Surface damage through grazing incidence ions investigated by scanning tunneling microscopy

Untersuchung des Oberflächen schadens streifend einfallender Ionen mittels Rastertunnelmikroskopie

Von der Fakultät für Mathematik, Informatik und Naturwissenschaften der RWTH Aachen University zur Erlangung des akademischen Grades eines Doktors der Naturwissenschaften genehmigte Dissertation

vorgelegt von
Diplom Physiker Alex Redinger
aus Luxemburg

Berichter: Universitätsprofessor Dr. Thomas Michely
Universitätsprofessor Dr. Markus Morgenstern

Tag der mündlichen Prüfung 10.07.2009

Diese Dissertation ist auf den Internetseiten der Hochschulbibliothek online verfügbar.
Prüfungskommission:

Prof. Thomas Michely (Betreuer und Berichter)
Prof. Markus Morgenstern (Berichter)
Prof. Matthias Wuttig (Vorsitzender)
Prof. Walter Selke
Datum der mündlichen Prüfung: 10 Juli 2009
Abstract

Surface damage, caused by grazing incidence ions, is investigated with variable temperature scanning tunneling microscopy. The experiments are carried out on a Pt(111) crystal. The kinetic energy of noble gas ions is varied between 1-15 keV and the angle of incidence can be adjusted between $\vartheta = 78.5^\circ$ and $\vartheta = 90^\circ$ measured with respect to the surface normal.

The damage patterns of single ion impacts, on flat terraces and at step edges of monoatomic height, are investigated at low surface temperatures. Ions hitting a flat terrace are usually specular reflected. The energy transfer from the ion to the crystal atoms is small and only little damage is produced. In contrast, at ascending step edges, which are illuminated by the ion beam, large angle scattering events occur. Sputtering, adatom and vacancy production is induced. However, a significant fraction of the ions, which hit step edges, enter the crystal and are guided in between two atomic layers parallel to the surface via small angle binary collisions. This steering process is denoted as subsurface channeling. The energy loss per length scale of the channeled particles is low, which results in long ion trajectories (up to 1000 Å). During the steering process, the ions produce surface damage. Depending on the ion species and the ion energy, adatom and vacancies or surface vacancy trenches of monoatomic width are observed. The surface damage can be used to track the path of the ion. This makes the whole trajectory of single ions with keV energy visible.

The number of sputtered atoms per incident ion at ascending step edges, i.e. the step edge sputtering yield, is measured experimentally for different irradiation conditions. For $\vartheta =86^\circ$, the sputtering yield is determined from the fluence dependent retraction of pre-existing illuminated step edges. An alternative method for the step edge sputtering yield determination, is the
analysis of the concentration of ascending steps and of the removed amount of material as a function of the ion fluence. This method is also applicable under less grazing angles of incidence. The investigations show that the sputtering yield at step edges depends on the azimuthal orientation of the impinging ions with respect to the surface. This change is attributed to the orientation dependence of subsurface channeling.

The step edge sputtering yield at small adatom clusters is measured. In this case, the topmost layer (which forms the step edge) has a small lateral extension in ion beam direction. The evaluation shows that the step edge yield is, compared to step edges with a long upper terrace, decreased by a factor of three. The physical reason can be traced back to subsurface channeling. The ions are able to pass underneath the cluster and exit the crystal without a large scattering event. Little energy is transferred to the crystal which results in a low sputtering yield.

The influence of adsorbates on sputtering and surface damage in grazing incidence ion erosion is studied for the case of oxygen and carbon monoxide. A partial surface coverage with adsorbates causes an enhancement of the erosion rate (the amount of removed material per ion fluence) by a factor of up to 40 compared to the clean case. The study is performed for 5 keV Ar\(^+\) ions for various grazing angles between 81° and 87° and temperatures ranging from 400 K to 550 K.

Finally, coarsening of ion beam induced ripple patterns is analyzed. For surface temperatures of 450 K or below coarsening is athermal and kinetic, unrelated to diffusion and surface free energy. Similar to the situation of sand dunes, coarsening takes place through annihilation reactions of mobile defects in the pattern. The defect velocity derived on the basis of a simple model agrees quantitatively with the velocity of monoatomic steps illuminated by the ion beam.
# Contents

Frequently used symbols \hspace{1cm} viii

1 Introduction \hspace{1cm} 1

2 Introduction to the ion-surface interaction \hspace{1cm} 5

2.1 Interaction between two charged particles \hspace{1cm} 5

\hspace{1cm} 2.1.1 Energy transfer \hspace{1cm} 5

\hspace{1cm} 2.1.2 The screened Coulomb potential \hspace{1cm} 7

\hspace{1cm} 2.1.3 The shadow cone \hspace{1cm} 8

2.2 The interaction of charged particles with a solid \hspace{1cm} 9

\hspace{1cm} 2.2.1 Ion penetration depth \hspace{1cm} 9

\hspace{1cm} 2.2.2 Bulk channeling \hspace{1cm} 10

\hspace{1cm} 2.2.3 Production of defects by ion irradiation \hspace{1cm} 12

\hspace{1cm} 2.2.4 Ion induced desorption \hspace{1cm} 17

\hspace{1cm} 2.2.5 Molecular dynamics simulations \hspace{1cm} 18

2.3 Diffusion processes \hspace{1cm} 19

\hspace{1cm} 2.3.1 Diffusion on the terrace and at step edges \hspace{1cm} 21

\hspace{1cm} 2.3.2 Incorporation of adatoms and vacancies into step edges \hspace{1cm} 22

2.4 Grazing incidence ion erosion \hspace{1cm} 24

\hspace{1cm} 2.4.1 Ion-surface interaction \hspace{1cm} 24

\hspace{1cm} 2.4.2 Subsurface channeling \hspace{1cm} 27

\hspace{1cm} 2.4.3 Sputtering by grazing incidence ions \hspace{1cm} 30

2.5 Pattern formation by ion erosion \hspace{1cm} 32

\hspace{1cm} 2.5.1 The Bradley-Harper theory \hspace{1cm} 34

\hspace{1cm} 2.5.2 Pattern formation, an atomistic approach \hspace{1cm} 36
## CONTENTS

2.5.3 Pattern formation through grazing incidence ions on Pt(111)  37

2.6 Open questions:  43

### 3 Experimental Setup

3.1 The vacuum system  45
3.2 The sample holder  47
3.3 The Platinum evaporator  52
3.4 The Scanning Tunneling Microscope  53
3.5 Calibration of the ion beam  53
3.6 Experimental procedure  55

### 4 Surface damage by single ion impacts

4.1 Introduction  59
4.2 Bulk channeling versus subsurface channeling  63
4.3 Damage analysis for 5 keV projectiles  68
4.4 Energy dependence of subsurface channeling  76
4.5 Angular dependence of subsurface channeling  82
4.6 Influence of temperature on subsurface channeling  86
4.7 Single ion impacts of Neon and Helium  88
4.8 Increasing the visibility of surface trenches by Xenon adsorption  89
4.9 The ion fluence onto step edges  91
4.10 Discussion  92
4.11 Conclusion  93

### 5 Step edge sputtering through grazing incidence ions

5.1 Introduction  95
5.2 Step retraction due to ion bombardment  96
   5.2.1 Step edge yield from step concentration  100
   5.2.2 Molecular dynamics simulations  103
5.3 Discussion  107
5.4 Conclusions  111
CONTENTS

6 Effect of adatom cluster adsorption on surface damage 113
   6.1 Introduction ................................................. 113
   6.2 Experimental procedure ................................. 114
   6.3 Results ..................................................... 114
       6.3.1 Preparation of small adatom clusters .............. 114
       6.3.2 Sputtering at adatom clusters .................. 115
   6.4 Conclusion .................................................. 121

7 Terrace damage and the effect of adsorbates on its formation 123
   7.1 The effect of a CO background pressure ................. 124
   7.2 Oxygen covered surface ................................. 127
   7.3 Simulation results ........................................ 131
   7.4 Surface damage and sputtering as a function of the angle of incidence $\vartheta$ 134
   7.5 Discussion .................................................. 135
   7.6 Conclusion .................................................. 139

8 Rapid coarsening of ion beam ripple patterns by defect annihilation 141
   8.1 Introduction ............................................... 141
   8.2 Results .................................................... 142
   8.3 Discussion .................................................. 147

9 Summary and outlook 149
   9.1 Summary .................................................... 149
   9.2 Outlook ..................................................... 151

References 154

A Appendix 165
   A.1 Outgassing of UHV components ......................... 165
   A.2 Temperature calibration ............................ 166
   A.3 A scanning tunneling microscope for students........ 167

B Scientific publications 171

C Curriculum vitae (Lebenslauf) 173

D German abstract (Zusammenfassung) 175
<table>
<thead>
<tr>
<th>CONTENTS</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>E Acknowledgments</td>
<td>177</td>
</tr>
</tbody>
</table>
Frequently used symbols and abbreviations

$\alpha$ angle of incidence measured with respect to the surface

$\alpha_{\text{crit}}$ Lindhards critical angle for channeling

$\chi(\vartheta_{\text{chan}} - \vartheta)$ non-channeling fraction

$\Delta E/\Delta x$ averaged nuclear energy loss of one channeled projectile

$\eta(\vartheta_{\text{chan}} - \vartheta)$ channeling fraction

$\langle \Delta E/\Delta x \rangle$ averaged nuclear energy loss of many channeled projectiles

$\Theta$ Amount of removed material

$\vartheta$ angle of incidence measured with respect to the surface normal

$\vartheta_{\text{chan}}$ channeling direction measured with respect to the surface normal

$\vartheta_{\text{tot}}$ angle necessary to achieve total reflection

$R_{\text{SC}}$ shadow cone radius at a distance $d$ from the atom at rest

$x_{C}$ zone of influence of an ascending step edge

$Y^{\text{step}}$ step edge sputtering yield

$Y^{\text{terr}}$ terrace sputtering yield

$F$ ion fluence

LEIS low energy ion scattering

MD molecular dynamics

ML monolayer

STM scanning tunneling microscopy
CONTENTS

TDS  Thermal Desorption Spectroscopy
UHV  ultra high vacuum

\( E \)  kinetic energy of the ion
\( M_1 \)  mass of the projectile
\( M_2 \)  mass of the target atom
\( Y \)  erosion rate, average sputtering yield
\( A \)  Thomas-Fermi screening length
Chapter 1

Introduction

Grazing incidence ions scattered from metal surfaces provide a wealth of information on many aspects of the ion-surface interaction. The charge exchange mechanisms, electronic energy loss of the projectiles as well as ion induced electron emission have been extensively investigated by analyzing the scattered particles [1]. The reflection coefficient of the impinging ions is very close to unity which results in a high surface sensitivity.

Already decades ago it was noticed that surface defects give rise to specific peaks in energy and angular distribution of ions scattered under grazing incidence [2]. Butterfly like spectra [3] were observed which could be explained by the scattering of the ions at ascending and descending step edges. Low energy ion scattering spectroscopy is a commonly used technique to measure the chemical composition of the surface and the position of adsorbates [4]. It has been shown that through monitoring the intensity of the specular reflected ions epitaxial growth processes can be studied in real time [5].

On the other hand, ion erosion is a versatile tool for surface modifications. Almost fifty years ago ripple patterns parallel to the direction of the impinging ions have been observed after erosion with air molecules of keV energy. The investigations were carried out on a glass substrate at an angle of incidence of $80^\circ$ measured with respect to the surface normal [6]. Since then, pattern formation through grazing incidence ions has been observed on many metallic [7–11], semiconductor [12], non-conducting [13] and polycrystalline [14] substrates. The resulting morphology can be used as a template for the adsorption of large molecules [15], for the manipulation of magnetism [16] or for tuning the chemical reactivity of catalytically active surfaces [17]. Grazing incidence ion beams are also of interest in ion beam assisted deposition of thin films [18].

Glancing ions can also be used to efficiently clean and smoothen a surface, as shown on silicon surfaces [19], insulator crystals [20], metal thin films [21] and metal single crystals [1]. One example of the ion beam induced smoothening is the sputter deposition of ZnO on glass or sapphire [22]. The comparison of these films without and
1. INTRODUCTION

with concurrent 5 keV Ar\(^+\) ion bombardment at grazing incidence, shows a reduced roughness by more than one order of magnitude, enhanced film density and reduced residual stress.

Depending on the experimental conditions, like type of substrate, ion energy, angle of incidence and temperature, the use of grazing incidence ions leads to completely different results. On the one hand the reflection coefficient is close to unity, although morphological changes are commonly observed. In some cases the surface roughens whereas other experiments show very efficient smoothening. All these findings point to the importance of surface defects in grazing incidence ion erosion experiments.

The influence of steps on the ion surface interaction has already been investigated with the help of molecular dynamics simulations (MD) \([23]\) and by MARLOWE \([24]\) (computer code based on the binary collision approximation). These MD simulations where restricted to low-energy ions (<100 eV) due to their relevance for ion-beam assisted deposition and the binary collision simulations where focused to the angular distributions of the scattered particles at step edges.

Recently molecular dynamics simulations \([25]\) and experiments \([26]\) showed, for the first time, that the damage production by grazing incidence ions depends strongly on the impact position. The sputtering yield of glancing ions hitting monoatomic step edges shows an increase by a factor of 100 compared to terrace impacts where the reflection coefficient is close to one and only very little sputtering occurs.

In order to understand the mechanisms of ion induced surface changes and the limits of the application of such ion beams for measuring and manipulating surfaces, it is necessary to understand damage formation mechanisms on the level of the interaction of a single ion with the surface. The Pt(111) surface is used as a substrate and the surface damage is analyzed with a variable temperature scanning tunneling microscopy (STM) apparatus under ultra high vacuum conditions (UHV). The experimental results are compared to molecular dynamics simulation studies performed in cooperation with the group of Prof. H. M. Urbassek from the University of Kaiserslautern.

The Pt(111) single crystal is used because extensive studies have already been performed for normal and grazing incidence ion erosion. Scanning tunneling microscopy and molecular dynamics simulations have been frequently used to study the ion surface interaction. For normal incidence the sputtering yield, adatom production, bulk vacancy and interstitial production, lateral distribution of the damage around the impact point as well as for the consequences of the impact induced thermal spike on the formation of mesoscopic damage structures, have already been investigated in detail \([27–31]\). The morphological evolution during grazing incidence ion bombardment has also been studied on Pt(111) \([10; 25; 26; 32; 33]\).

It is the aim of this thesis to study the damage produced by single ion impacts (Chapter 4), to study the sputtering yield at step edges, on the terrace and at small
adatom clusters (Chapter 5, 6). The influence of adsorbates on sputtering on the flat terrace is studied for the case of oxygen and carbon monoxide (Chapter 7). Finally coarsening of ripple patterns is investigated in Chapter 8. Before the results are presented, Chapter 2 provides the necessary experimental and theoretical background for this work and Chapter 3 describes the setup and the experimental procedure.
1. INTRODUCTION
Chapter 2

Introduction to the ion-surface interaction

In this chapter the interaction of low energetic (keV) particles with a solid target is discussed.

The outline of this chapter is as follows. First, the interaction between two particles is introduced and the concept is then extended to the interaction of one ion with many substrate atoms. The energy loss and the ion penetration depth of particles in solids is described. Channeling in crystalline materials is explained and the mechanisms of defect production due to ion beams are discussed. A brief description of the relevant diffusion processes is necessary in order to understand the annealing of the ion induced defects. Then, the ion-surface interaction for glancing incidence ion erosion is presented. The sputtering yield, surface channeling and subsurface channeling are discussed. A introduction of molecular dynamics simulations is also performed since it is a very efficient tool to study the ion-surface interaction on the picosecond timescale. Pattern formation by low energy ions is discussed where the continuum and the atomistic models are presented. The chapter ends with a detailed description of pattern formation through grazing incidence ions on Pt(111).

2.1 Interaction between two charged particles

2.1.1 Energy transfer

The interaction of an ion with a target atom can be described by elastic two body scattering events, if the kinetic energy, of the particles involved, is in the keV range. This is valid because the interaction time for a collision is small compared to the period of phonon frequencies in the solid \([10^{-15} \text{ sec compared to } 10^{-13} \text{ sec [2]}}\). A primary particle (I) with mass \(M_1\), velocity \(\vec{v}_0\) and atomic number \(Z_1\) hits an atom at rest (II)
with mass $M_2$ and atomic number $Z_2$. After scattering particle I is deflected under an angle of incidence $\alpha_1$ with a velocity $\vec{v}_1$ and particle II has gained a velocity $\vec{v}_2$ and the angle equals to $\alpha_2$. The situation is sketched in Fig. 2.1. From energy and momentum conservation follows:

$$\frac{1}{2}M_1v_0^2 = \frac{1}{2}M_1v_1^2 + \frac{1}{2}M_2v_2^2 \quad (2.1)$$

$$M_1v_0 = M_1v_1 \cos \alpha_1 + M_2v_2 \cos \alpha_2 \quad (2.2)$$

$$M_1v_1 \sin \alpha_1 - M_2v_2 \sin \alpha_2 = 0 \quad (2.3)$$

Eliminating the velocity of the target atom and the angle $\alpha_2$ results in equation 2.4 which only depends on the scattering angle $\alpha_1$ and the velocities of the primary ion before and after deflection.

$$\frac{v_1}{v_0} = \frac{M_1 \cos \alpha_1 \pm \sqrt{M_2^2 - M_1^2 \sin^2 \alpha_1}}{M_1 + M_2} \quad (2.4)$$

The energy of the primary particle after deflection $E_1 = \frac{1}{2}M_1v_1^2$ can be calculated by

$$E_1 = E \left[ \cos \alpha_1 \pm \sqrt{\left(\frac{M_2}{M_1}\right)^2 - \sin^2 \alpha_1} \right]^2 \quad (2.5)$$

where $E$ equals to the initial energy of particle I. The elastic energy loss can therefore be calculated without knowing the interatomic potential between the colliding particles. At this point it is instructive to calculate the energy transfer of two colliding particles in the case of grazing incidence ion bombardment. If one assumes that the scatter-
2.1 Interaction between two charged particles

<table>
<thead>
<tr>
<th>angle $\alpha_0$ [$^\circ$]</th>
<th>energy transfer $\Delta E$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>60</td>
</tr>
<tr>
<td>10</td>
<td>122</td>
</tr>
</tbody>
</table>

Table 2.1: Energy transfer $\Delta E$ in a single collision for a 5 keV Argon particle hitting a Platinum atom at rest. The angle of incidence $\alpha_0$ equals to the angle of incidence of the incoming particle. Specular reflection is assumed.

ing proceeds specularly, the angle of incidence of the incoming ($\alpha_0$) and the outgoing particle ($\alpha_1$) follows the relation $\alpha_1 = 2 \cdot \alpha_0$. The energy transfer $\Delta E = E - E_1$ for different angles of incidence $\alpha_0$ for a 5 keV Argon atom hitting a Platinum atom at rest is tabulated in 2.1. Under specular reflection, $\Delta E$ is extremely sensitive on the angle of incidence. Changing $\alpha_0$ by only $8^\circ$ increases the energy transfer by a factor 25.

2.1.2 The screened Coulomb potential

The interaction of charged particles can be described by a Coulomb potential which is proportional to the atomic numbers of the species involved ($Z_1, Z_2$) and inversely proportional to the distance $r$ between these particles. If the kinetic energies of the particles are high, the interaction is determined by scattering between the nuclei. This leads to the well-known Rutherford scattering cross sections. For low energy ions (keV), the pure Coulomb potential is not a good approximation, since the electron cloud screens the positive charge of the nucleus. Different screened Coulomb potentials have been proposed in the literature which usually have the general form of 2.6. The elementary charge is denoted with $e$ and $\varepsilon_0$ is the dielectric constant. A summary of the different screened Coulomb potentials can be found in reference [34].

$$V(r) = \frac{Z_1 Z_2 e^2}{4\pi \varepsilon_0 r} \Phi \left( \frac{r}{A} \right)$$  \hspace{1cm} (2.6)

The screening length is denoted with $A$. In this thesis the Thomas-Fermi screening length is usually applied which can be calculated with formula 2.7.

$$A = \frac{\left( \frac{9\pi^2}{128} \right)^{1/3} a_0}{\left( Z_1^{2/3} + Z_2^{2/3} \right)^{1/2}}$$  \hspace{1cm} (2.7)
2. INTRODUCTION TO THE ION-SURFACE INTERACTION

The Bohr radius is denoted with $a_0$ and equals to 0.529 Å. The screening term $\Phi$ is often approximated by

$$\Phi \left( \frac{r}{\lambda} \right) = \sum_{i=1}^{n} c_i \exp \left( -d_i \frac{r}{\lambda} \right)$$  \hspace{1cm} (2.8)

where $c_i$ and $d_i$ are constants which depend on the approximation. Widely used potentials are the Molière approximation with coefficients $c_i = [0.35, 0.55, 0.1]$ and $d_i = [0.3, 1.2, 6]$ and the ZBL approximation with $c_i = [0.1818, 0.5099, 0.2802, 0.02817]$ and $d_i = [3.2, 0.9423, 0.4028, 0.2016]$.

2.1.3 The shadow cone

Figure 2.2: Sketch of the shadow cone formed by energetic particles hitting a target atom. The radius of the cone $R_{sc}$ at a distance $d$ from the atom at rest is indicated. Graph from reference [1].

If an ion hits a target atom, the repulsive interaction potential deflects the ion. A shadow cone is formed behind the rest atom as shown in Fig. 2.2 [1]. It results from the Coulomb repulsion and visualizes the forbidden zone where the impinging ion is not able to enter. The lines show many trajectories of an energetic particle impinging from the left hand side onto the rest atom. The shadow cone radius $R_{sc}$ can be parametrized with the distance $d$ from the rest atom. In the case of an unscreened Coulomb potential $R_{sc}$ can be calculated with formula 2.9.

$$R_{sc} = 2 \sqrt{\frac{Z_1 Z_2 e^2}{4 \pi \epsilon_0 E}} d$$  \hspace{1cm} (2.9)

The energy of the impinging particles is denoted with $E$. If the approximation of an unscreened Coulomb potential is poor, the universal shadow cone expression deduced
by Oen can be used [35]. A close inspection of Fig. 2.2 shows that at the rim of the cone the number of trajectories is enhanced which is called focusing effect.

The shadow cone formation is well-known from low energy ion scattering spectroscopy where, for example, the position of adsorbates on surfaces is investigated. The shadow cone width can be deduced with impact collision ion scattering spectroscopy [36].

2.2 The interaction of charged particles with a solid

Energetic particles impinging on a substrate, enter the crystal, where they are decelerated by transferring their kinetic energy to the crystal lattice via elastic (nuclear collisions) and inelastic (electronic excitation) processes. The energy loss per length scale \( \frac{dE}{dx} \) can be written as a sum of elastic (n) and inelastic losses (e) (the energy loss due to nuclear reactions can be neglected here).

\[
\frac{dE}{dx} = \left( \frac{dE}{dx} \right)_n + \left( \frac{dE}{dx} \right)_e
\] (2.10)

The energy losses can be rewritten in terms of a nuclear and an electronic cross section \( S_i(E) \) for a single collision times the number density of substrate atoms \( N \).

\[
\left( \frac{dE}{dx} \right)_i = -NS_i(E)
\] (2.11)

In the energy range considered in this work (max. 15 keV) the electronic losses can be considered to be proportional to the ion velocity and can be neglected for heavy projectiles (i.e Xenon and Argon) since the nuclear stopping dominates. However, in the case of very light ions (Hydrogen and Helium) the electronic energy losses are important. For the case of platinum erosion with 5 keV ions, the values for the nuclear and the electronic stopping are tabulated in table 2.2. The numbers have been calculated with SRIM [37], a Monte Carlo simulation based on the binary collision approximation. In this computer simulation the target is assumed to be amorphous. As we will see below, the energy loss, the ion penetration depth and the sputtering yield for crystalline materials deviate significantly from amorphous targets.

2.2.1 Ion penetration depth

The ion penetration depth follows immediately from the energy loss of the energetic particles in the crystal. The average path length \( R(E) \) can be derived analytically from the knowledge of the stopping cross sections \( S_i(E) \), assuming a continuous slowing
### 2. INTRODUCTION TO THE ION-SURFACE INTERACTION

<table>
<thead>
<tr>
<th>ion species</th>
<th>ion energy [keV]</th>
<th>( \left( \frac{dE}{dx} \right)_n ) [eV/Å]</th>
<th>( \left( \frac{dE}{dx} \right)_e ) [eV/Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>5</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>Ne</td>
<td>5</td>
<td>24</td>
<td>8</td>
</tr>
<tr>
<td>Ar</td>
<td>5</td>
<td>61</td>
<td>12</td>
</tr>
<tr>
<td>Xe</td>
<td>5</td>
<td>212</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 2.2: Calculated nuclear and electronic energy loss for different projectiles impinging on a platinum crystal. The energy of 5 keV corresponds to the energy most frequently used in the experiments. Values have been calculated by SRIM \([37]\).

down of the projectiles.

\[
R(E) = \int_0^E \frac{dE}{dx} = \frac{1}{N} \int_0^E \frac{dE}{S_n(E) + S_e(E)} \tag{2.12}
\]

For ion implantation applications the relevant penetration length is determined by the average projected range \( R_P \) which is defined as the projection of \( R \) on the incidence direction of the impinging ions. For the low energy regime an approximate formula has been derived by Schiøtt \([38]\):

\[
R_P = C_l \frac{M_2}{M_1} \frac{1}{M_2} \left[ \left( \frac{Z_1^{2/3} + Z_2^{2/3}}{Z_1 Z_2} \right) \right]^{2/3} \tag{2.13}
\]

where \( C_l \) is a material constant. The energy loss and the ion range discussed until now are only valid for amorphous materials. For single crystals, the ion ranges and the energy losses are influenced by channeling.

#### 2.2.2 Bulk channeling

An ion hitting the target in a direction equal or close to a low index direction of the crystal can be steered along rows (axial channeling) or planes (planar channeling) \([39; 40]\). The motion through the crystal proceeds via small angle binary collisions and the energy loss is dramatically reduced compared to amorphous substrates. As a consequence the ion penetration depth increases. Channeling occurs as long as the angle between the direction of the incident beam and the low index crystallographic orientation is small.

In order to describe channeling analytically, Lindhard introduced the concept of the continuum approximation \([39]\). The scattering from a row of individual atoms is substituted with a continuous potential field \( V(\rho) \). The distance \( \rho \) is defined normal to the string. The average potential field \( V(\rho) \) can be calculated by integrating over all atoms in the string. The nearest neighbor distance between two atoms in the string
2.2 The interaction of charged particles with a solid

Figure 2.3: Sketch of bulk channeling along a low index direction of a single crystal

(along the crystallographic \([uvw]\)) is denoted with \(t_{uvw}\).

\[
V(\rho) = \int_{-\infty}^{\infty} \frac{dz}{t_{uvw}} V(\sqrt{z^2 + \rho^2})
\]  
(2.14)

The potential \(V(\rho)\) has the form of eq. 2.6. The only effective forces are perpendicular to the row and the momentum parallel to the row is constant if inelastic energy losses are neglected. The continuum approximation is valid as long as the distance of closest approach \(\rho_{min}\) is large and no scattering with individual atoms in the string occurs.

The maximum transverse energy \(E_\perp\) is related to the distance of closest approach \(\rho_{min}\) via

\[
E_\perp = V(\rho_{min})
\]  
(2.15)

It is now possible to introduce the critical angle since

\[
E_\perp = E \cdot \sin^2 \alpha_{crit} = E \cdot \cos^2 \theta_{crit} = V(\rho_{min})
\]  
(2.16)

where \(\alpha_{crit}\) is the angle measured with respect to the string of atoms and \(\theta_{crit}\) is measured with respect to the string normal and \(E\) the kinetic energy of the projectile.

The critical angle for axial channeling \(\alpha_{crit}\) has been calculated analytically by Lindhard [39]. The resulting formula 2.17 is valid as long as the energy of the ions \(E\) is smaller than \(2Z_1Z_2e^2t_{uvw}/A^2\).

\[
\alpha_{crit} = \left[\frac{3A^2Z_1Z_2e^2}{4Et_{uvw}}\right]^{1/4}
\]  
(2.17)

The distance between two atoms in the string is denoted with \(t_{uvw}\) and the Thomas Fermi screening length is denoted with \(A\) (eq. 2.7). Table 2.3 summarizes the critical angles for 5 keV ions on Pt(111) along the dense packed \(<110>\) direction of the crystal.
2. INTRODUCTION TO THE ION-SURFACE INTERACTION

<table>
<thead>
<tr>
<th>ion species</th>
<th>ion energy [keV]</th>
<th>$\alpha_{\text{crit}}$ [$^\circ$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>Ne</td>
<td>5</td>
<td>13</td>
</tr>
<tr>
<td>Ar</td>
<td>5</td>
<td>14.9</td>
</tr>
<tr>
<td>Xe</td>
<td>5</td>
<td>18.7</td>
</tr>
</tbody>
</table>

Table 2.3: Critical angles for axial channeling calculated with formula 2.17 for 5 keV ion energy. The ions hit the Pt(111) crystal parallel to the $<110>$ direction.

As pointed out by Robinson [41], in the case of heavy projectiles and energies below 50 keV, the values derived from equation 2.17 should only be used as a rough estimate since the formula does not predict the correct minimum approach distance.

The critical angle for planar channeling is considerably smaller than for axial channeling since the ion encounters atoms at different positions in the plane. The continuum approximation is, therefore, never exact and will not be discussed in detail here. Approximations for the critical angles for planar channeling can be found for example in reference [42].

2.2.3 Production of defects by ion irradiation

During the deceleration of the projectile in the bulk, energy transfer to the crystal atoms occurs which results in ion induced defects as shown in Fig. 2.4. Bulk defects consist of interstitials and bulk vacancies. Interstitials are atoms which are not located on regular lattice sites. Missing atoms in the crystal are denoted as bulk vacancies. These defect couples are denoted as Frenkel-pairs. Moreover, adatom and vacancy production occurs at the surface. If the energy transfer to the near surface atoms is large ion bombardment leads to sputtering. The decelerated atom will be implanted deep in the crystal.

The minimum energy which is required to produce a stable interstitial vacancy pair (Frenkel pair) is denoted as displacement or threshold energy $E_{\text{th}}$. In the case of metals and semiconductors $E_{\text{th}}$ is between 15 eV and 40 eV [43].

For light keV ions (H$^+$,He$^+$) only isolated recoils (atoms set in motion) are produced. This is denoted as near threshold regime and is also valid for heavy ion erosion with ion energies in the eV range. In the case of heavy ions with somewhat higher energies a collision cascade is induced which can be described in the binary collision approximation. The collisions take place between a moving and a stationary particle. For heavy ions with keV energies the collision cascade is followed by a state where collisions between two moving particles occur frequently. This energy regime is denoted as non-linear or thermal spike regime which cannot be described by the binary collision approximation. In the non-linear regime, after the collision cascade, the kinetic...
2.2 The interaction of charged particles with a solid

Figure 2.4: Sketch of the ion induced defects. In the bulk, the ion creates interstitials and vacancies whereas surface vacancies and adatoms are created at the surface. After the deceleration of the projectile the ion is implanted.

and potential energy components of the crystal attain equilibrium with each other. This is reached after roughly 0.1 ps. The mean velocity $\bar{v}$ of the atoms equals to a temperature $T$ as shown in equation 2.18.

$$E_{kin} = \frac{1}{2} m \bar{v}^2 = \frac{3}{2} k_B T \quad (2.18)$$

The temperature $T$ is often higher than the melting temperature of the crystal. For several picoseconds a hot, liquid like zone, exists where all atoms are in motion (a thermal spike is induced). During the cooling and recrystallization phase most of the atoms regain a regular lattice site which results in a decrease of the Frenkel pair density. Molecular dynamics simulations showed that during the cooling phase most Frenkel pairs in the melted regime recombine and only those located at the rim of the impact zone will not be annihilated [43].

If the collision cascade intersects the surface, which is usually the case for keV ions, extended defect production at the surface originates. Atoms, usually originating from the first three layers [29], can gain enough kinetic energy to be pushed towards the surface. If the kinetic energy perpendicular to the surface is larger than the surface
2. INTRODUCTION TO THE ION-SURFACE INTERACTION

binding energy sputtering occurs. If the transverse kinetic energy of the recoils is smaller than the binding energy and larger than the energy for adatom formation, the atom is pushed onto the surface.

The average number of sputtered particles per incident ion defines the sputtering yield $Y$.

$$Y = \frac{\text{number of removed atoms}}{\text{number of incident ions}} \quad (2.19)$$

The sputtering yield is proportional to the nuclear stopping power $S_n(E)$. Since the induced collision cascade intersects the surface, the sputtering yield will be inversely proportional to the surface binding energy $U_0$. This leads to the first general predictive equation for the sputtering yield of amorphous targets developed by Sigmund [44].

$$Y = 0.042\alpha S_n(E) / U_0 \quad (2.20)$$

The dimensionless factor $\alpha$ is a function of the angle of incidence. Increasing the angle of incidence $\vartheta$ measured from the surface normal leads to an increase of the sputtering yield. The projected ion penetration depth decreases and more energy is deposited at the surface which increases $Y$. Sigmund estimated the sputtering yield for oblique ion incidence $Y(\vartheta)$ to be equal to

$$Y(\vartheta) = Y(\vartheta = 0^\circ) \cdot (\cos \vartheta)^{-1} \quad (2.21)$$

where $Y(\vartheta = 0^\circ)$ is the sputtering yield at normal incidence. For grazing incidence, assumption 2.21 fails, since the reflection coefficient increases which results in a decrease of the deposited energy in the crystal. Some typical angular dependent measurements are shown for heavy ions with keV energies in Fig. 2.5(a). Depending on the experimental parameters, like ion energy and ion/substrate combination, the maximum of the sputtering yield is between 60$^\circ$ to 80$^\circ$ measured from the surface normal. At glancing incidence the measured sputtering yields drop sharply.

Sputtering yield measurements in the case of single crystals show a strong dependence on the crystallographic orientation of the crystal. Along low index directions of the crystal, channeling occurs. The energy loss of the projectiles decreases which results in an increase of the ion penetration depth. As a result the intersection of the collision cascade with the surface shrinks, which results in less sputtering. Along low index crystallographic orientations the crystal appears “open” which is denoted as transparency.

In the following a simple model, proposed by Onderdelinden [46], is introduced which connects the concept of transparency with the channeling theory of Lindhard. The model allows to evaluate the fraction of channeled particles along a certain crystal-
2.2 The interaction of charged particles with a solid

Figure 2.5: (a) Angular dependent measurements for various projectile/substrate combinations [45]. The dashed curve shows the prediction of Sigmund (formula: 2.21). The substrates were of polycrystalline or amorphous form (b) Angular dependent measurements on Cu(100). The inset shows the stereographic projection. The dashed line shows the sputtering yield measurements on polycrystalline Cu.

lographic orientation [uvw]. The idea is that the ion beam is split into two components, the channeling and the non-channeling fraction. A beam of ions impinging parallel or close to parallel to a low index direction of the crystal has a random distribution of impact parameters with respect to the surface atoms. The angle of the low index direction measured with respect to the surface normal is denoted with $\vartheta_{\text{chan}}$. As a consequence of the random distribution of the impact parameters, only those ions which fulfill the channeling condition, i.e. whose minimum approach distance to the substrate atoms is large, are steered along the atomic strings or planes. Only the non-channeling fraction of the ion beam contributes to sputtering. The channeled fraction enters deeper into the bulk and the collision cascade does not intersect the surface anymore. For a polar angle $\vartheta$, the sputtering yield $Y(\vartheta)$ equals to the fraction of non channeled particles $\chi(\vartheta_{\text{chan}} - \vartheta)$ times the sputtering yield for a structureless medium $Y_{\text{amorph}}$ times a fitting parameter $\beta$ which accounts for the fact that the yields for amorphous and
crystalline targets deviate.

\[ Y(\vartheta) = \chi(\vartheta_{chan} - \vartheta) \cdot \beta \cdot Y_{amorph} \quad (2.22) \]

The non-channeling fraction of particles \( \chi(\vartheta_{chan} - \vartheta) \) can be estimated via a screened Coulomb potential (In this case a Thomas-Fermi Potential is used). In the case of perfect alignment of the ion beam and the low index direction, i.e. \( \vartheta_{chan} = \vartheta \), the non-channeling fraction \( \chi(\vartheta_{chan} - \vartheta) = \chi(0) \) equals to

\[ \chi(0) = \pi N t_{uvw}^{3/2} \left[ \frac{3A^2 Z_1 Z_2 \left( \frac{e^2}{4\pi \epsilon_0} \right)}{E} \right]^{1/2} \quad (2.23) \]

where the distance between two atoms in the string or plane is denoted with \( t_{uvw} \). \( N \) equals to the atomic density. The Thomas Fermi screening length is denoted with \( A \) (see eq. 2.7), \( Z_1 \) and \( Z_2 \) are the the atomic numbers of the target and the ion. Since channeling also exists when the ion beam is not perfectly aligned with the atomic strings, the non-channeling fraction \( \chi(\vartheta_{chan} - \vartheta) \) can be estimated with formula 2.24 where \( f \) is a constant which can be used to fit the calculated curve to the experimental data. Throughout this thesis \( f=1 \) is assumed.

\[ \chi(\vartheta_{chan} - \vartheta) = \frac{\chi(0)}{1 - [1 - \chi(0)] \cdot \left[ f \frac{1}{\alpha_{crit}} \right]^{2}} \quad (2.24) \]

The critical angle \( \alpha_{crit} \) is equal to Lindhards approximation, e.g. formula 2.17.

