NEWTON] A quite different behaviour was seen with a pure palladium sample. [AAS] The adsorption of CO on Cu$_{86}$Pd$_{15}$ (110)-p(2x1) was compared with the adsorption on pure Cu and Pd crystals. At 300 K, CO adsorption on Pd (110) has a sticking coefficient close to unity for an appreciable coverage range. There is no CO adsorption on Cu at 300 K. With TDS, no CO desorption was found on the Cu$_{86}$Pd$_{15}$ (110)-p(2x1) surface at 300 K [HOLMES]. Low Energy Ion Scattering (LEIS) measurements were done by measuring the energy of the scattered ions from the sample, when a beam of 1 keV He ions was directed towards the surface in the [001] direction [NEWTON]. The scattering angle was fixed at 90 degrees. The ratio of the palladium to the copper signal was measured as a function of the angle of incidence, see figure 6.3. A maximum in the Pd/Cu ratio was observed at an angle of incidence of 45 degrees. A sharp drop in the Pd signal compared to the Cu signal is observed for grazing angles.

All these results, except the LEED [HOLMES], favour the highly copper enriched first layer model. The proposed Cu$_{86}$Pd$_{15}$ (110) - p(2x1) surface is shown in figure 6.4. No indication of a reconstruction was found for this surface.

### 6.2. Measurements

Low Energy Ion Scattering (LEIS) measurements were done with the Energy and Angle Resolved Ion Scattering Spectrometer (EARISS) and the Time Of Flight ion scattering and recoiling spectrometer (TOF), to make a quantitative analysis of the concentrations of Cu and Pd in the first and second layer of the Cu$_{86}$Pd$_{15}$ crystal. Cleaning was done with 2 keV Ar ion bombardment at approximately 650 K followed by annealing at the same temperature for 30-45 minutes. Unless
otherwise indicated, all measurements were done at room temperature (300 K).
After annealing, a sharp p(2x1) pattern was observed and only very small amounts
of contaminations with C or O were seen with the TOF, see figure 6.8. The crystal
orientation was determined with LEED within 5 degrees accuracy.

6.2.1. EARISS measurements

The Energy and Angle Resolved Ion Scattering Spectrometer (EARISS) has
already been described in chapter 3. The sensitivity of the two-dimensional
detection system is not homogeneous. Therefore, it is essential to correct the measured azimuthal distribution for the apparatus profile. This is done as follows. Spectra are taken at different azimuthal positions of the sample. This is done with azimuthal steps of equal length. Afterward, these spectra are shifted corresponding to their rotation and summed [BERGMANS]. In this way, the apparatus profile is averaged. This correction method was checked on a polycrystalline Cu sample, where a uniform azimuthal distribution was found when a rotation with steps of 24 degrees was used. In this way, the full 360° distribution is obtained. Integration over the energy range of a certain peak gives the average azimuthal distribution of the ion signal from the corresponding element in the surface. The correction method is used to obtain the azimuthal distribution of both the Cu and the Pd signal from the Cu₈₅Pd₁₅ (110) crystal. The results are shown in figure 6.5 and 6.6. The measurements are done at different temperatures. The azimuthal angle, used with the EARISS measurements, has an offset with respect to the TOF angle.
The disturbing in the EARISS spectra below 180 degrees is caused by the thermocouple, mounted on the manipulator. Therefore, only the right part of the figure is used for the calculations.

The open fcc (110) structure of the CuPd surface gives a contribution of scattered ions from both the first and the second layer. Depending on the positions of the atoms in the first layer, the ions scattered from the second layer can be blocked in certain crystal directions. This causes azimuthal variations in the ion signal, which are measured with the EARISS. The ions which are scattered from the first layer, cannot be blocked in any direction. Therefore, these ions give rise to an azimuthal independent signal. The contributions from the first and second layer can be seen in the Cu and Pd signals in figure 6.5 and 6.6.

For the Cu$_{85}$Pd$_{15}$ (110) sample, 2 keV Ne ions were used, for which total blocking of the ion signal occurs in 4 azimuthal directions. The maxima in the signal are
caused by the open [110] and [001] directions of the fcc (110) surface, see figure 6.1. In these directions, no blocking of the ions occurs. The maxima in the azimuthal distribution of the ion signal are repeated every 90°, because the fcc (110) structure has a rectangular unit cell. The minima however, will be separated by 71° and 109°, due to the place of the atoms in the first layer, see figure 6.7.

