Ultrathin KCl films on Cu(110) and Cu(111) studied by low-temperature scanning tunneling microscopy

THÈSE No xxxx (2005)
présentée à la Faculté Science de Base
Institut de Physique des Nanostructures
Section de Physique
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

pour l’obtention du grade de Docteur ès sciences
par
Michael Vogelgesang
Diplom-Physiker, Universität des Saarlandes, Allemagne
et de nationalité allemande

jury:
Prof. K. Kern, directeur de thèse
Prof. W.D. Schneider, rapporteur
PD Dr. D. Grützmacher, rapporteur
Dr. M. Wenderoth, rapporteur

Lausanne, EPFL
2005
Abstract

In this work the development of a low-temperature scanning probe microscope and the investigation of thin insulating films at the atomic limit is presented.

The scanning probe microscope has been designed in a modular way to provide large flexibility for the implementation of different types of measurements. The design provides high stability as well as a large field of view. In the present stage of development the instrument is used as a scanning tunneling microscope which has been used for all experiments presented.

Two different systems of insulating films on at the atomic limit have been investigated for the first time: KCl(100) on Cu(110) and KCl(100) on Cu(111).

Depending on the deposition parameters KCl(100) on Cu(110) shows different types of growth. This includes step decoration and modification at low coverage as well as growth of islands with monolayer or bilayer height at higher coverage. The islands appear with a stripe structure in STM. In the case of bilayer islands atomic resolution was achieved and the stripe structure has been identified as an electronic Moiré-pattern caused by the incommensurable lattice constants of salt an copper. The growth is not perfect, hence it was possible to identify defects like grain boundaries and point defects.

KCl(100) on Cu(111) has been shown to grow in large islands or closed layers. Similar to the bilayers on Cu(110) atomic resolution has been achieved. This system provides an interface state which is related to the Cu(111) surface state. The interface state shows nearly the same dispersion relation as the surface state of pristine copper but with a different onset energy. This dispersion relation is discussed in the framework of different dielectric layers on metal substrates.

Different electronic structures have been observed for the salt islands on both substrates: field resonances and an intrinsic salt state. Both systems have been shown to be transparent for electron tunneling within their bandgap. The latter has been determined for salt bilayers on Cu(110). Compared to the case of pristine copper, the imagestates on the pristine copper surfaces are shifted to lower energies. This energy shift is discussed in detail.
The growth of cobalt phthalocyanine on Cu(110) and Cu(111) at low coverage has been studied. In the case of Cu(111) the center of the molecule has been identified as the main scattering center.
Dans ce travail, le développement d’un microscope à sonde locale à basse température et l’étude de films minces isolants à la limite atomique sont présentés.

Le microscope à sonde locale a été conçu d’une manière modulaire afin de permettre une grande flexibilité dans la mise en œuvre de différents types de mesure. De par sa conception, le microscope est très stable et possède un large rayon de balayage. Avec l’étage d’extension actuel, l’instrument est utilisé en tant que microscope à effet tunnel qui a été utilisé pour toutes les expériences présentées ici. Deux systèmes différents de films isolants à la limite atomique ont été étudiés pour la première fois : KCl(100) sur Cu(110) et KCl(100) sur Cu(111).

KCl(100) sur Cu(110) montre, selon les paramètres de dépôt, différents modes de croissance, comme la décoration et modification de marche à faible recouvrement, ainsi que la croissance d’îles de hauteur monocouche ou bicouche à plus fort recouvrement. En utilisant le microscope à sonde locale, les îles apparaissent avec une structure en “rayures”. Dans le cas des îles bicouches, la résolution atomique a été atteinte et la structure en rayures a été identifiée comme un motif électronique de Moiré causé par l’incommensurabilité des paramètres cristallins du sel et du cuivre. La croissance n’est pas parfaite, par conséquent il était possible d’identifier les défauts tels que les joints de grain et les défauts ponctuels.

Sur KCl(100) sur Cu(111), la croissance de grandes îles ou de couches fermées a été démontrée. Tout comme pour les bicouches sur Cu(110), la résolution atomique a été atteinte. Ce système possède un état d’interface qui est lié à l’état de surface de Cu(111). L’état d’interface montre quasiment la même relation de dispersion que l’état de surface du cuivre originel, mais avec une énergie initiale différente. Cette relation de dispersion est discutée dans le contexte de plusieurs couches diélectriques sur un substrat métallique.

Plusieurs structures électroniques ont été observées pour les îles de sel sur les deux substrats: résonances de champ et état intrinsèque de sel. On a montré que les deux systèmes sont transparents au transport électronique par effet tunnel dans leur gap.
de bande. Ce dernier a été déterminé pour les bicouches de sel sur Cu(110). Comparées au cas du cuivre originel, les états images sur le cuivre originel sont déplacés vers les basses énergies. Ce décalage en énergie est discuté en détail.

La croissance de phthalocyanine de cobalt sur Cu(110) et Cu(111) à faible recouvrement a été étudiée. Dans le cas du Cu(111), le centre de la molécule a été identifié comme le principal centre de diffusion.
Zusammenfassung

In dieser Arbeit werden die Entwicklung eines Tieftemperatur-Rastersondenmikroskops und die Untersuchung von dünnen isolierenden Schichten am atomaren Limit präsentiert.

Das **Rastersondenmikroskop** wurde modular konstruiert um eine hohe Flexibilität für verschiedene Messmethoden zu garantieren. Die Konstruktion verbindet sowohl hohe Stabilität als auch einen großen Messbereich. In der derzeitigen Ausbaustufe arbeitet das Instrument als Rastertunnelmikroskop, das für alle hier präsentierten Experimente eingesetzt wurde.