For convenience the channeling fraction is defined as:

\[ \eta(\vartheta_{chan} - \vartheta) = 1 - \chi(\vartheta_{chan} - \vartheta) \quad (2.25) \]

Fig. 2.6 shows an example where the Onderdelinden approach was used to study the different axial channels on Cu(001) by focused ion beam milling [47]. The stereographic projection in Fig. 2.6(a) shows the major axial channeling directions in the case of 30 keV Ga\(^+\) ions. Fig. 2.6(b) shows a cross section along the \(<110>\) direction where the non-channeling fraction is plotted against the tilt angle \( \vartheta \) measured with respect to the surface normal. At the low index directions the non-channeling fraction is reduced. As already discussed, a decrease of the non-channeling fraction leads to a decrease of the sputtering yield.
2.2 The interaction of charged particles with a solid

Figure 2.6: (a) Stereographic projection of the axial channeling directions on Cu(001). (b) Cross section of the stereographic projection along the <110> tilt angle. At the low index directions the non-channeling fraction is strongly reduced. Graph from reference [47]

2.2.4 Ion induced desorption

Figure 2.7: The three contributions of the total desorption cross section. (a) the direct knock-off contribution, (b) the reflected ion contribution, (c) the sputtered atom contribution. The ion is denoted with (1), the substrate atoms with (2) and the adsorbate with (3). Graph from reference [48]

Adsorbates present on the surface can be very efficiently removed with ion erosion which is called ion impact desorption [48]. Whereas the amount of removed atoms per ion in the case solid targets is quantified with the sputtering yield, ion impact desorption is quantified by the desorption cross section $\sigma$. It is defined as the average number of adsorbates desorbed per incident ion $Y_{Ad}$, normalized with the adsorbate concentration $\rho_{Ad}$:

$$\sigma = \frac{Y_{Ad}}{\rho_{Ad}} = \frac{Y_{Ad}}{\Theta_{Ad}} \cdot \Omega \quad (2.26)$$

Here $\Omega$ denotes the area of one surface atom. $\sigma_0$ can be interpreted as the average...
2. INTRODUCTION TO THE ION-SURFACE INTERACTION

surface area depleted from adsorbates by a single incident ion. This definition is meaningful because at the beginning of the experiment when the adsorbate concentration is high, the average sputtering \( Y_{Ad} \) is high. The ion removes adsorbates and the concentration decreases. This results in a decrease of the average sputtering yield. The normalization of \( Y_{Ad} \) with \( \rho_{Ad} \) leads to a coverage independent number for the ion impact desorption.

The ion induced desorption can be described analytically with the Winters and Sigmund theory [49] which treated the interaction of the ions with the adsorbates via elastic binary collisions. Three contributions to the total desorption cross section \( \sigma \) are distinguished. They are denoted with \( \sigma_I, \sigma_{II}, \sigma_{III} \) and are sketched in Fig. 2.7.

\[
\sigma = \sigma_I + \sigma_{II} + \sigma_{III} \quad (2.27)
\]

The first contribution \( \sigma_I \) is due to direct knock-off processes. The adsorbate is hit by the primary ion and desorbs either immediately or after an additional collision with substrate atoms. The second contribution \( \sigma_{II} \) is due to reflected ions, i.e. ions which enter the crystal, are scattered in the crystal and on their way out cause in a further collision the adsorbate to desorb. The third contribution to desorption \( \sigma_{III} \) is due to collisions by the outward flux of sputtered substrate atoms in consequence of the bulk collision cascade.

2.2.5 Molecular dynamics simulations

A powerful tool to investigate the ion-substrate interaction is molecular dynamics simulations (MD). For this reason, most experiments, which will be described in this thesis, are supplemented with MD simulations. They result from a collaboration between the group of Prof. Herbert M. Urbassek at the University of Kaiserslautern and the group of Prof. Thomas Michely at the University of Cologne. In the following paragraph the concept of molecular dynamics simulations is briefly described.

Although the exact MD simulation procedure depends on the experiment, the following features are usually valid. The Pt(111) crystallite consists of a large number of atoms (50000 or more) [25, 26] arranged in at least 15 layers. The Pt interatomic interaction is modeled with a many body interaction potential which is splined to a ZBL potential [34] at higher energies. The projectile-Platinum interaction is modeled to be purely repulsive. The simulation times are roughly 20 ps. This is long enough to get reliable results of damage patterns, sputtering- adatom-, and vacancy yields. Most simulations are performed at 0 K. If a finite temperature is required, velocity scaling is used. The calculations are performed in the following way. For fixed time steps the forces resulting from the interaction of the ion with the substrate are calculated. Afterwards the new velocities and the displacements are calculated. This calculation
is performed for all substrate atoms until the end of the simulation. Details of the molecular dynamics simulations procedure and results for the Pt(111) can be found in reference [25; 50–53].

2.3 Diffusion processes

Figure 2.8: Relevant diffusion processes after ion irradiation. The graph illustrates the diffusion of adatoms, surface vacancies, bulk vacancies, interstitials and implanted atoms. For further details see text.

Until now the production of defects by ion irradiation has been treated without taking into account that all experiments are carried out at a finite temperature. Fig. 2.8 shows a sketch of an ion impact which leads to the production of a large number of interstitials, adatoms and vacancies. The ion induced defects are situated at energetically less favored positions with a reduced number of nearest neighbors. If diffusion is thermally activated, the defects move in order to gain an energetically more favorable position. Fig. 2.8 shows a sketch of the relevant diffusion processes after ion irradiation. Inside the bulk interstitials and vacancies move, which leads to annihilation or clustering. The bulk defects can also anneal to the surface which leads to adatoms and vacancies. If surface diffusion is activated annealing and clustering of the adatoms and vacancies occur.

The diffusion of surface defects such as adatoms and vacancies can be fairly accurately described by a two-dimensional random walk on the lattice of preferential adsorption sites. The mean square displacement of a moving particle \( \langle (r(t) - r(0))^2 \rangle \) is linearly proportional in time \( t \). The proportionality factor equals to the mean square
2. INTRODUCTION TO THE ION-SURFACE INTERACTION

distance per jump $l^2$ times the jump rate $\nu$. This leads to equation 2.28

$$\langle (r(t) - r(0))^2 \rangle = \nu l^2 t = 4Dt$$ (2.28)

where the surface diffusion coefficient $D$ equals to

$$D = \frac{1}{4} l^2 \nu$$ (2.29)

The movement can be described by a transition from the initial state to a final state where the particle has to pass over a saddle point in configuration space. In between both states the atom has to overcome the diffusion barrier $E_D$. The jump rate $\nu$ can be expressed in terms of the universal Arrhenius law which is valid for thermally activated processes

$$\nu = \nu_0 \exp\left(\frac{-E_D}{k_B T}\right)$$ (2.30)

where $\nu_0$ equals to the attempt frequency and $k_B$ the Boltzmann constant. The attempt frequency is of the order of the surface phonon frequency of the substrate. In the case of Pt(111) $\nu_0$ has been measured experimentally by field ion microscopy and STM. A value of $\nu_0 = 5 \cdot 10^{-12} \pm 0.5$ 1/s has been deduced [54].

The question immediately arises at which surface temperature different diffusion mechanisms become relevant. Usually a process $i$ is considered to be relevant if the hopping frequency $\nu_i \geq 1$ Hz. This is reasonable if the surface morphology prepared by deposition of atoms from the gas phase or creation of defects by ion bombardment is also on the time scale of seconds. The onset temperature for a process with an activation energy $E_i$ (in eV) can then be calculated using formula 2.31.

$$T_{onset} = 400K/eV \times E_i$$ (2.31)

The first diffusion process which becomes thermally activated is the migration of interstitials. STM measurements performed by Morgenstern et al. [30] showed that, at a surface temperature of 22 K, interstitials, created by ion erosion, appear on the Pt(111) surface. The energy barrier $E_D$ and the attempt frequency $\nu_0$ have been estimated to be $E_D=50$ meV and $\nu_0 = 6 \cdot 10^{-11}$ s$^{-1}$.

In contrast to interstitials, bulk vacancy diffusion has a much higher activation energy. For single vacancies the onset temperature is roughly 500 K [55] and vacancy cluster diffusion requires a sample temperature of roughly 500 K-850 K [31] (The onset temperature depends on the cluster size).
2.3 Diffusion processes

In addition to bulk diffusion, the ion induced surface defects are also influenced by diffusion processes. The first surface diffusion processes which become thermally activated are single adatom, adatom cluster and vacancy diffusion as shown in Fig. 2.9 [processes (1)-(3)] together with the corresponding onset temperatures calculated with formula 2.31. Single adatom diffusion starts at 100 K whereas vacancy diffusion is activated at 180 K. Adatom cluster diffusion requires higher temperatures depending on the cluster size ($T_{onset}=160-390$ K). If the movable species on the flat terrace meet, clustering occurs which results in adatom and vacancy islands. Annihilation occurs if adatoms and vacancies meet.

The resulting adatom and vacancy islands which are produced by agglomeration of many atoms or vacancies are also influenced by diffusion at the step edges. The shape of the islands is therefore strongly temperature dependent (see reference [54] for details). The most important step adatom diffusion processes, together with the

<table>
<thead>
<tr>
<th>process</th>
<th>$T_{onset}$ [K]</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. adatom diffusion</td>
<td>100</td>
<td>[56; 57]</td>
</tr>
<tr>
<td>2. adatom cluster diffusion (sizes=2-7 atoms)</td>
<td>160-390</td>
<td>[58]</td>
</tr>
<tr>
<td>3. surface vacancy diffusion</td>
<td>180</td>
<td>[59]</td>
</tr>
<tr>
<td>4. step adatom diffusion</td>
<td>250-350</td>
<td>[60; 61]</td>
</tr>
<tr>
<td>5. full edge mobility</td>
<td>500</td>
<td>[62-64]</td>
</tr>
<tr>
<td>6. detachment from kinks</td>
<td>700</td>
<td>[65-67]</td>
</tr>
</tbody>
</table>

Figure 2.9: Diffusion processes of adatoms and vacancies relevant in ion erosion experiments. The onset temperatures are calculated from eq. 2.31.

2.3.1 Diffusion on the terrace and at step edges

In addition to bulk diffusion, the ion induced surface defects are also influenced by diffusion processes. The first surface diffusion processes which become thermally activated are single adatom, adatom cluster and vacancy diffusion as shown in Fig. 2.9 [processes (1)-(3)] together with the corresponding onset temperatures calculated with formula 2.31. Single adatom diffusion starts at 100 K whereas vacancy diffusion is activated at 180 K. Adatom cluster diffusion requires higher temperatures depending on the cluster size ($T_{onset}=160-390$ K). If the movable species on the flat terrace meet, clustering occurs which results in adatom and vacancy islands. Annihilation occurs if adatoms and vacancies meet.

The resulting adatom and vacancy islands which are produced by agglomeration of many atoms or vacancies are also influenced by diffusion at the step edges. The shape of the islands is therefore strongly temperature dependent (see reference [54] for details). The most important step adatom diffusion processes, together with the
corresponding onset temperatures, are shown in Fig. 2.9. At roughly 250 K, laterally twofold coordinated step edge atoms become mobile which is in the following denoted as step edge diffusion [process (4)]. Full edge mobility, i.e. creation of step adatoms from kinks starts at roughly 500 K [process (5)]. Detachment from kinks, which leads to an adatom lattice gas starts at 700 K [process (6)]. Many other diffusion processes at step edges, such as the motion of step adatoms around corners, can be found in reference [54].

2.3.2 Incorporation of adatoms and vacancies into step edges

The incorporation of surface vacancies into ascending steps is somewhat different to adatom incorporation as shown in Fig. 2.10. Adatoms exhibit no additional barrier to be incorporated into an ascending step i.e. the energy barrier is comparable to the energy barrier for terrace diffusion with an onset temperature of 100 K [process (1) in Fig. 2.10]. Vacancies, however, can only be incorporated into the step by moving an adatom from the step into the vacancy as illustrated in Fig. 2.10 [process labeled (2)]. This means that for a short time a laterally fourfold coordinated step edge atom has to break all lateral bonds in order to gain the vacancy position. This process requires a much higher activation energy and the onset temperature is roughly 600 K-700 K [68; 69]. In contrast, the incorporation of vacancies into lower terraces [process (3) in Fig. 2.10] is much easier since no bonds have to be broken. The process is very similar to the diffusion of single vacancies on the flat terrace where the same exchange mechanism occurs. The onset temperatures should therefore be similar, e.g. 180 K. Finally the incorporation of adatoms into descending steps has been studied extensively in the past by field ion microscopy. The studies showed that the adatoms are very often

Figure 2.10: Incorporation of adatoms and vacancies into step edges
2.3 Diffusion processes

reflected from descending step edges [process (4) in Fig. 2.10, the curved arrow indicates the reflection]. Ehrlich et al. [70] were the first to observe this process for tungsten adatoms on tungsten. This work was followed by Schwoebel et al. [71] who introduced a schematic potential energy landscape for adatoms at step edges. The ad-particles have to overcome an additional energy barrier, called Ehrlich-Schwoebel barrier, in order to jump over the step edge (whether the process is determined by jumps or by an exchange mechanism is often unclear). The jump rate $\nu'$ can again be expressed by an Arrhenius law with the corresponding attempt frequency $\nu'_0$ and energy barrier $E_S$.

$$\nu' = \nu'_0 \exp\left(\frac{-E_S}{k_B T}\right)$$

(2.32)

The additional energy barrier due to the step equals to

$$\Delta E_S = E_S - E_D$$

(2.33)

The attempt frequency is defined as the number of attempts by the adatom to cross the barrier. In that sense $\nu'_0$ is, in contrast to the attempt frequency on the terraces, a directed move. The additional energy barrier at the step edges strongly depends on the atomic structure of the step edge. Whereas a straight B-step (a microfacet on the \{111\}-plane) has a large energy barrier $\Delta E_{SB}$, a straight A-step (a microfacet of the \{001\}-plane) has, according to density functional theory calculations, a much lower energy barrier $\Delta E_{SA}$ [72]. Moreover, kink positions reduce the Schwoebel barriers significantly, since they provide an energetically low pathway to overcome the step edge. At last the energy barriers are all influenced by adsorbates present at the step edge as shown by Kalff et al. [73]. As a result, the determination of accurate numbers for $\Delta E_S$ is rather difficult [for further details see [54]].
2. INTRODUCTION TO THE ION-SURFACE INTERACTION

2.4 Grazing incidence ion erosion

2.4.1 Ion-surface interaction

![Graph showing maximum transverse energy versus projectile atomic number for different f.c.c. metals. The graph is labeled with the equation \( E_{\perp} = E_0 \cos^2 \theta_{\text{tot}} \) for calculating the critical angle for total reflection.]

Figure 2.11: Maximum transverse energy in order to achieve total reflection versus the projectile atomic number for different f.c.c. metals. The ion beam direction was parallel to the [110] direction. Graph from reference [74]. The table shows the critical angles for total reflection in the case of 5 keV ions on Pt(111).

Until now the discussion of ion induced defects has been limited to normal or near normal incidence, where extensive studies have been performed during the last decades and the available theories are mostly in good agreement with the experimental results. We will now focus on the regime of grazing incidence ion erosion where the analytical theories developed for sputtering usually break down.

In the literature the polar angle of incidence is sometimes denoted with respect to the surface normal and sometimes measured with respect to the surface. Therefore the angle measured with respect to the surface normal is always denoted as \( \theta \) and the angle measured with respect to the surface is denoted as \( \alpha \).

As already addressed in section 2.2.3, if the angle of incidence \( \theta \) between the ion and the surface becomes too large, the deposited energy per ion drops since the reflection coefficient increases. At roughly \( \theta = 80^\circ \) it reaches a value close to one. This is shown in Fig. 2.11 where the maximum transverse energy in order to achieve total reflection is plotted as a function of the atomic number of the projectiles for various fcc (111) substrates [74]. The calculations have been performed parallel to the [110] direction. From the maximum transverse energy, the critical angle for total reflection \( \theta_{\text{tot}} \) can be calculated from \( E_{\perp} = E_0 \cos^2 \theta_{\text{tot}} \). For Pt(111) and ions with \( E_0 = 5 \text{ keV} \) the values are tabulated in 2.11. Increasing the angle of incidence \( \theta \) even further leads to surface channeling since the repulsive potential of the individual atoms are smeared out. The
interaction of the ion with the substrate proceeds with many surface atoms via small angle binary collisions. Fig. 2.12 shows a sketch of the ion trajectories in the case of 1 keV Argon on Aluminum. For an angle of incidence of $\vartheta = 60^\circ$ measured from the surface normal [Fig. 2.12(a)], the ions are able to enter the crystal, since the overlap of the shadow cones which are generated at each atom is small. Large scattering events at individual atoms occur which result in terrace erosion. If the angle of incidence is changed to $\vartheta = 70^\circ$ [Fig. 2.12(b)] the overlap of the shadow cones becomes larger and the ions are not able to enter into the crystal. However, significant energy transfer still occurs since the trajectories of the reflected ions show a large spread. By changing the angle of incidence to $\vartheta = 80^\circ$ [Fig. 2.12(c)] the scattering proceeds specularly. No large scattering events occur which results in surface channeling.

Ions impinging at grazing incidence are therefore very surface sensitive and large scattering processes only occur at surface imperfections as for instance steps. This property can be used to study the morphology of single crystals with the help of glancing incidence ions. As an example, Fig 2.13 shows the intensity of 25 keV He$^+$ ions scattered from a Fe(001) surface as a function of the polar angle [75]. The angle indicates the deviation from the specular reflected beam which is set to zero. An angle of incidence of $\vartheta = 88^\circ$ - $89^\circ$ has been set. The reflected ions are collected under specular reflection with the help of a channeltron detector. The experimental results are supplemented with
2. INTRODUCTION TO THE ION-SURFACE INTERACTION

Figure 2.13: (a) Intensity of a 25 keV He$^+$ ion beam scattered from Fe(001) surface at a polar angle of $\vartheta=88.25^\circ$. The graph shows the experimental results (dots) and the results from computer calculations (solid curves). The sharp solid peak (where specular reflection (C) occurs) results from calculations assuming a flat surface at $T=0$ K. Peak C is broadened if temperature is included. The experimental curve can be well reproduced if steps are included in the calculation. The under-specular peaks (A),(B) are due to scattering at downward steps whereas peak (E) is due to scattering at upward steps. The different trajectories are shown in (b). Graph from reference [75].

Computer calculations based on the binary collision approximation which give insight into distinct features of the surface morphology. Specular reflection leads to one peak (peak C in Fig. 2.13) in the angular distribution of the reflected ions. However the experimental results show a much richer curve with ions scattered over-and under-specular. Ions hitting downward steps are deflected at a polar angle smaller than specular reflection (trajectories A and B), whereas upward steps lead to over-specular reflection (trajectory E). Scattering of ions at ascending steps leads to large scattering events. They are not captured in the measured intensity of the specular ion beam shown in Fig. 2.13. These experiments also show that the scattered ion signal significantly broadens due to the surface temperature (in this case the temperature was set to 600 K). Labanda et al. [5] showed that measuring the specular reflected ion current is a versatile tool to study the growth of thin films. In the case of layer by layer growth\(^1\),

\(^1\)In these experiments GaAs was deposited onto a GaAs substrate
the reflected ion current signal oscillates with a period of one monolayer in agreement with the Reflection High Energy Electron Diffraction oscillations. Surface defects as adatoms and step edges disturb the specular reflection of the ions on the flat terrace. Large scattering events occur and the ions are not reflected specularly. This results in a decrease of the reflected ion current. As soon as one layer is filled, the number of ascending step edges decreases and this results in an increase of the reflected ion current signal. The oscillations of the step density are mirrored in the oscillations of the scattered ion beam.

2.4.2 Subsurface channeling

Figure 2.14: Sketch of a grazing ion which enters between the first and the second layer of the crystal. The phenomenon is denoted as subsurface channeling.

Ions hitting ascending step edges under a grazing angle of incidence are able to enter the crystal where they are guided between two layers parallel to the surface. This is possible since the angle of incidence with respect to the strings or planes of the surface atoms is small. This phenomenon, denoted as subsurface channeling, is schematically shown in Fig. 2.14. The impinging ion enters the crystal and performs an oscillatory motion between the strings or planes of atoms of the first two layers. After some distance the ion dechannels. Subsurface channeling has already been described by Fujii et al. [76] who measured the reflection of swift He$^+$ ions (0.7 MeV) from a SnTe surface. With the help of Monte Carlo simulations the reflected ion current could be divided into two contributions; ions scattered from the topmost layer performing surface channeling and contributions resulting from subsurface channeling. The experimental results are shown in Fig. 2.15(a) where a 700 keV Helium beam is scattered under an angle of incidence of $\alpha=5$ mrad from a stepped SnTe(001) surface. By changing the azimuthal direction of the crystal a sharp peak in the total ion current at the dense packed [100] direction is observed. By performing computer simulations this peak could be attributed to ions entering the crystal at surface steps [Fig. 2.15 (a) (III)] whereas the rest of the signal is due to ions performing surface channeling [Fig. 2.15 (a) (II)].

Planar subsurface channeling has also been observed for 30 keV H$^+$ ions scattered from a rough SnTe surface [78]. Moreover subsurface channeling has been reported by Kimura et al. [77] who measured the energy distribution of the reflected Helium ions after they have been scattered from the surface [see Fig. 2.15(b)]. The energy
2. INTRODUCTION TO THE ION-SURFACE INTERACTION

Figure 2.15: (a) Calculated reflected ion yield for 700keV He\(^+\) ions impinging onto a SnTe(001) surface at an angle of incidence of \(\alpha = 5\) mrad measured from the surface plane. (I) shows the total ion current, (II) shows the contribution of the topmost layer, (III) shows the contribution of ions performing subsurface channeling. Graph from reference [76]. (b) Energy spectrum of the reflected 2 MeV He\(^{2+}\) ions from a SnTe(001) surface at an angle of incidence of 3 mrad. The peak at 1980 keV results from ions scattered from the surface layer. The peaks at 1940 keV and 1900 keV result from subsurface channeling. Graph from reference [77].

Spectrum shows three maxima where the high energy peak is attributed to ions which have scattered specularly from the surface layer. The other two peaks are attributed to ions which entered the crystal at an ascending step edge and performed subsurface channeling. The energy loss depends on the number of oscillations in the subsurface before dechanneling occurs. Energy loss measurements of highly charged ions impinging on a stepped Pt(110) surface performed by Robin et al. [79] also suggest the existence of subsurface channeling.

Recently Rosandi et al. [52] studied subsurface channeling for 5 keV Ar\(^+\) ions on Pt(111) by molecular dynamics simulations. Fig. 2.16 shows a simulation event where a 5 keV Argon ion hits a monoatomic ascending step edge. The direction of the ion beam was parallel to the [\(\overline{1}1\overline{2}\)] direction. The simulations were carried out at an angle of incidence of 83° with respect to the surface normal. Similar to swift ion bombardment, the ion is able to enter the crystal and perform subsurface channeling. The oscillation period equals to 24 Å with an energy loss of 22.5 eV/nm for well channeled projectiles.
2.4 Grazing incidence ion erosion

Figure 2.16: Sideview of a 5keV Ar\(^+\) single ion impact at an ascending step edge. The oscillatory motion of the projectile inside the channel is shown together with the ion induced adatom vacancy production on the surface. This is shown in the topview of 2.16(b).

During the movement of the ion in the channel, the energy transfer to the uppermost layer leads to periodic adatom and vacancy production as shown in Fig. 2.16(b).

The effect of temperature on subsurface channeling has also been investigated by molecular dynamics [33; 52]. Fig. 2.17 shows a typical result of such a simulation performed at 550 K. It was found that temperature reduces the mean channeling distance of the projectiles. This observation is, similar to bulk channeling, due to thermal vibrations of the substrate atoms. This increases the probability for large scattering events. Moreover, the periodic adatom vacancy production, as shown in Fig. 2.16, for 0 K, is lost. At the end of the channeling trajectory, i.e. at the dechanneling point, a big adatom vacancy cluster has been created. Moreover, one has to keep in mind that the damage shown in Fig. 2.17 does not take into account surface diffusion processes which act on a totally different timescale. The MD simulations follow the motion of adatoms and vacancies for 20 ps. Surface diffusion leads to coalescence or annihilation of the adatoms and vacancies.

The experiments and simulations discussed in this section show that a grazing ion beam is very sensitive to surface imperfections. The extent to which the large angle scattering events lead to ion induced morphology changes, sputtering in particular, will be discussed in the next section.
2. INTRODUCTION TO THE ION-SURFACE INTERACTION

Figure 2.17: Topview of a molecular dynamics simulation result of a 5keV Ar\textsuperscript{+} single ion impact at an ascending step edge. The angle of incidence was $\theta = 83^\circ$ with respect to the surface normal [33] and a surface temperature of 550 K was used.

2.4.3 Sputtering by grazing incidence ions

From the discussion of the ion-surface interaction under grazing incidence erosion it is somewhat clear that the sputtering yield will also depend on the roughness of the surface. Sputtering yield measurements in grazing incidence geometry have been carried out by molecular dynamics simulations and scanning tunneling microscopy by Friedrich et al. [25] and Hansen et al [26]. In particular, the effect of ascending step edges have been investigated.

The simulations showed that, for angles of incidence larger than the critical angle for total reflection $\theta_{\text{tot}}$, no sputtering on the flat terrace occurs. In contrast, at ascending steps the energy transfer to the crystal is very efficient and large sputtering yields are observed. The simulations showed that even a thermal spike is induced at the step edges, very similar to normal incidence ion erosion. Fig. 2.18 (a) shows a typical simulation result of an ion impact at an ascending step edge. The image is a top view of the simulation cell where at the impact point sputtering occurred and a large number of adatoms and vacancies were created.

Since terrace and step impacts lead to very different sputtering yields, the ion beam can be split into two classes of trajectories. The first class consists of ions hitting an ascending (illuminated) step edge either indirectly, after reflection from the lower terrace [trajectory 1 in Fig. 2.18(b)], or directly [trajectory 2 in Fig. 2.18(b)]. The second class consists of all other ions from which the majority consists of ions hitting the terrace [trajectory 3 in Fig. 2.18(b)]. Also, ions approaching the surface at or close to descending steps, belong to this class. The distance of the ion penetration point through the plane of the upper terrace layer nuclei [dashed horizontal line in Fig. 2.18(b)] to the step edge atom nucleus is labeled by $\xi = x/\Delta x$ (where $x$ denotes
Figure 2.18: (a) Molecular dynamics result of a single ion impact at an ascending step edge. The resulting vacancy island at the step edge is surrounded by a ring of adatom clusters. Graph from ref.[25]. (b) Sketch of the geometrical model proposed by Friedrich et al.. Direct step impacts (2), step impacts after specular reflection (1) and terrace impacts (3) are indicated. (c) Step edge sputtering yield measured by molecular dynamics simulations for 5 keV Ar$^+$ ions impinging at 83°. The plot shows the dependence of $Y_{step}$ as a function of the impact point $\xi = x/\Delta x$. Direct impacts (2) and indirect impacts (1) lead to large sputtering yields. Terrace impacts (3) do not induce sputtering. Decrease between $\xi=-5..-11$ results from subsurface channeling. Graph from ref. [26].

The distance measured from the step and $\Delta x$ equals to the interatomic spacing along the projectile direction). All ions with $\xi \in [-x_c,0]$ belong to the first class. Here, $x_c$ characterizes the width of the zone of influence; with $\Delta h$ being the step height. From geometry $x_C$ can be simply calculated.

$$x_C = 2 \cdot \Delta h \cdot \tan \vartheta$$  \hspace{1cm} (2.34)

The ions of the first class enter the zone of influence in front of an illuminated step edge. Thus, they hit the step edge and cause step edge sputtering with a yield $Y_{step}$. 

2. INTRODUCTION TO THE ION-SURFACE INTERACTION

For all other ions a terrace impact takes place with a low sputtering yield $Y_{\text{terr}}$. If $A_{\text{step}}$ is the fractional area of the zones of influence of the ascending steps, $1 - A_{\text{step}}$ is the fractional area of the remaining surface. With these definitions the average sputtering yield $\bar{Y}$ is simply

$$\bar{Y} = A_{\text{step}} Y_{\text{step}} + (1 - A_{\text{step}}) Y_{\text{terr}}$$  \hspace{1cm} (2.35)

Note that $\bar{Y}$ is identical to the average erosion rate

$$\bar{Y} = \frac{d\Theta}{dF},$$  \hspace{1cm} (2.36)

if the eroded amount $\Theta$ and the ion fluence $F$ are measured in monolayers (ML) and monolayer equivalents (MLE) $^1$, respectively. Hansen et al. deduced an average step edge sputtering yield $Y_{\text{step}} = 8.4 \pm 1.5$ and an average terrace sputtering yield of $Y_{\text{terr}} = 0.08 \pm 0.03$ for the case of 5 keV Ar$^+$ erosion at 83° on Pt(111) by applying formula 2.35. Molecular dynamics simulations for the same set of parameters deduce a step edge sputtering yield of $Y_{\text{step}} = 8.3$ and $Y_{\text{terr}} = 0$. However, as shown in Fig. 2.18(c), the step edge sputtering yield is far from being constant over the length of the zone of influence $x_C$. The ion impact point $\xi$ has been continuously varied from $\xi = 0$ to $\xi = -x_C$. For low values and large values of $\xi$ the sputtering yield is large, however, for $\xi \in [-5, -11]$ the sputtering yield drops to almost zero. The physical mechanism responsible for this drop has first been described by Friedrich et al. $^2$, who attributed this to subsurface channeling. The energy transfer to the crystal lattice is drastically reduced, compared to direct impacts, since no large scattering events occur. As a consequence the sputtering yield is reduced. At this point of time, it was not clear whether this decrease, due to subsurface channeling, is only a “zero kelvin” molecular dynamics simulations effect or also apparent in the experiments.

A detailed investigation of the sputtering yield on Pt(111) for different angles of incidence and different azimuthal directions will be presented in chapter 5.

2.5 Pattern formation by ion erosion

In the last part of this chapter the temporal evolution of the surface during ion erosion will be discussed. It is well known that after prolonged ion bombardment surface roughening occurs which is often accompanied by self organized periodic patterns. The resulting morphology strongly depends on the experimental parameters such as type of substrate, ion energy, angle of incidence and temperature. One of the first experiments where self-organization by ion erosion was observed was performed by Navez et al. $^6$ who bombarded a glass substrate with charged air molecules. As shown in Fig. 2.19,

$^1$The ion fluence $F = f \cdot t$ (flux \times erosion time) is measured in MLE where one MLE equals to the areal density of surface layer atoms on Pt(111) $\left(1.504 \times 10^{19} \text{atoms/m}^2\right)$
Figure 2.19: Ion erosion on a glass substrate with 4 keV air molecules for a duration of 6 hours for different angles of incidence measured with respect to the surface normal. (a) experimental setup, (b) 30°, (c) 0°, (d) 80°. The direction of the ion beam is indicated with a white arrow. Graph from ref. [6].

the ion induced morphology strongly depends on the angle of incidence. Whereas for normal incidence ion erosion the morphology consists of a dot-pattern, the experiments at 30° and 80° show a regular spaced ripple pattern. The orientation of the ripples at 30° is perpendicular to the ion beam direction, whereas grazing incidence ion erosion leads grooves parallel to the beam direction.

These early observations have been confirmed for many different ion substrate combinations where usually for normal or near normal incidence regular dots [80; 81] or pits [66] are formed, whereas off normal incidence leads to a periodic ripple pattern. In agreement with the observations by Navez, off normal incidence leads to ripples orientated perpendicular to the ion beam direction [82] and grazing incidence to ripples parallel to the beam direction [7–11].

In the literature the destabilization of the surfaces by ion erosion is treated in two different ways. The morphological evolution is either explained by elementary atomic processes or by continuum theories. For single crystal materials, which during ion erosion stay crystalline, the morphological evolution near normal incidence is in most cases
explained with elementary atomic processes \([67; 68; 83–91]\). On the other hand pattern formation on amorphous substrates or substrates which upon ion erosion amorphize, e.g. semiconductors, are usually interpreted with the help of a continuum theory (for a recent review see \([9]\)). In the following the two approaches are briefly described. Afterwards pattern formation through grazing incidence ions on Pt(111) is presented in detail.

2.5.1 The Bradley-Harper theory

In Fig. 2.20(a) an ion impact onto a curved surface is sketched. The angle of incidence with respect to the surface normal equals to \(\vartheta\) and the position of the impact point is denoted with \((x_0, y_0)\). Sigmund's theory of sputtering \([44]\) is now applied and the kinetic energy \(E\) of the ion is distributed to many substrate atoms. The distribution...
is described by a Gaussian function. The center is located at a distance $R$ from the surface and the width and height are denoted with $b$ and $a$. In a coordinate system $(z, \zeta)$, where $z$ is chosen parallel to the beam direction and $\zeta$ perpendicular to the beam direction, the energy distribution can be described by:

$$E(z, R) = \frac{\epsilon_0}{(2\pi)^{3/2}} \exp \left( -\frac{(z - R)^2}{2a^2} - \frac{\zeta^2}{2b^2} \right)$$

As shown in Fig. 2.20 (a) an ion impact at the position $(x_0, y_0)$ deposits energy not only at $(x_0, y_0)$ but also at other places of the crystal surface, for instance $(x, y)$. Energy deposition at the surface leads to sputtering. The temporal evolution of the height $\frac{\partial h}{\partial t}$ at the position $(x, y)$ is calculated by adding up the whole deposited energy of all ions hitting the substrate at $(x_0, y_0)$.

Under the assumption that the surface curvature is much larger than the influenced area of one ion impact, the temporal evolution of the height can be solved analytically. A detailed evaluation can be found in reference [92] or review articles by Valbusa et al. [8] and Chan et al. [9]. The result of this calculation is shown in equation 2.38.

$$\frac{\partial h}{\partial t} = -v_0 + \frac{\partial v_0}{\partial \vartheta} \frac{\partial h}{\partial x} + v_x \frac{\partial^2 h}{\partial x^2} + v_y \frac{\partial^2 h}{\partial y^2}$$

The Cartesian coordinate system is used in the differential equation and indicated in Fig. 2.20(b). The erosion rate is denoted with $v_0$ which depends on the angle of incidence $\vartheta$. The parameters $v_x$ and $v_y$ depend on the ion beam parameters such as, for instance, the ion penetration depth, the width of the collision cascade etc. The main result of this equation is that the change in height is a function of the local curvature on the surface. This is illustrated in Fig. 2.20(b) where a curved surface is shown together with some ion impacts indicated with their energy distribution. The change in height on the hill, which is denoted with $\Delta h_H$, is determined by the sum of all surrounding ion impacts $\Delta h_{H1} + \Delta h_{H2} + \Delta h_{H3}$. The same is valid for ion impacts in the valley of a curved surface where $\Delta h_{V1} + \Delta h_{V2} + \Delta h_{V3}$ determines the change in height. Comparing the two sums shows that the distance is smaller in the valley than on the hill which is the geometrical interpretation of equation 2.38. The important message is that the valleys are eroded faster than the hills.

Diffusion is incorporated by BH with the Herring and Mullins approach [93; 94] who showed that for mildly curved surfaces that the rate of height change on the surface is proportional to the divergence of the curvature 2.39.

$$\frac{\partial h}{\partial t} = -B \nabla^4 h$$

The proportionality factor $B$ is a function of the surface diffusion coefficient, the average
number of diffusing particles and the surface free energy. The evaluation is only valid for isotropic amorphous substrates since for example the effect of steps is completely ignored. The combination of equation 2.38 and 2.39 leads to the basic formula deduced by Bradley and Harper:

\[ \frac{\partial h}{\partial t} = -v_0 + \frac{\partial}{\partial \vartheta} \frac{\partial h}{\partial x} + v_x \frac{\partial^2 h}{\partial x^2} + v_y \frac{\partial^2 h}{\partial y^2} - B \nabla^4 h \]  

(2.40)

By converting equation 2.40 in Fourier space, the time dependence of each wave vector can be calculated. If one assumes that the initial surface, which has a very low roughness, is described by a large number of wave vectors then eq. 2.40 yields the time dependence of each component. The wavelength, which has the largest velocity is the one, which after prolonged ion erosion, dominates the surface morphology. One of the main results of this equation is that it predicts a rotation of the ripple pattern from perpendicular to the beam direction at off normal incidence to parallel to the beam direction in the case of grazing incidence. This is in accordance with many experimental findings. Moreover, the theory predicts that for a certain temperature a fluence independent wavelength results whereas the roughness increases exponentially with erosion time. This situation has been observed for a variety of substrates. However, on crystalline materials a number of experiments show that the ripple wavelength depends on the ion fluence \[7; 9; 10\]. This can not be explained by the BH theory. In these experiments, the wavelength increases with ion fluence according to a power law behavior. Attempts have been made to incorporate these effects into the BH theory by adding higher order terms in equation 2.40. However a analytical model which covers all observed phenomena is still not available. Therefore, a second approach which is based on atomistic processes is discussed in literature and is presented in the next section.

2.5.2 Pattern formation, an atomistic approach

In the case of Pt(111), the different morphologies after ion erosion at normal incidence with 1keV Xenon ions and 5keV Argon erosion at grazing incidence (\(\vartheta = 83^\circ\)) are shown in figure 2.21. The morphology changes from a regular spaced pit pattern to a groove pattern parallel to the ion beam direction. The physical mechanisms responsible for destabilization at normal incidence can be summarized as follows [66]: at sufficiently high temperatures the ion induced surface vacancies diffuse over the surface and agglomerate to stable big vacancy islands. The presence of a step edge barrier for vacancies, as discussed in section 2.3.2, promotes the nucleation of new vacancy islands at the bottom of the structures. This leads to an overall downhill flux of vacancies at the step edges since the number of vacancies which anneal at a descending step exceeds the number of vacancies which are incorporated into ascending steps [Fig.2.21(c)]. Moreover
2.5 Pattern formation by ion erosion

adatoms formed during ion erosion can be quickly incorporated into ascending steps but the Schwoebel-barrier (see section 2.3.2) prevents incorporation into descending steps. This leads to an adatom uphill current which is equal to a downhill vacancy current [Fig. 2.21(d)]. Ion induced roughening, i.e. destabilization, at moderate temperatures is therefore governed by the existence of step edge barriers.

At higher substrate temperatures (in the case of Pt(111) higher than 700 K) the ion induced roughening diminishes and the surface stays flatter. This can be attributed to the onset of kink detachment which results in an adatom lattice gas formation. The annealing of most surface vacancies becomes very efficient which keeps the surface flat. These atomistic processes, which have mostly been derived from normal incidence ion erosion, can also be used to explain destabilization in grazing incidence ion erosion experiments which will be discussed in the forthcoming section.

2.5.3 Pattern formation through grazing incidence ions on Pt(111)

A detailed investigation of pattern formation through grazing incidence ions has been performed by Hansen et al. [10] with the help of scanning tunneling microscopy and molecular dynamics simulations. Fig. 2.22 shows an experimental series performed with a fixed ion fluence of 20 MLE, an angle of incidence of 83° and 5 keV Ar⁺ ions. The surface temperature has been varied from 250 K to 720 K. The experiments performed at temperatures between 250 K and 625 K show a regular spaced three dimensional
ripple pattern oriented parallel to the direction of the impinging ions (in this case the [\bar{1}12] direction is used). At 720 K [Fig. 2.22(f)] the resulting morphology is almost flat. The number of open layers is small and no periodic pattern is visible in the STM topography. The analysis of the dominant wavelength shows that two distinct regimes of pattern formation can be identified. For surface temperatures between 250 K and 450 K the ripple wavelength is temperature independent [Fig. 2.22 ((a)-(c))]. The second regime, at surface temperature between 450 K and 700 K shows an increase of the ripple wavelength with increasing temperature. Finally above 700 K no more ripple patterns are induced by the ion beam. The roughness analysis of the temperature dependent morphological evolution shows a continuous increase from 100 K (data not shown) to 550 K. For higher temperatures the roughness decreases rapidly. This leads to an overall bell shaped curve.