The height of the minimum in the azimuthal distribution, named $h_\parallel$ in figure 6.7, of Pd or Cu, can be considered as a measure for the amount of Cu or Pd in the first layer. The difference between the maximum and the minimum, named $h_\perp$ in figure 6.7, of Cu or Pd, can be considered as a measure for the amount of Cu or Pd in the second layer.

Before quantitative results can be extracted from these measurements, corrections have to be made for the relative sensitivities of Cu and Pd. Therefore, the signals from a poly-crystalline copper and palladium sample have been measured under the same circumstances as with the Cu$_{96}$Pd$_{16}$ (110) sample. The integrated number

---

Figure 6.6: Azimuthal distribution of Pd, measured with the EARISS.
of counts of the Cu and the Pd peak have been corrected for the surface density of both materials and for the difference in initial ion dose. From this, it is estimated that the EARISS is 1.5 times more sensitive for Pd than for Cu at the surface.

The measurements shown in figures 6.5 and 6.6 consist of spectra taken at different temperatures. The first one is measured at a temperature of approximately 700 K, the second one at approximately 650 K (only for palladium) and the last one at room temperature (=300 K). It can be seen that the Pd signal changes for different temperatures. The fact that the ratio of the palladium signal from the first and from the second layer doesn't change, and that the copper signal stays almost the same, rules out the possibility of a compositional change of the first or second layer. The measurements of the 650 K measurement is done much faster after cleaning of the sample than the 300 K and 700 K measurement. Because the copper signal changes much less with temperature and the fact that the signal from the 650 K measurement is higher than the 300 K and 700 K
signal, the difference in signal height may be due to selective contamination of the palladium atoms. To minimize this effect as much as possible, the 650 K measurement of palladium is used for the determination of the concentrations of Cu and Pd in the first and second layer. The 700 K measurement of copper is used for the calculations, because no 650 K temperature measurement of copper is done and the Cu signal stays almost the same. The height of the different peaks in figures 6.5 and 6.6 are measured and corrected with the factor 1.5 for the relative sensitivity of Cu and Pd. The assumption is made, that the relative neutralization probability for the second layer of copper and palladium is the same as for the first layer. The calculated concentrations of Pd in the first and second layer for the different temperatures, are shown in table 6.1.

Table 6.1 : Calculated Pd concentrations for different temperatures.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pd conc. 1st layer</th>
<th>Pd conc. 2nd layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 K</td>
<td>&lt; 11 at.%</td>
<td>35 at.%</td>
</tr>
<tr>
<td>300 K</td>
<td>&lt; 8 at.%</td>
<td>30 at.%</td>
</tr>
<tr>
<td>650 K Pd with 700 K Cu data</td>
<td>&lt; 14 at.%</td>
<td>41 at.%</td>
</tr>
</tbody>
</table>

Because the time after cleaning with the 650 K measurement is the shortest, the result of the 650 K Pd, together with the 700 K Cu measurement is the best estimation of the concentrations of Pd of the clean surface.

6.2.2. EARISS discussion

As a result of the selective Pd contamination, the Pd signal drops, causing a lower calculated Pd concentration in first and second layer.

The azimuthal resolution is approximately 15 degrees. This causes a broadening of peaks in the azimuthal spectra, resulting in a signal from the second layer,
which is not zero in the blocking directions. This creates errors in the determination of the contributions of Cu and Pd, resulting in changes in the calculation. If the broadening of the peaks is the same for Cu as for Pd, which is a reasonable assumption, a lower minimum has only effect on the calculation of the concentration in the first layer and not of the second layer. Due to this broadening, the Pd concentration in the first layer is calculated too high. Therefore, the 14 at.% is an upper limit.

In general, an enrichment of Pd in the second layer is observed. The concentration is almost 50 at.%, but due to the contamination of palladium, the Pd signal drops, resulting in a lower calculated concentration. In the first layer, a depletion of Pd is observed. The concentration is found to be less than 14 at.%.