Zwei verschiedene Systeme von dünnen isolierenden Schichten wurden erstmals untersucht: KCl(100) auf Cu(110) und KCl(100) auf Cu(111).


**KCl(100) auf Cu(111)** wächst als große Inseln oder als geschlossene Lagen. Ähnlich zu den Doppellagen auf Cu(110) wurde atomare Auflösung erreicht. Dieses System zeigt einen Grenzflächenzustand, der aus dem Cu(111)-Oberflächenzustand hervorgeht. Der Grenzflächenzustand zeigt fast die gleiche Dispersionrelation der sauberen Kupferoberfläche, hat aber eine andere Onset-Energie. Diese Dispersionrelation wird im Rahmen verschiedener dielektrischer Lagen auf Metallen diskutiert.

Bei Substraten wurden für die Inseln unterschiedliche **elektronische Strukturen** beobachtet: Bildzustände und ein instrischer Salzzustand. Beide Systeme sind innerhalb ihrer Bandlücke für elektronisches Tunneln transparent. Die Bandlücke wurde im Fall
der Doppellagen auf Cu(110) bestimmt. Verglichen mit der sauberen Kupferoberfläche sind die Bildzustände zu kleineren Energien verschoben. Diese Veränderungen werden im Detail diskutiert.

Das Wachstum von Cobalt-Phthalocyanine auf Cu(110) und Cu(111) wurde für den Grenzfall kleiner Bedeckungen untersucht. Im Fall der Cu(111)-Oberfläche wurde das Zentrum des Moleküls als Haupt-Streuzentrum identifiziert.
# Contents

Abstract iii
Résumé v
Zusammenfassung vii
Contents ix

1 Introduction 1

2 Scanning Probe Microscopy 5
  2.1 Principles ......................................................... 6
      2.1.1 Scanning tunneling microscopy ............................ 7
      2.1.2 Tunneling - the Tersoff-Hamann approach ............... 7
      2.1.3 Imaging of surfaces ....................................... 8
      2.1.4 Spectroscopy .............................................. 9
      2.1.5 Atomic force microscopy ............................... 11

3 Instrumental development 13
  3.1 Modular Design ................................................. 15
      3.1.1 Scanner module .......................................... 16
      3.1.2 Tipholder section ....................................... 19
      3.1.3 AFM-Optics .............................................. 21
      3.1.4 Future possibilities .................................... 22
  3.2 Connection between Cryostat and Instrument .................. 23
  3.3 UHV-Chamber ................................................... 25
      3.3.1 Preparation chamber .................................... 27
      3.3.2 Analysis chamber and cryostat .......................... 29
      3.3.3 Damping issues .......................................... 32
  3.4 Scanning probe control unit .................................. 35
## Contents

3.4.1 Plane substraction circuit ................................. 38  
3.5 Setup testing .................................................. 40  
3.5.1 Piezo calibration .......................................... 41  
3.5.2 Spectroscopy .................................................. 46  

4 Thin insulating layers ............................................. 47  

5 Morphology of KCl on Cu(110) and Cu(111) .................. 51  
5.1 Potassium chloride on Cu(110) ................................. 54  
5.1.1 Islands type I: KCl - Bilayer ............................... 55  
5.1.2 Islands type II: Monolayers of KCl ....................... 60  
5.2 Potassium chloride on Cu(111) ................................. 64  

6 Electronic structure ............................................... 67  
6.1 Bandgap determination ........................................ 68  
6.2 Imagestates on pristine and potassium covered copper  .................. 74  
6.3 KCl on Cu(111) interface state ............................... 84  
6.4 Defects on KCl on Cu(110): ring-structures ................ 87  

7 Molecules on surfaces: Cobalt Phthalocyanine .............. 91  
7.1 Cobalt phthalocyanine on Cu(110) ............................... 92  
7.2 Cobalt phthalocyanine on Cu(111) ............................... 93  

8 Conclusion ........................................................... 99  

Bibliography .......................................................... 103  

Acknowledgements .................................................... 111  

Curriculum vitae ..................................................... 113
Chapter 1

Introduction

Nanometer scale structures are a key issue in modern technology and research. This length scale is targeted from different directions and the attempts are converging to an area of research where different disciplines like physics, biology and chemistry meet. Modern electronics already uses technology on length scales of less than 100 nm [1]. Electronic devices at this lateral length scales have even smaller heights. Accordingly a vital element of any modern electronics, the thin insulating films, has shrunk to a few atoms thickness. These films are not only important for current MOSFETs but will play a major role in future electronic components made of molecules. At this scale one cannot expect the films to behave like bulk like insulators any more. Their insulating behavior will be changed and can break down because of imperfections or the tunneling effect.

There is a huge variety of insulating films on conducting surfaces. Accordingly they show different kinds of growth and different electronic structures. An interesting family of insulators on conducting substrates are the ionic alkali halides on metal surfaces. The prototype of this family, the sodium chloride, has been widely studied and is known to grow suitable films. The close relative $KCl$ has nearly been ignored although it offers the possibility for direct comparison to other systems like the $NaCl$ or to the isoelectronic but non-ionic argon films. This study is a first attempt to close this gap.

If one wants to meet the challenge of investigation at the atomic limit one has to choose dedicated measuring instrument. The prototype of surface tools is the scanning probe microscope invented by Binnig et al. [2]. Besides offering atomic resolution, it becomes an even more powerful tool if used at low temperatures. Under these conditions it is on one hand possible to use the instruments to characterize the local density of states with high lateral resolution. On the other hand it is possible to manipulate adsorbates or induce chemical reactions with the tip.
A complementary technique co-invented by the same author is the scanning force microscope [3]. It provides the same resolution limit but is based on mechanical interactions. The information obtained by this technique do normally not contain information about the electronic structure, but a variety of mechanical properties can be investigated. The advantage of this technique is that it does not need conducting surfaces.