These measurements can be explained as follows: The ion induced instability re-
2.5 Pattern formation by ion erosion

sults, in analogy to normal incidence ion erosion, from step edge barriers present on Pt(111). As already discussed in the preceding section and visualized in Fig. 2.21, the step edge barrier for vacancies promotes preferential nucleation at the bottom of the structures, i.e., a downward vacancy flux. The step edge barrier for adatoms depends on the atomic structure of the step. For the experiments performed at low temperatures the Schwoebel barrier is not relevant since the ion erosion had been performed parallel to the [1\overline{1}2] direction. This leads to step edges with a high number of kinks which provide a low energetic pathway for adatom migration over step edges. The destabilization is only governed by the existence of a step edge barrier for vacancies. The roughness of the resulting morphology is low. Increasing the temperature leads to an increase of step edge diffusion which reduces the number of kinks. At 550 K [Fig. 2.22(d)] the ripples even start to deviate from the ion beam direction where clear portions of <110> oriented steps are visible. Dense packed steps have a significant step edge barrier. Destabilization is enhanced since the step edge barrier for vacancies and the Schwoebel barrier are active. As a consequence the roughness increases. At 650 K vacancy incorporation into ascending steps starts. This decreases the destabilization mechanism which decreases the surface roughness. Finally at temperatures larger than 720 K adatom lattice gas formation becomes relevant and the ripple pattern vanishes. The surface destabilization and the increase of roughness can therefore be understood with the same mechanisms as for normal incidence ion erosion. The continuum approach cannot be used to explain the surface destabilization on Pt(111). The sputtering yield is close to zero for terrace impacts and comparable to normal incidence ion erosion at step edges (no curvature dependent sputtering yield, see section 2.4.3). Already after less than one monolayer of removed material a ripple pattern develops (this will be shown in this section) which is not in accordance with the Bradley Harper theory, where a much longer induction time is needed. At last for a fixed temperature, the wavelength of the ripple patterns increases with increasing ion fluence. The continuum approach predicts a fluence independent wavelength for a fixed temperature.

A clear difference between grazing incidence and normal incidence ion bombardment is the resulting morphology. Pits are formed at normal incidence and ripples are formed at grazing incidence. Therefore the onset of ripple pattern formation has been investigated and a small part of the experimental series is shown in Fig. 2.23. The morphologies after an ion fluence of 0.5 MLE at a surface temperature of 450K [Fig. 2.23(a)] and at 550K [Fig. 2.23(b)] are shown. In both cases the angle of incidence has been set to 83° and 5 keV Argon ions have been used. For 450 K the terrace and the ascending step edges show elongated grooves oriented parallel to the ion beam direction. This can be understood as follows. Although sputtering on the flat terraces is small, a small fraction of the impinging ions create adatom and vacancy clusters. A subsequent impact at the vacancy cluster leads to sputtering. The vacancy
2. INTRODUCTION TO THE ION-SURFACE INTERACTION

Figure 2.23: Morphology of Pt(111) after an ion fluence of 0.5 MLE at (a) 450 K, (b) 550 K. The ion beam direction is indicated with a white arrow. The image sizes are $1650\,\text{Å} \times 1650\,\text{Å}$, (c) sketch of vacancy groove formation at 450 K, (d) sketch explaining the positional alignment of the vacancy islands at 550 K. (a) and (b) from reference [10]

is elongated in the direction of the ion beam as shown in the sketch of Fig. 2.23(c). An elongated vacancy cluster and a rim of adatoms is visible. Step edge diffusion of one and twofold coordinated step atoms is activated which smoothens the rough step edges. Full edge mobility is not active which means that the global shape of the ion induced vacancy clusters stays unchanged. As a result subsequent ions are able to form elongated structures as shown in the sketch of Fig. 2.23(c). This is the physical reason for the appearance of the elongated vacancy grooves in ion beam direction visible in the STM topography of Fig. 2.23(a).

The situation is different for 550K, where the surface consists of small hexagonally shaped vacancy islands. No elongated vacancy grooves are visible on the surface. However, the vacancy clusters are not randomly distributed on the surface but show a positional alignment in ion beam direction. The physical interpretation of the tran-
Pattern formation by ion erosion

formation from vacancy grooves to compact hexagonal islands can be traced back to the onset of full edge mobility at 550 K. The ion induced vacancy clusters are very efficiently reshaped and the step edges are oriented along dense packed $<110>$ directions. The positional alignment of the vacancy islands can be traced back to subsurface channeling which has already been discussed in Section 2.4.2. A possible scenario for the positional alignment of the vacancy clusters is sketched in Fig. 2.23(d). Ions hitting the flat terrace have a very low sputtering yield. However, adatom and vacancy production is possible which eventually results in stable vacancy clusters [situation 1. in Fig. 2.23(d)]. An ion that hits the illuminated step edge of the cluster performs subsurface channeling. This leads to damage production on the surface [see Fig. 2.16]. At the dechanneling point, which usually consists of a large scattering event, enough energy is transferred to the crystal in order to produce a new stable vacancy cluster [situation 2. in Fig. 2.23(d)]. This cluster grows by subsequent impacts [situation 3. in Fig. 2.23(d)] until a new channeling event occurs which leads again to a vacancy cluster aligned in ion beam direction [situation 4. in Fig. 2.23(d)].

In order to study the positional alignment in more detail angular dependent measurements have been performed [33]. By changing the angle of incidence from $83^\circ$ to $79^\circ$ the influence of subsurface channeling could be diminished. The result is shown in Fig. 2.24 where a fluence dependent measurement for both angles of incidence is visible. After an ion fluence of 0.5 MLE at $83^\circ$ [Fig. 2.24(a)] a positional alignment of the vacancy clusters, similar to Fig. 2.23(b), is observed. Increasing the fluence to 1 MLE leads to a preferential coalescence in ion beam direction. The small vacancy clusters have grown to big vacancy islands. Since they are positioned in ion beam direction coalescence takes place mainly in the same direction (the anisotropy is well visible in the power spectral density shown in the inset of Fig. 2.24(b)). For even larger ion fluences [Fig. 2.24(c)] a three dimensional ripple pattern is observed already quite similar to the Fig. 2.22 where a fluence of 20 MLE was used.

Ordering of the vacancy grooves in the direction normal to the ripple ridges is caused by vacancy depletion in the terraces between the grooves and the adatom repulsion effect. Details can be found in [10].

In contrast to the experiments at $83^\circ$, the experiment at $79^\circ$ [Fig. 2.24(d)] shows no positional alignment of the vacancy clusters. The image shows a similar amount of removed material, however the clusters are randomly distributed. At larger ion fluences [Fig. 2.24(e)] all vacancy clusters have grown due to sputter erosion and coalescence starts. No preferential orientation is observed in the STM images and in the power spectral density. Higher ion fluences [Fig. 2.24(f)] lead to a three dimensional ripple pattern with a reduced grade of quality compared to $83^\circ$. The ripples have a large number of defects.

It can be concluded that the alignment of a three dimensional ripple pattern is
2. INTRODUCTION TO THE ION-SURFACE INTERACTION

Figure 2.24: STM topographs of Pt(111) after exposure to (a) 0.5 MLE, (b) 1.0 MLE, (c) 2.0 MLE, (d) 0.25 MLE, (e) 0.5 MLE and (f) 1.0 MLE of 5 keV Ar$^+$ at 550 K. The ion beam has an angle of incidence with respect to the surface normal of (a)(c) $\vartheta=83^\circ$ and (d)(f) $\vartheta=79^\circ$. The ion exposures were chosen to yield similar eroded amounts in each row. The direction of the ion beam is indicated by a white arrow in (a). All steps visible are of monolayer height. The image size is always $2200\,\text{Å} \times 1800\,\text{Å}$. Insets: power spectral densities of the topographs shown. Graph from reference [33].

significantly influenced by subsurface channeling which initiates a positional alignment of the vacancy clusters at low ion fluences. This alignment of the vacancy islands promotes coalescence in ion beam direction. At higher ion fluences a three dimensional ripple pattern is formed induced by the step edge barriers for adatoms and vacancies.

In order to corroborate the existence of subsurface channeling a series of single ion impact experiments at 350 K have been performed [33]. The damage at illuminated step edges has been analysed. In Fig. 2.25 the result of such an experiment is shown. The experiment has been performed in two steps. First, high temperature sputtering
2.6 Open questions:

The preceding discussion gives rise to a number of questions:

1. Molecular dynamics simulations of single ion impacts performed at 0 K show aligned adatom vacancy production during subsurface channeling. There is a need for low temperature single ion impacts in order to study the surface damage in detail. The results are presented in chapter 4.

2. Molecular dynamics simulations suggest that the sputtering yield is influenced by subsurface channeling. Changing the impact position at the step edge changes the
sputtering yield significantly. Direct impacts and impacts after reflection at the lower terrace show large sputtering yields. However, ions hitting the bottom of the step edge perform subsurface channeling and the sputtering yield decreases. The question arises whether this is only a “zero kelvin” molecular dynamics effect or whether the sputtering yield depends on the subsurface channeling probabilities. An experimental and molecular dynamics study has been performed and the results are presented in chapter 5.

3. What about impacts at single adatoms or at small adatom clusters? Is the sputtering yield at these defects also enhanced in comparison to the terrace sputtering yield? Chapter 6 shows experimental results in order to clarify this issue.

4. There is a discrepancy between terrace sputtering yields in molecular dynamics simulations and experiment. MD measures no terrace sputtering yield at 83°. However, pattern formation has been demonstrated experimentally. The question arises whether adsorbates influence the terrace sputtering yield. This issue is addressed in Chapter 7.

5. Finally, chapter 8 shows how coarsening of the ripple patterns through grazing incidence ion erosion takes place.
Chapter 3

Experimental Setup

3.1 The vacuum system

The experiments described in this thesis are performed in a ultra high vacuum variable temperature scanning tunneling microscopy apparatus with a base pressure in the low $10^{-11}$ mbar range. A sketch of the chamber is shown in Fig. 3.1. The system is briefly described in the following. A more detailed review can be found in [32; 95].

A stainless steel chamber (1) is mounted on a frame (2) which is connected to the ceiling via four springs (3). The springs act as very efficient mechanical vibration isola-
tion damping due to their low resonance frequency ($\leq 0.5$ Hz). During the experimental procedure, i.e. sample preparation and ion erosion experiments, the chamber is fixed to the ground via four posts (4). During the STM imaging, the chamber is disconnected from the ground and thereby decoupled from most mechanical vibrations.

In order to keep the pressure in the chamber as low as possible a number of different pumps are used. The backbone of the pumping system consists of a turbo molecular pump (5) and an ion getter pump (6). The necessary fore-vacuum for the turbo pump is generated via a rotary vane pump. A titanium sublimation pump (8), which is embedded into a large cold trap (7a) is also part of the vacuum system. Moreover a non-evaporable getter pump (9) is connected to the chamber. A second smaller cold trap (7b), which surrounds the STM (25), is filled during STM imaging. It efficiently decreases the local pressure at the sample since most trajectories of the residual gas molecules are blocked. The sample stays free of adsorbates for a longer period.

Inside the vacuum system the sample (10) is mounted on a sample holder (11) which is mounted on a big stainless steel block (12). The block which rests on Viton pieces is part of a large aluminum manipulator (13). The Viton pieces improve the vibrational isolation damping. The cooling of the sample is accomplished via an evaporator cryostat (15). The cryostat is connected to the sample holder via a flexible copper braid.

In order to perform grazing incidence ion bombardment a differentially pumped ion gun (16) is mounted horizontally on the chamber. The ion gun setup is sketched in Fig 3.2. For ion erosion experiments, the ion source is backfilled with noble gas atoms which are ionized (28) and accelerated towards the sample (10). The Wien-filter (27) selects the ions according to their mass/energy ratio and afterwards the deflection unit (26) scans the ions over the entire sample.

The ion current can be measured with a Faraday cup (14) mounted on the manipulator. As in most UHV chambers, a residual gas analyzer (QMS) is available. The QMS is mounted on a one inch manipulator (19) in order to approach the ionization volume to the sample. This is necessary for the Thermal Desorption Spectroscopy (TDS) experiments. The sensitivity of the QMS is increased with the help of a gold plated shield (20) which surrounds the ionization volume [96]. A 5.5 mm hole at the front end of the shield assures that only the gases which desorb from the sample are measured during TDS. Moreover, the ionization probability of these gases is increased due to the shielding.

The UHV chamber is equipped with two gas inlet systems. The first dosing system consists of a long thin glass tube (21) which is connected to the chamber via a leak valve (22). A small gold plated reservoir (23) is connected to this valve as shown in Fig. 3.1. It can be filled with gases and the pressure insight the volume is controlled with a spinning rotor gauge (24). This inlet system is particularly useful if small amounts of gases (well below 1 monolayer) have to be deposited with a high accuracy onto the
3.2 The sample holder

The sample holder of a UHV scanning tunneling microscopy apparatus has to fulfill a number of prerequisites.

1. It has to be mounted mechanically rigid, in order to achieve a high STM resolution.

2. The thermal conductivity of the sample holder to the cryostat has to be as large as possible in order to reach low temperatures.

3. Special care has to be taken to minimize the heat losses from the sample to the environment.

4. The scanning tunneling microscope used in this thesis is a homebuilt inverted
3. EXPERIMENTAL SETUP

Figure 3.2: (a) Cross section through the UHV chamber. The ion gun, the sample holder, the wobble-stick and the Pt evaporator are shown. (b) Enlargement of the dashed box shown in Fig. 3.2(a). The tilt mechanism of the sample holder is illustrated. Original drawing from reference [32] modified to the current setup. Details see text.

beetle-type STM [97–99]. As a consequence the sample holder needs three small ramps which are necessary for the coarse approach of the STM to the sample.

5. During the heating cycles the outgassing rate of the sample holder has to be as low as possible in order to stay at a low pressure during the cleaning process.

The first point to be addressed is the mechanical stability. The sample holder, as it had been used in [32] was made from copper and showed a good mechanical stability for room temperature experiments. However, low temperature experiments were hardly possible since here the evaporator cryostat has to be filled with liquid nitrogen or liquid helium in order to decrease the sample temperature. The cooling process leads to mechanical vibrations which are well distinguishable in the STM images and which prevent high resolution images.

In order to increase the resolution of the STM at low temperatures the three outer piezos of the beetle STM, which are in contact with the sample holder, are equipped with small magnets. They are glued in between the piezos and the steel balls. The steel balls, which are in contact with the sample holder, are magnetized. If the sample holder material is magnetizable an attractive force between the piezos and the holder results which increases the contact pressure. This concept has been introduced by Rost et al. [100] and is a very efficient method to increase the mechanical stability of the STM without increasing the STM mass (which decreases the resonance frequency of the piezos).
3.2 The sample holder

Magnetizable stainless steel (as for instance EN 1.4021) is a good material from which a sample holder can be fabricated. It is UHV compatible and relatively easy to process mechanically. The drawback of a pure stainless steel sample holder is the bad thermal conductivity. Therefore only the ramps have been fabricated from stainless steel and the rest is made from oxygen free high conductivity copper (OFHC). This concept combines the good mechanical stability without losing the good thermal conductivity of copper. The top view of the new sample holder is shown in Fig. 3.3(a). The Pt(111) single crystal (1) is fixed with three tungsten leaf springs (2). The three stainless steel ramps (3) are fixed to the copper part of the sample holder (4) by stainless steel screws (5). As illustrated in the sketch of Fig. 3.3(b), the two parts of the holder are fixed on the backside with a screw (5), two screw nuts and a spring washer (6). The thermocouples, which have been spot welded to the sample, are guided through the sample holder with the help of Aluminum oxide tubes (7).

Fig 3.4 shows the improvement of the STM resolution due to the enhanced mechanical stability. All three images are raw data. Imaging has been performed at (a) 120K, (b) 105K, (c) 18K. Fig. 3.4(a) shows an STM image recorded during liquid nitrogen cooling (here the lowest possible temperature was 120 K) and the sample holder was made from copper (old setup). A big hexagonal vacancy island together with a profile analysis is shown. The root mean square deviation of the vibrations equals to roughly 0.6 Å.

Figure 3.3: (a) Topview of the new sample holder design. (b) Side view of the sample holder with the copper braid attached to the sample holder and the cryostat, details see text.
In contrast to the pure copper sample holder, STM imaging with the new sample holder [Fig. 3.4(b)] shows a reduction of the noise by a factor of six, i.e. 0.1 Å root mean square deviation. The last Fig. 3.4(c) shows the performance of the new sample holder with liquid helium cooling. The resolution is again improved by a factor of two (liquid helium cooling produces less vibrations in the evaporator cryostat). The image shows the Pt(111) crystal in atomic resolution imaged at 18 K.

The second condition to be fulfilled is a good thermal conductivity from the cryostat to the sample holder. For this purpose a flexible braid has been fabricated from roughly 700 high purity cooper wires with a diameter 0.125 mm. The braid is shown in Fig. 3.3(b) (8). The contact to the sample holder and to the cryostat is done in the same way as the connection of the ramps to the copper part of the holder, i.e. a screw, two screw nuts and a spring washer. The lowest possible temperature which can be achieved is 105 K with liquid nitrogen cooling and 18 K with liquid helium cooling. The temperature calibration has been performed with the help of thermal desorption spectroscopy of noble gases from the Pt(111) crystal (for details see Appendix A.2).

The third issue deals with the minimization of the heat sinks. No major changes have been performed during this thesis and the reader is referred to [32; 101] for details.
The last important property of a sample holder is the low outgassing rate of the material during heating. Whether a surface is clean depends crucially on the base pressure increase during flash annealing. In order to decrease the outgassing rate of the sample holder, all parts have been degassed in a separate vacuum chamber under UHV conditions (for details see Appendix A.1). In order to check the cleanliness of the stainless steel/copper holder, the outgassing has been recorded with the residual gas analyzer during flash annealing of the Pt(111) sample to 1273 K. Two different

![Figure 3.5: Partial pressure increase of the most prominent gas species during flash annealing of the Pt(111) sample to 1273 K. (a) with pure iron sample holder, (b) with stainless steel/copper sample holder. The recorded gas species are, 2 a.m.u \equiv H_2, 28 a.m.u \equiv CO, 16 a.m.u \equiv CH_4, 44 a.m.u \equiv CO_2, 18 a.m.u \equiv H_2O.](image)

sample holders are compared. Fig. 3.5(a) shows the outgassing of pure iron sample holder which has been used during an intermediate stage of this thesis and Fig. 3.5(b) shows the outgassing from the stainless steel/copper holder. The most prominent gas species are recorded during flash annealing. In both cases the base pressure prior to the heating cycle was in the $10^{-11}$ mbar range. Only relative changes are analyzed due to the different sensitivity of the residual gas analyzer in both experiments. The partial pressure increase for hydrogen $\Delta p_{H_2}$ (green curve) stays roughly constant for both holders and equals to a factor of 11 in case (a) and 9 in case (b). The most important difference is the increase of the carbon monoxide partial pressure $\Delta p_{CO}$ (red curve). Whereas the CO increases by a factor of 16 in case (a) (the iron sample holder), an increase by a factor of 6 is measured for the stainless steel/copper holder. The total base pressure increase with the new sample holder equals roughly $1.5 \cdot 10^{-10}$ mbar, the pressure increase in example (a) equals to $2.0 \cdot 10^{-9}$ mbar. As a result, a clean sample, where no impurities are visible with STM, could only be achieved with the stainless steel/copper sample holder.
3. EXPERIMENTAL SETUP

3.3 The Platinum evaporator

![Image showing the Platinum evaporator](image)

Figure 3.6: The image shows the home built Pt evaporator used in this thesis. Details see text.

Physical vapor deposition of platinum has been performed by resistive heating of a platinum wire in a home built evaporator shown in Fig. 3.6. The main part of the evaporator consists of a long stainless steel tube (1) which can be mounted into a z-translator. The front end consists of a heating shield (3) which is cooled by a water circuit (2). Inside the heating shield two tantalum tubes (4) are mounted in between sapphire plates (5) and marcor plates (6). The sapphire plates electrically insulate the filament.

Platinum evaporation is a challenge since the filament has to be made extremely hot (i.e. roughly 200 K below the melting point) in order to achieve a decent evaporation rate of roughly 1 monolayer (ML) per minute\(^1\). At high temperatures, the Pt filament is extremely soft and therefore instable. In order to stabilize the filament a 0.25 mm diameter Pt wire is wrapped around a 0.25 mm tungsten wire. Both wires are then wrapped around a M4 screw to form a spiral like filament which is clamped into the tantalum tubes [Fig. 3.6(4)]. This leads to a stable filament which operated at deposition rate of 0.02 ML/s. The total deposited amount before destruction with one filament was roughly 2500 ML.

\(^1\)The deposition rate depends strongly on the distance between the filament and the sample and on the shape of the filament. The numbers indicated here refer to this particular setup.
3.4 The Scanning Tunneling Microscope

As already mentioned, the scanning tunneling microscope used in this thesis is a homebuilt inverted beetle type STM. For details the reader is referred to [97–100]. The only point which is discussed here, is the temperature dependence of the piezo deflections shown in Fig. 3.7. The deflection is normalized to room temperature and the values have been deduced from atomically resolved STM images at different surface temperatures. The temperatures indicated are the sample temperatures. The temperatures of the piezos are not known. These values are extremely important in order to calibrate the STM images recorded at low temperature. The deflection drops from 100% at room temperature to roughly 73% at 20 K. The inset of Fig. 3.7 shows the calibration of the piezo scanner. The column denoted as electronics refers to the coding used by the STM electronics.

### 3.5 Calibration of the ion beam

The adjustment of the ion beam is of crucial importance for the ion beam erosion experiments. Especially in the grazing incidence geometry, the ion induced damage is extremely sensitive to changes of the angle of incidence. In order to characterize the angle of incidence, two parameters have to be known. The relationship between the rotation of the setting screw [(38) in Fig. 3.2] and the tilt angle, in the following
denoted as slope $U$, and the horizontal position of the sample, i.e. $\vartheta=90^\circ$. The slope, is
determined with Laser pointer. The sample is positioned at two opposite UHV windows
as shown in Fig. 3.8(a). The laser beam is directed on the sample and is fixed. With the
help of the manipulator [(13) in Fig. 3.1] the sample is moved away from the window.
The Laser is now shining on the opposite window and the spot position is marked.
The sample holder is tilted and moved back to the Laser pointer position at the UHV
window. Specular reflection at the sample surface occurs and the spot of the deflected
beam is marked on the window. This procedure is repeated for many different settings
of the screw. Since the distance $l$ from the sample holder to the UHV window is known
and the height $\Delta h$ is measured, the slope $U$ of the screw setting can be deduced from
trigonometry. In this case $U$ equals to 1.17°/turn $\pm$ 0.07°/turn and the result is shown
in Fig. 3.9. The number of turns $U$ is plotted against the calculated angle of incidence
$\vartheta$. This evaluation does not yield the proper angle of incidence since the data refers to
the zero position of the setting screw and not to $\vartheta=90^\circ$.

Therefore the second parameter (the horizontal position of the sample holder) has
to be deduced. The sample holder has been adjusted horizontally with great care and
the zero position has been defined identically to the stopping position of two screw
nuts which are shown in Fig 3.2 (40) (in the ideal case the horizontal position equals
to $U=0$ turns). This procedure has been performed ex-situ. In the UHV chamber the
horizontal position was cross checked with a laser pointer. This time the spot has been
directed onto the sample under an angle of incidence of 45° as shown in Fig. 3.8(b).
The pointer is adjusted in the middle of the UHV window, is reflected from the sample
and collected on the other side at the second window (both windows have a angle of
45° with respect to the horizontal position of the UHV chamber). If the position of the
reflected beam in the second window is also situated in the middle then the adjustment
was successful. A slight offset of 0.2° is deduced from this evaluation. This leads to
3.6 Experimental procedure

the following formula for the calculation of the angle of incidence.

\[ \vartheta = 90 - 1.17 \cdot (U + 0.2) \]  \hspace{1cm} (3.1)

Taking into account all possible errors which are the horizontal position, the slope and the possible offset induced by the ion gun which might not be perfectly aligned with the sample holder then the absolute error of the angle of incidence is ±0.5°.

The ion flux on the sample is measured in the following way. First the total ion current I is measured in the Faraday-Cup which is positioned normal to the ion gun. The Faraday Cup hole has a diameter of 0.9 mm. The vertical position of the Cup hole is identical to the vertical position of the sample in the chamber. Details can be found in [32]. From geometry the ion flux on the sample can then be calculated using formula 3.2

\[ f = \frac{4 \cdot I}{\frac{1}{2} \cdot d^2 \cdot N \cdot e \cdot \cos \vartheta} \]  \hspace{1cm} (3.2)

where the d denotes the Faraday cup diameter, N the ionization state of the ion, e the elementary charge and \( \vartheta \) the angle of incidence measured with respect to the surface normal. The ion fluence \( F = f \cdot t \) (flux \( \times \) erosion time) is measured in MLE where one MLE equals to the areal density of surface layer atoms on Pt(111) \( (1.504 \times 10^{19} \text{ atoms/m}^2) \).

3.6 Experimental procedure

The experimental procedure can be described as follows. Sample cleaning is accomplished by ion bombardment at room temperature with 5keV Ar\(^+\) ions under an angle of incidence \( \vartheta = 81.5^\circ \) measured with respect to the surface normal. An ion flux \( 5.8 \times 10^{16} \text{ ions/cm}^2 \text{per}

Figure 3.9: Calculated angle of incidence \( \vartheta \) versus the number of turns U of the screw.
ions/m²s and an ion fluence of 14 MLE is used. Afterwards the sample is flash annealed to 1273 K. If previous experiments showed small traces of carbon impurities on the sample, the sample is treated under an oxygen atmosphere of roughly $1 \cdot 10^{-6}$ mbar for a duration of 5 minutes at a sample temperature of 500°C. Afterwards the sample is again flashed to 1273 K. The cleaning procedure is completed and the experiment can be performed.

Therefore the sample is tilted to set the desired angle of incidence and then the Faraday cup is moved in front of the ion gun. The desired ion current is set and monitored for at least five minutes. During that time slight changes in the ion current are corrected by adjusting the gas flux into the ion gun. Afterwards the desired sample temperature is set and the ion beam is blanked\textsuperscript{1}. The sample is moved to the ion gun (blanking is switched off) and the ion bombardment is performed. Immediately after the end of the ion erosion, the heating of the sample is switched off. Experiments performed at high temperatures are cooled down to room temperature. Experiments below room temperature are quenched down as low as possible (105 K in the case of liquid nitrogen cooling and 18 K in the case of liquid helium cooling). The ion current is cross checked in order to assure that no ion flux changes occurred. Afterwards the ion gun is switched off and the sample is tilted back into the horizontal position in order to perform STM.

The alignment of the sample with respect to the ion beam direction is either parallel to the $[-112]$, or the $[110]$ or the $[110]$ crystallographic orientation of the crystal. The ion beam direction is always indicated in the different chapters. It has to be noticed here that a mirror operation on the $[110]$ leads to the $[110]$ direction. This property is used in Chapter 4 where the ion erosion has been performed along the $[110]$ in experiment and parallel to the $[110]$ in the molecular dynamics simulations. The STM images have been mirrored in order to compare the results with MD.

The experimental procedure which is used to study the damage of single ion impacts at low temperatures, where the experimental procedure is more elaborate, is described next.

After the preparation the sample is bombarded with 5 keV Ar\textsuperscript{+} ions at a temperature of 750 K with a total ion fluence of 0.75 MLE at an angle of incidence of $83°$. This leads to well separated big hexagonal vacancy islands \cite{26} which are necessary in order to study subsurface channeling at ascending step edges. Then the large cooling trap is filled in order to decrease the base pressure as quick as possible. The sample is moved towards the STM position where the second small cooling trap is located. This trap is also filled with liquid nitrogen and acts as a hood which prevents the adsorption of molecules on the surface. At this point in time the base pressure is always well below

\textsuperscript{1}Blanking is referred to the ion gun control unit. If activated the deflection voltage in the Wien-filter unit is set to maximum. The ion beam is deviated considerably and cannot pass the Wien-filter anymore. The ions do not enter into the main chamber anymore.
3.6 Experimental procedure

the measuring limit of a standard Bayard-Alpert pressure gauge which is $2 \cdot 10^{-11}$ mbar [102]. Afterwards the sample is cooled down with liquid nitrogen or liquid helium and during the whole cooling phase the sample rests under the hood. After the minimum temperature is reached, the sample is moved to the wobble stick position, titled and then moved to the Faraday cup. Then the sample is flash annealed to 750 K in order to desorb the occasionally adsorbed molecules. The ion gun is switched on and the desired ion current is set. During this procedure the sample is cooling down again and regulated to the desired temperature. The ion bombardment is performed and afterwards the gas flux to the ion gun is quickly switched off. The ion fluence is set to $1.3 \cdot 10^{-3}$ monolayer equivalents (MLE) if not otherwise indicated. The sample temperature is usually kept constant for 1-2 minutes in order to pump away the noble gas atoms. This is necessary in order to prevent adsorption of the noble gases on the Pt(111) surface. At a base pressure below $5 \cdot 10^{-11}$ mbar the sample heating is switched off in order to reach the lowest possible temperature. During STM imaging of the single ion impacts the base pressure is always well below $2 \cdot 10^{-11}$ mbar.

The bombardment temperature is on the one hand chosen as low as possible in order to prevent annealing of the ion induced surface defects through diffusion. On the other hand the temperature is chosen high enough to prevent adsorption of the noble gas atoms. This is inevitable since these gases are used for the ion exposure. For Ar the surface temperature was set to 62 K, which is well below the onset temperature of single adatom diffusion [56; 57]. For Xe 115 K is used as Xe starts to adsorb at about 110 K on the flat terraces [103]. After ion bombardment the surface is quenched to 20 K in the case of the Ar single ion impacts and to 105 K in the case of Xe impacts. The temperature was always low enough to prevent surface vacancy diffusion [59].
3. EXPERIMENTAL SETUP
Chapter 4

Surface damage by single ion impacts

4.1 Introduction

In this chapter the damage of single ion impacts is analyzed at low temperatures in order to better understand the physics of the ion-solid interaction under grazing incidence conditions. Analyzing the ion-induced damage in solids allows one to gain insight into the mechanisms of energy transfer, particle ejection and ion induced defect formation. The investigations presented here show that under specific conditions the whole trajectory of single keV ions in the solid can be made visible at the surface.

Tracks of individual ions can be observed on many different materials in the case of swift ion erosion (MeV to GeV range). The deceleration of these ions in the solid is dominated by electronic stopping while nuclear energy losses are marginal. In a narrow cylinder centered around the ion trajectory, electrons from substrate atoms are very efficiently removed resulting in large number of positively charged ions. Due to Coulomb interaction repulsion, these ions repel which leads to damage formation $[$104$]$. By means of chemical etching the resulting damaged cylinder, denoted as ion track, can be removed and well defined hole diameters on the nanometer scale are produced. These tracks can be observed by electron microscopy $[$105–107$]$. Applications range from porous membranes particle counters to radiation dosimetry $[$108; 109$]$. The entrance spot of a swift heavy ion may be visualized by scanning probe microscopy as a hillock or crater $[$110–112$]$. Chains of dots due to grazing incidence swift heavy ions passing near the surface through layers of different electron density in SrTiO$_3$ have also been reported $[$113$]$. In contrast, ions with energies of a few keV have large nuclear but negligible electronic stopping. The ion penetration depth is small ($\leq 100 \text{ Å}$ for normal incidence ion bombardment) and tracks of individual particles in the solid are not observed. Only
the collective damage of keV ions can be analyzed by transmission electron microscopy [114]. Using scanning tunneling microscopy or atomic force microscopy it is possible to observe in great detail the surface damage of individual impacts which allows insights into adatom production, sputtering and thermal spike formation [28; 31; 115]. This experimental data complements molecular dynamics simulations of the interaction of keV ions with solids [25; 29; 116]. For oblique ions with energies above 50 keV impinging on graphite, chains of small hillocks in ion beam direction could be associated with interstitial cluster formation along the ion path [117].

In this study the damage produced by single keV ions is investigated by scanning tunneling microscopy and supplemented by molecular dynamics simulations. The simulations have been performed in a collaboration with the group of Prof. Herbert Urbassek. A Pt(111) crystal is chosen and the angle of incidence \( \vartheta \), measured with respect to the surface normal is varied between 78.5\(^\circ\) and 88\(^\circ\). The azimuthal orientation of the crystal is parallel to the \([\overline{1}10]\) direction. In order to compare the results to the MD simulations (performed parallel to the \([\overline{1}10]\) direction) all STM images have been mirrored. Therefore the azimuthal direction is from now on always denoted with \([\overline{1}10]\).

At grazing angles of incidence the ions are extremely surface-sensitive and the damage on flat terraces is absent or marginal (depending on \( \vartheta \)). Only ions encountering monoatomic steps are able to initiate damage as already discussed in chapter 2. The experiments are performed at low temperatures in order to diminish annealing of ion-induced damage and to make the experimental data comparable to MD simulations performed at 0 K.

A typical STM topography after an ion exposure experiment is shown in Fig. 4.1. In a first experimental step the large hexagonal vacancy islands were formed by sputtering at 750 K. The vacancy islands display well defined step edges serving as locations of attack for the subsequent low fluence and low temperature ion exposure. Here the Pt(111) surface was subject to a fluence of about \( 6 \cdot 10^{16} \) ions/m\(^2\) 2.5 keV Ar\(^+\) ions with \( \vartheta = 86\(^\circ\) \) at 62 K [no surface diffusion on Pt(111)]. Statistically under these conditions only one out of 250 surface atoms is hit by an ion. The damage resulting from the low temperature single impacts visible in Fig. 4.1 is located behind the ascending step edges if viewed in ion beam direction. Three events which can be unambiguously attributed to single ion impacts are highlighted. Event (1) in Fig. 4.1 shows a piece of step edge nibbled off and surrounded by a large adatom island. This direct hit event is characteristic for localized energy deposition with a subsequent thermal spike [25]. Event (2) in Fig. 4.1 shows a chain of adatoms and adatom cluster extending over a distance of about 220 Å from the step edge away in ion beam direction. Here an ion entered the crystal at the step edge and was steered in a channel formed through chains of atoms of the two topmost layers in \( \langle \overline{1}10 \rangle \) direction until it presumably left the crystal again. Subsurface channeling occurs. The energy transfer from the ion to the surface...
Figure 4.1: STM topography after 2.5 keV Ar$^+$ ion exposure at a surface temperature of 62 K. The direction of the ion beam is indicated with the black arrow. Three different impacts are highlighted (details see text). The image size equals to 1280Å × 1280Å

Layer atoms when they are gently hit from below result in adatoms and hardly visible surface vacancies. The pattern resembles the molecular dynamics simulations shown in Fig. 2.16.

Event (3) in Fig. 4.1 shows a smaller ensemble of adatom clusters elongated in ion beam direction and extending over a distance of about 80 Å behind the step. Close to the end of the adatom cluster ensemble a small vacancy crater is visible. This is again a channeling event but with a shorter channeling length. Apparently, at the end of the channeled trajectory a large angle scattering event took place, resulting in significant energy transfer causing the crater and the accumulation of adatom clusters around the crater. Many other ion impacts are visible in Fig. 4.1. Most of them can be attributed with little ambiguity to single ion impacts, but for some of them it is uncertain whether damage patterns of several impacts overlap. Also a few lonely atoms on the terrace are seen which can hardly be attributed to an impact at an ascending step. They may
originates from the formation of an adatom vacancy pair in a terrace impact (though with small probability and possibly influenced by an adsorbate). Alternatively, one has to consider that once adatoms are created through an ion impinging at a step they may be displaced by long distances by another arriving ion with a small probability.

The adatom formation in ion beam direction is explained by subsurface channeling. For grazing incidence keV ions on Pt(111) evidence for the presence of subsurface channeling and its importance for pattern formation has already been discussed in section 2.5.3. However, in these experiments no low temperature single ion impact study was performed. The single ion impacts shown there were done at 350 K where surface diffusion changed the damage pattern considerably (compare Fig. 2.25 and Fig. 4.1). However one has to keep in mind that these experiments have been performed parallel to the $[\overline{1}12]$ direction of the crystal. The comparison is therefore not straightforward.

The experimental procedure has already been introduced in section 3.6. A remark with regard to STM image interpretation is in place here. The finite size of the STM tip strongly affects imaging of adatoms (or small adatom clusters) and of surface vacancies (or small clusters of them). However, in opposite directions for the two species. Fig. 4.2 shows a side view sketch of an imaging situation with adatoms and surface vacancies assuming for simplicity a constant density of states at all positions of the surface. The dashed line in Fig. 4.2 indicates the position of the tip apex moving over the surface resulting from the convolution of tip and surface shape. Due to its finite size the tip is unable to reach the bottom of surface vacancies or surface vacancy clusters. Consequently the apparent depth is reduced significantly (see $\Delta h_{\text{vac}}$) compared to the expected height of a monoatomic step. In contrast the apparent height of small elevations $\Delta h_{\text{ad}}$, i.e. adatoms or small adatom clusters is comparable to the step edge height. They cannot be overlooked in STM topographs, especially since their apparent lateral size is largely exaggerated due to the adatom tip convolution. As a consequence a small vacancy cluster in the direct vicinity of an adatom is usually invisible in STM as shown in Fig. 4.2. Finally, due to tip surface convolution the

![Figure 4.2: Imaging small surface defects with STM (see text). The resulting corrugation of a vacancy is denoted with $\Delta h_{\text{vac}}$ and the one of an adatom cluster with $\Delta h_{\text{Ad}}$.](image)
distinction of adatom and adatom clusters becomes difficult as their size is similar and depends strongly on the tip shape.

The MD simulation procedure is briefly described in the following. Details can be found in [51] (see also section 2.2.5). All simulations are performed at 0 K. The simulations do not model electronic energy loss.