The disappearance of the LEED (2x1) pattern above 700 K, observed by [FRANCIS], is not followed by a measurable change in the concentrations in the first and second layer. Therefore, the disappearance of the (2x1) structure is probably due to a disordered second layer above 700 K, but no mobility in the direction perpendicular to the layers.

6.2.3. TOF measurements

The set-up of the Time Of Flight ion scattering and recoiling spectrometer (TOF) was already described in chapter 3. In order to separate the Cu and Pd scattering peak in the spectrum, a heavy ion and a low mass have to be used. The separation is a problem, because of the worse mass resolution for small scattering angles. When 1.5 keV Ar ions are used to analyze the Cu$_{24}$Pd$_{16}$ (110) sample, the separation between the Cu and Pd single scattering peak should theoretically be 627 ns. No lower energies can be used, because already with 1.5 keV Ar ions the pulse becomes broader, due to the energy spread in the pulse, see chapter 5. Another drawback of a low energy is the dimension of the shadowcone. At this energy, the width of the shadowcone becomes comparable to the lattice constant. Specular reflection is used to minimize the negative effects of the large
shadowcones at this energy. This means that the angle of incidence and the exit angle are both 17.5°. When a smaller angle of incidence is used, atoms are in almost every crystal direction in the shadowcones of their neighbour atoms, which is not useful when analyzing the surface. A measured TOF spectrum of the Cu₈₅Pd₁₅ (110) sample in the [114] direction is shown in figure 6.8.

![TOF Spectrum](image)

**Figure 6.8** : Example of a TOF spectrum of Cu₈₅Pd₁₅ (110).

Around \( t = 3.5 \) us, small amounts of C or O recoil signal (\( C_r \) or \( O_r \)) can be seen. Because the width of the shadowcone at 1.5 keV is comparable to the lattice constant, it is unlikely that a pure single collision will occur. Due to multiple collision on Cu, two peaks can be observed (see chapter 2). These peaks are named quasi single and quasi double, or \( \text{Cu}_{qs} \) and \( \text{Cu}_{qd} \). These peaks are in the spectrum at \( t = 7.9 \) us and \( t = 7.3 \) us, respectively. The \( \text{Pd}_{qs} \) scattering peak, should be at the same place as the \( \text{Cu}_{qd} \) peak and the \( \text{Pd}_{qd} \) peak should be 413 ns to the left of the \( \text{Pd}_{qs} \) peak. At \( t = 12 \) us, a peak is seen, which is caused by recoiled copper atoms (\( \text{Cu}_r \)). \( \text{Pd}_r \) is not visible in any azimuthal direction. The azimuthal dependence of
the TOF signal is analyzed. Every 2 degrees, a TOF spectrum was taken. This is done in the azimuthal range of 124° to 360°. In the region from 245° to 290°, the particles from the sample are "blocked" by the thermocouple, which is mounted on the manipulator. When the height of the Cu_{\text{q}}/Pd_{\text{q}}-peak at \( t = 7.3 \) us is plotted as a function of the azimuthal angle, figure 6.9 is created.

![Figure 6.9: Azimuthal plot of the combination of the Pd_{\text{q}} and the Cu_{\text{q}} peaks in the TOF spectrum.](image)

With LEED the maximum at 178° (and 358°) could be assigned to the [001] direction of the surface. When the azimuthal dependence of the Cu_{\text{r}} peak is plotted, see figure 6.10, a lot of peaks occur. These peaks can be assigned to different crystal directions of the surface.

### 6.2.4. TOF discussion

Because the shadowcones are broad at this energy, a lot of multiple collisions occur. The shorter the distance between the atoms is, the more multiple collision
will occur. Therefore, azimuthal distribution of the Cu$_q$-peak shows a maximum when the atoms in the surface are aligned. Because the top layer is enriched with copper, the main contribution comes from the Cu$_q$ peak. This means that the highest signal belong to the [110] and [001] directions. In these direction the specular reflection is optimal. The calibration of the azimuthal angle is done in this way with 1 degree accuracy. The peak of the [110] direction should be at 268°, but it is not visible, due to the blocking of the thermocouple.