Thin insulating layers are at the border of being insulating and providing conductivity. Hence it is consequent to develop an instrument which is combining both, scanning tunneling and force microscopy, to be able to switch between both modes to meet the requirements of the sample.

This thesis is divided into two major parts: the instrumental development and studies of insulating films and adsorbates on copper surfaces.

In the first part, the basics of STM, STS and AFM are addressed (chapt. 2). This basic knowledge leads to the development of the modular low temperature scanning probe microscope used for the investigations presented in this thesis (chapt. 3). Chapter 3 does not only involve the framework directing the development process of the instrument itself (sec. 3.1, 3.2) but also of the infrastructure like the UHV-chamber (sec. 3.3) and the home built scanning probe control unit (sec. 3.4). A last section of the first part is devoted to the testing and calibration of the instrument (sec. 3.5).

The second part of this thesis involves the investigations of thin insulating layers on copper surfaces. The first chapter gives a motivation and introduction to this field (chapt. 4). Two different systems have been investigated in detail: \( \text{KCl} \) on \( \text{Cu}(110) \) and on \( \text{Cu}(111) \). Deposited on the copper substrate, the salt forms islands of different geometries (chapt. 5). According to the copper surface geometries this leads to different STM topographies of the salt layers. On the \( \text{Cu}(110) \) surface the one-dimensional character of the substrate is partially transferred to the adlayer (sec. 5.1) whereas the higher symmetry of the \( \text{Cu}(111) \) surface leads to smooth films (sec. 5.2).

A topic of special interest are the electronic properties of the films deposited (chapt. 6). As the films are expected to be insulating layers, they show an electronic structure reminiscent of a band-gap (sec. 6.1). The salt layers are not only interesting because of their intrinsic structures. Furthermore they influence electronic states situated in front of the copper surface. This perturbation is discussed in the case of field resonances (sec. 6.2). A related state to the field resonances is the surface state of \( \text{Cu}(111) \). This state is transferred by the salt into an interface state which is discussed in detail (sec. 6.3).

A final chapter is concerned with the adsorption of molecules on both surfaces \( \text{Cu}(111) \) and \( \text{Cu}(110) \) which will lead to future experiments combining both, molecules
and thin salt layers.
Chapter 2

Scanning Probe Microscopy

Since the invention of the scanning tunneling microscope (STM) by Binnig and Rohrer in 1981 [2] a lot of different types of scanning probe microscopes (SPM) have been developed. They vary in the type of interaction between a tip and the surface used for imaging. Prominent members of this family are the STM, the scanning force microscope or atomic force microscope (AFM) [3], the magnetic force microscope [4], scanning nearfield optical [5] or acoustical microscope [6, 7]. Other interactions used are the temperature [8] or the ionic currents through membranes [9].

For imaging the interaction between tip and sample surface should be as small as possible to not damage the surface. However, part of the attractiveness of SPM in the area of nanotechnology stems from the fact that the samples or adsorbates on the sample can be modified in a controlled way. These modifications include cutting of strip lines [10], scratching [11] or indenting [12] the surface to analyze its mechanical resistance and selective chemical modifications. Even moving single atoms or molecules as well as synthesis of molecules [13] has been reported. Some of these experiments require the use of liquid helium temperatures to minimize the thermal motion of adsorbates on the sample surfaces. In the following a short overview of the theoretical background of the operation of the STM at low temperatures is given and in chapter 3 the construction of a Low-Temperature-UHV-STM is described which is foreseen to also operate as a LT-AFM and is used for the experiments described in chapters 4-7.
2.1 Principles

All scanning microscopes are based on the same idea sketched in figure 2.1. A probe (tip) is placed in front of a sample surface. One chooses a physical quantity like current or force, which depends on the distance due to a localized interaction between the probe and sample. The probe is approached to the sample surface until the quantity meets a predefined value. To image the sample surface one rasters the sample line by line with the probe and forms an image from the change of interaction strength during the scan. Dependent on the application one scans at a constant high and records the interaction as a position dependent function or one tries to keep the interaction constant by appropriate changes of the tip sample distance. In the first case one can scan extremely fast but one is limited to flat surfaces and one obtains a map for the varying interaction strength with position which rarely allows a quantitative analysis of the surface structure. In the second case the elongation of the scanpiezo is recorded as a function of the position of the tip. This surface maps corresponds to surfaces of constant interaction which can in some cases be interpreted as the real topography. In the case of STM for example this image reflects a map of constant local density of states (LDOS) and hence of the electronic structure rather than geometrical structure. In this work constant current STM topographies are shown and mostly plotted as gray scaled height maps where black corresponds to the lowest and white to the highest positions of the probe in the direction normal to the surface.

Figure 2.1: Principle of scanning probe microscopes: Probe interacting with sample while rastering the surface.
2.1 PRINCIPLES

2.1.1 Scanning tunneling microscopy

The scanning tunneling microscope is based on the quantum mechanical tunneling effect. A metallic tip, mostly an etched tungsten or ground \( Pt_{90}Ir_{10} \) tip, is placed at a distance of several Ångstroms above the surface of a conducting sample. If a voltage is applied to this contact a current can flow. This current shows an exponential dependence on the distance between sample and tip. Typical conditions used are voltages in the range from several millivolts up to several volts at a current of several picoamperes up to nanoamperes. Using parameters like 1 nA setpoint and 300 mV bias voltage, about 90% of the current will be carried by the tip atom closest to the sample [14] explaining the high lateral resolution.