Subsurface channeling is simulated for 5 keV Ar\textsuperscript{+} and Xe\textsuperscript{+} ions impinging on a kinked ascending step (parallel to the [1\textbar10] direction) at a glancing incidence of 86\degree. The target crystallite has a size of 298 Å along the ion direction and is 86 Å broad, consisting of 18 Pt(111) layers. The topmost layer ends at 120 Å to form an ascending step; behind the step the crystal extends for 178 Å. Ions channeling farther exit the simulation cell. In total, 625 ion trajectories have been simulated, which varied in the location of the ion impact point with respect to the step edge. These simulations follow the trajectory of the ion and the motion of all target atoms for 25 ps. This is long enough to get reliable results for the defect production (sputtered atoms, adatom and vacancies).

Terrace impacts have also been investigated. The angle of incidence of 5 keV ions is varied, and the trajectories are evaluated. The impact point of the projectile is varied over a unit cell of the surface mesh to gather sufficient statistics. Here, for each angle, 100 trajectories were simulated. In these simulations the trajectories are followed only for 1 ps. This is long enough to investigate the ion trajectories. No reliable results for defect production can be deduced from these measurements.

In order to analyze the energy loss behavior of ions inside a channel, they are directly injected into a channel, with direction parallel to the surface plane. The initial position of the ion is chosen in the approximate center of the channel. In this series of simulations, a thick target crystallite consisting of 54 layers with a length of 110 Å along the ion flight direction is used. The trajectories are followed for 2 ps. This is long enough to follow the trajectory of the ion and to measure the energy loss.

### 4.2 Bulk channeling versus subsurface channeling

Since bulk channeling is a well studied phenomenon, the discussion of subsurface channeling starts by analyzing bulk channeling with the help of molecular dynamics simulations. The results are then extended to subsurface channeling. As shown in Fig. 4.3(a) bulk channeling is simulated by injecting a particle parallel to the surface plane into different layers of the crystal along the [1\textbar110] direction. By changing the entrance layer depth of the projectile, in this geometry, the transition from bulk channeling to subsurface channeling can be monitored. Figure 4.3(b) shows a simulation result in the case of 5 keV Ar\textsuperscript{+}. The ion moves 12 layers underneath the surface and performs an oscillatory
4. SURFACE DAMAGE BY SINGLE ION IMPACTS

Figure 4.3: Bulk and subsurface channeling for 5 keV Ar\(^+\) and Xe\(^+\). (a) Sketch of the simulation geometry. For subsurface channeling the ion is injected into the crystal at the ascending step edge under an angle of incidence of 86°. Bulk channeling is simulated by injecting a particle parallel to the (111) plane deep inside the crystal. (b) Trajectory of 5 keV Ar\(^+\) ion performing bulk channeling (sideview). The ion has been injected in the crystal 12 layers below the surface. The straight fat lines denote the positions of the atomic layers and the full curved line the ion trajectory. (c) STM topography of damage patterns of 5 keV Ar\(^+\) incident at \(\vartheta = 86^\circ\). The marked chain of adatom clusters decorates a trajectory of a long channeling event. (d) Corresponding MD simulation in (d) topview and (e) sideview [118]. (f) STM topography of damage patterns of 5 keV Xe\(^+\) incident at \(\vartheta = 86^\circ\). (g) Corresponding MD simulation in (d) topview and (h) sideview. The full dots above the crystal in (e) and (h) represent adatoms created and are located at the x-position of their creation, the open circles in (h) represent the additionally sputtered atoms at the x-position of their creation. STM image size in (c) and (f) is 580 Å \(\times\) 580 Å.

For this type of trajectory an average nuclear energy loss of 1.3 eV/Å independent of the depth of the layer of injection is measured. No damage is created along the trajectory and the mean oscillation period is \(\lambda = 23\) Å. The energy loss is measured by dividing the initial energy of the projectile by the channeling length. In this case the target crystallite is 110 Å long. This means that on average the 5000 eV projectile, which enters on the one side of the crystal exits on the other side with 4857 eV left. The averaged nuclear energy loss for one ion trajectory is in the following denoted...
4.2 Bulk channeling versus subsurface channeling

as $\Delta E/\Delta x$. If the energy loss is averaged over many trajectories then the following abbreviation is used $\langle \Delta E/\Delta x \rangle$.

In Fig. 4.3(c) the damage of a well channeled $\text{Ar}^+$ ion incident on $\text{Pt}(111)$ at $\vartheta = 86^\circ$ is highlighted. A chain of adatom clusters decorates the ion track. A rough estimate shows that this particular channeling event created $\approx 38$ adatoms (the evaluation is described in detail below). The ion track extents over a length of 320 Å. The damage pattern, resulting from an MD simulation of a comparable event, is shown in a topview in Fig. 4.3(d). Similarly to the experiment, a chain of adatom clusters forms along the ion track. The vacancy clusters in the MD simulation, resulting from adatom production, are not observed in the experiment; most likely due to tip-surface convolution. The side view of the MD simulation in Fig. 4.3(e) displays the irregular oscillations of the ion between the two topmost layers with an average period of $\lambda = 33$ Å for this particular event (note that the average over many well channeled trajectories leads to a value of roughly $\langle \lambda \rangle = 20$ Å analogous to the bulk channeling simulations). It is apparent from Fig. 4.3(e) that adatoms are created whenever the ion hits the top layer atoms from below. The full green dots in Fig. 4.3(e) indicate the x-position and the number of adatoms produced. No damage is formed in deeper layers. The average energy loss for the particular MD simulation event is $\Delta E/\Delta x = 1 \text{eV/Å}$. The energy loss averaged over many trajectories equals to $\langle \Delta E/\Delta x \rangle = 1.3 \text{eV/Å}$.

Within the statistical uncertainties, the energy loss and oscillation period of the channeled particles in bulk and just underneath the surface are identical. However, while damage is absent in bulk channeling, adatoms and surface vacancies are formed in significant numbers in subsurface channeling. This difference can be traced back to different bonding for surface and bulk atoms. Surface atoms are marginally stabilized against motion normal to the surface if energized from below: there are no atoms above the surface layer which exert a restoring force. As a consequence, the “surface displacement threshold” is similar to the work needed for adatom creation of $\approx 2.4 \text{ eV}$ in Pt [29]. In contrast the bulk displacement threshold is $\approx 37 \text{ eV}$ and thus more than an order of magnitude larger [119]. In consequence, the damage during channeling and dechanneling depends on the depth of the channel inside the crystal. It is pronounced if the ion moves just underneath the surface and diminishes with increasing depth.

In Fig. 4.3(f) a characteristic damage pattern produced by a well channeled 5 keV $\text{Xe}^+$ ion incident at $\vartheta = 86^\circ$ is shown. The damage pattern consists of adatom clusters (similar to $\text{Ar}$) and a continuous groove of surface vacancies aligned in ion beam direction. Since the Xe ions induce surface vacancy trenches, the interaction is in the following denoted as ploughing of the surface.

The topview of a comparable MD damage pattern [Fig. 4.3(g)] shows, in striking agreement with the experiment, a continuous one atom wide vacancy groove in ion beam direction. Such continuous vacancy grooves are never observed for Ar impacts,
either in experiment or in MD simulations, while they are frequent for Xe impacts, both in experiment and in simulation. The side view of the MD simulation event in Fig. 4.3(h) exhibits a strongly reduced oscillation amplitude and period of the ion trajectory compared to the Argon case. The Xenon ion creates more adatoms than the Argon ion [compare full dots above surface layer in Fig. 4.3(h) and in Fig. 4.3(e)]. Moreover sputtering takes place [open blue dots above surface layer in Fig. 4.3(h)] which has not been observed for Argon. For this specific molecular dynamics event 30 atoms have been sputtered. A close inspection of Fig. 4.3(h) reveals that atoms are preferentially sputtered, whenever the Xe ion hits the top layer atoms from below. In the case of the 5 keV Argon impact [Fig.4.3(e)] adatoms are created at these positions. In the case of Xenon, adatoms are formed even when the ion trajectory is most distant from the surface atoms. The Argon projectile induces no surface damage at these positions. For this type of Xe trajectories an average nuclear energy loss of $⟨ΔE/∆x⟩=11$ eV/Å is measured which is approximately eight times larger than the Ar one (1.3 eV/Å). For the specific event shown the energy loss amounts to $ΔE/Δx=7.6$ eV/Å.

The adatom clusters visible in Fig. 4.3(f) appear to be larger than for the Ar event shown in Fig. 4.3(c). Probably due to the higher bombardment temperature for Xe (115 K instead of 62 K) single adatoms are absent and only clusters of at least two adatoms are visible. Statistically, the Xe ion track is considerably shorter than the aligned adatom vacancy production in the case of Ar. This indicates that the energy loss is larger for Xenon ions than for Argon ions (a detailed investigation will be presented below).

The marked difference in the damage pattern of 5 keV Ar$^+$ and 5 keV Xe$^+$ impacts is apparently due to the larger energy loss during channeling. MD simulations show that the energy loss is enhanced by a factor of 8. The larger energy loss of the 5 keV Xe$^+$ supplies sufficient energy to individual surface atoms to overcome the sputtering threshold, which is of the order of the cohesive energy [5.8 eV/atom for Pt(111)]. This energy is considerably larger than the threshold for adatom vacancy pair production of about 2.4 eV. The smaller oscillation amplitude of the channeled Xe ion and the fact that adatoms are formed even at locations, where the Xe ion is most distant from the surface atoms appears to indicate that, loosely speaking, the Xe ion is “too big” for the channel.

This idea can be visualized and quantified analytically using the shadow cone concept [39]. A shadow cone represents the ensemble of trajectories from a binary collision for varying impact parameters. Fig. 4.4 shows the calculated shadow cone for a 5 keV Xe projectile hitting a Pt atom at rest. A ZBL interaction potential has been used to calculate the trajectories. To characterize the size of the shadow cone in Fig. 4.4 its radius $R_{sc}$ at the Pt nearest neighbor distance $d = 2.78$ Å behind the target atom is specified. A quick estimate of the shadow cone radius can be performed by assuming an
4.3 Damage analysis for 5 keV projectiles

Figure 4.4: The shadow cone around a Pt atom (full circle) resulting from scattering of a Xe$^+$ ion. The open circle denotes the neighboring atom in the [110] direction of the crystal (at 2.78 Å). The shadow cone at the distance $d$ which is equal to the next surface atom measures $R_{SC} = 1.45$ Å. For an Ar$^+$ ion, the shadow cone looks qualitatively similar, but is narrower, i.e. $R_{SC} = 1.23$ Å [118].

unscreened Coulomb potential (see chapter 2). The relationship between the shadow cone radius $R_{sc}$, the ion energy $E$, the atomic numbers $Z_1$ and $Z_2$ of the projectile and the target atoms and $d$ the distance from the target atom is given in equation 4.1.

$$R_{sc} = 2\sqrt{\frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 E}}d$$

(4.1)

The calculation shown in Fig. 4.4 is based on a ZBL interaction potential and results in $R_{sc} = 1.45$ Å for 5 keV Xe$^+$ and $R_{sc} = 1.23$ Å for 5 keV Ar$^+$. The ions in the channel “feel” the superposition of all shadow cone radii. From $R_{SC}$ follows that the Xe ion has a smaller channel and thereby the amplitude of its channeling oscillation is strongly reduced compared to Ar. Moreover the Xe ion, moving in the channel, will hit the shadow cone of each individual ion at a larger angle which corresponds to larger momentum and energy transfer.

In conclusion subsurface channeling and bulk channeling are very similar in view of the ion motion through the crystal. However, the damage left behind by the ion differs markedly. For bulk channeling damage is usually absent whereas subsurface channeling leaves a trail of damage on the surface making keV ion tracks visible. Most striking is ion ploughing which results from well channeled Xe ions.
4. SURFACE DAMAGE BY SINGLE ION IMPACTS

Figure 4.5: (a) STM topography of 5 keV Xe\(^+\) single ion impact. The corresponding sketch below highlights the surface trench and the adatom clusters on both sides, image size: 500 Å × 230 Å. (b) MD simulation where the crystal top view is shown in two different representations. Upper image shows a ball model where the surface trench and the adatoms are visible, lower sketch shows the ion trajectory.

4.3 Damage analysis for 5 keV projectiles

Figure 4.5(a) shows a zoom in of Fig. 4.3(f) where the surface trench produced by a 5 keV Xe\(^+\) single ion impact is shown in more detail. The corresponding sketch below the STM image [Fig. 4.5(b)] highlights the surface trench, and the position of the adatom clusters. Two interesting observations can be made. (i) The distribution of adatom clusters on both sides of the surface trench is asymmetric. (ii) The surface trench is not straight but shows kinks where apparently the ion switches between different atomic rows. Fig 4.5(c) shows another molecular dynamics simulation where again a surface trench is visible. As in the experiments, the number of adatoms is not equally distributed on both sides of the groove [also compare Fig. 4.3(g)]. In this specific case 32 adatoms are located on the right hand side of the trench and 46 on the left hand side of the trench (if observed in ion beam direction). In the STM image 9 adatom clusters are on the left hand side and 3 adatom clusters are on the right hand side. Moreover, as shown in the top view of the molecular dynamics simulations [Fig. 4.5 (d)], the ion switches between different rows while channeling.

First the anisotropy of the adatom production is discussed. For this purpose the distribution of adatom clusters has been analyzed from STM images. The result is shown in Fig. 4.6(a) where the weighted difference between the number of adatoms on the left \(A_{d_{left}}\) and on the right \(A_{d_{right}}\) is plotted versus the number of counts. If the
adatoms would be equally distributed the curve should follow a binomial distribution centered around zero. It is clearly visible that this is not the case and most channeling events produce more adatom clusters on the left hand side. The plot is intended to give a qualitative picture of the anisotropy since it is not possible to distinguish between single atoms, dimers or small adatom clusters in the STM images. The measured anisotropy is only valid if one assumes that statistically the ratio of adatoms to adatom clusters is identical on both sides of the surface trench. A quantitative analysis from MD simulations shows that 66% of the adatoms are situated on the left hand side and 34% on the right hand side of the surface trench.

The measured anisotropy of adatom creation can be traced back to the asymmetry of the $\langle 110 \rangle$ channel. In order to visualize this channel Lindhards continuum approximation, introduced in section 2.2.2, is used. The scattering from a row of individual atoms is substituted with a continuous potential field. A ZBL potential is used to describe the the interaction of the ion with the string. Fig. 4.6(b) shows the result of such a calculation where different equipotential curves are shown. A channeled ion moves almost perpendicular through this cut. The kinetic energy transverse to the plane of drawing is large and the energy in the plane is low. The equipotential curves indicate the minimum approach distance of the ions with an in-plane kinetic energy of $E_\perp = E_0 \cos^2 \vartheta$. The angle $\vartheta$ is measured normal to the string and the energy $E_0$ corresponds to the total kinetic energy of the projectile. A particle hitting the string at 86° with an energy $E_0=5000$ eV has a transverse energy of 24 eV. This corresponds to the inner equipotential curve shown in Fig. 4.6(b). The ion oscillates inside the equipo-
4. SURFACE DAMAGE BY SINGLE ION IMPACTS

Figure 4.7: The two sub-channels along the [110] channeling direction. (a) The ion is confined in the lower part of the channel. The interaction with the substrate atoms is limited to $A_l \Rightarrow$ asymmetric damage. (b) The ion is confined in the upper channel. Interaction with $A_l$ and $A_r \Rightarrow$ damage more symmetric potential curve which is not symmetric but has the form of a dumbbell [see Fig. 4.6(b)]. The overall shape for Argon and Xenon is identical; however, the width of the dumbbell becomes larger if the atomic number of the impinging particle decreases. As a consequence the Argon ions have more space to move in the channel than the Xenon ions.

Due to the asymmetric channel, the distance of closest approach of the oscillating ion to the surrounding atoms is not equal. This results in different impact parameters which leads to different energy losses. Molecular dynamics simulations show that the Xe ion can be confined in different regions of the dumbbell. This could not be expected from Fig. 4.6(b). In the continuum approximation, it has been assumed that the ion has a constant $E_\perp$ which results in the dumbbell like channel. It is clear that this is a simplification. The exact number of $E_\perp$, which has been defined as the transverse energy of the impinging ion, exhibits significant changes during the entry in the channel. This of course influences the width of the dumbbell. In Fig. 4.7 the channel (red dashed line deduced from the continuum approximation) is indicated together with the centers of the two sub-channels [blue dots in Fig. 4.7(a),(b)]. The ion is confined in one of the channels and performs an oscillatory motion in there. The green points denote the crystal atoms. The arrows indicate the oscillation in the sub-channels. The exact amplitudes are not known and work is still in progress to clarify this issue.

However, ions confined in the lower channel shown in Fig. 4.7(a) interact effectively with surface atoms on left side, i.e. $A_l$. No or only little interaction between the ion and $A_r$ occurs (compare the distance between the center of the sub-channel and $A_l$ and $A_r$). The surface atom marked with $A_l$ is sputtered or pushed onto the surface.
4.3 Damage analysis for 5 keV projectiles

Figure 4.8: (a) STM topography of 5keV Ar$^+$ single ion impact. The corresponding sketch below highlights the adatom clusters, dashed line indicates the trajectory of the ion. Image size: 640Å × 260Å. (b) corresponding MD simulation where the crystal top view is shown in two different representations [118]. Upper image shows a ball model where the surface trench and the adatoms are visible, lower sketch shows the ion trajectory.

depending on the impact parameter. In this case a groove with single-atom width will be produced with preferential adatom production on the left hand side. When the ion propagates in the upper sub-channel [Fig. 4.7(b)], it propagates in the intersection zone of two atomic rows, i.e. $A_I$ and $A_r$. According to the MD simulations, a groove with double-atom width is created. The production of adatoms is more symmetric with a slight preference to the right.

Fig. 4.5 shows that the channeled ion switches between different rows of atoms while channeling [observation (ii)]. Already in their early computer simulations Robinson et al. [120] observed that two classes of axial channeling can be distinguished: channeling confined in one potential valley between the atomic strings (also denoted as proper channeling or hyperchanneling) and channeling where the ion switches between different atomic strings without violating the channeling condition. The reason is that the potential at the saddle point between the atomic strings is much smaller than the critical value of the potential for “normal” axial channeling.

In order to quantify the switching of the ions between different atomic strings, the same set of impacts as used in Fig. 4.6(a) has been evaluated. At least 70% of the trajectories show kinks.

It can be concluded that crossing of the projectiles between different rows in one surface plane is clearly visible in the experiment. The question immediately arises
whether switching is also observed between different layers i.e. deeper layer subsurface channeling. Fig. 4.8(a) shows a 5 keV Argon single ion impact at 86° ion incidence. The sketch shown in Fig. 4.8(b) highlights the adatoms/adatom clusters produced. Although Argon does not induce surface trenches [dashed line in Fig. 4.8(b) is to guide the eye], the projectile trajectory can be followed from the alignment of the adatoms in ion beam direction. The image shows a channeling event which starts at an ascending step. After a distance of 250 Å the trajectory crosses a descending step edge. If the projectile had been confined between the first and the second layer, the adatom production should have ended at the descending step. This is obvious since the ion would simply escape out of the crystal. However, the adatom production continues in the layer below and even crosses an ascending step edge before dechanneling occurs. This STM topography shows that deeper layer channeling is indeed visible in experiment. The channeling condition is not violated when the ion switches from the first layer to the second layer.

The same phenomenon is also observed in the molecular dynamics simulations as shown in Fig. 4.8(c),(d). On the surface adatom vacancy production is observed. However, the side view [Fig. 4.8(d)] shows that switching between layers occurs without a large scattering event. Although the simulations show that the long channeling events are mostly confined between the first and the second layer, some trajectories enter deep inside the bulk. For Argon ions switching down to the 10th layer and for Xenon ions switching down to the 4th layer has been observed. Since the lighter Argon ion produces a smaller shadow cone it has more freedom to move inside the crystal channels. The potential walls are thinner and switching is easy. The Xenon shadow cone is larger and therefore the ion is confined stronger in the channels which results in less switching.

Deeper layer channeling events induce less surface damage. Surface atoms can move more freely towards the vacuum than bulk atoms. The threshold energy for damage production in the case of surface atoms is close to the adatom formation energy. In the deeper layers, surface effects are negligible and the channel walls are not damaged by the projectile (for well-channeled motion). The energy for damage formation increases up to the value of the bulk displacement threshold energy.

Until now only the well channeled long trajectories have been analyzed. In the next paragraph the different damage patterns induced at the step edges are discussed.

In Fig. 4.9 a STM image and six molecular dynamics snapshots are shown for the case of 5 keV Xe at 86° ion incidence. Until now only those impacts have been discussed which showed long channeling distances (i.e. damage pattern IV in Fig. 4.9). However, the ion trajectory depends strongly on the impact position at the step edge. If the step edge is hit directly no channeling occurs and the damage is induced at the impact point. These trajectories show efficient sputtering and lead to step edge erosion (Fig. 4.9 I). Ions hitting the step edge somewhat farer away from the step enter into the crystal but
4.3 Damage analysis for 5 keV projectiles

Figure 4.9: STM topography of 5keV single ion impacts at 86° ion incidence together with six molecular dynamics simulations. Different damage patterns are highlighted in the STM image which are comparable to the simulation snapshots below. Image size 1370Å × 620Å. The six MD snapshots show the final damage as obtained after 25 ps simulation time; the different patterns result from different impact positions at the step edge. The top views show: (I) step edge erosion, (II) peninsula vacancy island, (III) isolated vacancy island, (IV) single-row trench, (V) double-row trench, (VI) sporadic damage. MD simulations from [118].

As a consequence of this diversity the damage resulting from step impacts is spread
over large distances. Fig 4.10 shows the experimental and simulated channeling length distribution for the case of 5 keV Xenon at 86° ion incidence. The strong peak at 170 Å in the simulated results arises from the finite size of the simulation cell and can be considered as an artifact.

The channeling length distribution shows that a lot of impacts don’t lead to long surface vacancy trenches. The damage is directly situated at the step edge (the maximum in the histogram is located 35 Å). These damage patterns result from direct impacts at the step edge. Fig. 4.10 shows that the experimental distribution extends up to roughly 400 Å away from the step edge. For short channeling distances the experimental and molecular dynamics results are in good agreement. The long channeling events observed in the experiment are not reproduced by the MD simulations due to the finite size of the simulation cell.

Finally, it is highly desirable to get an estimate of the amount of adatom production in the case of well channeled projectiles. This cannot be done for the Xenon impacts since the surface temperature during ion erosion was higher than the onset temperature of single adatom diffusion. The clusters visible in the STM images consist of an unknown size of adatoms. In contrast, the Argon experiments are performed at a temperature lower than the onset temperature of single adatom diffusion. Here a rough estimation can be done by assuming that the smallest adatom “clusters” visible in STM are single adatoms. In Fig. 4.11(a) the damage of a well channeled projectile is shown. Adatom clusters with different sizes are visible in the STM image. The small black arrow in Fig. 4.11(a) indicates one adatom with a very small size. Probably this
4.3 Damage analysis for 5 keV projectiles

Figure 4.11: (a) STM topography of the damage induced by a 5 keV Ar$^+$ ion hitting the surface at 86° ion incidence. Image size: 580 Å × 190 Å. (b) Number of adatoms produced during subsurface channeling (here: 38). (c),(d) profile analysis of all adatoms is a single adatom. Fig. 4.11(c) and (d) show a profile analysis of the small adatoms. The graph shows that the height of the adatom clusters is not identical (variations of roughly 1 Å are observed). This is probably due to the different density of states of single adatoms compared to small adatom clusters. The small elevations have a smaller apparent height compared to the bigger elevations. A flooding algorithm to determine the cluster area is therefore not applicable. It can only be used if the heights of all clusters are equal. This would make the evaluation independent of the chosen threshold value.

Therefore the following method has been used to get an estimate of the adatom yield. The smallest visible clusters are assumed to be single adatoms and the area is filled with a circle. The sizes of all other clusters are compared to the size of this circle. The bigger clusters are filled with the circles until the whole area is covered. This is shown in Fig. 4.11(b). For this particular event 38 adatoms are counted which equals to a density of 0.12 adatoms/Å. This number is a lower bound since the overestimation of the adatom clusters, due to the finite size of the tip, is largest for the smallest clusters. It is likely that the bigger clusters contain more adatoms. Evaluating five high quality images of long channeling trajectories leads to a value of 0.08 1/Å ± 0.04 1/Å. The evaluation relies on the assumption that these channeling events have similar trajectories with similar energy losses. Since this cannot be judged from the STM data, the investigation gives only a rough estimate of adatom production. The error is large and averaging over different impacts is dangerous since the trajectories will always differ slightly which leads to different amount of adatoms produced.
4. SURFACE DAMAGE BY SINGLE ION IMPACTS

4.4 Energy dependence of subsurface channeling

![Image showing STM topographs of damage produced by Xenon single ion impacts at different energies.](image)

Figure 4.12: STM topographs of the damage produced by Xenon single ion impacts at $86^\circ$ ion incidence for different ion energies, ranging from (a) 1 keV, (b) 2.5 keV, (c) 5 keV, (d) 10 keV to (e) 15 keV, (f) 15 keV zoom in of (e). The sample temperature while bombarding was set to 115 K for a fixed ion fluence of $1.4 \times 10^{-3}$ MLE. Image size: (a)-(d),(f) $580\,\text{Å} \times 580\,\text{Å}$ (e) $1300\,\text{Å} \times 1300\,\text{Å}$.

The energy dependence of subsurface channeling will be discussed mainly for the case of Xenon ions impinging at an angle of incidence of $86^\circ$ measured with respect to the surface normal. Fig. 4.12 shows the evolution of the ion induced damage for different ion energies ranging from 1 keV to 15 keV. In the case of 2.5 keV and 5 keV well developed vacancy channels are observed [Fig. 4.12(b),(c)]. The experiment with 1 keV energy [Fig. 4.12(a)] shows no production of vacancy trenches. The damage is exclusively situated at the step edge. At energies of 10 keV and 15 keV [Fig. 4.12(d),(e)] the vacancy channels become longer (Note the different image size in Fig. 4.12(e)). Moreover, in both cases the grooves are not well developed at the beginning of the trajectory but only at the end. This is particularly visible in Fig. 4.12(f) which consists of a zoom-in of Fig. 4.12(e). The damage changes from adatom vacancy production at the beginning of the trajectory to a fully developed vacancy groove at the end of
4.4 Energy dependence of subsurface channeling

in the trajectory. Finally, in Fig. 4.12(e) two subsurface channeling events, which cross a descending step edge are visible in one STM image. This is an indication of a large probability for deeper layer channeling.

How can it be understood that subsurface channeling at an ion energy of 1 keV is suppressed? The prerequisites are (i) the ion has to be able to enter into the crystal, (ii) the channel has to be “large” enough in order to allow a guided motion of the energetic particle. In order to check condition (i) molecular dynamics simulations for 1 keV Xenon impinging at 86° have been performed. We find that the impinging ion misses the channel entry point. It is reflected too early by the repulsive interaction of the surface atoms. The minimum approach distance to the flat terrace is relatively large and equals to roughly 2.3 Å. This means that specular reflection occurs at a distance comparable to the Pt(111) interlayer distance. The ion collides immediately with the step edge atoms, which results in the typical step erosion damage [peninsula-like surface vacancy cluster similar to Fig. 4.9 II]. Prerequisite (ii) for channeling, i.e. the width of the channel inside the crystal, is therefore irrelevant since large scattering events already occur at the entry point.

This result can be compared to an analytical formalism developed for bulk channeling introduced by Onderdelinden [46]. It explains the sputtering yield decrease along low index directions of a single crystal and it has already been introduced in section 2.2.2. The formalism gives an analytical expression for the channeled fraction \( \eta(\vartheta_{chan} - \vartheta) \) of ions hitting the substrate along a low index direction. In the case of subsurface channeling \( \vartheta_{chan} = 90° \) and the channel is parallel to the <110> direction. Fig. 4.13 shows the result of the calculation where \( \eta \) (deduced from formula 2.25) is plotted versus the ion energy. An angle of incidence of \( \vartheta = 86° \) has been assumed for the calculation.

In the case of Xenon the channeling fraction changes from \( \eta = 0.7 \) in the case of 15 keV to \( \eta = 0 \) below 1.1 keV. This result is in excellent agreement with the experimentally observed energy threshold for subsurface channeling. In the case of Argon, the energy threshold for subsurface channeling equals to roughly 500 eV. This lower threshold compared to Xenon is evident since the channeling fraction scales with the shadow cone radius \( R_{SC} \). The value of \( R_{SC} \) is smaller for Argon than for Xenon. The excellent agreement might be partially fortunate since no experiments were performed between 1 keV and 2.5 keV ion energy. Even taking this into account one can conclude that the analytical theory reproduces the energy dependence of subsurface channeling with fairly good accuracy.

The high energy results (10 keV and 15 keV) are discussed in the next paragraph [Fig. 4.12(d)-(f)]. An increase of the channeling length with increasing ion energy is observed. As already shown in Fig. 4.10 the channeling length distribution is very broad. The discussion is therefore limited to a small number of events, i.e. the five
Figure 4.13: Channeling fraction $\eta(\vartheta_{\text{chan}} - \vartheta)$ as a function of the ion energy $E$ in the case of Xenon and Argon ions impinging parallel to the $<110>$ direction. In this case $\vartheta_{\text{chan}} = 90^\circ$ and $\vartheta = 86^\circ$. see formula 2.25 for details.

longest channeling events observed in experiment. Thereby, the energy dependence of the maximum channeling length $l_{\text{chan}}$ and the amount of damage induced at the surface by the well channeled projectiles can be investigated. By averaging it is assumed that these five trajectories, which arise from well channeled particles exhibit similar energy losses and similar surface damage. The result is shown in Fig. 4.14 where $l_{\text{chan}}$ is plotted versus the ion energy (black solid curve). The data confirms the trend already visible in the STM data of Fig. 4.12. The channeling distance becomes longer with increasing ion energy. For 15 keV, $l_{\text{chan}}$ equals to roughly 1100 Å whereas the 5 keV channeling length distribution, already discussed, shows a maximum of 350 Å [compare Fig. 4.10].

This behavior is nothing but expected; the higher the initial energy the longer the channeling length. However, by taking a closer look at the data one realizes that the higher initial energy can only partially explain the increase of $l_{\text{chan}}$. The reason is indicated by the dashed black line in Fig. 4.14 which shows the calculated evolution of the channeling length assuming a constant, energy independent, energy loss.

The calculation has been performed as follows. The mean energy loss $\langle \Delta E/\Delta x \rangle$ for 2.5 keV Xenon ions is estimated by dividing the initial energy $E_0$ of the projectile by $l_{\text{chan}}$. A value of $\langle \Delta E/\Delta x \rangle=20$ eV/Å is deduced. This is of course a rough approximation since the channeled particles will probably not loose the entire energy during
4.4 Energy dependence of subsurface channeling

channeling. During the deceleration, the energy drops which increases the shadow cone radius. At a critical energy the channel is completely blocked and a large scattering event occurs. The ion will either deposit the rest of the energy in the bulk or it exits the crystal with some kinetic energy left. Assuming that the critical energy for dechanneling is independent of the initial energy of the ion, which is reasonable, and that the energy loss is constant, then the maximum channeling length can be extrapolated to higher energies. As shown in Fig. 4.14, this procedure fails and underestimates the channeling length at 15 keV by roughly 35% (dashed black line).

This qualitative analysis shows that an energy dependent energy loss has to be assumed in order to explain the experimental findings. This is corroborated by analyzing the number of adatom clusters formed on the surface by a channeled particle. If the energy loss is constant, the number of adatom clusters normalized by the channeling length $\rho_{Ad}$ should also be constant. The result is shown in Fig. 4.14 (red dashed line) where $\rho_{Ad}$ is plotted versus the ion energy. The sharp drop from 1 keV to 2.5 keV shows the transition from step edge impacts to subsurface channeling followed by a gradual decrease up to an energy of 15 keV. This again points towards an energy dependent energy loss which decreases with increasing ion energy.

Molecular dynamics simulations for 10 keV and 15 keV ion energy have been performed in order to analyze the energy losses in more detail. Since the complete trajectory of the ions cannot be followed (the simulation cell is roughly 180 Å in length),

Figure 4.14: Solid black line shows the maximum channeling length $l_{chan}$, resulting from an average of the five longest trajectories, as a function of the ion energy. Black dotted line extrapolation of $l_{chan}$ by assuming a constant energy loss. Red dashed line number of adatom clusters $\rho_{Ad}$ as a function of the ion energy.
only the energy loss from *proper-channeling* trajectories have been analysed. They are defined as those that stay inside the [110] channel until they reach the end of the simulation crystallite. The Xe stopping force drops from $\langle \Delta E/\Delta x \rangle = 11$ eV/Å at 5 keV to only $\langle \Delta E/\Delta x \rangle = 3.7$ eV/Å at 15 keV. The reason can again be traced back to the energy dependence of the shadow cone (eq. 4.1) where the radius $R_{SC}$ decreases with increasing ion energy. The ions have more space to move and the interaction with the cones decreases which decreases the energy loss.

This finding also explains the transition from surface vacancy trenches to adatom vacancy production at 10 keV and 15 keV [Fig. 4.12(d)-(f)]. In experiment, a transition from adatom vacancy production at the beginning of the trajectory to a fully developed vacancy trench at the end has been observed [Fig. 4.12(f)]. The smaller energy loss at higher energies suppresses to a certain extend damage production. A 15 keV Xe$^+$ ion with $\langle \Delta E/\Delta x \rangle = 3.7$ eV/Å shows a similar damage pattern as a 5 keV Argon impact. MD simulations show that a 10 keV Xe ion produces no longer double-row grooves since the two sub-channels have coalesced. A typical simulation is shown in Fig 4.15(a) for 10 keV Xenon and Fig 4.15(b) for 15 keV Xenon. In contrast to the surface vacancy trench for 5 keV ions [see Fig. 4.3(c)], 10 keV impacts produce only partial vacancy trenches and 15 keV Xenon is similar the 5keV Argon [see Fig. 4.3(b)].

![Figure 4.15: Topview of two molecular dynamics snapshots after a (a) 10keV Xenon single ion impact and (b) after a 15keV Xenon single ion impact](118)

Fig. 4.12(e) shows two channeling events which cross a descending step edge. This indicates an increase of the probability for deeper layer channeling. An increase of the projectile energy for a fixed angle of incidence leads to an increase of the energy normal to surface plane $E_\perp$. Changing the energy from 5 keV to 15 keV increases $E_\perp$ from 24 eV to 73 eV. From Fig. 4.12(e) one can speculate that deeper layer channeling is more probable at higher energies since two events crossing a descending step edge are observed in one image. However it is very hard to quantify this from experiment since deeper layer channeling is only visible if the trajectory of the ion crosses a descending step edge. This is of course much more likely at higher energies where the channeling distance is longer. Molecular dynamics simulations, performed for a limited set of trajectories, indicate a slight increase in the deeper layer channeling probabilities (5 keV: 27%,

80
4.4 Energy dependence of subsurface channeling

Figure 4.16: STM topographs of Ar\textsuperscript{+} single ion impacts at 86\textdegree ion incidence for different ion energies, (a) 1.25 keV Ar\textsuperscript{+}, (b) 2.5 keV Ar\textsuperscript{+}, (c) 5 keV Ar\textsuperscript{+}, (d) 10 keV Ar\textsuperscript{+}, sample temperature 62 K. The ion fluence was set to of 4.2 \times 10^{-3} MLE. The direction of the ion beam is indicated with a white arrow. Image size: 1280 Å × 1280 Å

10 keV: 33\%, 15 keV: 32\%). It is doubtful that this small increase can be corroborated experimentally.

Finally, the differences between Argon and Xenon single ion impacts are discussed. The energy dependent measurements for Ar\textsuperscript{+} ions and 86\textdegree ion incidence are shown in Fig. 4.16. In these experiments the ion fluence was higher by a factor of three compared...
4. SURFACE DAMAGE BY SINGLE ION IMPACTS

to the Xenon experiments. In all images the aligned adatom vacancy formation is
clearly visible. For the 5 keV and the 10 keV impacts long channeling trajectories can
be identified. However the density of the adatom clusters is too large to evaluate the
channeling length distribution in detail. For lower ion energies the channeling distance
decreases in complete analogy to Xe. For 2.5 keV [Fig. 4.16(b)] the evaluation of the
channeling length is feasible since the channeling distances are small. Therefore the
2.5 keV Xenon and the 2.5 keV Argon channeling lengths are compared. The evaluation
is again restricted to the five longest trajectories. For Ar $l_{\text{chan}}$ equals to 330 Å whereas
for Xenon a value of 123 Å is measured. The ratio equals to 2.7 which is a measure for
the different stopping powers of Argon and Xenon.

4.5 Angular dependence of subsurface channeling

The angular dependence of subsurface channeling is investigated for the case of 5 keV
Xeon impacts. The angle of incidence has been varied from 88° to 78.5° with respect
to the surface normal for a fixed ion fluence of $1.4 \cdot 10^{-3}$ ML. Fig. 4.17 shows a
part of the experimental results for 83° [Fig. 4.17(a)], 80° [Fig. 4.17(b),(c)] and 78.5°
[Fig. 4.17(d)] and one MD simulation snapshot performed at 78.5° on the flat terrace.
In all images subsurface channeling is clearly visible. Two important observations can
be made.

First, decreasing the angle of incidence $\vartheta$ increases the surface damage. Whereas at
83° the damage almost exclusively results from subsurface channeling at step edges, 80°
and 78.5° show an increased number of adatoms and vacancies resulting from terrace
impacts. The energy of motion in the direction normal to the surface becomes larger
if the angle of incidence is decreased ($E_{\perp} = 74$eV for 83°, $E_{\perp} = 151$eV for 80°, $E_{\perp} =
199$eV for 78.5°). This results in an enhanced probability for large scattering events on
the terrace. This result is also in accordance with previous research where the angular
dependent morphological evolution has been investigated for grazing incidence ions [33].

The second observation is linked to Fig. 4.17 (c),(d) at 80° and 78.5°. Here surface
trenches are visible on the terraces which cannot be linked to ascending step edges. For
80° the number is still very low but at 78.5° most trenches start and end on the flat
terrace. Two scenarios can be imagined in order to understand this observation.

The first possibility is based on a two-event scenario. A large scattering event on
the terrace creates a stable adatom-vacancy cluster. Then a subsequent impact into
the vacancy or at the adatom cluster leads to a significant change of the ion trajectory
which results in a penetration into the subsurface. It is however hard to imagine how
a large scattering event at a surface defect results in a stable channeling trajectory in
the subsurface.