When the azimuthal distribution of the Cu$_q$-peak is analyzed (figure 6.10), the peaks can be assigned to the different crystal directions for the unreconstructed (110) surface. The recoil signal is created by ions which are focused at the right impact parameter for the copper atoms to be kicked out of the surface under the right angle, see figure 6.11.

For this effect, there is an optimal distance between the atoms. When the atoms are too close to each other, the edge of the shadowcone cannot come underneath
the atom to "kick it out". When the atoms are too far separated, the distance between the edge of the shadowcone and the atom is too large to have an interaction. The maximal recoil signal appears in the [114] direction. The distance between two atoms in the [114] direction is 8.2 Å. When a simulation is done with 1.5 keV Ar on Cu atoms in the [114] direction, figure 6.12 is created. It can be seen that the edge of the shadowcone falls under the Cu atom of the first layer.

![Figure 6.11: The recoil effect.](image)

![Figure 6.12: Shadow effects on Cu atoms in the [114] direction of Cu_{55}Pd_{15} (110).](image)
7. Conclusions / Recommendations.

A new pulsing method for the Time of Flight ion scattering and recoiling spectrometer (TOF), based on switching on and off the ionization process, could not produce ion pulses of the desired length, for fundamental reasons. The measured rise and fall times of the ion pulse are 50 µs and 15 µs, respectively, which is at least a factor of 1000 too long for the TOF experiments. The optimalization of the old pulsing method, which uses deflection of the ion beam and a slit, to make pulses, was successful. For 2 keV Ne ions, the measured pulse width is 54 ns (FWHM). This width is small compared to the width of the peaks in the spectrum. Therefore no further optimalization is needed. When lower energies or heavier ions are used, the relative energy spread in the ion pulse becomes larger. The chopping method introduces an intrinsic energy spread of at least 10 % of the used deflection voltage. A possible solution for minimizing this energy spread, is decreasing the deflection voltage.

With the EARISS, measurements were done on the Cu₈₅Pd₁₅ (110) sample at 700 K, 650 K and 300 K, using 2 keV Ne ions. The variations, mainly in the Pd signal were found to be dependant of the time between cleaning and the measurement, instead of being a temperature effect. The Pd showed a large decrease while the copper signal remained almost the same. A reasonable explanation for this is a selective contamination of Pd. The measurement taken the shortest after cleaning, gives a calculated Pd concentration of the first layer of < 14 at.% and of the second layer of 41 at.%. Due to the contamination, the value for the Pd concentration decreases. Therefore it is likely that for a really clean Cu₈₅Pd₁₅ (110) sample the measured second layer concentration of Pd will be close to 50 at.%, which is expected to be the origin of the (2x1) structure. Because the azimuthal resolution of the EARISS is only 15 degrees, the broadening of the spectra causes a higher calculated Pd concentration in the first layer. Therefore, 14 at.% is an upper limit. At 700 K no significant change in the palladium concentrations is measured, under the assumption that the Pd is contaminated preferentially. The disappearing of the (2x1) LEED pattern at this temperature, as seen by
[FRANCIS], is therefore due to a disordering of the second layer. To obtain a better estimation of the concentrations in the first and second layer, the EARISS measurements have to be repeated with a short time between cleaning and measurement. The source of the contamination is the EARISS analyzer, which gives rise to an increase of the pressure from $5 \times 10^{-10}$ to $3 \times 10^{-9}$. It has to be investigated, to decrease the contamination level, for future measurements. The TOF measurement were done at room temperature (300 K) with 1.5 keV Ar ions. The plot of the azimuthal distribution of the Cu recoil signal showed large variations. The peaks could be assigned to the crystal directions of the unreconstructed (110) surface, of which the [114] direction had the highest peak in the plot. The thermocouple has to be removed, because it influences both the EARISS as well as the TOF measurements. To measure the azimuthal distribution of the signal near the [110] direction, the TOF measurements have to be repeated. Also higher energies have to be used to decrease the dimensions of the shadowcone. Then, the angle of incidence can be varied, to measure distances on the surface. In the future, the TOF can prove its value when oxygen or hydrogen adsorbed surfaces are investigated, for instance for the oxygen adsorption on the Cu$_{86}$Pd$_{15}$ sample. The place of the adsorbate on the surface can then be determined, by varying the azimuth and the angle of incidence.


8. References


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