An important spectroscopic mode is the scanning tunneling spectroscopy (STS). This mode gives access to the LDOS of an predefined energy range and is used extensively in this thesis.

2.1.2 Tunneling - the Tersoff-Hamann approach

The model mostly used to understand the tunneling current has been developed by Tersoff-Hamann [15]. The approximation of a spherical tip leads to the following expression for the tunneling current [17,18]:

\[
I \propto \int_{-\infty}^{\infty} \rho_s(E)\rho_t(E - eV)T(E,V,z) (f(E - eV,T) - f(E,T)) dE
\] (2.1)

The basic parameters are the density of states (DOS) of sample \( \rho_s(E) \) at the actual lateral position of the tip and the DOS of the tip \( \rho_t(E) \), the Fermi functions \( f(E,T) \) at the temperature \( T \) and the distance \( z \) between tip and sample.

The Fermi function leads to a broadening of the structures at \( T > 0K \) in the DOS and thus is limiting the spectral resolution of the STM. Expanding equation 2.1 to different temperatures of tip and sample clearly shows that the limiting factor for the resolution is the temperature of the tip only. LDOS features of the sample can be broadened by different processes, but due to the convolution of the tip and sample DOS and Fermi-function these features can only be imaged correctly if the Fermi-function of the tip is sharp enough. This clearly explains the necessity to cool the sample as well as the tip.

Working at low temperatures below 10K the Fermi-functions line width is below \( kT \approx 1 \text{meV} \). If one is interested in features larger than \( kT \) it is possible to simplify
equation 2.1 to
\begin{equation}
I \propto \int_{0}^{eV} \rho_s(E)\rho_t(E-eV)T(E, V, z)dE
\end{equation}
by substituting the Fermi functions with stepfunctions. A commonly used approximation for the transmission function $T$ is given by [19]:

\begin{equation}
T(E, V, z) = \exp \left( -2z \sqrt{\frac{m_e}{\hbar^2}} (\Phi_s + \Phi_t - 2E + eV) \right)
\end{equation}

$T$ obviously depends on the work functions of tip $\Phi_t$ and sample $\Phi_s$, but it mainly depends on the tip-sample distance $z$. Using these equations experiments can often be explained qualitatively. At small bias voltages the voltage dependence in equation 2.3 becomes negligible and thus it is possible to assume an energy independent $T$

\begin{equation}
T(z) = \exp \left( -2z \sqrt{\frac{m_e}{\hbar^2}} (\Phi_s + \Phi_t) \right)
\end{equation}

which gives:

\begin{equation}
I \propto T(z) \int_{0}^{eV} \rho_s(E)\rho_t(E-eV)dE
\end{equation}

### 2.1.3 Imaging of surfaces

As mentioned, surfaces can be imaged by STM in two different ways: constant height and constant current mode. In the constant height mode the surface is scanned by moving the tip on a predefined plane and the tunneling current is recorded. This mode allows fast scanning but due to the exponential behavior of the tunneling current it is restricted to flat surfaces.

In this work all measurements are taken in the constant current mode where the tunneling current is kept constant by a feedback loop. The topographic images for this mode can be calculated using the equations above. Assuming a constant current one can invert equation 2.1 to get $T(z)$ which is carrying the information about the tip sample distance. In the limit of low temperatures and small voltages the equation can be solved numerically:

\begin{equation}
z(V, x, y) = z_0(x, y) + \frac{1}{2 \sqrt{\frac{m_e}{\hbar^2}} (\Phi_s(x, y) + \Phi_t(x, y))} \cdot \ln \left( \frac{\int_{-\infty}^{\infty} \rho_s(E)\rho_t(E-eV, x, y)dE}{I_0} \right)
\end{equation}
The LDOS of the sample can show significant changes as a function of the position of the tip and is in most cases the main component for corrugations. Workfunction changes are normally small. Nevertheless in the case of thin insulating films they can play an important role.

2.1.4 Spectroscopy

The power of the STM is not only the ability to image surfaces. It furthermore is able to gather spectroscopic information about the LDOS at different energies. As the tunneling current can be easily understood with equation 2.5 this is also true for the different spectroscopy modes.

$I(z)$ at constant bias voltage

Current-distance curves taken at a small bias voltage basically have an exponential dependence [16]. For data analysis they are $\ln(I(z))$ curves resulting in a linear function. To understand this behavior, from equation 2.5 it follows:

$$\ln(I) = -2 \sqrt{\frac{m_e}{\hbar^2}} (\Phi_s + \Phi_t) \cdot z + A = -MZ + A$$

which is a function depending on the workfunction of both tip and sample. Extracting the slope $M$ of $\ln(I(z))$ gives access to the work function of the sample:

$$\Phi_s + \Phi_t = \frac{\hbar^2}{4m_e} M^2$$

This equation is giving a measure of the effective tunneling barrier height $\Phi_{eff} = \frac{1}{2} (\Phi_s + \Phi_t)$. In general the tip is prepared by controlled tip-sample crashes. Therefore one can assume the frontmost part of the tip to be of the same material as the sample. This simplification leads to

$$\Phi = \frac{\hbar^2}{8m_e} M^2$$

for the local workfunction $\Phi$.

d$I$/d$V$-curves

d$I$/d$V$-curves taken at fixed tip-sample distance give direct access to the LDOS of the sample. This can be explained by differentiation of equation 2.5 if one assumes $T$ and $\rho_T$ to be constant in the energy range if interest:

$$\left. \frac{dI(V_0)}{dV} \right|_{z=\text{constant}} \propto \sigma_s(V_0)s_t(0)$$
This equation states that the dI/dV-signal is proportional to the samples LDOS at the energy $V_0$.