The most plausible scenario is that the ion is able to enter the crystal without a large
4.5 Angular dependence of subsurface channeling

Figure 4.17: STM topographs of the damage produced by 5keV Xenon single ion impacts at different angles of incidence. (a) 83°, (b) 80°,(c) Surface trench on the flat terrace at 80° and many surface trenches on the flat terrace at 78.5°(d). Image sizes: 650Å × 650Å. (e) Molecular dynamics snapshot after an ion impact on the flat terrace. An angle of incidence of 78.5° and 5keV Xenon ions have been used [118].

scattering event. Due to the relatively large angle of incidence of the ions with respect to the surface strings, the crystal becomes partially transparent and the ion enters into the subsurface. This scenario is very similar to deeper layer channeling events already discussed in the preceding sections and is well known from surface channeling experiments [74; 79] (see also section 2.4.1). The ions are able to enter most easily in
the subsurface if they hit the crystal parallel to a close packed direction between two atomic rows. Here the repulsive potential of the surface atoms reaches its minimum. Danailov et al. [74] deduced the maximum transverse energy, in order to achieve total reflection on Pt(111) along the [110] direction, from computer calculations [see section 2.4.1]. This transverse energy defines the critical angle for total reflection [formula 2.16]. For the case of Xenon a value of 79° is deduced. This is in nice agreement with the experimental finding which shows surface trenches on the flat terrace at an angle of incidence of 80°.

In order to corroborate this finding we analyzed the damage on the flat terrace by molecular dynamics simulations. At an angle of incidence of 80° no surface trenches are observed on the flat terrace. Specular reflection occurs and no damage is induced at the surface. By reducing the angle of incidence to 78.5° the situation changes and trenches are produced by the impinging ions on the flat terrace. A snapshot of such a simulation is shown in Fig. 4.17(e) where the ion entered the subsurface without a large scattering event and induces a surface trench of 310 Å before leaving the simulation cell. In total, 24% of all ions hitting the flat terrace at an angle of 78.5° enter into the subsurface. They perform at least one oscillation between the strings of atoms before dechanneling occurs.

Summarizing, the angle of incidence necessary to induce surface trenches on the flat
4.5 Angular dependence of subsurface channeling

terrace with 5 keV Xenon ions, has been estimated with STM to lie between 83°-80°. From MD simulations an angle between 80° to 78.5° has been deduced. However one has to keep in mind that no experiments have been performed between 80°-83° and no simulations between 80°-78.5°. Since the experimentally measured number of surface trenches at 80° is low and with the input from literature (79° from ref. [74]) the onset of surface vacancy trenches on the flat terrace is most probably between 80°± 1°. The MD simulations performed at 0 K probably underestimate the angle of incidence (T=0 K). Moreover one has to keep in mind that the calibration of the angle of incidence in experiment has an error of ±0.5°.

The distribution of the five longest channeling events has been investigated as a function of the angle of incidence and is shown in Fig. 4.18. The graph has to be treated with proper skepticism since the evaluation suffers from severe simplifications, i.e. the five longest channeling events are the result of similar ion trajectories, similar energy loss etc. In the case of the angular dependent measurements this is very doubtful. Still, the graph shows a trend towards longer channeling distances at less grazing angles. At 78.5° most channeling events enter on the terrace in contrast to larger angles of incidence where this is not the case. It is very likely that the ions at 78.5° are not only confined in one layer during channeling but switching between different layers frequently occurs. Deeper layer channeling might lead to an enhanced probability to be captured longer in the channel since a switching event upwards will not lead to dechanneling. An event of deeper layer channeling at 78.5° (the longest trajectory found in the experiment) is shown in Fig. 4.19 (a). The surface trench is visible over a length of 760 Å and crosses a descending step edge. The channeling distance is roughly 50% longer as the longest channeling event shown for 88° [Fig. 4.19]. The number and the position of the adatom clusters are shown in Fig. 4.19(b),(d) (red dots). The blue dots mark the clusters which have a significantly lower apparent height. They are probably due to occasionally adsorbed Xenon atoms as it will be discussed in section 4.8. The distribution of the adatom clusters in Fig. 4.19(b) differs from the 88° adatom distribution shown in Fig. 4.19(d). At 78.5° the number of adatom clusters per length scale on the upper terrace is smaller than at the lower terrace. The lower terrace adatom density is comparable to 88°. This points towards deeper layer channeling at 78.5° since the adatom yield decreases in the deeper layers.
4. SURFACE DAMAGE BY SINGLE ION IMPACTS

Figure 4.19: (a) STM topography of 78.5° 5 keV Xenon impacts. The ion trajectory crosses a descending step edge and the channeling distance equals to 760 Å. (b) Corresponding sketch of the adatom cluster distribution (red dots). The blue small dots indicate the position of Xenon adsorbates decorating the surface trench (see section 4.8). (c) Channeling event at 88° ion incidence with the corresponding sketch (d). Image size: 1010 Å × 1010 Å.

4.6 Influence of temperature on subsurface channeling

Figure 4.20: STM topographs of the damage produced by 5keV Xenon single ion impacts at 86° ion incidence for different surface temperatures. (a) 120 K, (b) 323 K. The ion fluence was set to 1.410⁻³ MLE. The azimuthal direction of the impinging ions is parallel to [110] direction and is indicated with a black arrow. Image size: 650Å × 650Å.

The temperature dependence of subsurface channeling is discussed for the case of
5 keV Xenon at 86° ion incidence. Fig. 4.20 shows two experiments performed at a surface temperature of (a) 115 K, and (b) 323 K. In both cases a surface trench is visible however the number of adatoms on the surface is drastically decreased in case (b). The surface trench at low temperatures is almost continuous and surrounded by many adatoms, the experiment near room temperature only shows a partial trench and two big adatom islands. This shows that subsurface channeling is active at higher temperatures and also visible at higher surface temperatures. These experiments corroborate the findings in [33].

However a detailed investigation of these single ion impact experiments is not feasible. The reason is the enhanced mobility of the adatom clusters and vacancies at higher temperatures. At a surface temperature of 323 K, vacancy diffusion, and adatom cluster diffusion is active which leads to coalescence and annihilation of the surface defects. An experiment at a surface temperature of 450 K has also been performed (data not shown); however, no surface trenches where visible. Since surface diffusion was even higher at this temperature it is very likely that the damage has been annealed. The effect of subsurface channeling at higher temperatures can only be studied from experiments at higher ion fluences as shown in [33].
4.7 Single ion impacts of Neon and Helium

Two experiments have been performed in order to investigate the surface damage at ascending step edges of lighter ions. Fig. 4.21(a) shows the result for 5 keV Neon single ion impacts and Fig 4.21(b) for 5 keV Helium single ion impacts at 86° ion incidence. For Ne aligned adatom vacancy production is observed at the ascending step edges very similar to the Ar experiments. The highlighted event in Fig. 4.21(a) shows that the damage is crossing a descending step edge which indicates deeper layer channeling. The experiment is consistent with Lindhards critical angle (see table 2.3) which predicts that $\phi_C$ equals to 13°. The experiments are performed at 86° and subsurface channeling is observed. Moreover no aligned adatom vacancy clusters are observed on the terrace which is consistent with the finding of Danailov et al. [74] who estimated the angle for total reflection on the Pt surface to be 84° for Ne on Pt(111). This value is smaller than the experimental value of 86°. The He single ion impacts [Fig. 4.21(b)] show no aligned adatom vacancy production. This is probably due to a drastic increase of the deeper layer channeling events and the reduced energy transfer from the He ions to the Pt atoms (see formula 2.5). Moreover adatoms on the flat terrace are observed in a higher density than for the Neon impacts. This is due to the larger critical angle for total reflection which is, in the case of He, 89° (see table 2.11) larger than the angle of incidence used in the experiment. The crystal is therefore partially transparent and
the ions are able to enter the crystal on the flat terrace.

4.8 Increasing the visibility of surface trenches by Xenon adsorption

![Figure 4.22](image)

Figure 4.22: (a) STM topographies after ion erosion with 5 keV Xe at a surface temperature of 105 K, quenched to 20 K. Image size: 640Å × 640Å. (b) Zoom in of Fig. 4.22(a). (c) 10 keV Xenon erosion at 115 K quenched to 105 K, image size: 960Å × 960Å. (d) Zoom in of Fig. 4.22(c). The arrows in (d) mark the preferential adsorption of Xenon at the B-steps. Circled area shows the bimodal size distribution of adatom clusters.

This section describes some observations which are not directly connected to subsurface channeling but they are, although not studied in detail, worth mentioning. Ion
erosion with Xenon has been performed at a surface temperature of 115 K. This usually leads to clean surfaces which are free of adsorbates. It would have been desirable to decrease the temperature during ion erosion in order to prevent single adatom diffusion. Fig. 4.22 shows an experiment performed at 105 K which has been quenched to 20 K for STM imaging. Unlike the experiments performed at 115 K quenched to 105 K, the surface is covered with adsorbates. They do not show a regular superstructure. Moreover, the damage distribution induced by subsurface channeling visible in Fig. 4.22(a) and (b) shows a bimodal size distribution of adatom clusters around the surface vacancy trench. The height of the big clusters is comparable to the step edge height. The small clusters show a reduced apparent height. The small clusters are probably single adsorbates which decorate the surface damage. The most plausible adsorbate is Xenon since it is known that below 110 K adsorption of Xenon on the terrace starts [103]. A certain background pressure of Xenon is inevitable since the ion erosion is performed with Xenon.

Fig. 4.22(c) shows an experiment performed at 115 K with 10 keV Xenon ions. The ion gun efficiency decreases for ion energies higher than 5 keV. This means that a higher Xe pressure has to be used in order to reach the desired ion flux. This leads to a higher Xenon background pressure in the main chamber compared to the 5 keV experiments. The image shows the big vacancy islands together with some single ion impact events. Interestingly, as indicated by the arrows in Fig. 4.22(d), the step edges are decorated by a thin line. This is a well known phenomenon which occurs during Xenon adsorption on Pt(111) [121; 122]. The decoration is almost exclusively situated at B-steps. The chain which is of monoatomic width is bonded to the upper part of the step edge. The bimodal size distribution of the adatom clusters is again visible at the ion induced damage [see circled region in Fig. 4.22(d)]. It is tempting to assign the decoration of the ion induced damage to Xenon adsorption since a clear fingerprint of Xenon is visible (the decoration of steps). However the decoration of the vacancy islands is not visible in Fig. 4.22(a).

One could of course try to attribute this to the different bombarding and imaging temperatures; however, the decoration of the step edges with Xenon has been observed down to very low temperatures (4 K) [122]. This has been explained in terms of a transient mobility gained by the Xenon atoms as a result of the conversion of the binding energy released upon adsorption into lateral kinetic energy [122]. This means that if adsorption of Xenon occurs then the decoration of the step edges should always be visible.

At this point it is not clear whether the decoration of the surface damage visible in the experiments can be attributed to the adsorption of Xenon. It appears likely since the bimodal distribution was usually accompanied with the Xenon step decoration with the exception of the experiment shown in Fig. 4.22(a). Further measurements are required
4.9 The ion fluence onto step edges

in order to clarify this issue. However, the phenomenon observed in these experiments could be used to track very small surface defects (for example single vacancies).

4.9 The ion fluence onto step edges

Figure 4.23: (a) STM topography after ion erosion with 5keV Xe at 86° ion incidence. The numbers in the vacancy islands indicate the number of impacts at the illuminated step edges. Image size: 1500Å × 1500Å.

How many ion impacts are visible in the STM topographs compared to the total ion fluence at the ascending step edges? In order to answer this question the mean number of ions hitting the step edges is compared to the mean number of damage events. In order to illustrate this, Fig. 4.23 shows an STM image after Xenon 5 keV ion erosion at 86° with a total ion fluence of $1.3 \cdot 10^{-3}$ MLE. The numbers in the vacancy islands indicate the number of visible impacts. This evaluation is rather rough since it cannot be excluded that the observed damage has been created by more than one ion impact. The numbers therefore give a lower bound of the step edge impacts. In this case, a mean number of 0.8 events per vacancy island is deduced. Due to the zone of influence $x_C$ (see section 2.4.3) of each step edge the step ion fluence $F_{\text{step}}$ is strongly enhanced compared to the terrace fluence $F$ and can be calculated with formula 4.2

$$F_{\text{step}} = F \cdot \frac{x_C}{\Delta x} \quad (4.2)$$

In this case $F_{\text{step}}$ equals to 0.03 MLE with $x_C=64$ Å and $\Delta x=2.776$ Å. This means that
the fluence is enhanced by a factor 23 compared to the ion fluence on the flat terrace. The average area of the big vacancy islands evaluated by grey-scale discrimination of the STM images equals to 217 nm ± 73 nm. This results in an average edge length of 91 Å ± 15 Å. Since two ascending steps of the hexagon are illuminated by the ion beam, statistically each vacancy islands consists of 76 ± 13 illuminated step edge atoms. From $F_{\text{step}}$ follows that statistically one out of 33 atoms is hit with an ion. This results in a mean number of impacts per vacancy island of 2.3 ± 0.75. This number differs with the average number of impacts measured in experiment by roughly a factor of 3.

From this evaluation follows that at least one third of all step edge impacts can be observed in experiment. Since the experimental evaluation is a lower bound, the difference between the calculated step edge fluence and damage observed with STM is even lower.

4.10 Discussion

One of the questions which has not been fully discussed until now is the atomic structure of the surface trenches in the experiments. Do we observe trenches which consist of only one removed atomic string or do we observe the removal of a double row. This can only be clarified unambiguously from atomically resolved surface trenches. This has not been achieved. However the anisotropy of the adatom cluster production to one side of the channel points towards single rows. As shown in the molecular dynamics snapshots in Fig. 4.7 the removal of a single atomic row leads to adatom clusters which are mainly formed on the left side of the trench whereas a double row leads to a more uniform adatom production with a tendency to more adatom production to the right side. Since more adatoms are observed on the left side as shown in Fig. 4.5(a) it can be concluded that we mostly observe single row surface trenches. This is also supported from overlaying an STM image in atomic resolution recorded at the same surface temperature over a surface vacancy trench. However, in most STM images the surface vacancy trench is not visible in identical resolution over the whole channeling length [for instance Fig. 4.5(a)]. This points to a non-uniform surface vacancy trench with portions where only one row is removed and portions where two rows are removed. By having a closer look to the MD snapshots in Figs. 4.3(c) 4.17(e), 4.7(VI) and 4.5(c) one realizes that all theses trajectories show the same non-uniformity. The atomic structure can therefore be assumed to consist of mainly one atomic string removed with portions where two rows are missing.

The second point to discuss is the contribution of the inelastic (electronic) energy loss which was neglected in the MD simulations. It is obvious that neglecting this contribution does not change the damage induced on the surface (in this energy regime). The excited electrons will be emitted in form of secondary electrons or will couple to the
phononic system which results in heat. The main change will be the length distribution of the channeled projectiles. However, for well channeled projectiles, which were the only ones considered for the calculation of the energy loss, the ions vanish from the simulation cell with still a large amount of energy left. A variation of the channeling length due to the negligence of the electronic energy loss is therefore not visible in the simulations.

This leads directly to the next question which is related to the energy loss. Due to the energy dependence of the energy loss it is obvious that it cannot be estimated from experiment by dividing the initial energy of the projectile by the total channeling length. This only leads to an average energy loss for a specific ion energy. The data from the simulations exhibit the same problems. Here, the energy loss is determined by measuring the difference of the initial and the final energy (at the end of the simulation cell) and dividing by the simulation cell length. For 5 keV Xenon an energy loss of \( \langle \Delta E / \Delta x \rangle = 11 \text{ eV/Å} \) has been deduced. The simulation cell is 180 Å long. This means that the ion exits the cell with roughly 3000 eV left. The energy loss indicated is therefore the mean energy loss for ion energies between 5000 eV - 3000 eV. In the case of 15 keV Xenon with an energy loss of \( \langle \Delta E / \Delta x \rangle = 3.7 \text{ eV/Å} \) the ion exits the simulation cell with over 14000 eV left. This immediately shows that it is hard to compare these values. The simulations and the experiments provide important informations on the damage pattern (which is directly connected to the energy loss); however, they can not be used to estimate straightforwardly the energy loss. This is only possible from simulations if the energy of the projectile is measured in small steps during the channeling event. The numbers given here are always averaged values for a specific energy interval and a specific channeling length (in this case the simulation cell).

4.11 Conclusion

By analyzing the surface damage of grazing incidence single ion impacts the trajectories of the ions during subsurface channeling can be analyzed in detail. Experiments and molecular dynamics simulations are in excellent agreement. In experiments the ion induced damage can be followed for distances larger than 1000 Å away from the impact position. The ions enter into the crystal at ascending step edges and are guided between the collective repulsive potential of the surface atoms with very little energy loss. Most physical processes are similar in bulk channeling and subsurface channeling. However, the energy threshold for damage formation is drastically reduced for subsurface channeling. This leads to the unique opportunity to study the switching of ions in between different rows and planes, the energy dependence, angular dependence and temperature dependence of channeling through the analysis of the surface damage. Some of these quantities are inaccessible in bulk channeling experiments. One could
4. SURFACE DAMAGE BY SINGLE ION IMPACTS

rephrase this by saying that grazing incidence single ion impacts is a tool to study bulk channeling with a reduced energy threshold for damage formation.
Chapter 5

Step edge sputtering through grazing incidence ions

5.1 Introduction

A practical prerequisite for future applications of grazing incidence ion beams is knowledge of how fast the surface erodes for a given ion flux of a specific energy. This chapter describes two new methods to determine the step edge sputtering yield $Y_{\text{step}}$. The evaluations are based on the geometrical model introduced by Friedrich et al. (see section 2.4.3). The first method visualizes $Y_{\text{step}}$ by measuring step retraction through scanning tunneling microscopy topographs. This method is only applicable under extreme grazing incidence conditions where only a little terrace damage is produced by the ion beam. The second method is generally more applicable and relies on the determination of the step concentration and on measuring the removed material. The measurements will show that with knowledge of the step-edge concentration and of the normal incidence amorphous yield $Y_{\text{amorph}}$, the erosion rate $\bar{Y}$ may be predicted with an accuracy of a factor of 2. Finally, with the help of molecular-dynamics (MD) simulations performed in the group of Prof. H.M. Urbassek, the significant dependence of $Y_{\text{step}}$ on the azimuthal direction can be understood. Moreover a significant dependence of the yield on temperature is observed. Section 2.4.3 already introduced the geometrical model, the step edge sputtering yield $Y_{\text{step}}$ and terrace sputtering yield $Y_{\text{terr}}$. From these measurements, one would expect that:

1. the sputtering yield does not depend on the value of $\xi$ as long as $\xi \in [-x_c,0]$,

2. the step-edge sputtering yield does not depend on the azimuthal angle,

3. $Y_{\text{step}}$ is largely temperature independent,
4. The step-edge sputtering yield is largely independent of the angle of incidence as long as the terrace damage is negligible. It will be shown below that all four expectations fail. The common origin of these failures is the neglect of planar and axial subsurface channeling. Subsurface channeling has been introduced in section 2.4.2 and axial channeling has already been discussed extensively in Chapter 4.

5.2 Step retraction due to ion bombardment

Figure 5.1: STM topographs after exposure to (a) 0.25 MLE, (b) 1.0 MLE, (c) 1.5 MLE 5 keV Ar$^+$ at 550 K along the [\(\bar{1}\bar{1}2\)] azimuth with \(\vartheta = 86^\circ\). The direction of the ion beam is indicated by a white arrow in (a). The ion flux was set to 1.0 \(\cdot\) \(10^{16}\) ions / (m$^2$s). All steps visible are of monolayer height. The inset in (a) shows vacancy clusters (circled) in front of an ascending step edge. Image size 2450 Å \(\times\) 2450 Å, size of inset 700 Å \(\times\) 700 Å.

Fig. 5.1 shows a series of experiments with the ion beam along the [\(\bar{1}\bar{1}2\)] azimuth after ion exposure at a grazing angle of \(\vartheta = 86^\circ\) and a surface temperature of 550 K. All STM images show one or more preexisting steps. The direction of the ion beam is indicated with a white arrow in Fig. 5.1(a). For the lowest fluence in Fig. 5.1(a) almost no damage is present on the terraces. However, as highlighted in the inset small vacancy islands and a few adatom islands are visible behind the exposed preexisting steps. Close inspection shows that in front of the preexisting steps small vacancy islands are also apparent [circled in Fig. 5.1(a)]. Increasing the ion fluence [compare Fig. 5.1(b) and (c)] causes a pronounced growth in number and size of the vacancy islands in front of the preexisting steps. In addition, large vacancy islands with low number density are also present on terraces.

The appearance of vacancy islands on the terraces in Fig. 5.1(b) and (c) may be understood as follows. For \(\vartheta = 86^\circ\) with \(E^\perp = 24\) eV sputtering from clean terraces is
5.2 Step retraction due to ion bombardment

zero (compare also Sect. 5.2.2). However, due to thermal vibrations adatom-vacancy pairs may be produced. The liberated adatoms - also occasionally adsorbed molecules from the background gas - may cause few sputtering events to occur. This results in an excess of surface vacancies (see chapter 6 and chapter 7 for details). After a considerable induction time these mobile surface vacancies may be sufficient in number to form small vacancy clusters. As these vacancy clusters expose themselves as an ascending step to the ion beam, once formed, they rapidly grow to the visible size through step edge impacts.

The presence of vacancy clusters behind the step edges is apparent in all three topographs of Fig. 5.1. They result from subsurface channeling. Ions hitting the ascending steps at the bottom of the step enter into the crystal with high probability and are guided in between the planar potentials of the first and the second layer. Due to the higher temperature, the channeling distance is decreased considerably compared to the low temperature single ion impacts presented in chapter 4. Moreover one has to keep in mind that the experiments, shown here, are performed in a different azimuthal direction, i.e. the $[\overline{1}\overline{1}2]$ direction. During subsurface channeling, the ions produce adatoms and vacancies [see Fig. 2.16]. These defects will not be stable at 550 K. However, at the location of dechanneling adatom and vacancy clusters are created large enough to be stable at 550 K. Subsequent impacts enlarge the surface vacancies to a visible size.

Important for the following is the appearance of vacancy islands in front of the step edge, which grow in number and size with ion fluence. The dashed lines in all topographs of Fig. 5.1 indicate the positions where the density of vacancy clusters starts to increase in comparison to the flat terrace. These dashed lines mark the initial positions of the preexisting steps according to the following arguments. Step edge impacts cause thermal spikes which results in a large number of adatoms and vacancies. Molecular dynamics simulations show that vacancies are not only created in the upper terrace, but also in the lower terrace and to a certain extent in subsurface layers [10; 25] [compare also Fig. 2.18(a)]. Due to the step edge barrier for vacancies, the lower terrace vacancies do not anneal at the nearby ascending step edge [66; 69] and thus form with significant probability stable vacancy islands. These islands grow through subsequent step edge impacts to the large structures visible in Fig. 5.1(b) and (c). Through diffusion they also efficiently collect the lower terrace vacancies originating from step edge impacts into the preexisting steps at other locations.

As the positions of the dashed lines in Fig. 5.1 mark the initial positions of the step edges, measuring their average distances from the preexisting steps in ion beam direction allows to obtain the step retraction $x_{\text{step}}$ as a function of fluence $F$. It has to be noted that for a given fluence the average distance traveled by a preexisting step in ion beam direction does not or only marginally depend on the step orientation, as long as the angle between step normal and the projection of the ion beam on the surface is
5. STEP EDGE SPATTERING THROUGH GRAZING INCIDENCE IONS

Figure 5.2: Step retraction \( x_{\text{step}} \) as a function of the ion fluence \( F \). A linear fit to the data yields a step retraction of \( 270 \pm 9 \, \text{Å} \) per MLE.

As shown in Fig. 5.2, the step retraction \( x_{\text{step}} \) is a linear function of \( F \) resulting in a step velocity \( v_{\text{step}} = x_{\text{step}}/F = 270 \pm 9 \, \text{Å MLE}^{-1} \) for the \([\bar{1}12]\) azimuth [compare Fig. 5.2] and \( 216 \pm 45 \, \text{Å MLE}^{-1} \) for the \([1\bar{1}0]\) azimuth (data not shown). The geometrical model links \( x_{\text{step}} \) with \( Y_{\text{step}} \) through

\[
x_{\text{step}} = \frac{x_c}{\Delta x} F Y_{\text{step}} \Delta x \tag{5.1}
\]

where \( \Delta x \) is the distance between two atoms on the surface parallel to the ion beam direction (\( \Delta x = 2.40 \, \text{Å} \) in the \([\bar{1}12]\) direction and \( \Delta x = 2.78 \, \text{Å} \) in the \([1\bar{1}0]\) direction). The zone of influence \( x_C \) can be calculated from geometry and equals to \( x_C = 2d \tan \theta \) (see section 2.4.3). Equation 5.1 attests that the step retraction \( x_{\text{step}} \) is the number of ions entering the zone of influence \( x_cF/\Delta x \) times the retraction of the step edge in ion beam direction \( Y_{\text{step}} \Delta x \) caused by each of these ions. Rewriting (5.1) leads to

\[
Y_{\text{step}} = \frac{x_{\text{step}}}{x_c F} \tag{5.2}
\]

The application of (5.2) results in \( Y_{\text{step}} = 4.2 \) and \( Y_{\text{step}} = 3.3 \) for the \([\bar{1}12]\) azimuth and \([1\bar{1}0]\) azimuth, respectively. However, these numbers are not yet the proper values
5.2 Step retraction due to ion bombardment

Figure 5.3: (a) STM topograph of Pt(111) after exposure to 1.5 MLE of 5 keV Ar$^+$ at 550 K along the [\bar{1}\bar{1}2] azimuth with $\vartheta = 86^\circ$. (b) After additional annealing for 120 s at 720 K. The direction of the ion beam is indicated by a white arrow in (a). The image size is 2450 Å x 2450 Å. Inset in (a) 500 Å x 500 Å

for $Y_{\text{step}}$ as they do not take into account that at 550 K the subsurface vacancies created during step retraction do not completely anneal to the surface and are thus not counted [28]. Figure 5.3 compares STM topographs after exposure to 1.5 MLE 5 keV Ar$^+$ at 550 K [Fig. 5.3(a)] and with additional annealing for 120 s at 720 K [Fig. 5.3(b)]. Annealing to 720 K is sufficient to remove all subsurface vacancies and to make them visible as surface vacancies [28]. Due to annealing the apparent removed amount increases by 35%. Taking this into account $Y_{\text{step}}$ is 5.7 ± 0.2 along the [\bar{1}\bar{1}2] azimuth and 4.5 ± 0.9 along the [1\bar{1}0] azimuth. Moreover, Figs. 5.1(b), (c) and 5.3(a) show that the large vacancy islands on the terraces are usually accompanied by small daughter vacancy islands situated behind the large ones if viewed in ion beam direction. These daughter vacancy islands originate from the dechanneling damage caused by ions hitting the illuminated steps of the large mother vacancy islands [10; 33; 123].

Finally the inset in Fig. 5.1(a) shows that in the vicinity of the big vacancy islands the well-known platinum reconstruction can be observed in complete analogy to normal incidence single ion impacts [28]. The reason is, that the ion induced interstitials migrate to the surface where they are trapped forming surface interstitials. Since the Pt(111) surface layer is under tensile stress, the surface reconstructs in the presence of the ion induced interstitials.
5. STEP EDGE SPUTTERING THROUGH GRAZING INCIDENCE IONS

5.2.1 Step edge yield from step concentration

Figure 5.4: STM topographs of Pt(111) after exposure to (a) 0.5 MLE, (b) 1.0 MLE, (c) 2.0 MLE, (d) 0.57 MLE, (e) 1.1 MLE, (f) 2.3 MLE of 5 keV Ar⁺ at 550 K. For (a)-(c) the ion bombardment is along the [\bar{1}1\bar{2}] azimuth with \( \vartheta = 83^\circ \) and for (d)-(f) along the [1\bar{1}0] azimuth with \( \vartheta = 82^\circ \). The direction of the ion beam is indicated by a black arrow in (a) and (d). The image sizes are 1200 Å × 1600 Å in (a),(d) and 1840 Å × 2450 Å in (b),(e),(c),(f).

Figure 5.4 shows two series of topographs after exposure to increasing ion fluences. The upper row [Fig. 5.4(a)-(c)] displays the effect of ion bombardment along the [\bar{1}1\bar{2}] azimuth with \( \vartheta = 83^\circ \) and the lower one [Fig. 5.4(d)-(f)] along the [1\bar{1}0] azimuth with \( \vartheta = 82^\circ \). In comparison with Fig. 5.1 the number of vacancy islands on the terraces, in Fig. 5.4, is dramatically higher for similar ion fluences. This increase is due to the
5.2 Step retraction due to ion bombardment

lowering of \( \vartheta \) by a few degrees. It results in an enhanced production of mobile vacancies on the terraces \( (Y_{\text{ter}} \neq 0) \) which aggregate to small vacancy islands and subsequently grow by step edge impacts\(^1\). Under such conditions \( Y_{\text{step}} \) can no longer be obtained through monitoring of step retraction.

The three columns of Fig. 5.4 represent the three stages of pattern formation onset: (i) aligned formation of vacancy islands through subsurface channeling (ii) preferential coalescence of the vacancy islands along the ion beam direction as a consequence of their alignment and (iii) onset of multilayer groove formation through the step edge barrier for vacancies. For a detailed description of these morphological stages the reader is referred to ref. [10; 33] or section 2.5.3.

However, a striking difference in the pattern evolution for the two azimuthal orientations has to be mentioned here. Aligned formation of vacancy islands (chains of vacancy islands) is much more pronounced in the [1 \( \bar{1} \) 0] azimuth [Fig. 5.4(d)] than in the [\( \bar{1} \) \( \bar{1} \) 2] azimuth [Fig. 5.4(a)]. This difference causes, in the subsequent stages of pattern formation, a better alignment in ion beam direction. A higher pattern regularity for bombardment along the [1 \( \bar{1} \) 0] azimuth is always observed. This better alignment can be traced back to the fact, that axial subsurface channeling takes place along the [1 \( \bar{1} \) 0] direction, leading to a better aligned and more distant damage production behind a vacancy island, which initiates a better aligned growth of a daughter vacancy island. In contrast, in the [\( \bar{1} \) \( \bar{1} \) 2] direction planar subsurface channeling takes place, which is less efficient and where the ion trajectories are much easier deflected from their initial direction through thermal vibrations (compare also the discussion in the next Section).

For the two sequences of experiments partly visualized in Fig. 5.4 the increase of the removed amounts \( \Theta \) with \( F \) was measured in incremental steps through greyscale discrimination of STM topographs. Fig. 5.5(a) displays the change of \( \Theta \) with \( F \) for the two different azimuths. After an initial slow onset of erosion, \( \Theta \) increases linearly with ion fluence for \( F \geq 0.75 \text{ MLE} \). According to \( (2.36) \) the erosion rate \( \bar{Y} \) is the slope of change of \( \Theta \) with \( F \). Thus for both azimuths \( \bar{Y} \) is initially small and then saturates to \( \bar{Y} = 1.5 \) for the [\( \bar{1} \) \( \bar{1} \) 2] azimuth and to \( \bar{Y} = 1.0 \) for the [1 \( \bar{1} \) 0] azimuth. The values given are the results of linear fits for \( F \geq 0.75 \text{ MLE} \).

The concentration of ascending steps was analyzed for the two sequences of experiments in the following way. As shown in Fig. 5.4 lines parallel to the ion beam direction, in a distance below and incommensurate with the ripple pattern wavelength, are overlayed to each topography. Counting the number of ascending steps divided by the total line length along the projection of the ion beam direction onto the surface results in a density of ascending steps \( \rho_{\text{step}} \). In Fig. 5.5 (b) \( \rho_{\text{step}} \) is plotted versus the \( F \). It increases rapidly with \( F \) and saturates for \( F \geq 0.75 \text{ MLE} \) at \( \rho_{\text{step}} \approx 6 \cdot 10^{-3} \text{ 1/Å} \).

---

\(^1\)To a certain extent the larger vacancy island density is also caused by the ion flux which was larger by a factor of 2 for \( \vartheta = 82^\circ - 83^\circ \) in comparison to that of \( \vartheta = 86^\circ \).
5. STEP EDGE SPUTTERING THROUGH GRAZING INCIDENCE IONS

Figure 5.5: (a) Removed material $\Theta$ versus fluence $F$ for bombardment conditions as in Fig. 5.4. (b) Concentration of ascending steps $\rho_{\text{step}}$ parallel to the ion beam direction versus $F$. Solid black squares denote data for the $[\bar{1}\bar{1}2]$ azimuth and solid red circles data for the $[1\bar{1}0]$ azimuth.

From the comparison of Fig. 5.5(b) with Fig. 5.5(a) it is apparent that the increase of the step edge concentration is mirrored in the increase of the slope of $\Theta$ versus $F$, i.e. of $\bar{Y}$. The simultaneous saturation of $\rho_{\text{step}}$ and the slope of $\Theta$ versus $F$ visualizes directly that $\bar{Y}$ is determined by $\rho_{\text{step}}$. Using the linear fits for $\bar{Y}$ and $\rho_{\text{step}}$ for $\Theta \geq 0.75$ MLE and with the application of

$$Y_{\text{step}} = \frac{\bar{Y}}{\rho_{\text{step}} x_c} \quad (5.3)$$

we obtain $Y_{\text{step}} = 7.4 \pm 0.3$ for the $[\bar{1}\bar{1}2]$ azimuth and $Y_{\text{step}} = 4.5 \pm 0.2$ for the $[1\bar{1}0]$ azimuth.

An error discussion is in place here. With the application of (5.3) terrace sputtering is neglected. As the terrace yield is small it contributes only insignificantly to sputtering. Here $Y_{\text{terr}} = 0.08$ [26] and as $A_{\text{step}} \approx 25\%$, the contribution of terrace sputtering to $\bar{Y}$ is roughly 5%, causing a slight overestimation of $Y_{\text{step}}$. On the other hand, all ascending steps are counted for the determination of $\rho_{\text{step}}$. However, due to
Step retraction due to ion bombardment

multiple steps or shadowing by ascending steps the zone of influence is smaller than \(x_c\) for some of them. This causes an underestimation of \(Y_{\text{step}}\). A detailed analysis of the step distribution shows that roughly 8% of the ascending step edges have a smaller zone of influence than that of the geometrical model. Since both errors counteract each other, the overall underestimation of the sputtering yield is 3%.

Finally for establishing \(Y_{\text{step}}\) the low fluence data below \(\Theta \leq 0.75\) MLE has been neglected. As already pointed out above, step edge impacts also cause production of subsurface vacancies invisible at the surface. However, after a certain ion fluence their concentration saturates due to a dynamic equilibrium between damage production and annealing of subsurface damage to the surface. Previous normal incidence experiments indicate that the subsurface damage saturates for ion fluences well below 0.75 MLE [124; 125]. Therefore for \(\Theta \geq 0.75\) MLE the erosion rate is fully represented by changes at the surface. Neglecting the low fluence data makes additional annealing avoidable.

Taking into account all errors described above, the step edge sputtering yields parallel to the [1\(\bar{1}\)2] azimuth equals to 7.7 \(\pm\) 0.9 and along the [1 \(\bar{1}\)0] azimuth to 4.6 \(\pm\) 0.6.

5.2.2 Molecular dynamics simulations

![Figure 5.6: (a) Terrace adatom yield \(Y_{\text{terr},\text{ad}}\) and (b) terrace sputter yield \(Y_{\text{terr}}\) as a function of the polar angle \(\vartheta\) for 5 keV Ar\(^+\) incident on Pt(111) along the [1\(\bar{1}\)2] azimuth. Circles: MD simulations at 0 K; triangles: MD simulations at 550 K.](image)

In a first set of MD simulations the dependence of the terrace yield for sputtering \(Y_{\text{terr}}\) and of the terrace yield for adatom production \(Y_{\text{terr},\text{ad}}\) on the incidence angle \(\vartheta\) has been investigated. The simulations were performed for the [1\(\bar{1}\)2] azimuth and each data point represented in Fig. 5.6 averages over 50 ion impacts. Figure 5.6 visualizes the strong decrease of these yields as the polar angle approaches \(\vartheta = 90^\circ\). Independently of the temperature of simulation \(Y_{\text{terr}}\) ceases for smaller \(\vartheta\) than \(Y_{\text{terr},\text{ad}}\). This result reflects the fact that less kinetic energy needs to be transferred for the production of an
adatom, still bound to the surface, compared to the sputtering of an atom. Compared to the 0K simulations, the 550 K yields diminish only for larger $\vartheta$. The significant vibration amplitude of surface atoms at 550 K causes for the arriving ions deviations from the planar surface potential and the probability for large angle scattering events increases.

The presence of terrace vacancy islands in Fig. 5.1 observed in experiments performed at $\vartheta = 86^\circ$ appears to contradict the absence of sputtering and adatom production for $\vartheta \geq 84^\circ$ found in the simulation. However, the density of vacancy clusters on the terrace (away from preexisting steps) after a fluence of 0.25 MLE in Fig. 5.1 is only $9.0 \times 10^{-6} \text{Å}^{-2}$. Dividing the cluster density by the number of ions incident on the terrace yields a probability of $5 \times 10^{-4}$ for the initiation of vacancy cluster formation through terrace impacts. Assuming a vacancy cluster to result from a single adatom production event gives a lower bound estimate $Y_{\text{terr,ad}} \approx 5 \times 10^{-4}$. An upper bound estimate results from dividing the terrace area covered by vacancy islands of 0.2% by the ion fluence resulting in $Y_{\text{terr,ad}} \approx 5 \times 10^{-3}$. Both numbers are consistent with the limited statistics of the MD simulations. Moreover, as pointed out above, a very small concentration of adsorbed molecules from the background gas might also be of relevance for initiating vacancy island formation on terraces.

Fig. 5.7 summarizes the simulation results for sputtering through 5 keV Ar$^+$ on a stepped Pt(111) surface. As the amounts of sputtering and adatom production are roughly proportional to each other, with the ratio of sputtered atoms to adatoms being $\cong 3 \ldots 4$, the discussion is limited to the sputter yields. First the 0 K data are discussed. The expectations for the zones of influence from the geometrical model for the 0 K yield are indicated by dashed lines in Fig. 5.7. Along the [112] azimuth the geometrical zone of influence agrees rather well with an accuracy of about one lattice spacing with the $\xi$-range of significant sputtering according to the MD simulations. In contrary, along the [110] azimuth the $\xi$-range of significant sputtering according to the MD simulations extends much further in front of the step than expected from the geometrical model.