$dI/dV$-curves with variable $z(V)$ give access to larger voltage ranges. In this case the assumption of constant transmission coefficient is no longer valid and its change cannot be neglected. This measurement type as well as the case of large voltage ranges will be discussed in chapter 6.1.
2.1.5 Atomic force microscopy

The interaction used to define the tip sample distance in atomic force microscopy (AFM) are mechanical forces acting on the sensor. These forces can be for example of chemical, van-der-Waals, electrostatic or magnetostatic nature. According to the way of detecting the interaction one can mainly distinguish two different possible modes: the contact mode and the dynamical non-contact mode.

Contact mode measurements are characterized by constant tip sample force in the repulse force regime. The signal used for feedback is the deflection signal which represents the bending of the cantilever. Knowing the force constants and hence the sensitivity of the sensor one can easily calculate the force acting on the surface. The torsion of the sensor can be used to obtain data about lateral forces caused by friction between tip and sample when scanning.

The main drawback of this mode is the comparable large forces applied to the surface. While quasi-atomic resolution is possible, true atomic resolution has not been reported. The spectroscopic data which can be obtained in this mode are force-distance curves. They mainly contain information about the sample and tip properties in the contact regime.

Another mode commonly used is the non-contact mode. In this case, the tip is oscillating normal to the surface in front of the sample. The interaction between tip and sample is occurring mainly in the last few nanometers above the sample. This interaction changes the oscillatory properties of the cantilever as there are phase shift, amplitude and resonance frequency in dependence of the tip-sample distance.

A widely used variant is the frequency modulation mode. In this mode, the oscillation of the sensor is maintained with a feedback loop using a fixed phase shift between excitation and tip oscillation. The amplitude of the oscillation is kept constant with a feedback loop. Hence the amplitude of the excitation is representing the damping of the sensor and thus non-conservative force. A second feedback loop is adjusting the tip sample distance to keep a fixed frequency shift and thus constant conservative forces [20].

Different kind of detection schemes have been developed. The first AFM invented by Binnig et al. [3] used an STM on top of the cantilever to measure its displacement. Being too complicated, this method has been replaced by different new techniques. The only scheme using commercial cantilevers which is also able to determine lateral forces is the beam deflection mode shown in figure 2.2. Its idea is to measure the bending of a cantilever by reflecting a laser beam on the backside of the cantilever to a 4 quadrant diode. The foreseen AFM-operation of the system described in chapter 3 also uses this technique. Calculating different combinations of sensor quadrants signals
allows to determine both possible bending directions: the bending caused by the force perpendicular to the surface \( \frac{(A+B)-(C+D)}{A+B+C+D} \) and parallel to the surface \( \frac{(A+C)-(B+D)}{A+B+C+D} \). Other approaches are discussed in chapter 3.

Figure 2.2: AFM: principle. The mechanical state of the cantilever is read out with a laser beam reflected from its backside.
Chapter 3

Instrumental development

In the framework of this thesis a low temperature scanning probe microscope (SPM) for ultra-high vacuum conditions was realized. To get a suitable instrument which is extremely flexible, the following design considerations had to be taken into account:

1. STM and AFM mode available
2. In situ sample preparation and transfer to the SPM
3. Large coarse movement range, i.e. movements of millimeter dimensions well controlled on a 100 nm scale
4. Large scanning range at low temperatures
5. High resolution and stability
6. In-situ tip exchange
7. Effective damping of vibrations

None of these requirements can be considered independently. A particular solution to one of them restricts some or all of the other specifications. For example a large scanning range (4) will decrease the lateral resolution (5).

In the case of atomic force microscopy one can choose between several different techniques. The first group of AFMs is getting the information about the status of the probe using electro-mechanical effects. Commonly available sensor techniques are piezoresistive cantilevers [21] and piezoelectric sensors [20, 22, 23]. Despite their big advantage of structural simplicity, they have the disadvantage of limited commercial availability and hence choice of sensor properties.

The second group is reading the information in an optical way. There are two principle methods employed: the interferometric approach and the beam-deflection mode.
Both modes can use the same kind of cantilever sensor. Theoretically both can achieve the same resolution limit [24].

The mechanically simpler method is the interferometric approach. In this case one approaches the facet of a cleaved glass fiber to the backside of the cantilever to get a Fabry-Perot type interferometer consisting of the facet and the cantilever. The information can be extracted outside of the vacuum chamber using the glass fiber. The advantage of this system is its simplicity, but it is not capable to detect lateral forces.

If one is constrained to commercially available sensors, there is only one realization which gives full information about the probe: the beam deflection mode described in chapter 3.1.3.

At a first glance one can choose between the possibilities of scanning with the sample or scanning with the tip. Nevertheless there is a major difference in the mechanical stability.

As the tip-sample interaction is kept constant by a feedback loop one wants to keep the gain parameters as high as possible. On the other hand the gain has to be chosen small enough to avoid feed-back oscillations. This limit is mostly defined by the mechanical resonant frequency of the scanner. A good compromise is trying to get frequencies of more then $\approx 1$ kHz.

If one loads the scanpiezo with a certain mass, the resonant frequency $f$ will change according to equation 3.1 [25]

$$f = f_0 \sqrt{\frac{m_{\text{eff}}}{m_{\text{eff}} + M}}$$

(3.1)

In this equation $f_0$ is the resonant frequency of the unloaded piezo, $m_{\text{eff}}$ its effective mass which is about $1/3$ of its real mass, and $M$ the additional mass. As $m_{\text{eff}}$ is in the order of 1 g, even a small load in the order of several grams will dramatically decrease the resonant frequency. These circumstances imply that one has to keep the mass added to the piezo as small as possible.

Therefore it is tempting to scan with the tip which is in general, but especially in the case of an STM-tip, much lighter than the sample with sampleholder. Nevertheless this is problematic for any AFM with optical detection as one has to move the whole optics synchronously with the scanning tip. To avoid this problem the SPM is designed to scan with the sample as done for example by Hug et al. [26].

The decision to scan with the sample implies an extremely light and thus small sample holder. Furthermore one has to take into consideration the sample-transfer mechanism to the AFM because one is directly operating on top of the brittle piezotube.
3.1 Modular Design

Facing a completely new construction which is meant to offer a big variety of different possibilities to enhance the instruments abilities (see for example chapter 3.1.4), a modular design has been chosen. As shown in figure 3.1, the SPM can be divided into three subassemblies:

1. The scanner module containing all parts needed for sample scanning and coarse movement (chapt. 3.1.1).

2. The tip holder section, needed as a spacer between the two other parts. It contains a retainer for the tipholder as well as the electrical contacts (chapt. 3.1.2).

3. The AFM-optics section which contains the AFM optics as well as all motors needed to operate this module (chapt. 3.1.3).

Every single unit can be tested, modified or replaced easily without having a big impact to the other parts. In principle this guarantees short cycle times for evolutionary development.

One drawback of this construction is the reduced thermal connection due to a lot of different interfaces. This is important as all parts a cooled from the top where the instrument is attached to the cryostat. Furthermore, the modular design causes an increased size and makes the construction more vulnerable to oscillation than a monolithic design as for example used in [27].
3.1.1 Scanner module

The scanner module has to provide all degrees of freedom needed for the sample movements (x, y, z). This involves the scanning movement as well as the coarse motion in the millimeter regime.

Nearly all scanning probe microscopes working under UHV-conditions use coarse movement motors based on piezoelectric actuators. In principle one can choose between two general classes of motor for coarse movement.

The first one is the so called “beetle-typ” motor [28]. It realizes all coarse movements with a disk sitting loosely on three piezo tubes. This approach provides high stability due to compact design and high resonant frequency and good balancing of thermal changes. Its disadvantages are the limited range of the coarse approach in the direction normal to the surface, commonly in the order of a few tenths of a millimeter, and limited possibilities to attach the AFM optics.

The motor type chosen here belongs to a second class of motors developed by Pan [29]. In contrast to the beetle type, this motor provides a purely linear motion. The main advantage of the construction is the large traveling range possible. The main disadvantages of this motor type are the limitation to one respectively two axis per motor and the larger volume of the motor.

The z-approach motor is based on two vital parts: a sapphire prism with polished faces and a set of 6 shear-piezo stacks with amorphous Al₂O₃ slabs as faces which are clamping the prism.

Using a defined motion sequence of the piezo stacks causes a movement of the sapphire prism. Different types of movement sequences are known. The instrument is driven in the “slip-stick” mode sketched in figure 3.2. This mode requires only one cable for the piezos as all piezostacks are moved simultaneously. A typical step in this
3.1. MODULAR DESIGN

Figure 3.3: Scanner module. Left: tube scanner with connections; Right: Scanner module (test version).

mode would be: First slowly moving all piezos simultaneously together with the prism (“stick”), then tearing all piezos to the other side, leaving the prism at the current position due to its inertial mass (“slip”).

A crucial point of this kind of motor is the appropriate selection of materials and geometries. This incorporates the choice of different materials for the sliding interfaces as well as the motion range of the piezo actuators. Working at low temperatures the thermal properties are of special importance. As the tension of the spring clamping the prism is the most critical parameter, the combination of the materials of clamping springs and motor housing has to be chosen very carefully. In the present case the material combination is UHV compatible aluminum for the housing and molybdenum for the springs.

The movement in the sample plane is less critical as it has not to work against gravity. This 2D-motor has been realized in a similar way as the motor described above: the whole z-motor housing is clamped with piezo stacks consisting of two doublelayers of shearpiezos slabs. The translation directions of the doublelayers are rotated by \(90^\circ\) with respect to each other to allow two orthogonal directions of movement. The sliding interfaces are \(Al_2O_3\) ceramic half spheres on polished sapphire faces glued to the housing. This construction is placed in a can-like housing made of OFHC-copper, the spring is made of \(CuBe\).

In order to make the STM as compact as possible, the scanpiezo tube is placed inside the sapphire prism.

The steel sample holder is placed on top of the scanpiezo. To center the sample in this position, the sample and sample holder have conical chamfers fitting within some
CHAPTER 3. INSTRUMENTAL DEVELOPMENT

Figure 3.4: Sampleholder with crystal. (1) electrical insulated thermocouple contact; (2) crystal clamped with Mo-plate which is fixed with 3 M0.8 screws (3); (4) chamfer; (5) lug for sample transfer. Diameter of sampleholder without lug: 8 mm, height with crystal: approx. 3 mm.

Figure 3.5: Scanner module: Left image: z-motor on testing stage; Right image: opened scanner module from top. (1) scanpiezo; (2) sapphire prism; (3) piezo stack for z-motor; (4) sapphire slabs for xy-motor; (5) z-motor housing.

tenth of a millimeter. Inside the piezotube underneath the chamfer a small magnet is placed to fix the sample. This connection is stiff enough to ensure stable operation. On the other hand it avoids a too strong coupling to the scanpiezo while sample exchange. The sample holder itself is shown in figure 3.4. Even though it is extremely small (diameter without lug 8 mm, mass with crystal less than 3 g, consists of 11 separate parts) it provides direct thermocouple connection.
3.1. Tipholder section

The tipholder section shown in figure 3.6 consists of a circular housing with a plane inside the instrument. The central part is a drawer for the tip holder. The tip holder is clamped by four electrically insulated CuBe springs which can be used to connect the tipholder electrically.