To obtain a clue on this MD result Fig. 5.8(a) and (b) show the channels in the Pt crystal along the [112] azimuth and along the [110] azimuth are shown, respectively. The contour lines displayed indicate the turning points in the motion of a 5 keV Ar$^+$ ion with $83^\circ$ incidence angle (transverse energy $E_\perp = 74$ eV); i.e., at these positions the ion is reflected from the channel walls. For ions in front of the step edge outside the crystal only the lower (red) contour lines are relevant. The corrugation of the potential perpendicular to the plane of drawing is small; it amounts to only 0.053 (0.013) Å for the [110] (112) azimuth. The energy of 74 eV corresponds to $E_\perp$ of the 5 keV Ar$^+$ ions impinging with $\vartheta = 83^\circ$. The corrugation of the contour lines amounts to 0.12 Å in the [112] azimuth and 0.64 Å in the [110] azimuth. Thus, ions impinging along
5.2 Step retraction due to ion bombardment

The [112] azimuth are guided by an almost planar potential in front of the step edge, whereas ions impinging along the [110] azimuth experience a corrugated potential. As a consequence ions impinging on the ridges of the structure are reflected early, while the ion trajectories become extended when they impinge into a valley. The surface corrugation in front of a kinked step causes strongly dispersed ion trajectories and the $\xi$-range of significant sputtering along the [110] azimuth deviates from the zone of influence derived from the geometrical model. In agreement with this discussion, the total extent of the zone of influence – defined as the zone, where ion impact leads to a nonzero sputter yield – amounts to 43 Å for ions along the [112] azimuth (impacting a \{111\}-microfaceted step) and to 58 Å along the [110] azimuth (impacting a fully kinked step).

![Figure 5.7: Sputtering yields of 5 keV Ar$^+$ on Pt (111) for $\theta = 83^\circ$ as a function of the distance $\xi$ to the step edge. (a) [112] azimuth (impacts on dense packed step) and (b) [110] azimuth (impacts on kinked step). The dashed lines in (a) and (b) represent the estimate of $Y^{\text{step}}$ at 0 K according to the geometrical model and as obtained from the simulation results via Eq. (5.4).](image)

Fig. 5.7 displays for both azimuthal directions a clear dependence of the sputtering yield on $\xi$, contrary to the expectation (1) from the geometric model (compare Sect. 5.1). The largest yields are obtained for ions directly impinging on step atoms with a small impact parameter and $\xi$ in the range of 0 Å to -10 Å. Minima in the sputtering yield are observed for $\xi$ in the range of -10 Å to -20 Å. These minima are attributed to subsurface channeling. During channeling the Argon ions produce almost exclusively adatom vacancy pairs [see Chapter 4]. The sputtering yield is dramatically decreased compared to direct step edge impacts. Only at the dechannelling position sputtering occurs due to a large scattering event. Moreover, the dechanneled ion leaves the crystal with a significant amount of kinetic energy which is lost for sputtering. The channeling dip at about $\xi = -15$ Å is considerably more pronounced along the [110] azimuth.
5. STEP EDGE SPATTERING THROUGH GRAZING INCIDENCE IONS

Figure 5.8: Representation of the contour lines at $E^\perp = 74$ eV in the channels of a Pt crystal for (a) the [\bar{1}\bar{1}2] azimuth and (b) the [1\bar{1}0] azimuth. $E^\perp$ is the transverse energy of 5 keV Ar$^+$ with $\vartheta = 83^\circ$. The view is along the projection of the ion direction onto the surface plane, i.e. the ions are moving into the plane of paper. Circles show the Pt atom positions and the different shadings indicate that the atoms have different positions in the direction normal to the paper plane.

[Fig. 5.7(b)] compared to the [\bar{1}\bar{1}2] azimuth [Fig. 5.7(a)]. This difference may again be traced back to the differences in the 74 eV contour lines shown in Fig. 5.8. Ions traveling along the [\bar{1}\bar{1}2] direction are guided in between planar potentials of the first and the second layer with only minor perturbations originating from the crystal atoms. Therefore ions performing subsurface channeling along the [\bar{1}\bar{1}2] azimuth have to overcome the planar potential in order to dechannel. This transfers a significant amount of energy to the crystal which results in sputtering at the dechanneling point. In contrast, along the [1\bar{1}0] azimuth the potential is not planar, but strongly corrugated. Due to the strong corrugation ions performing axial channeling along the [1\bar{1}0] azimuth are able to change their axial channel without significant energy loss. This implies that such ions may leave the crystal causing no or only little damage, but also that these ions may penetrate to deeper layers; both effects are observed in the simulations [126] and in the low temperature single ion impacts [see chapter 4]. They contribute to make the channeling dip of the [1\bar{1}0] azimuth more pronounced.

The sputtering yield along the [\bar{1}\bar{1}2] azimuth has a bimodal structure with a second peak in the sputtering yield appearing for $\xi \equiv (-30 \ldots -20)$ Å. This maximum shows up because in this $\xi$-range the projectile atom hits the step after reflection from the lower terrace [see section 2.4.3]. This second maximum is considerably smaller for the [1\bar{1}0] azimuth as indirect hits lead to comparatively less sputtering. The rougher surface potential (Fig. 5.8) steers projectiles into axial channels on the lower terrace; these ions then have a decreased probability of hitting step edge atoms, and hence sputtering is reduced.
To compare the results of the MD simulations with the experimental \( Y^{\text{step}} \) the \( \xi \)-dependent yields are integrated and divided by \( x_c \) resulting from the geometrical model:

\[
Y^{\text{step}} = \frac{\int Y(\xi) d\xi}{x_c}.
\]  

Using (5.4) at 0 K, we obtain \( Y^{\text{step}} = 11.8 \) for the \([\overline{1}12]\) azimuth and \( Y^{\text{step}} = 5.6 \) for the \([1\overline{1}0]\) azimuth. This strong azimuthal dependence is mainly owed to the fact that sputtering due to indirect hits is strongly reduced for the \([1\overline{1}0]\) azimuth, cf. Fig. 5.7.

Taking temperature into account changes the situation (compare blue circles in Fig. 5.7). The most important effect of temperature is an increase of the yields, such that at 550 K \( Y^{\text{step}} = 15.8 \) for the \([\overline{1}12]\) azimuth and \( Y^{\text{step}} = 11.8 \) for the \([1\overline{1}0]\) azimuth. This increase amounts to 34 \% for the \([\overline{1}12]\) azimuth and to 112 \% for the \([1\overline{1}0]\) azimuth. The increase results from step roughening and atomic vibrations which significantly increase the probability of large angle scattering events. This strong temperature dependence is at variance with the expectation (iii) of the geometric model that \( Y^{\text{step}} \) is temperature independent (compare Sect. 5.1). The increase of the yields at \( \xi = 0 \), i.e., when hitting the step edge directly, are primarily due to step roughening. Most noticeably, the channeling dip at \( \xi \approx -15 \) Å is largely filled for both azimuthal directions. Here thermal roughening increases the probability for large scattering events while the ions are guided between the first two layers of the crystal. Subsurface channeling probabilities do not decrease significantly with increasing temperature,[33]; however, the distance a particle channels is strongly reduced and more violent dechanneling events take place.[52] The increase of yield with temperature for the \([1\overline{1}0]\) azimuth is stronger than for the \([\overline{1}12]\) the azimuthal anisotropy of the yield decreases toward higher temperature. At still higher temperatures, the surface will probably appear rather isotropic to the ion beam and all azimuthal dependence will disappear.

Finally, for 0 K the angular dependence of \( Y^{\text{step}} \) has also been investigated by MD simulations. For the \([1\overline{1}0]\) azimuth the yield for \( \vartheta = 86^\circ \) is with \( Y^{\text{step}} = 5.7 \) within the limits of error identical to the one obtained for \( \vartheta = 83^\circ \). Similarly the sputter yields for the \([\overline{1}12]\) azimuth change only little.

### 5.3 Discussion

The experimental and simulation results for \( Y^{\text{step}} \) in both azimuthal directions are summarized in table 5.1. It is obvious from table 5.1 that \( Y^{\text{step}} \) depends on the azimuthal angle. In the range \( \vartheta = 82^\circ - 86^\circ \) experiments and simulations agree that in the \([1\overline{1}0]\) azimuth \( Y^{\text{step}} \) is significantly lower compared to the \([\overline{1}12]\) azimuth by about 20-30 \% at 550 K and even 50 \% for 0 K (simulations only). In the channeling picture (see section 2.2.3) this difference is nothing but expected, as in an fcc metal
5. STEP EDGE SPUTTERING THROUGH GRAZING INCIDENCE IONS

<table>
<thead>
<tr>
<th>angle $\vartheta$</th>
<th>beam direction</th>
<th>$Y_{\text{Step}}$</th>
<th>$\Delta Y_{\text{Step}}$</th>
<th>MD (550K)</th>
<th>MD (0K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>83°</td>
<td>[112]</td>
<td>7.7</td>
<td>0.9</td>
<td>15.8</td>
<td>11.8</td>
</tr>
<tr>
<td>82° 83°</td>
<td>[110]</td>
<td>4.6</td>
<td>0.6</td>
<td>11.8</td>
<td>5.6</td>
</tr>
<tr>
<td>86°</td>
<td>[112]</td>
<td>5.7</td>
<td>0.6</td>
<td>n.a.</td>
<td>10.7</td>
</tr>
<tr>
<td>86°</td>
<td>[110]</td>
<td>4.5</td>
<td>0.9</td>
<td>n.a.</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Table 5.1: Experimental data (550 K) and MD simulation results for 5 keV Ar$^+$ on Pt(111) for the [112] and the [110] azimuth.

Figure 5.9: channeling fraction $\eta(90 - \vartheta)$ versus the angle of incidence $\vartheta$. The channeling fraction has been calculated with formula 2.25.

the [110] direction is the most transparent direction with the largest acceptance angle for channeling.

The lower yields in the [110] azimuth are thus due to a larger channeling fraction of ions, which contribute less to sputtering. In fact, using Ounderdelinden’s transparency concept, (see section 2.2.3) the channeling fraction $\eta(0)$ of 5 keV Ar$^+$ in Pt equals to $\eta(0) = 0.7$ for the [110] azimuth and $\eta(0) = 0.3$ for the [112] azimuth. The angular dependence of $\eta$ is shown in Fig. 5.9. The channeling fraction is calculated with the help of formula 2.25. As already mentioned, for $\vartheta = 90$, the channeling fraction $\eta(90 - \vartheta) = \eta(0)$ is more than a factor of two larger for the [110] direction than for the [112] direction. The angular dependence of the channeling fraction is also different
for the two azimuthal directions. In the case of the $[\bar{1}\bar{1}2]$ azimuth channeling ceases for angles larger than $10^\circ$. In the axial channeling geometry channeling ceases only at angles larger than $15^\circ$. The channeled ions contribute less to sputtering as they lose energy through less violent mechanisms (electronic stopping and non-sputtering surface damage production) and eventually leave the crystal again with a high probability and a significant amount of energy left; lost for sputtering. Contrary to bulk sputtering, ions performing subsurface channeling are not lost entirely for sputtering.

One of the key results of the MD simulations is the temperature dependence of $Y_{\text{step}}$. As visible from table 5.1, $Y_{\text{step}}$ drops by 50% due to lowering the temperature from 550 K to 0 K. This decrease is caused by thermal vibrations, which reduce the channeling fraction of particles. A similar, though weaker, dependence of sputtering on temperature was found also for non-grazing incidence directions close to a channeling direction.\[127]\] The decrease in this case is essentially caused by a decrease of the penetration depth of the ions due to thermal vibrations of the crystal atoms.\[128]\] More energy is transferred closer to the surface resulting in an increase of the sputtering yields. Future experimental and theoretical work is certainly necessary to fully exploit the mechanisms and the relevance of the temperature dependence of sputtering under grazing incidence conditions.

According to table 5.1, $Y_{\text{step}}$ depends on the polar angle $\vartheta$ along the $[\bar{1}\bar{1}2]$ azimuth, but not or to a much lesser extent for the $[1\bar{1}0]$ azimuth. Using the channeling picture again, this fact may be understood from the azimuth dependence of the channeling fraction $\eta$. Fig. 5.9 shows the calculated angular dependence of the channeling fraction. Changing the angle of incidence to smaller $\vartheta$ leads to a decrease of the channeling fraction $\eta$. A decrease of $\eta$ leads to an increase of the sputtering yield. As indicated in Fig. 5.9, the change of the angle of incidence from 86° to 83° changes $\eta$ only by 6% for the $[1\bar{1}0]$ azimuth. However $\eta$ decreases by 32% in the case of the $[\bar{1}\bar{1}2]$ azimuth. The sputtering yields along the $[1\bar{1}0]$ direction are therefore less influenced by subsurface channeling for angles between 86° and 82°.

The trends of MD simulations and experiment are consistent with each other. However the MD simulations tend to overestimate the experimental yields roughly by a factor of two. Similar deviations between simulation and experiment are known from previous work.\[28; 29; 31; 116]\] The origin of this quantitative discrepancy is mainly attributed to an incomplete knowledge of the interatomic interaction potential of Pt. Interatomic potentials are usually fitted to the bulk properties of the material. This also applies to the Pt potential used here; they describe surface properties less reliably. In the present application, however, the properties of surfaces and surface defects play
5. STEP EDGE SPUTTERING THROUGH GRAZING INCIDENCE IONS

...a major role. Moreover, the electronic stopping was ignored in the simulations. This may affect in particular long-ranged channeled projectile trajectories and may lead to an overestimation of sputter yields. Two further issues may affect the quantitative reliability of a molecular-dynamics simulation: (i) the crystallite is too small to contain all projectile trajectories, even though it was as large as appeared justifiable (computing times are of the order of a few weeks / impact angle and azimuth direction on a 100 node PC cluster, in order to gather sufficient statistics). Around 37 % of the ion trajectories for 83° incidence in the [112] azimuth are not contained in the crystallite, i.e. they leave the crystallite via subsurface channeling along a side. Hence the finite size of the simulation volume underestimates the sputter yields by (at most) approximately 37 %. The corresponding numbers for the [110] azimuth have not been evaluated. (ii) Each molecular-dynamics simulation neglects the quantum mechanical zero-point motion of atoms at low temperatures. Typically, above the Debye temperature (240 K for Pt) thermal vibrations may be treated classically, which gives confidence to our 550 K results. However, our 0 K simulations treat the crystal in an idealized way as completely motionless; in the real low-temperature solid, the atoms would not be on ideal lattice positions; the resulting disorder would increase the sputter yield.

Comparing the present experimental results for the [112] azimuth at 83° with the previous experimental results [26] the agreement is satisfactory. The present value obtained at 550 K $Y_{\text{step}} = 7.7 \pm 0.9$ agrees within the limits of error with the previous one of $Y_{\text{step}} = 8.4 \pm 1.5$ obtained at 720 K. The somewhat higher yield, resulting from the higher temperature experiments, could be due to the increase of $Y_{\text{step}}$ with temperature because of the amplitude increase of thermal vibrations.

Finally, the discussion allows to obtain straightforwardly an estimate of the erosion rate $\dot{Y}$ at grazing incidence. Under grazing incidence conditions $Y_{\text{terr}}$ is of the order of zero. Therefore $\rho_{\text{step}}x_{\text{c}}$, the product of step density $\rho_{\text{step}}$ and the width of the zone of influence in front of an illuminated step, gives the fraction of the surface area subject to ion sputtering. The product of this fraction of surface area subject to sputtering with the step edge yield $Y_{\text{step}}$ is the average erosion rate $\dot{Y}$, Eq. (2.35).

In lack of better knowledge, $Y_{\text{step}}$ itself may be well approximated by a TRIM calculation for $Y_{\text{amorph}}(\vartheta)$ at the chosen angle of incidence.[37] TRIM grossly fails to calculate the average yield $\dot{Y}(\vartheta)$ for grazing incidence, as it does not take into account surface channeling. Even under grazing incidence TRIM calculates for every impact random collision cascades involving large angle scattering events. Such cascades are characteristic for step edge impacts, but not for surface impacts. Therefore the source of failure, making TRIM calculations unsuitable to estimate $\dot{Y}$ at grazing incidence makes them suitable to estimate $Y_{\text{step}}$ under these conditions. At grazing incidence, TRIM accounts in a reasonable way for energy loss through the primary ion or other high energy recoils scattered into the vacuum. However, the TRIM values derived
5.4 Conclusions

in such a way for $Y_{\text{step}}$ suffer from two fundamental deficits, which fortunately cause errors of opposite sign. The amorphous yield calculated by TRIM generally underestimates the crystalline yield obtained for identical parameters in a non channeling direction.\[28; 127]\ As an example, the normal incidence yield of 5 keV Ar$^+$ onto Pt(111) is calculated by TRIM to be 5.4, while the experimental result is 7.4. For the same reason TRIM neglects subsurface channeling and therefore tends to overestimate the experimental yield. As both errors are of opposite sign and similar magnitude they tend to cancel. For example TRIM yields for $Y_{\text{amorph}}(83^\circ) = 6.5$ which compares reasonably well with the values of 7.7 and 4.6 (see table 5.1) for the $[\bar{1}12]$ and $[1\bar{1}0]$ azimuth, respectively. The estimate can be expected to predict the grazing incidence erosion rate in a wide parameter range correctly to within a factor of 2. However the estimates have to be treated with care, as subsurface channeling is different from bulk channeling. Channeling particles are not lost entirely for sputtering and the extent to which these particles contribute to sputtering depends strongly on temperature.

5.4 Conclusions

With the onset of surface channeling for grazing incidence, ion sputtering from flat surface regions of crystals ceases and the average erosion rate is exclusively determined by sputtering of step edges illuminated by the ion beam. The sputtering of these steps results not only from direct impacts but also from ions reflected by surface channeling on the lower terrace near the step. Here two new experimental methods to obtain the step edge yield $Y_{\text{step}}$ have been applied for grazing incidence conditions. The results of these methods are consistent with each other and also agree with previous measurements \[26]. Step edge yields display a clear dependence on the azimuthal angle. Molecular dynamics simulations evidence that this dependence is due to the azimuthal dependence of surface and subsurface channeling. They also display a strong dependence of $Y_{\text{step}}$ on temperature, primarily caused by the influence of vibrations on channeling. A simple procedure to estimate the average erosion rate under grazing incidence is given, which needs as input only the step concentration and the sputtering yield as calculated by TRIM for the chosen angle of incidence.
5. STEP EDGE SPUTTERING THROUGH GRAZING INCIDENCE IONS
Chapter 6

Effect of adatom cluster adsorption on surface damage

6.1 Introduction

The experimental results presented in the preceding chapter show that the sputtering yield at step edges is roughly two orders of magnitude larger than at the flat terrace in the case of grazing incidence ion bombardment. However, even for 86° ion incidence, terrace sputtering is not completely absent since vacancy island formation is observed. This is not in accordance with the molecular dynamics simulations [compare Fig. 5.1 and Fig. 5.6]. The hypothesis is as follows: although the reflection coefficient is very close to zero, some ions eventually create some adatoms and vacancies. Some of them form stable clusters whereas others recombine. These small adatom and vacancy clusters, which are hit by subsequent ions, grow due to sputtering.

Therefore it would be very interesting to study the influence of single adatoms on the terrace sputtering yield experimentally. For a recent molecular dynamics study, the reader is referred to [53]. However, there are a number of experimental difficulties that rule out a measurement with reasonable precision for the near future. A surface with a small coverage of randomly adsorbed Pt adatoms on Pt(111) is easy to prepare at temperatures below 100 K, where Pt adatoms are immobile [28]. One can also measure the sputtered material by investigating the surface, after bombardment, by STM. However, each ion interaction with an adatom changes the local situation, causing sputtering, damage creation (adatom-vacancy pairs) or at least adatom relocation. Thus after a very small number of impacts, much less than one ion interaction with each adatom, the surface situation will deviate drastically from the situation initially prepared.

Therefore the influence of single adatoms on the sputtering yield is not investigated. Instead, the influence of small adatom clusters is analyzed. At first glance, this situation
appears to be even more complicated. However, it will be shown below that preparing a surface with adatom clusters is feasible and the sputtering yield on the flat terrace is significantly influenced by the presence of small adatom clusters.

6.2 Experimental procedure

The experimental procedure is described in detail in chapter 3. Here, only the additional information is mentioned. The adatom clusters have been prepared by physical vapor deposition of platinum on Pt(111). A surface temperature of 150 K has been chosen. At this temperature single adatom diffusion is activated but small adatom clusters are immobile. The deposition rate has been set to $2.4 \cdot 10^{-3}$ ML/s. After the preparation of the adatom clusters, the surface has been exposed to a fluence of 0.5 MLE at 83°. In this case 5 keV Ar$^+$ ions have been used and the azimuthal orientation of the crystal was parallel to the [110] direction. The bombardment and the subsequent STM imaging is performed at 150 K in order to prevent annealing of the ion induced defects. In order to characterize the amount of removed material the surface is annealed to 720 K for 120s. The topography and the amount of removed material is analyzed again. The results of this investigation are compared to an experiment where no adatom clusters were present at the surface prior to ion erosion.

6.3 Results

6.3.1 Preparation of small adatom clusters

Fig. 6.1(a) shows a scanning tunneling microscopy image after deposition of 0.1 ML Pt on Pt(111) at a surface temperature of 150 K. The surface is covered with a large amount of small adatom clusters which are mostly of monoatomic height. The cluster size distribution is broad. Annealing to 650 K for 120 s [Fig. 6.1(b)] has been performed in order to quantify the deposited amount of Pt. The small adatom clusters have coalesced and adatom islands of hexagonal shape have been formed. The size of these islands is large enough to deduce the deposited amount accurately.

In order to estimate the cluster sizes the following procedure has been used. First the area of each cluster is estimated with the help of a flooding algorithm implemented in WSxM [129]. Since the clusters are extremely small, the finite size of the tip over-estimates the deposited amount and the cluster size significantly. The evaluation with the flooding algorithm yields cluster sizes which are too large. In order to correct this error the apparent deposited amount, measured at low temperature [Fig. 6.1(a)], is compared to the measured deposited amount after annealing to 650 K [Fig. 6.1(b)]. The resulting ratio is used to scale the cluster sizes down to a realistic value. The result is shown in Fig. 6.2 where the cluster sizes are plotted versus the number of counts.
6.3 Results

Figure 6.1: (a) STM topographs after deposition of 0.1 ML Pt on Pt(111) at a surface temperature of 150 K. The image size equals to 750 Å × 750 Å. (b) Annealing of experiment shown in Fig. 6.1(a) to 650 K for 120 s. Image size: 1750 Å × 1750 Å.

The cluster size distribution is very broad with a maximum at roughly 20 atoms per cluster followed by a long tail up to 150 atoms per cluster. The evaluation is intended to yield a rough estimate on the cluster size present in the experiment. The error is quite large which becomes evident from Fig. 6.2 where some adatom clusters show an area which is smaller than the area of one atom. This is certainly not physically meaningful. One assumption, which is not valid, is that the overestimation of the STM tip is independent of the cluster size. Moreover, adsorbates and small adatom clusters cannot be distinguished in the STM images. Therefore adsorbates are also counted as adatom clusters which might influence the cluster size distribution.

6.3.2 Sputtering at adatom clusters

After the characterization of the adatom clusters two experiments have been performed. First, a reference measurement without adatom clusters has been done. An ion fluence of 0.5 MLE, an angle of incidence of 83° and a surface temperature of 150 K have been chosen. The result is shown in Fig. 6.3(a). The morphology consists of small adatom- and vacancy clusters. An alignment of the adatom and vacancy clusters in the direction of the ion beam is visible. It results from subsurface channeling. The amount of removed material is measured from Fig. 6.3(b) where the morphology, shown in Fig. 6.3(a), has been annealed for 120 seconds to 720 K. The total amount of removed material in this experiment equals to $\Theta_{\text{terr}}=0.17$ ML.
The result of this experiment is surprising. Although the terrace sputtering yield is very low (compare with results in chapter 5), the surface has roughened considerably. The enhanced roughening compared to 550 K is a result of the reduced surface diffusion. The ion induced surface damage is not annealed efficiently, as at 550 K, but stays on the surface. Large scattering events at those defects occur which results in sputtering.

The second experiment is performed in a similar way except that prior to ion erosion the surface has been covered with the adatom clusters shown in Fig. 6.1(a). The result after ion erosion is shown in Fig. 6.3(c). No big difference to the experiment without adatom clusters is apparent at first glance [Fig. 6.3(a)]. Small adatom clusters and surface trenches produced by the ion beam are visible. In order to quantify the amount of removed material the sample is annealed to 720 K for 2 minutes and the result is shown in Fig. 6.3(d). The amount of removed material equals to 0.24 ML. If one takes into account that, prior to the ion bombardment, the surface was already covered with 0.1 ML of adatom clusters the total amount of removed material equals to $\Theta_{ad}=0.34$ ML. Comparing this result to the experiment where a clean surface has been used, shows an increase of the amount of removed material by a factor of two.

However, it is not possible to deduce from $\Theta_{terr}$ and $\Theta_{ad}$ immediately the sputtering yield at small adatom clusters. The reason is the quick roughening of the initially flat surface. After a very short induction time (well below the fluence of 0.5 MLE),
6.3 Results

Figure 6.3: STM topographs after ion erosion with 5keV Argon at a surface temperature of 150 K. (a) Ion erosion on an initially flat surface. (b) Annealing of the experiment shown in (a) at 720K for 120s. (c) Ion erosion on surface covered with small adatom clusters. (d) Annealing of experiment (c) at 720K for 120s. The direction of the ion beam is indicated with a white arrow. The image size in (a),(c) 750Å × 750Å, (b),(d) 1750Å × 1750Å.

Sputtering on the flat terrace proceeds via impacts at adatom clusters. The experiment performed without adatoms is therefore a mixture between terrace sputtering and adatom cluster sputtering. The quick roughening does not result from a larger terrace sputtering yield at lower temperatures. The terrace sputtering at 150 K is even lower than at 550 K (compare Fig. 5.6). Subsurface channeling, which produces damage over long distances, is responsible for the quick production of many surface defects. In contrast to high temperature ion erosion, where this damage quickly anneals, low temperature erosion leads to stable defects. At the adatoms and vacancies large scattering events occur which increase the terrace erosion rate. From the single ion impact experiments and from the sputtering yield evaluations discussed in the preceding
chapters, we know that the terrace sputtering yield is very close to zero. The terrace damage $\Theta_{\text{terr}}$ can therefore be attributed almost exclusively to sputtering at surface defects which have been created shortly after the ion erosion started.

The sputtering yield of small adatom clusters is therefore not deduced with the help of the reference measurement. It is estimated with the same evaluation as in the case of step edge sputtering presented in chapter 5. In the case of a constant number of ascending step edges, the erosion rate $\bar{Y}$ (i.e. the removed material per ion fluence) is constant. The adatom cluster concentration is measured before [Fig. 6.1(a)] and after the ion erosion [Fig. 6.3(c)] from profile lines in ion beam direction as shown in Fig. 6.3(c). The analysis shows that the cluster density after deposition equals to $\rho_{\text{ad}}=0.019 \pm 0.001$ 1/Å, and after subsequent ion erosion to $\rho_{\text{ad}+\text{ions}}=0.016$ 1/Å $\pm$ 0.002 1/Å. This shows that the cluster density stays roughly constant, which is the prerequisite for the evaluation of the sputtering yield at the adatom clusters with the help of formula 6.1 (see chapter 5 for derivation of the formula).

$$Y_{\text{ad}} = \frac{\bar{Y}}{\rho_{\text{ad}} \cdot x_C}$$

(6.1)

The erosion rate has been measured experimentally and equals to $\bar{Y} = \Theta_{\text{ad}}/F=0.68$. The one dimensional step edge concentration in ion beam direction is denoted with $\rho_{\text{ad}}$ and $x_C$ denotes the zone of influence of an ascending step edge. The zone of influence in the case of 83$^\circ$ equals to 36.65 Å mean step edge concentration of $\rho_{\text{ad}}=(\rho_{\text{ad}}+\rho_{\text{ad}+\text{ions}})/2=0.0175$ 1/Å is assumed.

Applying formula 6.1 results in a sputtering yield at small adatom clusters of $Y_{\text{ad}}=1.1 \pm 0.2$. Comparing this result with the step edge sputtering yield at 82$^\circ$ and 550 K ($Y_{\text{step}}=4.6$) shows a significant deviation. In the case of small adatom clusters the sputtering yield is decreased by a factor of 4.

An error discussion is in place here. The evaluation assumes that the zone of influence $x_C$ of an adatom island is identical to the zone of influence of an ascending step edge. Since $x_C$ does only arise from the height of a surface defect, which is identical in the case of adatoms and step edges, and from the angle of incidence, this assumption is justified. Moreover molecular dynamics simulations suggest that in the case of adatom clusters $x_C$ is identical to the value for step edges [51].

The second question is related to the effect of shadowing. Since the density of clusters is large, the open space between two adjacent clusters is small. The question arises whether the zone of influence is partially blocked by descending step edges. From $\rho_{\text{ad}}$ one deduces a mean distance between the clusters of 57 Å. The shadowing length $l_{\text{shadow}}$ of a step edge has to be at least $l_{\text{shadow}} = d \cdot \tan \theta = 18$ Å from geometry. Adding $l_{\text{shadow}}$ to $x_C$ leads to the minimum distance of 55 Å between two adjacent clusters. This evaluation shows that from geometry the zone of influence should be fully active.
6.3 Results

However, one has to take into account that rainbow scattering at the descending step edges [1] changes the trajectories of the impinging ions considerably. This error cannot be estimated from experiment. Molecular dynamics simulations could clarify this issue.

Moreover the experiments in this chapter have been performed at a surface temperature of 150 K, whereas the step edge sputtering yield has been measured at 550 K. Molecular dynamics simulations showed that the sputtering yield is temperature dependent (see chapter 5). In order to check how large the influence of temperature is, the following assumption has been made: the sputtering yield increase caused by an increase in temperature is proportional to the root mean square phonon amplitude $\Delta \mu$ which can be calculated with the help of formula 6.2.

$$<\Delta \mu>^2 = \frac{3h^2T}{4\pi^2mk_BT_{Debye}^2}$$  \hspace{1cm} (6.2)

$T$ is the crystal temperature, $m$ the atomic mass and $T_{Debye}$ the Debye temperature. The assumption is justified since the sputtering yield depends on the subsurface channeling probabilities and the dechanneling characteristics. As the effect of temperature in channeling related effects is usually described by the rms phonon amplitudes [42], the assumption is realistic. The calculation shows that the decrease of the surface temperature from 550 K to 150 K decreases the sputtering yield by 25%. The step edge sputtering yield $Y_{step}$=4.6 can be scaled down to $Y_{step}$= 3.5.

This error discussion shows that the sputtering yield for small adatom clusters $Y^{rad}$ is roughly three times smaller than the sputtering yield $Y_{step}$ at ascending step edges which have an extended upper terrace. This statement relies on the assumption that the shadowing effect is not too large.

In order to find a physical explanation for the different sputtering yields at small adatom clusters and at step edges with an extended upper terrace, the following experiment at a higher surface temperature has been performed. First, 0.1 ML Pt is deposited on Pt(111) at a surface temperature of 300 K. The surface is then heated up to 550 K. Thereby the small adatom clusters coalesce to bigger adatom islands. Afterwards the sample is exposed to 5 keV Argon ions with a fluence of 0.5 MLE. The result of the experiment is shown in Fig. 6.4(a). Big adatom islands together with aligned vacancy cluster formation can be seen in the STM topography. Two interesting observations can be made. (I) In a significant number of adatom islands small vacancy clusters can be found resulting in a “donut” like shape. (II) Aligned adatom and vacancy formation preferentially occurs behind the adatom islands. Both observations are highlighted in Fig. 6.4(a).

The creation of small “donut” adatom islands can be explained by subsurface chan-
6. EFFECT OF ADATOM CLUSTER ADSORPTION ON SURFACE DAMAGE

Figure 6.4: (a) STM topography after deposition of 0.1 ML Pt on Pt(111) at 300K followed by 5keV Ar$^+$ sputtering at 83° and 550K. The ion fluence was 0.5 MLE. “Donut” formation (I) and aligned vacancy formation behind the adatom islands (II) are observed. Black arrow indicates the direction of the ion beam. Image size: 1750Å × 1750Å. (b) Sketch of the physical mechanisms which explain the observed morphology in Fig. 6.4(a), details see text.

neling at the illuminated ascending step edges of the islands as illustrated in Fig. 6.4(b). The ions channels in between the first and the second layer [Fig. 6.4(b) (Ia)] and creates adatoms and vacancies [Fig. 6.4(a) (Ib)]. These defects diffuse over the small terrace of the island and are either annihilated at the descending step edges or create stable clusters on the island. Adatom clusters are illuminated by the ion beam. It is very likely that these defects will be quickly irradiated away. Small vacancy clusters do not have a full zone of influence due to shadowing and are therefore much more stable. This mechanism could explain the “donut” formation observed in the STM topographs.

The same mechanism explains the lower sputtering yield at adatoms clusters ($Y^{ad}$) compared to step edges with an extended upper terrace ($Y^{step}$). A lot of subsurface channeling events occur between the first and the second layer of the crystal. At the small adatom clusters the ions enter into the crystal and after a short channeling distance, they exit the cluster on the other side. No dechanneling event occurs here. This means that only little energy transfer to the crystal occurs. This decreases the sputtering yield at extended upper terraces since there the ion often exits the crystal by large scattering event, which leads to sputtering.

The second observation is the formation of chains of vacancy clusters in ion beam direction behind the adatom islands. This is at first glance strange since one would
assume that the descending step edge creates a shadow where the ion is not able to induce damage. However, from the single ion impact investigations, we know that deeper layer channeling is possible, which leads to a possible explanation of the observed morphology. As illustrated in Fig. 6.4(b) the ion performs deeper layer channeling (IIa) with results in damage behind the adatom island. The produced adatoms can diffuse to the step edges where they are annihilated. The vacancies remain behind the step edge (they cannot be annealed at the step due to the step edge barrier) and grow due to subsequent impacts. This explains the formation of the vacancy chains in ion beam direction situated behind the adatom islands.

6.4 Conclusion

The experiments presented in this section show that the terrace is eroded faster if small adatom clusters are present on the surface. However, the adatom cluster yield $Y_{\text{ad}}$ is roughly three times smaller than $Y_{\text{step}}$ deduced in chapter 5. Ions hitting the small adatom islands cause either large scattering events, which results in sputtering, or subsurface channeling occurs. Due to the small lateral extension of the adatom cluster the channeled ions have a large probability to exit the cluster on the other side. The ion exits the crystal without a large scattering event. As a consequence, very little energy is deposited in the crystal and the sputtering yield is low. This mechanism, which could explain the smaller yields at small adatom clusters compared to $Y_{\text{step}}$, is supported by molecular dynamics simulations which can be found in [51].

The adatom cluster sputtering yield $Y_{\text{ad}}=1.1$ is roughly a factor of 13 larger than the terrace sputtering yield $Y_{\text{terr}}=0.08$ deduced by Hansen et al. [26] for the case of 5 keV Argon impinging at 83° on a flat terrace. It can be concluded that small adatom clusters present on the flat terrace increase the probability for large scattering events which results in a larger terrace yield.
6. EFFECT OF ADATOM CLUSTER ADSORPTION ON SURFACE DAMAGE
Chapter 7

Terrace damage and the effect of adsorbates on its formation

Whether adsorption influences the sputtering yield is a question rarely posed and usually considered to be irrelevant. Indeed there is very little reason to believe that adsorbates influence the sputtering yield and surface damage at normal incidence. The energy of the primary ion is efficiently transferred to the substrate atoms causing thereby sputtering, irrespective of whether adsorbates are present or not. As a consequence of the large amount of energy transferred to the substrate, a collision cascade and a subsequent thermal spike develop ensuring efficient adparticle desorption from the surface. Therefore even in the presence of a background pressure only a moderate adsorbate concentration will establish.

As already discussed in the preceding sections, grazing incidence ion bombardment is very surface sensitive which results in a large reflection coefficient of the impinging ions, surface channeling and only little terrace sputtering. Adsorbates present on the surface disturb the planarity of the surface potential and large angle scattering events take place. Ions hitting the adsorbates become scattered and will energize the adsorbate, thereby causing not only a vastly increased energy transfer to the surface with the consequence of sputtering, but also adsorbate desorption. This property is used in low energy ion scattering measurements (LEIS) to determine the structure, coverage and sticking coefficient of adsorbates [4; 130; 131]. The ion induced desorption has been studied in detail; however, morphology changes due to large scattering events have not been studied extensively.

This chapter shows a combined scanning tunneling microscopy and molecular dynamics study where adsorbate induced sputtering on the flat terrace and ion induced desorption are investigated. In this case 5 keV Ar$^+$ ions impinging at angles between 81° and 87° with respect to the surface normal on Pt(111). Molecular oxygen ($O_2$) and carbon monoxide (CO) are used to study the ion-adsorbate interaction. The surface
changes due to adsorbates are investigated for low ion fluences and initial flat surfaces as then adsorbates disturb surface channeling most significantly.

The effect of a carbon monoxide background pressure on surface damage and sputtering is tested by exposing the surface to a carbon monoxide partial pressure $P_{CO} = 1 \cdot 10^{-8}$ mbar starting 300 s prior to ion erosion. This is enough time to establish an initial adsorption-desorption equilibrium at 400 K with a molecular coverage $\Theta_{CO} = 0.12$ ML, as estimated on the basis of the data of Poelsema et al. [132]. An ion exposure $F = 1$ MLE and $\vartheta = 87^\circ$ were used. Due to repulsive CO-CO interaction [133] and at $\Theta_{CO} = 0.12$ ML the CO overlayer must be assumed to be disordered, however with a preferential adsorption to step edges. At the temperature of 400 K, used in the adsorption experiments, the initial sticking coefficient $S_{CO}$ of CO differs only little from 0.8, the value measured at room temperature. The results are presented in Section 7.1. The experiments investigating the effect of an oxygen background pressure on surface damage and sputtering are described in Section 7.2. A clean, adsorbate free surface is prepared by sputtering and annealing. Afterwards the sample temperature is set to 550 K and then the sample is exposed to a preset oxygen partial pressure $P_O$ up to $1 \times 10^{-5}$ mbar through backfilling of the vacuum chamber. Immediately after establishing $P_O$ the ion bombardment with $\vartheta = 85.5^\circ$ started and terminated after $F = 0.5$ MLE was reached. Oxygen adsorbs dissociatively on the Pt(111) surface at temperatures above 150 K forming an adlayer with a saturation coverage of oxygen amounting to $\Theta_O = 0.25$ ML. At 550 K the oxygen adlayer forms a disordered adsorbate layer, as the p(2×2) adlayer spots diminish with temperature in intensity and are already at 400 K only faintly visible [134]. At 550 K the initial sticking coefficient $S_O$ of oxygen molecules is 0.03 [135]. Desorption of oxygen becomes significant at 600 K [136; 137]. For the experiments investigating the effect of the incidence angle on surface damage and sputtering at 550 K described in Section 7.4 an adsorbate free situation is compared to one with the sample exposed to $P_O = 5 \times 10^{-6}$ mbar and $\vartheta$ was varied from $\vartheta = 81^\circ - 87^\circ$. In order to achieve comparable results $F$ was selected such that the removed amounts of material $\Theta_S$ were comparable and well below 1 ML. STM imaging was performed at room temperature, where the surface morphology is frozen. The experiments are supplemented with molecular dynamics simulations performed by the research group of Prof. Urbassek. A detailed description of the simulation setup can be found in reference [51].