There are two different kinds of tipholders which can be used with the instrument: STM- and AFM-tip holders. The coaxial construction of the STM-tip holder is shown in figure 3.7. The innermost part is a copper tube holding the STM tip. This tube is insulated with a ceramic tube against the grounded shielding. The connection to the spring contact is made via a small contact area. Having a small effective area coupling to the sample, this construction shows a minute capacitive coupling of high frequency signals from the sample to the STM-tip.

The AFM-tipholder uses the same base-plate like the STM-tipholder, but with a window for the laser beam. Underneath the plate the AFM-tip is mounted with an alignment chip [30] under an angle of 5° according to the AFM-optics requirements. The tip can be excited with a piezo-slab between the alignment chip and the wedge defining the angle and the distance perpendicular to the sample surface.

As an extension it is possible to exchange the position of tip and sample. As the “normal” tip holder is based on the sample holder design from Omicron [23], this offers the chance to use larger samples or samples from other instruments. However this exchange is limited to the STM mode only.
Figure 3.6: Tipholder section with STM-tip: (1) z-motor housing; (2) sapphire prism; (3) scanpiezo; (4) sampleholder; (5) tip holder.

Figure 3.7: STM-tipholder: (1) copper shielding; (2) ceramic tube; (3) copper tube with etched tip; (4) contact pad.
3.1.3 AFM-Optics

The AFM module has two functions. The main task is to house the AFM-optics. Furthermore it is the central interface and last cooling stage for the electrical connections as will be described in chapter 3.2.

The beam deflection mode provides the possibility to get the all information on the motion of the cantilever used as sensor. While realizing the idea shown in chapter 2.1.5, one has to care about a number of different degrees of freedoms for the optical path. Most of them can be eliminated by pre-adjustment of optical components and the cantilever and by using a fault-tolerant optics.

The pre-adjustable parameters are the relative position and angle of the glass fiber to the first lens and the position of the parallel beam on the second lens. Using these parameters one can focus the beam to the cantilever and define the angle of incidence on the cantilever. Tolerances of the tip position in the beam direction are compensated by using an optic which is providing a focal spot smaller than 30 $\mu$m over a range of about 0.3 mm along the laser beam.

Some parameters have to be adjusted during the instruments normal operation. The first one is the position of the four-quadrant diode with respect to the laser spot. The second one is the position of the focused last beam compared to the cantilever. In both cases 2D-motors similar the ones described in chapter 3.1.1 are used.

The implementation is shown in figure 3.8. As mentioned above, the light is delivered by a glass fiber. A first lens is bundling the divergent light to a parallel beam. This beam is reflected on a mirror to a off-centric position on the second lens. Focused on the cantilever it is reflected by the sensor. A second mirror transmits the divergent beam to the four quadrant photodiode [31].

Besides being simple to connect, using a laser source in vacuum as done for example in [23] suffers from different drawbacks which are prohibiting this basic approach in the framework of the actual development. First, laser diodes react quite sensitively to thermal stress and high temperatures. Furthermore commercial laser diodes are normally not designed to work at temperatures like 4K. Finally, a future goal, as described in chapter 3.1.4, is to incorporate optical spectroscopy. Laser diodes emit light with a rather broad bandwidth superimposing the optical range of interest. Therefore a HeNe-Laser [32] equipped with an attenuator unit and intensity sensor [33] situated outside the vacuum was chosen. The light is guided by a metal coated glass fiber [34] into the vacuum system. As the HeNe laser offers a quite sharp wavelength distribution, it is possible to filter its light with a notch filter without loosing the signal of interest.
3.1.4 Future possibilities

Designed in a modular way, the instrument can easily be upgraded in different ways.

In a first step the system will be equipped with the possibility to transfer samples from another system. As the samples are based on the Omicron sampleholder-design this requires the exchange of the tips and sample position as well as minor modifications on the sample transfer system.

Due to the optical access foreseen for the AFM optics one can also add optical components to collect light emitted from the tunneling contact. This method allows to gather information about inelastic processes as has been demonstrated by different authors [35–38].

Also the reverse is possible mainly to couple light to the gap between scanning probe tip and sample. This offers access to light-matter interaction at the nanometerscale [39].

Due to the extremely open design further additions like an evaporator installed in front of the SPM for in-situ investigation of growth processes at low temperatures, are possible.
3.2 Connection between Cryostat and Instrument

The aim of the designed system is to work at 5 K. To reach this temperature at tip and sample special care has to be taken to avoid heat flow exceeding the cooling power of the cryostat which is in the order of 50 mW only.

This had to be taken into account while modifying the cryostat as described in chapter 3.3.3. On the other hand it limits the possibility for electrical connections. This is even more important in the present case as there are a large number of connections to be made for i.e. the motors of the lateral positioning system and the AFM module.

A prerequisite to reach the low temperature is a decent cooling of the cables. In the present case this cooling was achieved by connecting the cables to 4 anchoring points with decreasing temperature: the room temperature flange, one of the radiation shields, the top of the helium reservoir and the AFM-optics module of the SPM. At these points the thermal resistance to the cold reservoir has to be minimized. As these connections have to be insulating, the resulting thermal resistance will be quite high. Therefore one has to care of high thermal resistances of the cables. Due to the Wiedemann-Franz law cables with low electrical and thus thermal resistance have to be avoided and materials with higher electrical resistance like manganin or stainless steel have to be chosen.