7.1 The effect of a CO background pressure

Figure 7.1 compares the surface morphology after 1.0 MLE 5 keV Ar$^+$ ions incident at 87° on Pt(111) at 400 K in the absence [Fig. 7.1(a)] and in the presence [Fig. 7.1(b)] of a CO partial pressure of $P_{CO} = 1 \cdot 10^{-8}$ mbar. From the comparison of the topographs
7.1 The effect of a CO background pressure

Figure 7.1: STM topographs after 1.0 MLE of 5 keV Ar\(^+\) ions incident at 87° on Pt(111) at 400 K. (a) Ion exposure in the absence of a CO partial pressure, (b) \(P_{CO} = 1 \cdot 10^{-8}\) mbar. The direction of the impinging ions is indicated with a black arrow. The image size is 1750 Å \(\times\) 1750 Å. The dotted line is the projection of the preexisting step edge to the position where the number of vacancy islands starts to increase (see text).

It is obvious that the removed amount of surface layer Pt is substantially increased through the presence of the \(P_{CO}\). While in Fig. 7.1(a) only small vacancy islands of monolayer depth are visible, in Fig. 7.1(b) both number and size of the vacancy islands are largely increased. The vacancy islands are frequently elongated along the ion beam direction. Also a few adatom islands are visible, which result from the nucleation of atoms pushed onto the surface in consequence of large angle scattering events. The CO background pressure causes an enhancement of the visible removed material by a factor of 7. The removed amount \(\Theta_S\) is increased from \(\Theta_{S,clean} = 0.04\) ML to \(\Theta_S = 0.28\) ML which corresponds to an adsorbate induced increase of \(\Delta \Theta_S = 0.24\) ML. Due to the admittance of the CO 300 s prior to the beginning of ion exposure a coverage \(\Theta_{CO} = 0.12\) ML is established [132]. Although this coverage diminishes under the action of the ion beam, it must be concluded that the adsorbed molecules are the origin of the enhanced \(\Theta_S\). The CO molecules are highly mobile on the surface and form no ordered structure.

How do the adsorbed CO molecules increase the amount of removed material \(\Theta_S\)? To this end we first consider the interaction of the ion beam with the clean, adsorbate free substrate. The ions arriving at the surface are almost perfectly reflected from the surface (surface channeling). At \(\vartheta = 87°\) the kinetic energy of motion along the surface
normal

\[ E_\perp = E_0 \cdot \cos^2 \vartheta \]  

(7.1)

amounts to only 14 eV and is not sufficient to induce sputtering on a perfect terrace. At most occasionally adatom – surface vacancy pairs are created. Although these pairs most frequently recombine due to diffusion eventually a few vacancy and adatom clusters form. Adatoms and adatom clusters are elevations exposed to the ion beam. Thus they are efficiently sputtered through large angle scattering processes of impinging ions. Also larger vacancy clusters expose an illuminated step to the ion beam allowing impinging ions to transfer significant amounts of kinetic energy to the substrate through large angle scattering processes which cause sputtering. Let us now consider the interaction of the ion beam with a surface of randomly positioned adsorbates. The adsorbates are illuminated by the ion beam and large angle scattering processes take place right from the beginning and in large numbers at the adsorbate locations. These scattering processes have two consequences (i) the adsorbed molecules are partially desorbed from the surface and (ii) the scattered primary ion or the energized molecule transfers a significant amount of energy to substrate atoms causing sputtering and adatom formation. Note that the desorbed CO molecules are partly replenished from the CO background pressure. An indirect consequence of the adsorbate induced sputtering is the rapid formation of vacancy islands (and to a lesser extent of adatom islands), which themselves display steps to the ion beam and are sputtered. In this sense the direct adsorbate induced sputtering is amplified by the ensuing formation of steps illuminated by the ion beam.

An interesting detail is visible in Fig. 7.1(b). The descending step edge displays in the shadow of the ion beam on the lower terrace a depletion zone where the number of vacancy islands is reduced in comparison to the flat terrace. The dotted line indicates the boundary of the vacancy depleted shadow zone. Through the step shadow ions do not or only with lower probability hit the terrace and adsorbed particles. The distance between the step edge and the dotted line is 137 Å ±10%.

As CO is one of the major components in the background gas of ultra high vacuum systems and as CO has typically a large initial sticking coefficient on metal surfaces [e.g. \( S_{CO,0} = 0.8 \) for Pt(111)], CO adsorption cannot be avoided at room temperature [73]. Therefore ion scattering experiments on metal surfaces using the grazing incidence geometry are always subject to enhanced surface sputtering and roughening due to adsorbate scattering. It is likely that the removed material under nominally clean conditions as visible in Fig. 7.1(a) is to a significant extent caused by a minute and unavoidable amount of adsorbed particles from the background gas.
7.2 Oxygen covered surface

Figure 7.2: STM topographs after a fluence of 0.5 MLE 5 keV Ar$^+$ ions at 550 K and 85.5° with respect to the surface normal. (a) No oxygen partial pressure $P_O$, (b) $P_O = 1 \cdot 10^{-7}$ mbar, (c) $P_O = 1 \cdot 10^{-6}$ mbar, (d) $P_O = 1 \cdot 10^{-5}$ mbar. In (a) the direction of the ion beam is indicated by an arrow. The insets display the corresponding topographs after annealing to 720 K for 120 s. The image sizes are 1750 Å × 1750 Å, the inset sizes are 1000 Å × 1000 Å.

7.2 Oxygen covered surface

Figs. 7.2(a-d) compare the surface morphology after exposure to 0.5 MLE 5 keV Ar$^+$ at 550 K in the absence of an oxygen partial [Fig. 7.2(a)] and in the presence of oxygen.
7. TERRACE DAMAGE AND THE EFFECT OF ADSORBATES ON ITS FORMATION

partial pressures $P_O = 1 \cdot 10^{-7}$ mbar [Fig. 7.2(b)], $P_O = 1 \cdot 10^{-6}$ mbar [Fig. 7.2(c)] and $P_O = 1 \cdot 10^{-5}$ mbar [Fig. 7.2(d)]. It is obvious that the amount of removed material visible as the dark surface vacancy islands of monolayer depth depends dramatically on the oxygen partial pressure. Already for $P_O = 1 \cdot 10^{-7}$ mbar in Fig. 7.2(b) the number density of vacancy islands increased by a factor of six compared to the clean experiment represented by Fig. 7.2(a). The higher oxygen partial pressures of Figs. 7.2(c-d) increase the size of the vacancy clusters, whereas their number density stays roughly constant. For $1 \cdot 10^{-5}$ oxygen partial pressure in Fig. 7.2(d) also a significant number of adatom clusters is visible [small bright dots in Fig. 7.2(d)]. To establish the amount of removed material $\Theta_S$ quantitatively, after imaging, the samples were annealed for 120 s to 720 K and subsequently re-imaged (insets in Fig. 7.2). The bulk vacancies created by ion impacts migrate during the annealing step to the surface such that afterwards the area of the monolayer islands represents to a very good approximation $\Theta_S$ [88]. $\Theta_S$ is plotted in Fig. 7.3 (full squares) as a function of $P_O$ on a logarithmic scale. It increases from 0.015 ML to roughly 0.20 ML for $P_O = 1 \cdot 10^{-3}$ mbar corresponding to an increase by a factor of 13 due to the presence of oxygen adsorbates on the surface. Qualitatively the increase of $\Theta_S$ with $P_O$ may be understood similar as for the case of adsorbed CO molecules: (i) It is due to direct sputtering caused by the energized adsorbate or the scattered primary ion. (ii) The direct sputtering associated with the adsorbate fosters formation of vacancy islands and adatom clusters which are sputtered by ions illuminating them.

In order to study the effect of adsorbates in more detail the time dependent oxygen coverage $\Theta_O(t)$ is calculated. It is determined by the balance of adsorption from the background pressure and desorption due to the impinging ions. Desorption due to impinging ions is quantified through the desorption cross section $\sigma_O$ being the average number of oxygen atoms desorbed per incident ion $Y_O$ normalized with the adsorbate concentration $\rho_O$ as introduced in section 2.2.4:

$$\sigma_O = \frac{Y_O(t)}{\rho_O(t)} = \frac{Y_O(t)}{\Theta_O(t)} \cdot \Omega.$$  (7.2)

Here $\Omega = 6.67$ Å$^2$ is the area of a Pt surface site. In the following analysis, we assume $\sigma_O$ to be independent of $\rho_O$. This is certainly valid for small $\rho_O$, but a serious approximation for large $\rho_O$. The oxygen coverage $\Theta_O(t)$ at a time $t$ results from the balance of adsorption from the background and desorption through the ion beam and depends on the adsorption and desorption history. To calculate the increase in the oxygen coverage $\Theta_O$ due to adsorption we assume simple Langmuir adsorption kinetics resulting in

$$\frac{d\Theta_O}{dt} = \frac{2}{\Theta_{sat,O}} \cdot \Omega \cdot \phi \cdot S_O \cdot (\Theta_{sat,O} - \Theta_O)$$  (7.3)
7.2 Oxygen covered surface

Figure 7.3: Amount of removed material $\Theta_S$ as a function of oxygen partial pressure $P_O$. The solid curve is a fit to the experimental data using equation 7.8. The inset shows the evolution of the oxygen coverage versus ion fluence $F$ for the values of $P_O$ used, calculated on the basis of (7.6) and the measured desorption cross section $\sigma$ (see text).

Here $\phi$ is the flux of impinging oxygen molecules. The product $\Omega \cdot \phi$ is the particle flux in units of ML/s and the factor of $\frac{2}{\Theta_{sat,O}} = 8$ in (7.3) takes into account that oxygen adsorbs dissociatively resulting into two adsorbed oxygen atoms and that the saturation coverage of oxygen $\Theta_{sat,O}$ is 0.25 ML with respect to the Pt surface sites. The flux of molecules $\phi$ is given by the Knudsen equation $\phi = \frac{P}{\sqrt{2\pi mk_bT}}$, with $P$ being the pressure, $m$ the molecular mass, $k_b$ the Boltzmann constant and $T$ temperature. The sticking coefficient $S_O$ in (7.3) is assumed to be coverage independent for simplicity (identical to the initial one of 0.03 [135]). The decrease of $\Theta_O$ due to the ion impingement is given by

$$\frac{d\Theta_O}{dt} = -f \cdot \sigma_O \cdot \Theta_O \quad (7.4)$$

In total the change of $\Theta_O$ is thus

$$\frac{d\Theta_O}{dt} = 8 \cdot \Omega \cdot \phi \cdot S_O (\Theta_{sat,O} - \Theta_O) - f \cdot \sigma_O \cdot \Theta_O \quad (7.5)$$

Experimentally adsorption and ion erosion both start at $t = 0$. With this boundary
condition the solution of this differential equation results in

$$\Theta_O(t) = \frac{8 \cdot \Omega \cdot \phi \cdot S_O}{8 \Omega \cdot \phi \cdot S_O + \sigma_O \cdot f} \cdot (1 - \exp \left[ -\left( 8 \Omega \cdot \phi \cdot S_O + \sigma_O \cdot f \right) \cdot t \right]) \cdot (7.6)$$

The simplest reasonable assumption on the dependence of the additional sputtering yield on $\Theta_O(t, \sigma_O)$ is a linear dependence, i.e.

$$Y_S(t) - Y_{S,clean} = \Delta Y_S(t) = \gamma \cdot \Theta_O(t, \sigma_O), \quad (7.7)$$

where $Y_S(t)$ is the number of surface atoms sputtered per incident ion for a given $\Theta_O$ (the sputtering yield for $\Theta_O \neq 0$), $Y_{S,clean}$ is the number of surface atoms sputtered per incident ion for $\Theta_O = 0$ (the sputtering yield of the clean surface), $\Delta Y_S$ is the number of additionally sputtered atoms per incident ion due to the presence of oxygen adsorbates (the additional sputtering yield) and $\gamma$ a proportionality factor. $\Theta_S$ measured in the experiment is the result of ion exposure to a fluence $F$ for a certain period of time $\tau$. Thus

$$\Theta_S = f \cdot \Omega \cdot \int_0^\tau Y_S(t) dt = f \cdot \Omega \cdot \int_0^\tau (\gamma \cdot \Theta_O(t, \sigma_O) + Y_{S,clean}) dt \quad (7.8)$$

Here $f \cdot \Omega$ is the flux of incident ions in units of MLE/s. The sputtering yield of the clean surface is measured experimentally to be $Y_{S,clean} = 0.03$. Equation (7.8) is fitted to the experimental data by adjusting the parameters $\gamma$ and $\sigma_O$. The best fit is plotted in fig.7.3 (solid curve) for $\gamma = 1.61 \pm 0.1$ and $\sigma_O = 2.0 \cdot 10^{-15} \text{cm}^2 \pm 1.4 \cdot 10^{-15} \text{cm}^2$. In view of the simplicity of our approach the experimental data are well reproduced by the fit. The proportionality constant $\gamma$ fitted above has also a substantial interpretation. To characterize the ability of an adsorbed oxygen to induce additional sputtering we may define in analogy to the desorption cross section the sputtering cross section

$$\sigma_S = \frac{\Delta Y_S(t)}{\rho_O(t)} = \frac{\Delta Y_S(t)}{\Theta_O(t)} \cdot \Omega. \quad (7.9)$$

The sputtering cross section $\sigma_S$ can be interpreted as the additional average surface area which is sputtered by a single ion due to adsorbed oxygen. Comparison of (7.9) with (7.7) makes plain that

$$\gamma = \frac{\sigma_S}{\Omega}. \quad (7.10)$$

Thus by fitting (7.8) to obtain $\gamma$ we also determined $\sigma_S = 1.07 \cdot 10^{-15} \text{cm}^2 \pm 0.06 \cdot 10^{-15} \text{cm}^2$. Some scatter of the data around the fit for larger $P_O$ is not surprising since the model used is crude. To derive an explicit expression for $\Theta_O(t)$ we assumed a coverage independent sticking coefficient, which is especially for larger $P_O$ a poor approximation.

Moreover, we attributed the entire increase of $Y_S$ implicitly to the large angle scattering processes of ions at adsorbates. However, the increased $Y_S$ in the presence of
7.3 Simulation results

Oxygen adsorbates leads to an increased number of steps illuminated by the ion beam. Due to the large angle scattering processes, enabled by steps in grazing incidence ion bombardment (not necessary involving O-atoms), $Y_S$ is further enhanced. We also note that the increased number of illuminated steps is not only due to vacancy islands. For the largest $P_O$ also tiny adatom islands are visible [compare Fig. 7.2(d)]. Apparently the presence of oxygen hinders recombination of impact induced atoms with surface vacancies by a reduced adatom diffusion. This effect further enhances surface roughening and thus the average sputtering yield. The inset in fig. 7.3 shows the calculated oxygen coverage $\Theta_O$ deduced from (7.6) for the different $P_O$. The comparison of this graph with the evolution of $\Theta_S$ as a function of $P_O$ explains why there is now further increase of $\Theta_S$ for large $P_O$. The surface is nearly saturated with adsorbates for most of the experimental time.

7.3 Simulation results

![Figure 7.4: Schematics of ion-adsorbate scattering dynamics above the Pt surface. Ion (full) and adsorbate (dashed) trajectories are taken from realistic MD simulations in the direct-hit (a) and the indirect-hit (b) regime. Open circles: Pt surface atoms. Full circle: adsorbate atom. Thin black lines denote the incoming asymptotes of the trajectories. Their intersection with the x-axis (at the height of the adsorbate atom) defines the impact points. These are at (a) $x = -12$ Å and (b) $x = 0$. Note the different scaling in horizontal and vertical direction.

Molecular dynamics simulations were performed for 5 keV Ar$^+$ ions incident at $\vartheta = 85.5^\circ$ on a Pt(111) simulation cell with a single adsorbed oxygen atom to gain a
deeper insight into the interaction of the primary ion with the oxygen adsorbate and its effect on substrate sputtering. Let us denote as $x$-axis a line parallel to the [110] azimuth and within a plane parallel to the surface passing through the adsorbate atom at $x = 0$ [see Fig. 7.4]. We first consider ion trajectories in a plane normal to the substrate surface containing the $x$-axis. As impact point we define the intersection of the $x$-axis with the straight extension of the initial trajectory as indicated in the sketch.

Fig. 7.4 shows realistic ion trajectories with impact points on the $x$-axis. The oxygen adsorbate is positioned at a height of $h_O = 1.13$ Å above the surface. The simulations show that the ion is reflected from the surface at about the same height. The ion trajectory may be classified into two categories: The ions hitting the adsorbate directly (‘direct-hit’) and the ions which hit the adsorbate after being reflected off the surface in front of the adsorbate (‘indirect-hit’). An analysis of the molecular-dynamics trajectories reveals that ions with impact points $x > -5$ Å belong to the first class, while those with impact points $x < -5$ Å belong to the second class.

Figure 7.5: Local sputter yield $Y_S(x)$ (a) and local oxygen atom desorption yield $Y_O(x)$ (b) in dependence of the ion impact point along the ion beam direction (see text). The data have been averaged in the direction perpendicular to the ion incidence plane.

Fig. 7.5(a) shows how sputtering of the Pt target and desorption of the O adsorbate depend on the impact position of the ion. Here, the ordinates show the laterally averaged (i.e. averaged along the coordinate normal to the $x$-axis in a plane parallel to the surface) local sputter and desorption yields $Y_S(x)$ and $Y_O(x)$. The simulations show that the projectile never induces sputtering directly, i.e., by being deflected towards the Pt substrate; rather it accelerates the adsorbate towards the surface, which in turn induces Pt sputtering. Consistent with the discussion above, the peaks of $Y_S(x)$ between $-25$ Å < $x$ < $-5$ Å correspond to sputtering induced by adsorbates which have been energized via indirect hits, i.e., by the primary ion after its reflection from the substrate (trajectory a in Fig. 7.4), while peaks between $-5$ Å < $x$ < $5$ Å are due
7.3 Simulation results

<table>
<thead>
<tr>
<th></th>
<th>(\sigma_S) ((\text{\AA}^2))</th>
<th>(\sigma_{ad}) ((\text{\AA}^2))</th>
<th>(\sigma_O) ((\text{\AA}^2))</th>
<th>(\sigma_{impl}) ((\text{\AA}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiment</td>
<td>10.7</td>
<td>n.a.</td>
<td>20</td>
<td>n.a.</td>
</tr>
<tr>
<td>Simulation</td>
<td>11.3</td>
<td>48.8</td>
<td>32.6</td>
<td>43.8</td>
</tr>
<tr>
<td>Simulation for Pt adatom</td>
<td>110</td>
<td>323</td>
<td>22.9</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Table 7.1: Cross sections for sputtering, adatom formation, oxygen desorption and oxygen implantation on a Pt(111) surface covered with a single adsorbate atom (5 keV Ar impact at 85.5° incidence). Experimental and simulational data for an O-covered Pt surface obtained in the present work. Simulation data obtained for Pt surface covered with a single Pt adatom (5 keV Ar impact at 83° incidence) taken from Ref. [53]); the adatom formation cross section has been determined at 10 ps after impact and may still somewhat change at later times.

to sputtering caused by the directly-hit adsorbate (trajectory b in Fig. 7.4). The O desorption yields displayed in Fig. 7.5(b) are rather structureless; here, all projectile impacts between -25 \(\text{\AA}\) < \(x\) < 7 \(\text{\AA}\) contribute to desorption, and no clear distinction between direct and indirect hits is discernible. The reason for this insensitivity is given by the weak bonding of the adsorbate and its exposed position above the surface, which allows for even weak energy transfers to desorb it.

The results are quantified by calculating the sputter and desorption cross sections, Eqs. (7.2) and (7.9). In analogy to these, one can also define the cross sections for damage creation (detecting by measuring the number of adatoms produced) and for adsorbate implantation into the substrate. All these cross sections can be extrapolated to a coverage of \(\Theta_{O,\text{sat}} = 0.25\) by assuming a linear dependence as in section 7.2. For the sputter yield, we thus obtain

\[
Y_{sp}(\Theta_{O,\text{sat}}) = \Theta_{O,\text{sat}} \frac{\sigma_{sp}}{\Omega},
\]

and analogous for the other quantities. Note that in these formulae one makes use of the fact that a flat clean terrace does neither sputter nor produce damage for the impact conditions analyzed. Our simulations give cross sections of \(\sigma_S = 11.3 \text{\AA}^2\), \(\sigma_O = 32.6 \text{\AA}^2\); the cross section for damage creation amounts to \(\sigma_{ad} = 48.8 \text{\AA}^2\), and the cross section for adsorbate implantation is \(\sigma_{impl} = 43.8 \text{\AA}^2\) (see Table 7.1). Extrapolation to the saturation oxygen coverage of \(\Theta_{O,\text{sat}} = 0.25\) gives the yields as \(Y_S = 0.42\), \(Y_O = 1.22\), \(Y_{ad} = 1.83\) and \(Y_{impl} = 1.64\).

The experimental value \(\sigma_O = 20 \text{\AA}^2\pm14 \text{\AA}^2\) agrees reasonably with the simulated desorption cross section of \(\sigma_O = 32.6 \text{\AA}^2\). The experimental value \(\sigma_S = 10.7 \text{\AA}^2\pm0.6 \text{\AA}^2\) agrees favourably with the simulated sputtering cross section of \(\sigma_S = 11.3 \text{\AA}^2\). As will be discussed in Section 8 the latter agreement is a fortunate coincidence and likely to result from different systematic errors in experiment and simulation, which
both enhance the magnitude of $\sigma_S$. An oxygen background pressure of $1 \cdot 10^{-5}$ mbar $\Theta_O$ is close to saturation for most of the erosion time as evidenced by the inset of Fig. 7.3. Experimentally under these conditions after an ion fluence $0.5$ MLE $\Theta_S$ equals to $0.2$ ML corresponding to an experimental yield of $Y_S \approx 0.4$ in good agreement with the simulations.

### 7.4 Surface damage and sputtering as a function of the angle of incidence $\vartheta$

Figs. 7.6(a) and (b) compare STM topographs after $0.25$ MLE $5$ keV Ar$^+$ incident at $\vartheta = 81^\circ$ and at $550$ K in the absence and in the presence of $P_O = 5 \times 10^{-6}$ mbar, respectively. Figs. 7.6(c) and (d) compare STM topographs after $1.5$ MLE $5$ keV Ar$^+$ incident at $\vartheta = 87^\circ$ and at $550$ K in the absence and in the presence of $P_O = 5 \times 10^{-6}$ mbar, respectively. As expected, in both cases the presence of the background pressure increases $\Theta_S$. To quantify the effect of the oxygen background pressure the ratio $\Delta \Theta$ of the amount of material removed $\Theta_S(P_O = 5 \times 10^{-6}$ mbar) from the oxygen covered surface to the amount of material removed from the clean surface $\Theta_S(P_O = 0)$ is plotted against the angle of incidence $\vartheta$ in fig. 7.4.

It increases from a factor of $2$ at $81^\circ$ and $83^\circ$ to about a factor of $40$ at $\vartheta = 87^\circ$. The question arises, why the enhancement of surface damage by adsorbates increases so strongly with the $\vartheta$. The answer is conceptually simple. While the contribution of adsorbed oxygen to sputtering is only moderately dependent on $\vartheta$ and never ceases, sputtering on a clean surface ceases with increasing $\vartheta$ [compare Fig. 7.6(a) and Fig. 7.6(c)], thus bringing the denominator in the ratio of $\Delta \Theta$ to zero and $\Delta \Theta$ to infinity. As pointed out already in Section 7.1 the kinetic energy of motion along the surface normal $E_\perp$ [compare (7.1)] becomes smaller and smaller with increasing $\vartheta$. The variation of $\vartheta$ from $81^\circ$ to $87^\circ$ changes $E_\perp$ from $122$ eV to $14$ eV in the case of $5$ keV Ar$^+$ ions. With increasing $\vartheta$ the transferred $E_\perp$ thus first drops below the sputtering threshold (The displacement energy equals to $34$ eV for Pt [119]) and then below the threshold for adatom production. In the molecular dynamics simulations sputtering ceases for $\vartheta > 82^\circ$ and adatom production for $\vartheta > 83^\circ$ if $5$ keV Ar$^+$ is used on Pt(111) (see section 7.3). Although experimentally we find indeed a drastic decrease of sputtering from $81^\circ$ and $87^\circ$ [compare Fig. 7.6(a) and Fig. 7.6(c)] it is not absent entirely at $\vartheta = 87^\circ$ thus keeping $\Delta \Theta$ finite. Similar to the CO case at $\vartheta = 87^\circ$ the reason for sputtering is likely unavoidable adsorption of trace amounts of gas species from the background and the ensuing adsorption induced sputtering.
Figure 7.6: STM topographs after 0.25 MLE 5 keV Ar$^+$ at $\vartheta = 81^\circ$ [(a),(b)] and 1.5 MLE 5 keV Ar$^+$ ions at $\vartheta = 87^\circ$ [(c),(d)]. In fig. (a), (c) the sample was exposed to the ion beam in the absence of an oxygen partial pressure, in (b),(d) $P_O = 5 \times 10^{-6}$ mbar. The direction of the ion beam is indicated by an arrow. The image size is 1750Å × 1750Å.

7.5 Discussion

A number of issues not yet discussed in the previous sections will be addressed here. Ion-induced adsorbate desorption may be simply calculated using classical-trajectory (or Monte Carlo) simulations, in which only binary collisions are taken into account, and
even the Pt substrate may be considered fixed during the simulation. Such a procedure is of course not possible for determining the sputtering of the substrate, and for this reason we started MD simulations of the entire process. A simple binary-collision description was developed by Winters and Sigmund [49] as introduced in section 2.2.4.

For grazing incidence ion erosion where the reflection coefficient is close to unity, the calculation of the three contributions of the cross section (direct knock-off, reflected ion contribution and the sputtered atom contribution) is reduced to the calculation of the direct knock-off contribution $\sigma_1$ since the scattered ions do not enter into the crystal on the flat terrace. This contribution to the desorption cross section is calculated by using a power potential for the interaction between the collision partners [ion $\equiv (1)$, surface atom $\equiv (2)$ and adsorbate $\equiv (3)$]. The direct knock-off contribution can be calculated by using formula 7.12.

$$\sigma_1 = \frac{C_{13}}{\cos \vartheta \cdot m} (EU_3)^{-m} \left(1 - X^{-m}\right)$$  \hspace{1cm} (7.12)$$

The coefficient $C_{13}$ depends on the mass ratio between the colliding particles and the nuclear charge and is specified in [48]. For a universal potential of the Lenz-Jensen type a value $m = 0.25$ results [138]. The kinetic energy of the impinging particles is denoted with $E$, $U_3$ is the binding energy of the oxygen adsorbate ($U_3 = 5.18$ eV), and the factor $X$ is defined as $X = \gamma_{13}(E/U_3)$ with $\gamma_{13} = 4M_1M_3/(M_1 + M_3)^2$. With (7.12), Winters
et al. were able to reproduce their experimental findings for nitrogen desorption on tungsten through keV ions with an accuracy better than a factor of two. Using (7.12) for our situation results in $\sigma_O = 36 \text{ Å}^2$. This value is in reasonable agreement with our experimental ($\sigma_O = 20 \text{ Å}^2$) and molecular dynamics ($\sigma_O = 32.6 \text{ Å}^2$) results.

The next issue we need to address is the reliability of the experimental and theoretical cross sections. The overall agreement for the desorption cross section $\sigma_O$ is satisfactory with $20 \text{ Å}^2$ and $32.6 \text{ Å}^2$ for experiment and simulation, respectively. Also the overall agreement for the sputtering cross section $\sigma_S$ in the presence of oxygen is rather good with $10.7 \text{ Å}^2$ and $11.3 \text{ Å}^2$ for experiment and simulation, respectively. As apparent from (7.8) the removed amount $\Theta_S$ depends on the product of $\sigma_S$ and $\Theta_O$. The latter quantity is exponentially dependent on $\sigma_O$ as apparent from (7.6). Therefore the rise of $\Theta_S$ in our fit is rather sensitive to $\sigma_O$. We are therefore confident that the experimental value for $\sigma_O$ is a reasonable estimate.

In simulation and experiment several possible sources of error must be discussed. As known Chapter 5, MD simulation has a tendency to overestimate sputter and adatom yields for grazing incidence. We discuss in the following several issues connected with the reliability of our MD simulations.

1. A prime source of systematic error in every simulation is the implementation of the interatomic potentials. In this case, the O-Pt potential appears particularly difficult to implement: it is known to be of many-body nature; its bond strength decreases strongly from the value of 3.81 eV in a Pt-O dimer bond [139] to 1.73 eV, as it is used here to describe the interaction with a Pt surface [140]. However, during the ion-surface interaction, the O atom may be dynamically exposed to different bonding environments, ranging from implantation (12 Pt neighbours) to desorption (0 Pt neighbours). We checked the influence of the bonding part of the Pt-O potential by performing a reference simulation (for a restricted number of events), in which bonding was entirely switched off. No statistically significant deviations from our result with the full (repulsive and attractive) potential were found. We conclude that it is mainly the repulsive part of the Pt-O interaction which is relevant for the fate of the adsorbate and the induced sputtering.

2. In the simulation, the fate of the adsorbate under irradiation can be easily followed. The cross section for implantation (43.9 Å²) is even larger than that for desorption (32.6 Å²). Experiment measures essentially the removal of O from the surface; hence the experimental desorption cross section of 20 Å² not only includes O desorption, but also O incorporation into the target. However, from an inspection of the depth distribution of implanted O atoms we find that 77% are ‘implanted’ into the first layer, 9% into the 2nd layer, and the remainder form a highly skewed distribution extending deep into the Pt crystal. We feel that our
7. TERRACE DAMAGE AND THE EFFECT OF ADSORBATES ON ITS FORMATION

potential cannot safely predict the fate of the shallow implanted O atoms; many of them may actually return to the surface in the course of time and will thus not be removed from the surface.

3. In experiment, only the effects of a finite adsorbate coverage can be determined, while for simulation it is most convenient – and also of fundamental interest – to study the effect of a single adsorbate atom. These two views can be combined as long as the linear relations (7.2) and (7.9) hold. From our previous work with isolated Pt adatoms on a Pt (111) surface we could derive a criterion for the maximum coverage $\Theta_{\text{lin}}$ for which the single adatom results could be extrapolated linearly to finite coverages,

$$\Theta_{\text{lin}} \cong \frac{\Omega}{A_{\text{infl}}}.$$  

(7.13)

Here $A_{\text{infl}}$ denotes the zone of influence around the adatom, into which the projectile must hit in order to collide with the adsorbate atom; depending on the process of interest (e.g., sputtering or adsorbate desorption), this zone of influence may assume slightly different values. The idea behind Eq. (7.13) is that linearity holds as long as the zones of influence of the individual adsorbate atoms do not overlap. In our case, we measure a value of $A_{\text{infl}} = 19 \text{ Å}^2$ for sputtering and $A_{\text{infl}} = 48.5 \text{ Å}^2$ for desorption. Thus we may trust our results up to coverages of $\Theta_{\text{lin}} \cong 0.35$ for sputtering; this includes the O saturation coverage of 0.25. For oxygen desorption, it is $\Theta_{\text{lin}} \cong 0.14$ and our linear extrapolation, Eq. (7.11), to the saturation coverage is subject to a larger error.

4. In (7.8) $\sigma_S$ is just a multiplier determining the magnitude of $\Theta_S$. As pointed out already in Section 7.2, our experimental $\sigma_S$ not only includes the additional sputtering at the locations of the adsorbed oxygen adatoms. The damage created by the presence of oxygen (adatoms, adatom clusters surface vacancy clusters) itself enhances $\Theta_S$, as the damage is illuminated by the ion beam and allows for large angle scattering events. This positive feedback mechanism is not included in our MD simulation. In the simulation always a single oxygen atom on a perfect surface is investigated. Thus $\sigma_S$ as derived in experiment significantly overestimates the true $\sigma_S$ and thus should also overestimate the value obtained in the MD simulations. This is not the case, most likely due to the general overestimation of sputter yields on Pt(111) through MD simulations.

A third issue to be addressed is how realistic experimental values for $\Theta_{S,\text{clean}}$ are in the light of our results on adsorbate enhanced sputtering. Indeed for $\vartheta > 83^\circ$ the MD simulations predict the absence of any surface damage (see chapter 5). Even when considering the MD simulations with proper skepticism, it appears unlikely that for
\[ \theta = 87^\circ \] 5 keV Ar\(^+\) ions are able to induce surface damage. Let us consider for instance the case of CO adsorption described in Section 7.1. Using the data of Poelsema et al. \cite{132} and a rough estimate for the sputtering cross section of adsorbed CO based on our data shown in Section 7.1 we find a partial pressure of \( P_{\text{CO}} \approx 3 \cdot 10^{-10} \text{ mbar} \) to be sufficient to induce the observed \( \Theta_{S,\text{clean}} = 0.04 \text{ ML} \) after 1 MLE at 400 K. Although the CO partial pressure in the absence of the ion beam is in low \( 10^{-11} \text{ mbar} \) range, turning on the ion beam results in a considerable increase of the CO background of about \( 1 \cdot 10^{-10} \text{ mbar} \). It is thus nothing but plausible that the removed material \( \Theta_{S,\text{clean}} \) at very large angles \( \theta \) is largely due to adsorbate induced sputtering resulting from the adsorption prior to the onset of ion exposure and the adsorption induced by the pressure rise of the ion beam itself. The adsorbate enhanced erosion is relevant in a number of situations. Among them is pattern formation under grazing incidence conditions, which might be accelerated under poor vacuum conditions. Also ion scattering experiments under grazing incidence conditions are always endangered to be obscured by effects of unwanted adsorption.

In the present context, it is particularly interesting to compare the effect of a single adsorbate on the surface with that of a single adatom; these latter simulations have been performed for the same Pt(111) surface as investigated here, but for another incidence angle (83°) azimuth ([112]); hence a comparison with those results can only be performed qualitatively. As Table 7.1 shows, the desorption cross sections for the adsorbate and the adatom are of similar magnitude. However, the Pt adatom gives rise to an order of magnitude larger sputter and adatom-creation effect, while the O adsorbate is implanted with an order of magnitude larger efficiency. The first feature can be understood by the small O/Pt mass ratio: even though the O adsorbate can receive quite large energies from the Ar projectile, its sputter efficiency is small. The larger implantation cross section of O can be traced back to the small atomic radius of O which lets it fit easier into the Pt crystal than a Pt atom.

### 7.6 Conclusion

Scanning tunneling microscopy experiments demonstrate that sputtering on terraces in grazing incidence ion erosion is dominated by adsorbed particles. Molecular dynamics simulations reveal that the physical mechanism responsible for adparticle induced sputtering is direct knock-off impacts of the impinging ions on the adsorbates. The energized adsorbates in turn transfer energy to substrate atoms which eventually become sputtered. At extremely grazing incidence we found an enhancement of the initial erosion rate by a factor of 40 through adsorbed oxygen atoms. A similar enhancement of the initial erosion rate is found for adsorbed carbon monoxide. This is particularly important since CO adsorbs with high sticking probability at room temperature on
7. TERRACE DAMAGE AND THE EFFECT OF ADSORBATES ON ITS FORMATION

many metal surfaces and it is at the same time a major component of the background gas in UHV systems. The desorption cross section and the related and adsorbate induced sputtering cross section for oxygen are extracted from experiment and molecular dynamics. Both numbers agree within the experimental uncertainties. The obtained desorption cross section also agrees reasonably with the one derived for knock-off desorption calculated within the Winters and Sigmund theory. Our results show that a reliable measurement of the sputtering yield of perfect crystalline terraces at grazing incidence is very difficult due to hardly avoidable minute amounts of adsorbed particles. However, as soon as a significant number of vacancy and adatom clusters are present on the substrate, the presence of adsorbates will be less important for the erosion rate.
Chapter 8

Rapid coarsening of ion beam ripple patterns by defect annihilation

8.1 Introduction

In this chapter coarsening of ion beam ripple patterns is described. The fluence dependent measurements presented here can also be found in [32]. The data have been used to develop a simple model, which explains athermal coarsening of ion induced ripple patterns.

Coarsening, i.e. the increase of the characteristic feature size with time, is a well known and ubiquitous phenomenon in the physics of structure formation. Ostwald ripening [141], grain growth [142] or grain boundary grooving [143] are examples for coarsening phenomena driven by the minimization of surface or interface energy in a system. Coarsening also takes place in systems far from equilibrium with nonconserved particle numbers, e.g. in molecular beam epitaxy (MBE) or ion beam erosion.

Siegert [144] and Moldovan and Golubović [145] first realized that coarsening in MBE and ion beam erosion under conditions where kinetically preferred facets are established is enabled by defects in the evolving pattern. The demand for reduction of effective system energy stored in the facet edges drives the reduction of edge length and gives rise to the motion of defects and their subsequent annihilation reactions. The facet edge mobility itself requires thermally activated surface diffusion and is thus dependent on the characteristic feature size λ of the pattern and on temperature T. The feature size is found to develop with time t according to a power law \( \lambda \propto t^n \) with coarsening exponents n ranging from 1/3 to 1/4 depending on the symmetry of the crystalline substrate [145; 146], in partial accordance with experiments [67; 147; 148].
However, there are also situations where coarsening is not an energy minimizing process. Using scanning tunneling microscopy (STM), here we show that under grazing incidence ion erosion of a crystalline surface rapid, athermal coarsening of the ripple pattern takes place through the annihilation of mobile defects, which are driven by the ion beam along the ripple direction. The mechanism is similar to that described by Werner and Kocurek [149] for coarsening in transverse aeolian sand dunes, where defects are driven by the wind perpendicular to the crest lines. This establishes a connection between coarsening of ion beam ripples ($\lambda \approx 10^{-8}$ m) and dunes ($\lambda \approx 10^3$ m), complementing existing theoretical attempts to use models of aeolian ripple formation for the description of ion beam ripples [150; 151].

Ripple patterns form under ion erosion of solid surfaces through a variety of different mechanisms [9], and in all cases such patterns contain a certain density of defects that reflect the random fluctuations during the initial stages of the evolution. Defect density has been used as a measure for the degree of order in ion-induced ripple patterns [152; 153], but the dynamical evolution of defects and their relation to coarsening behavior has so far been studied only on a qualitative level [13; 154]. In the specific case of grazing incidence erosion of crystalline surfaces considered here, the topography evolution can be largely reduced to the ion-induced propagation of surface steps.

This basic simplicity of the dynamics allows to quantitatively relate the coarsening behavior to the fundamental time constant of the process, the propagation velocity of individual steps.

### 8.2 Results

Coarsening during 5 keV Ar$^+$ grazing incidence ion exposure of Pt(111) is visualized in Figs. 1(a)-1(f) after fluences from 1 MLE up to 300 MLE. As visible in Fig. 1(a) after exposure to 1 MLE, the formation of a ripple pattern is rapid. The pattern is aligned along the projection of the ion beam direction on the surface. In the initial stage steps of monoatomic height can still be distinguished in the STM topography. Details of the pattern formation mechanism can be found in section 2.5.3 or in [10; 32]. Important for the following investigation is the ion beam induced motion of illuminated ascending step edges, i.e. the step edge velocity. In the case of the [112] azimuthal direction and at an angle of incidence of 83° a step edge sputtering yield of $Y_{\text{step}} = 7.7 \pm 0.9$ has been measured [see table 5.1]. The step edge velocity can be calculated with equation 5.2 and equals to $v = 28 \pm 3$ nm/MLE.

As visible in Figs. 1(b)-1(f) $\lambda$ strongly increases with $F$. Figure 2 represents the dependence of $\lambda$ on $F$ quantitatively. After a rapid initial increase of $\lambda$ up to 20 MLE it becomes a linear function of $F$. Within the limits of error the wavelength increase is identical for 350 K and 450 K evidencing the athermal nature of the coarsening. Above
8.2 Results

Figure 8.1: (a)-(f) STM topographs of Pt(111) after exposure to 5 keV Ar\(^+\) incident at an angle \(\vartheta = 83^\circ\) at 450 K. The scan size is always 2450 Å × 2450 Å. The ion fluences are (a) 1 MLE, (b) 5 MLE, (c) 20 MLE, (d) 70 MLE, (e) 160 MLE and (f) 300 MLE. The projection of the ion beam direction onto the surface is indicated by an arrow in (a). The four types of defects in the ripple pattern are circled in (c). They are start (S), end (E), bifurcation (B) and merger (M) defects. (g) displays a height profile along the coordinate \(X\) of the line indicated in (f). (h) A hexagonal vacancy island formed after sputtering and equilibration at 750 K \[87\] (indicated by the white hexagon) is elongated through the motion of the illuminated steps in beam direction during grazing incidence ion exposure at 550 K.
RAPID COARSENING OF ION BEAM RIPPLE PATTERNS BY DEFECT ANNIHILATION

Figure 8.2: Pattern wavelength $\lambda$ and roughness $\sigma$ (inset) as a function of ion fluence $F$ for 350 K (full dots), 450 K (full squares) and 550 K (full up triangles). Lines to guide the eye.

450 K step edge diffusion sets in causing a significant increase of the initial wavelength [10]. Besides an apparent upward shift, the functional dependence of $\lambda$ on $F$ in the thermal regime at 550 K is still similar to the lower temperature cases.

The inset of Fig. 2 displays the evolution of the surface roughness $\sigma$ with $F$. A power law behavior with $\sigma \propto F^\beta$ is found over a fluence range of more than two decades. The exponents $\beta$ are 0.50, 0.48 and 0.59 for 350 K, 450 K and 550 K, respectively. An exponent $\beta = 1/2$ results for a Poisson model, i.e. for a situation where material transport between different atomic layers is suppressed (large step edge barrier for surface vacancies) [155]. The observed preferential nucleation of surface vacancies at the bottom of grooves is consistent with this scenario.

The formation of stable kinetically preferred facets in the pattern (slope selection) would require the identity of the exponents $n$ and $\beta$, which is not observed here. Indeed, the height profile of Fig. 1(g) taken through the ripples of Fig. 1(f) does not display a single set of preferred facets but rather a parabolic ridge profile.

It is well visible in Fig. 1 that defects originating from the initial randomness of nucleation and coalescence of monolayer vacancy islands are present in all stages of pattern evolution. Four types of topological pattern defects are circled and labeled in Fig. 1(c). With respect to the ion beam direction we distinguish the start (S), end (E), bifurcation (B) and merger (M) of ridges. For clarity, the four defects are sketched...
8.2 Results

Figure 8.3: (a) Schematic representation of the start (S), end (E), bifurcation (B) and merger (M) defects pointed out in Fig. 1(c). Inset: Sketch for the quantitative distinction between S and B defects (see text). (b) Schematic sketch of a ripple pattern with S and E defects only (see text). The large arrow in (a) indicates the beam direction.

schematically in Fig. 3(a). Although the identification of these defects appears to be straightforward, the distinction between S and B defects requires a quantitative criterion to decide whether an emerging ridge (viewed in the downstream direction) branches off an existing ridge or starts anew in the valley between two ridges. The criterion used in this work is sketched in the inset of Fig. 3(a). If close to the defect but slightly downstream the height $\Delta r \leq \Delta h/2$ [as for a profile between the white arrows near B in Fig. 3(a)], we consider it as a B defect, and if $\Delta r \geq \Delta h/2$ as an S defect [as for a profile between the white arrows near S in Fig. 3(a)]. Similar considerations apply to E and M defects. As $\lambda$ is uniform over the sample for any topograph of lateral dimension much larger than $\lambda$ we obtain for the numbers of specific defects $N_S + N_B \approx N_E + N_M$, i.e. the number of ridges entering a topograph is approximately equal to that leaving it.

As a key to the understanding of coarsening through defect motion, we consider now a simple start S defect. It consists of an array of illuminated monoatomic steps which consequently will move in the beam direction with a speed similar to that of a single step. To the contrary, an end E defect consists of an array of steps not illuminated by the ion beam and is thus immobile. If the ridge originating from an S defect terminates in an E defect, the ion beam will move the S defect towards the E defect until they annihilate. As a consequence a ridge is removed and thus the average wavelength has increased.

We derive a simple analytical formula relating the defect concentration to coarsening (compare also [145; 149]) for the simplified defect pattern containing only S and E defects in Fig. 3(b). The field of area $A = X \times Y$ has a total ridge length $L$ with an average separation $\lambda$ such that $A = \lambda L$. The total number of defects in the field of area $A$ is $N$, the defect density $\rho$ correspondingly $\rho = N/A$. The S defects form a fraction
8. RAPID COARSENING OF ION BEAM RIPPLE PATTERNS BY DEFECT ANNIHILATION

\( \gamma (\gamma = 1/2 \text{ if we consider only S and E defects}) \) of all defects and move with a velocity \( v \). Therefore the total ridge length decreases with ion fluence according to

\[
\frac{dL}{dF} = -v\gamma N. \tag{8.1}
\]

In order to obtain the change of \( \lambda \) with fluence we rearrange the identity \( dA/dF = 0 = L(d\lambda/dF) + \lambda(dL/dF) \) to obtain

\[
\frac{d\lambda}{dF} = -\frac{\lambda}{L} \frac{dL}{dF} = \frac{\lambda}{L} v\gamma N = \lambda^2 v\gamma \rho. \tag{8.2}
\]

As we are able to measure \( \lambda \) and \( \rho \) as a function of \( F \) from our STM topographs, (3) allows us to obtain a quantitative value for \( v \).

Assuming the fraction of mobile S defects to be \( \gamma = \frac{1}{4} \) of all defects and the mobility of E, B and M defects to be negligible yields the velocities \( v \) represented in Fig. 4. The total defect density \( \rho \) as a function of ion fluence is plotted in the inset of Fig. 4. The evaluation of \( \rho \) was feasible for ion fluences of 5 MLE and larger. It decreases from 5 MLE to 300 MLE by more than a factor of 25. For 350 K, 450 K and 550 K the average \( v \) is \( 16 \pm 2 \text{ nm/MLE}, \ 16 \pm 1 \text{ nm/MLE} \) and \( 8 \pm 1 \text{ nm/MLE} \), respectively. For the athermal regime \( v \) resulting from our crude analysis agrees to better than a factor of 2 with the velocity \( v = 28 \text{ nm/MLE} \) of a single step driven by the ion beam. We consider this agreement as strong evidence for coarsening driven by defect motion, which itself results from step motion in the beam direction due to selective step erosion. Note that our analysis did not use any free parameter. Although the data scatter around the respective average value, there is no trend for a decrease of \( v \) with increasing \( \lambda \) for 350 K and 450 K. This is in contrast to continuum models for defect-driven coarsening of ripple patterns such as the model of Golubović and Levandovsky \[146\] for fcc(110) surfaces, which predicts that \( v \propto 1/\lambda^{3/2} \). The fact that the defect velocity is a constant in our system supplies further evidence for a distinct type of coarsening. In the thermal regime at 550 K coarsening is apparently influenced by diffusion giving rise to the smaller \( v \) and the tendency for a decrease in \( v \) with \( F \).

A characteristic feature of models for defect-mediated coarsening is the existence of multiple length scales which increase at different rates \[144–146\]. In the present case a second relevant scale is the mean spacing \( \lambda_{||} \) between defects along the direction of the ridges [compare Fig. 3(b)], which is related to the pattern wavelength \( \lambda \) and the defect density \( \rho \) through \( \rho = 1/(\lambda \lambda_{||}) \). Computing \( \lambda_{||} \) from the data for \( \lambda \) and \( \rho \) we find that \( \lambda_{||} \gg \lambda \) at all times, and for \( F \geq 20 \text{ MLE} \) \( \lambda_{||} \) generally exceeds the topography size, as is also evident from Figs.1(c)-(f). Inserting \( \rho = 1/(\lambda \lambda_{||}) \) on the right hand side of (8.2) shows that it is the ridge aspect ratio \( \lambda_{||}/\lambda \gg 1 \) which gives rise to the large factor relating the step velocity \( v \) to the coarsening rate \( d\lambda/dF \).
8.3 Discussion

The model presented above is oversimplified in several respects. A unique velocity $v$ in the beam direction and a fraction $\gamma = 1/4$ have been assumed here mainly in lack of an adequate description for the velocities of all defects. As described above, S and B defects differ for a large number of situations only gradually. While the extreme case of an S defect with $\Delta r \approx \Delta h$ will have a velocity not significantly different from that of a single step, the velocity of a B defect with $\Delta r \approx 0$ will vanish. The cases in between may have intermediate velocities. As S and B defects make up 1/2 of all defects, it appears still reasonable to assume $\gamma = 1/4$ with a uniform $v$. The neglected M defects also expose steps to the ion beam and must be assumed to move, create ridge length and thus reduce the coarsening rate. However, we rarely observe M defects in their pure form, as they tend to transform into immobile E defects when the groove cuts sideways through one of the branching ridges [see Fig. 3(a)]. Finally, even a perfect S defect is likely to move more slowly than a single illuminated step edge. Channeling ions (a significant fraction of all ions) entering the crystal at an isolated monoatomic step travel just one layer underneath the surface and are likely to cause significant sputtering when dechanneling. In contrast, channeling ions entering the crystal close
to the bottom of an S defect deposit their energy well below the surface of the ridge, cause little sputtering and therefore give rise to a comparatively lower step velocity, as observed.

In conclusion, for grazing incidence ion erosion there is a regime of athermal coarsening in the ensuing ripple pattern resulting from mobile defects with a velocity related to the velocity of a single monatomic step exposed to the ion beam. To obtain additional information on the mobility of complex defect structures experimental investigations applying in situ imaging of the developing pattern appear to be most suitable.
Chapter 9

Summary and outlook

9.1 Summary

Surface damage induced through grazing incidence ions has been studied with variable temperature scanning tunneling microscopy. A new sample holder has been designed in order to improve the mechanical stability of the STM system at low imaging temperatures. A combination of magnetizable stainless steel ramps with a high purity copper backbone assures an excellent thermal conductivity and an enhanced mechanical stability. Atomic resolution on Pt(111) can be achieved during liquid nitrogen and liquid helium cooling. The setup allows to study the damage of single ion impacts at a surface temperature low enough to prevent single adatom and vacancy diffusion.

At ascending step edges single ion impacts create damage due to large scattering events or perform subsurface channeling. In the first case the damage is situated exclusively at the step edge where a thermal spike, sputtering, adatom and vacancy formation occurs. However, many ions are able to enter the crystal and are guided between the open space of two crystal layers via small angle binary collisions, i.e. subsurface channeling. The energy loss is strongly reduced compared to direct impacts and the ion performs a steered oscillatory motion. Surface damage is induced due to the reduced energy threshold for damage formation. Compared to bulk channeling, the threshold energy is reduced by roughly one order of magnitude. In the case of Argon ions the damage consists of adatoms and vacancies aligned in ion beam direction. In contrast, Xenon ions produce surface vacancy trenches. This ploughing mechanism produces a one atom wide surface vacancy trench in ion beam direction. Almost the complete trajectory of the channeled particles is visible on the surface. Switching between different rows and different layers is observed with STM. The angular dependent measurements give insight into the terrace damage induced by grazing ions. For angles larger than 80° the damage is almost exclusively induced by the ascending step edges. In contrast, the experiments performed at 80° and 78.5° show that surface vacancy
trenches are induced on the flat terrace. Ions are able to enter the crystal without a large scattering event, with a subsequent stable channeling trajectory. The experimental results are supplemented by molecular dynamics simulations. Both experiment and simulations are in excellent agreement which enables to assign distinct features of the ion induced damage to differences in the ion trajectories which occur on a time scale not experimentally accessible.

The step edge sputtering yield has been measured experimentally for different angles of incidence and different azimuthal directions. At $86^\circ$ ion incidence and $550\ \text{K}$ almost no damage is formed on the flat terrace and $Y_{\text{step}}$ can be monitored by measuring the step edge retraction of preexisting step edges. This is possible since the vacancy clusters produced by ion impacts at the lower terrace of the step edge cannot anneal. As a consequence, they mark the initial position of the step edge. This method is not applicable at $83^\circ$ since the number of vacancy islands on the flat terrace is too large. Therefore, the step edge sputtering yield has been measured by means of the concentration of ascending steps, together with the removed amount as a function of the ion fluence. The evaluation shows that the erosion rate is determined by the number of ascending step edges. As soon as a dynamical equilibrium is reached on the surface the erosion rate is constant. Both evaluations have been performed along the $[1\bar{1}0]$ and $[\bar{1}1\bar{2}]$ direction. The results show that the step edge sputtering yield decreases with increasing $\vartheta$ and is larger for the $[\bar{1}1\bar{2}]$ direction than for the $[1\bar{1}0]$ direction. This can be traced back to the different subsurface channeling probabilities for the two azimuthal orientations. The $[1\bar{1}0]$ direction shows a large channeling fraction resulting in a low sputtering yield. The $[\bar{1}1\bar{2}]$ has a smaller channeling fraction which results in larger sputtering yield. The angular dependence of the step edge sputtering yield can be explained by the angular dependence of the channeling fraction. It the angle of incidence between the ion and the string is low (large angles of incidence measured with respect to the surface normal) the channeling fraction is large and the sputtering yield is low. Decreasing the angle of incidence, measured with respect to the surface normal, increases the angle on incidence between the ion and the string. The channeling fraction decreases which increases the sputtering yield. The results are corroborated by molecular dynamics simulations. Moreover the MD simulations predict a strong temperature dependence of the step edge sputtering yield. This is intuitively clear, since at higher temperatures, the vibrational amplitude of the target atoms is larger, which increases the probability for large scattering events during subsurface channeling.

The step edge sputtering yield has also been determined for small adatom clusters. Through deposition of a small amount of Pt, the surface has been covered with a large amount of clusters. Afterwards the surface has been bombarded with ions and the amount of removed material has been determined. Comparing the results with an experiment on an initially clean surface shows that the erosion rate is larger when
small adatom clusters are present on the surface. The step edge sputtering yield of the adatom clusters is determined. It is roughly a factor of three smaller than in the case of preexisting step edges with an extended upper terrace. This can be traced back to less violent dechanneling events. At the illuminated step edges of the small adatom clusters the ions enter into the crystal and perform subsurface channeling. Due to the small size of the adatom clusters, it is very likely that the ions escape the crystal on the other side without a large scattering event. This results in a decrease of the sputtering yield.

The effect of adsorbates on terrace erosion has been studied in the case of oxygen and carbon monoxide adsorption. In all cases, the terrace erosion rate increases when adsorbates are present on the surface. At 87° the erosion rate on the flat terrace has been increased by a factor of forty in the presence of oxygen adsorbates. A similar enhancement of the initial erosion rate is found for adsorbed carbon monoxide. Ions hitting the flat terrace are usually reflected without creating much damage. Adsorbates present on the surface disturb this planarity, which then results in an enhanced number of large scattering events. The desorption cross section and the sputtering cross section can be deduced from experiment and they are compared to molecular dynamics simulations and the analytical theory by Winters and Sigmund. The numbers agree within the uncertainties. The experiments show that the determination of the terrace sputtering yield under grazing incidence conditions is very difficult since a very small amount of adsorbates is always present on the terrace. These adparticles significantly influence the terrace sputtering yield.

Finally, coarsening of the ion beam induced ripple patterns has been analyzed. In a temperature regime where coarsening is not driven by surface diffusion or energy minimization, mobile defects are responsible for the increase of wavelength with ion fluence. On the basis of a rough model which is also used to explain coarsening in dune fields, the speed of the mobile defects can be estimated from the fluence dependent wavelength and defect density. The velocity of the defects agrees quantitatively with the speed of monoatomic step edges.

9.2 Outlook

The experiments described in this work are limited to one type of substrate, i.e. Pt(111), angles of incidence between 88°-78.5°, an energies between 1 to 15 keV. The question immediately arises if subsurface channeling is also present on other type of substrates. Although fingerprints from ion scattering experiments already exist on other metal surfaces, scanning tunneling microscopy investigations could unambiguously clarify this issue.

It would be very interesting to study grazing incidence ion erosion on low Z ma-
9. SUMMARY AND OUTLOOK

terials (low atomic number) like beryllium or carbon since they are frequently used as wall materials in fusion reactors. Due to plasma wall interactions sputtering and implantation occurs. Low Z materials have very small shadow cone which should result in large subsurface channeling probabilities. Subsurface channeling on HOPG (highly oriented pyrolytic graphite) could even be carried out under non UHV conditions. An ion gun and a small vacuum chamber could be used to perform the single ion erosion experiment and afterwards the sample could be investigated ex situ with the help of a scanning tunneling microscopy system. This has already been done for ion energies down to 50 keV [117]. Another possibility would be to grow isolated graphene flakes on Pt(111). For these experiments the recipe from [156], i.e. decomposition of hydrocarbons, could be used. No changes in the UHV chamber would have to be made in order to perform these experiments. It would be interesting to compare these experiments with the results on the Pt(111) system.

Changing the angle of incidence over a wider range could also give new insights into the ion surface interaction processes. Due to the limitations of the tilt angle in this UHV system it was not possible to investigate the breakdown of subsurface channeling (Surface vacancy grooves, created by single ion Xe impacts, were present down to an angle of incidence of 78.5°).

Different azimuthal orientations of the crystal with respect to the ion beam direction have to be investigated as well. A random orientation, where axial channeling does not exist, could be investigated. Until now, only room temperature experiments parallel to the [112] direction have been performed [33]. It would be interesting to investigate planar subsurface channeling since the critical angles are smaller, i.e. could be within the limits of the experimental setup and as pointed out by Gemmell [40] all planar channeling events are proper or hyper channeling events. This should be well visible in the STM images since the switching between different layers of the crystal should lead to large scattering events with subsequent dechanneling. Does Xenon erosion also lead to surface vacancy grooves under planar channeling conditions? This could be clarified as well.

The energy dependent single ion impact measurements showed that subsurface channeling ceases for energies lower than 1 keV in the case of Xenon. As subsurface channeling is of crucial importance for the regularity of ripple patterns [33], experiments performed at 550 K with 1 keV ions should show a much worse alignment of the groove patterns. These experiments where not possible here due to the limitations of the ion gun.

The recipes introduced here to measure the step edge sputtering yield at grazing incidence ion erosion could be used to extensively study the energy dependence of $Y_{\text{step}}^r$. This is particularly interesting for ion beam assisted deposition experiments where usually lower energies are used (a few hundred eV). Whether the temperature dependence
of $Y_{\text{step}}$ could be measured experimentally (to verify the molecular dynamics simulation results presented in chapter 5) is difficult to say, since the step edge density depends strongly on the surface temperature. Moreover both experiment (chapter 6) and MD [51] showed that the sputtering yield depends on the size of the adatom islands.

As already suggested by H. Hansen [32] coarsening of ripple patterns due to defect annihilation could be investigated in real time by scanning electron microscopy. These experiments could give insight into the annihilation processes and the movements of other defect types present in the ripple patterns. In the lack of an adequate description, a unique velocity $v$ and a fraction of $\gamma = 1/4$ of all defects has been assumed in the presented model.
References


155
REFERENCES


[37] http://www.srim.org. 9, 10, 110


REFERENCES


REFERENCES


REFERENCES


[102] A UHV-24 Bayard-Alpert Type Ionization Gauge is used, pressure range from Varian Inc. Vacuum Measurement Catalog. 57


161
REFERENCES

[118] courtesy of Y. Rosandi and H. M. Urbassek. 64, 67, 69, 71, 73, 80, 83


162


REFERENCES


Appendix A

Appendix

A.1 Outgassing of UHV components

Figure A.1: Sketch of the vacuum firing device used to reduce the outgassing rate of UHV components.

Vacuum firing is an efficient way to decrease the outgassing rate of UHV components. The UHV parts are heated in vacuum for a long period at the highest possible temperature. The temperature has to be chosen higher than the temperature during the operation in the UHV chamber. During the treatment, the amount of gas in the
A. APPENDIX

bulk is decreased substantially. Since the sample holder and the ramps are heated very often to high temperatures during the annealing and high temperature sputtering experiments, they have to be degassed prior to the first operation. The maximum operating temperature of the sample holder in this setup is roughly 600 K. Therefore the copper part, which is closest to the heating filament, has been degassed to 800 K for 8 hours, under UHV conditions in a separate chamber. The degassing setup is schematically shown in Fig. A.1. The sample holder (red) is suspended into the chamber with a tungsten wire. The sample holder has been biased to a positive voltage of roughly 1000 V. The heating is done with a commercially available halogen lamp where the glass tube has been cut off. The hot filament emits electrons which are accelerated towards the sample holder. This results in very efficient heating. The temperature is controlled via a NiCr-Ni thermocouple. Most wires are fed through aluminum oxide tubes in order to assure a good electrical insulation [see Fig. A.1]. The ramps of the sample holder, the cantilever and the setting screw have been degassed for 8 hours to 620 K. The outgassing temperatures for a large variety of materials can be found in [157; 158].

A.2 Temperature calibration

Figure A.2: Thermal desorption spectroscopy of Argon and Xenon desorption from the Pt(111) surface. Heating rate 1 K/s.

The accuracy of the temperature measurement with thermocouples without calibration is rather poor at low temperatures. As pointed out by Schlichting et al. [159] a bias deviation of only 10 µV at a sample temperature of 5 K leads to an error of 5 K
in the case of NiCr-Ni thermocouples. Therefore the system has to be calibrated by means of thermal desorption spectroscopy of thick noble gas layers. In order to check how much temperature offset is present in this setup, a few desorption spectra have been recorded. The measurements presented here were done to get a rough estimate of the temperature measurement error. If an exact temperature calibration is needed then the recipe introduced by Schlichting should be applied. Fig. A.2 shows two TDS spectra recorded for Argon and Xenon desorption from Pt(111).

In both cases the noble gas adsorption was performed by exposing the sample for a duration of 60 s to a pressure of $2.5 \cdot 10^{-9}$ mbar under the dosing tube. The heating ramp was roughly 1K/s. It has to be noted here that, especially between 20-50 K, the linear ramp was not well adjusted. The Xenon signal (black curve) shows a number of peaks which can be attributed to the desorption of the first monolayer at 108 K (I), the second monolayer at 72 K (II) and higher layers at 69 K (III). For Argon (red curve) one peak at 44 K and a small one at 57 K are observed. Comparing these results to the data available in literature [103; 160] shows that there is a huge offset. In the case of Xenon the peak temperature of the second layer desorption is 64.5 K (here: 72 K) and the multilayer desorption of Argon equals to 30 K (here: 44 K). Although differences in the peak temperatures occur from slightly different temperature ramps in this experiment and in the experiments from literature, one can still conclude that the sample temperature is largely overestimated by the uncalibrated thermocouples. In order to compensate this difference, the procedure described in [101] has been applied, where the mean value of the onset temperature and the peak temperature of the multilayer peak have been set to the sublimation temperature. From these values an offset voltage has been calculated which equals to -100 $\mu$V to -110 $\mu$V. This value is astonishingly large. However, a test experiment, where the thermocouples have been immersed into liquid nitrogen, shows that the main fraction of the offset results from the long thermocouple cable outside the UHV chamber. Therefore a value of -110 $\mu$V is used to roughly calibrate the temperature controller. The lowest possible temperature measured with the uncalibrated thermocouples was 37 K. After compensation the minimum temperature is lowered by a factor of two i.e. 18 K. The error can be assumed to be roughly $\pm$ 3 K. Further desorption spectra, with a much better control of the heating ramp, are necessary to improve the temperature calibration.

A.3 A scanning tunneling microscope for students

This section describes the development and the performance of a scanning tunneling microscope for practical courses. Special care was taken in order to simplify the handling of the STM and to assure the best possible mechanical vibration insulation damping. Fig. A.3 shows a sketch of the main parts of the STM setup together with some pho-
A. APPENDIX

Figure A.3: The scanning tunneling microscope for student practical courses. (a) Sketch of the setup, (b)-(e) Photographs of the main components (Details see text)

tographs. The four piezos are glued into a stainless steel block which rests on three viton damping stages. Measurements are performed in constant current mode, where the tunneling current is measured and compared to a reference current. A feedback loop regulates the voltage at the inner piezo in such a way that the actual current equals to the reference current. The sample holder consists of magnetizable stainless steel which is placed upside down onto the outer three piezos. In order to keep the resonance frequency of the STM as high as possible, the sample holder has a weight below 10 grams. It is shown in Fig. A.3(d)(e). The sample holder is placed into a z-translator (Fig. A.3(c)), which is used to place the holder onto the piezo tubes. In order to bias the sample for STM imaging, the following concept has been used. A thin wire is fed through one of the STM piezo tubes and connected to the steel ball at the end of the tube. With this technique the sample holder is biased without connecting an external wire to it. Fig. A.4 illustrates the performance of the STM which works under ambient conditions. Fig. A.4(a) shows the atomic resolution on HOPG. Fig. A.4(b) shows a large scale image of a 200 nm Gold film on mica. Grain boundaries, atomic step edges and slip planes are visible. Fig. A.4(c) shows a greyscale image of the gold film. Fig. A.4(d) shows an image of the herringbone reconstruction on a freshly cleaned Au on mica surface. Fig. A.4(e) demonstrates the performance of the STM in solution. The image shows the arrangement of Terephthalic acid on HOPG. The
Figure A.4: (a) Atomic resolution on HOPG, scan size: $76\,\text{Å} \times 76\,\text{Å}$, (b) Au on mica, scan size: $2\,\mu\text{m} \times 2\,\mu\text{m}$, (c) Au on mica, scan size: $2380\,\text{Å} \times 2380\,\text{Å}$, (d) Au on mica, scan size: $2380\,\text{Å} \times 2380\,\text{Å}$, the herring-bone reconstruction is visible, (e) Terephthalic acid on HOPG, scan size: $76\,\text{Å} \times 76\,\text{Å}$, (f) Decanthiol on Au, scan size: $600\,\text{Å} \times 600\,\text{Å}$

molecules which were solved in heptanoic acid form a hydrogen bonded network [161] visible in the STM image. Finally Fig. A.4(f) shows the arrangement of self assembled...
A. APPENDIX

Decanethiol molecules on Au. They form a $\sqrt{3} \times \sqrt{3} \ R30^\circ$. However, in this case the molecules are not well aligned which is most probably due to the preparation.
Appendix B

Scientific publications

The results presented in this thesis can be found partially in the following publications. A part from the surface damage induced by grazing incidence ions I also worked on the topic of homoepitaxial growth of Pt on Pt(111) in the presence of screw dislocations. The results can be found in: *Spiral Growth and Step Edge Barriers*. Water on Pt(111) has been studied by thermal desorption spectroscopy. The results are presented in the publication: *Desorption of H$_2$O from flat and stepped Pt(111)*.


B. SCIENTIFIC PUBLICATIONS

- Y. Rosandi, A. Redinger, T. Michely and H. M. Urbassek:  
  *Influence of single adatom on sputtering at grazing incidence: a molecular dynamics case study of 5 keV Ar impact on Pt(111)*,  

- H. Hansen, A. Redinger, S. Messlinger, G. Stoian, J. Krug und T. Michely:  
  *Rapid coarsening in ion beam ripple patterns by defect annihilation*  
  Phys. Rev. Lett. 102, 146103 (2009)

- A. Redinger, Y. Rosandi, H. M. Urbassek, and T. Michely:  
  *Grazing incidence ion erosion in the presence of adsorbates*  
  New J. Phys. 11, No 6, 063011 (2009)

- Y. Rosandi, A. Redinger, T. Michely, and H. M. Urbassek:  
  *Competition of terrace and step-edge sputtering under oblique-incidence ion impact on a stepped Pt(111) surface*  

- A. Redinger, S. Standop, T. Michely, Y. Rosandi and H. M. Urbassek:  
  *Trails of keV ions created by subsurface channeling*,  
  Phys. Rev. Lett., accepted
## Appendix C

### Curriculum vitae (Lebenslauf)

### Persönliche Daten:

<table>
<thead>
<tr>
<th>Name</th>
<th>Redinger</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vorname</td>
<td>Alex</td>
</tr>
<tr>
<td>Geburtstag</td>
<td>25.06.1981</td>
</tr>
<tr>
<td>Geburtsort</td>
<td>Esch/Alzette (Luxemburg)</td>
</tr>
<tr>
<td>Staatsangehörigkeit</td>
<td>Luxemburg</td>
</tr>
</tbody>
</table>

### Qualifikationen:

<table>
<thead>
<tr>
<th>Abitur</th>
<th>07/2000</th>
<th>Lycee Technique Esch/Alzette Luxemburg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Studium</td>
<td>10/2000</td>
<td>Inamatrikulation im Studiengang Physik, RWTH Aachen</td>
</tr>
<tr>
<td></td>
<td>05/2003</td>
<td>Vordiplom RWTH-Aachen Note: gut</td>
</tr>
<tr>
<td></td>
<td>11/2005</td>
<td>Diplom Physik, RWTH Aachen, Note: sehr gut</td>
</tr>
<tr>
<td>Promotion</td>
<td>12/2005-07/2009</td>
<td>wissenschaftlicher Mitarbeiter am I. Physikalischen Institut RWTH Aachen und am II. Physikalischen Institut Universität zu Köln</td>
</tr>
<tr>
<td></td>
<td>04/2006-11/2007</td>
<td>Promotionsstipendium der RWTH Aachen</td>
</tr>
<tr>
<td></td>
<td>10/07/2009</td>
<td>Doktorprüfung an der RWTH Aachen, Gesamtnote: „mit Auszeichnung“</td>
</tr>
</tbody>
</table>
Appendix D

German abstract
(Zusammenfassung)

Der Oberflächenenschaden von streifend einfallenden Ionen wird mittels temperaturvariabler Rastertunnelmikroskopie untersucht. Die Beschußexperimente werden auf einem Pt(111) Kristall durchgeführt. Die Edelgasionen haben eine Energie von 1 keV-15 keV und werden unter einem Winkel von $\vartheta = 78.5^\circ$ bis $\vartheta = 88^\circ$, bezogen auf die Oberflächennormale, auf das Substrat geschossen.


Die Anzahl der zerstäubten Atome pro einfallendes Ion (die Zerstäubungsausbeute) wird für aufwärtsführende Stufenkanten bestimmt. Bei einem Beschusswinkel von $86^\circ$ kann die durch Zerstäubung induzierte Wanderung von aufwärtsführenden Stufenkan-
ten ermittelt werden. Hieraus kann man unmittelbar die Zerstäubungsausbeute berech-
nen. Bei weniger streifenden Winkeln kann diese anhand der Stufenkonzentration und
der abgetragenen Menge bestimmt werden. Es zeigt sich, dass die Zerstäubungsaus-
beute von der Richtung der einfallenden Ionen abhängt. Dies kann auf unterschiedliche
Channeling Wahrscheinlichkeiten für die verschiedenen kristallographischen Orien-
tierungen zurückgeführt werden.

Die Zerstäubungsausbeute an Stufenkanten wird ebenfalls für kleine Adatomcluster
bestimmt. Die Ausdehnung der obersten Terrasse ist hier, im Vergleich zu großen
Inseln, sehr viel kleiner. Die Ionen, die an den Stufen eintreten und geführt werden,
besitzen eine hohe Wahrscheinlichkeit auf der anderen Seite wieder aus dem Kristall
auszutreten ohne Schaden zu erzeugen. Die Zerstäubungsausbeute an den Clustern ist
deshalb, ist im Vergleich zu großen Adatomseln, um einen Faktor drei kleiner.

Der Einfluss von Adsorbaten auf den Terrassen wird für den Fall der Sauerstoff-
und Kohlenmonoxidadsorption untersucht. Im Vergleich zu adsorbatfreien Terrassen
steigt die mittlere Zerstäubungsausbeute stark an. Es kann eine Erhöhung bis zu
einem Faktor vierzig ermittelt werden. Adsorbate erhöhen die Wahrscheinlichkeit von
Großwinkelstößen auf der Terrasse. Dies führt zu einer erhöhten Zerstäubungsausbeute
und Oberflächenschaden in Form von Adatomen und Leerstellen.

Schlussendlich wird die Vergrößerung von Wellenmustern, die durch streifenden
Ionenbeschuss erzeugt werden, untersucht. Für Substrattemperaturen unterhalb von
450 K erfolgt die Vergrößerung nicht durch Diffusion oder Minimierung der freien
Oberflächenergie, sondern athermisch. Die Auslöschung von Defekten im Wellen-
muster, und die damit einhergehende Vergrößerung der Wellenlänge, ist vergleichbar
mit Defekt-Reaktionen in Dünenfeldern. Es wird gezeigt, dass die, durch den Io-
nenbeschuss induzierte Bewegung von Stufenkanten, für die Auslöschung von Defekten
verantwortlich ist.
Appendix E

Acknowledgments

Finally, I would like to thank all the people who help me during the last three and a half years. This thesis would not have been possible without them.

- I would like to express my deep gratitude to Prof. Dr. Thomas Michely. I really enjoyed working on such an interesting topic. I cannot express how thankful I am for the support and the help he gave me during the whole period of this PhD. The numerous, or should I say, the countless pieces of advise he gave me were indispensiable for the success of this work.

- I would like to thank Prof. Dr. Markus Morgenstern for his willingness to accept the Korreferat of this thesis. I would also like to thank him for supporting me when I applied for a Promotionsstipendium at the RWTH Aachen.

- I am grateful to Prof. Dr. Herbert M. Urbassek and Dr. Yudi Rosandi from the University of Kaiserslautern who performed the molecular dynamics simulations. The collaboration enriched this thesis in many ways. The interpretation of the experimental data would not have been possible without the input from the simulations. The working atmosphere was extremely nice and I think our collaboration was very fruitful. I am also very thankful that I could present here, a number of unpublished simulation results, especially on the topic of the single ion impacts where the work is still in progress.

- I would like to thank Prof. Dr. Matthias Wuttig for giving me the possibility to use the infrastructure of the institute at the RWTH Aachen.

- I would like to thank the representative director of the II physics institute in Köln for giving me the possibility to finish my work there.

- I would like to thank Prof. Dr. Joachim Krug who supported me on many occasions. The study of the spiral growth in the presence of step edge barriers and
the study of the coarsening of ion induced ripple patterns benefited significantly from his input.

- I also would like to thank the diploma students who worked with me at the TUMA II. Dipl.-Phys. Oliver Ricken who worked on the spiral growth and the ion beam assisted deposition of Pt on Pt(111). Dipl.-Phys. Alexander Picolin who developed the thermal desorption spectroscopy setup and Sebastian Standop who worked quite a lot on the single ion impact experiments presented here.

- I would also like to express my gratitude to Dipl.-Phys. Alpha N’Diaye, Dipl.-Phys. Daniel Förster and Dipl.-Phys. Sebastian Bleikamp. We already worked together during our time as diploma students. I am very happy that we all spend three more years together and sharing many problems like bad base pressure, broken piezos, broken turbo pumps etc. The support and the discussions were essential for the success of this thesis.

- I would also like to thank Dr. Carsten Busse. I really enjoyed sharing the office with him and I am also very grateful for the help and support he provided on many different aspects technical and scientific or making our office look nicer by bringing a few plants.

- I also would like to thank Dr. Johann Coraux for the numerous discussions and the support he provided during his stay in Cologne.

- All the other members of our group especially Dipl.-Phys. Sven Macko, Rabia Djemour, Jürgen Klinkhammer, Timm Gerber and Ralf Schumacher.

- I would like to thank numerous people (Daniel R., Lindsay, Claudine, Alpha, Daniel F., Sven, Sebastian) for helping me getting rid of hopefully most typos in this thesis.

- The technical support has been extremely nice during the whole time. I would like to thank Stefan Hermes and Michael Huppertz who helped a lot during my time in Aachen. Especially when we moved to Cologne and the UHV chamber had to be unmounted the help and the support was really nice. I also would like to thank Norbert Henn. I really enjoyed the work and the discussions with him. The design and the construction of the STM for students we did together was really fun.

- The members of the mechanical and electrical workshop at the RWTH Aachen and at the University of Cologne for the construction and also for the repair of numerous parts. Thank you.
• All the members of the I. Physikalisches Institut from Aachen and from the II. Physikalisches Institut from Cologne, thank you for the nice and friendly atmosphere.

• I would of course also like to thank my entire family who supported me during the whole period.

• Finally I would like to thank my girlfriend Claudine. I think that this work benefited extremely from your help and support. I can only work hard if I am happy. Well you make me happy and this work would not have been possible without you. Thank you.