![Figure 3.9: Thermal coupling: radiation shield stage. To decrease the thermal resistance to the anchoring point the contact area has been maximized by coiling and gluing the cables. (1) radiation shield; (2) cable (left image: two quadruple ribbon cables, right image: coaxial cable); (3) coupling stage with cable coiled and glued.](image-url)
Figure 3.10: Thermal coupling: Anchoring points. Left image: He-cooling stage mounted in service frame. Right images: anchoring points. From top: flange, radiation shield, He-pot, AFM-optics module. Markers: anchoring level.
### 3.3 UHV-Chamber

The UHV chamber used (see fig. 3.11) consists of two main parts which can be separated by a gate valve [40]: the preparation chamber and the analysis-chamber. Both chambers have base pressures of $1 - 5 \cdot 10^{-10}$ mbar.

The preparation chamber (1) is equipped with different instruments for sample cleaning and preparation. It also includes a transfer mechanism (2) to transfer the sample to the second part of the UHV system. Furthermore it has a load-lock (3) to transfer samples and probes to the system. The analysis-chamber (4) mainly consists of the bath cryostat cooling the SPM itself.

The system is equipped with an oil free pumping system as sketched in figure 3.12. This system has different stages. The first pump is a membrane pump providing a pressure in the millibar range. This pressure is used as pre-vacuum for the next pumping stage as well as for the first differential pumping stage of the rotational feed-through of the manipulator (2). The second pumping stage is set up with a small turbo pump with drag-stage and provides a pressure in the $5 \cdot 10^{-6}$ mbar range. This vacuum can be connected to the systems main turbo, the load-lock turbo, the gas-lines and the second differential pumping stage of the manipulator. The chamber itself can be pumped with a turbo-pump with magnetic bearings [41] which can be separated from the chamber with a gate valve. During operation of the SPM, the chambers can be pumped with getter-pumps only to avoid mechanical vibrations.

![Figure 3.11: Sketch of UHV-system. 1: preparation chamber; 2: manipulator; 3: load-lock; 4: cryostat; 5: analysis chamber with cryostat; 6: damping system.](image-url)
3.3. UHV-CHAMBER

3.3.1 Preparation chamber

The preparation chamber is reserved for sample cleaning and preparation. The possible separation from the analysis-chamber is mandatory to avoid contamination of the cryostat with process gases as e.g. argon used for sputtering.

This chamber offers a variety of different possibilities to attach tools needed for sample preparation and investigation. At the moment it is equipped with evaporators, gas dosing equipment, a sputter gun, a mass spectrometer and an auger spectrometer. For sample handling a manipulator [42] with a sample heating stage included in the sample holder section 3.13 and a wobble-stick are installed. Finally a load-lock is attached to offer the possibility of sample and tip exchange.

Different types of evaporators have been attached according to the requirements of the different materials. The KCl used in this work has been evaporated with a homebuild Knudsen cell. Molecules have been filled into a homebuild Knudsen type double evaporator. Both evaporators use fused silica crucibles in order to separate the evaporant from the metallic holders. The third evaporator, an electron beam evaporator [23], has been equipped with metal rods. To be able to exchange the materials without breaking the vacuum of the chamber they are installed in small load-locks.

The load-lock has been connected at top of the chamber. Separated from the main chamber with an gate valve, it can be pumped with its own turbo pump [41] and baked without interfering other parts of the instrument. Using a wobble stick attached to the preparation chamber, the sample can be transferred to a storage storage connected to the load lock or to the linear manipulator.

Gas dosing is performed with two different gas lines. Both lines can be pumped via the pre-vacuum turbo to clean the tubes. The first line is connected to the sputter gun and supplies the argon needed for the sputtering process. The second line can be connected to different gases. The oxygen needed for the calibration experiments described in chapter 3.5.1 has been dosed with this line.

Sample transfer to the analysis-chamber is done with a linear manipulator attached to the system. It provides linear motion along all three directions in space as well as a rotation along the manipulators axis. The manipulators head can be cooled with liquid nitrogen or liquid helium.

The sample holder section is attached to the head of the manipulator. It provides a transfer mechanism for tip holders and samples as well as an electron beam heating stage for sample preparation and connections for the thermocouple of the sample holder.

As can be seen in figure 3.13, the sample sits in an insulating ceramic housing. It is fixed with a molybdenum spring which acts as a contact to the sample. A thermocouple
Figure 3.13: Manipulator head: sample holder section. Upper image: mechanics without shielding and sample or tip, Lower image: closed shielding; sample- and tipholder inserted. (1) thermocouple connection; (2) tipholder-connection; (3) sampleholder connection; (4) manipulator interface; (5) sampleholder; (6) tipholder.

clamping mechanism connects the sample from both sides. Underneath the sample a tantalum foil filament is placed inside a Wehnelt cylinder. The cylinder can be set to a negative voltage to ensure that all electrons emitted by the filament are accelerated towards the sample.
3.3. Analysis chamber and cryostat

The second part of the chamber shown in figure 3.11 is reserved for sample examination only. It can be separated by a gate valve [40] from the preparation chamber. If the valve is closed, the chamber is pumped with two pumps: an ion getter pump [43] and the cryostat which is acting as a cryo pump. This allows a base pressure of $1 \cdot 10^{-10}$ mbar in this part of the chamber.

The cooling stage of the cryostat itself consists of two parts: a radiation shield at liquid nitrogen temperature and the helium stage inside the radiation shield. The radiation shield consists of a tube like tank with an opening for the helium cooling stage. It has a capacity of 46 l filled with liquid nitrogen. The helium reservoir is an approximately 10 l pot inside the nitrogen shield which is only weakly coupled to the room temperature parts. The SPM is mounted on the baseplate of this pot.

Originally, the manufacturer [44] fixed this pot with a thin steel tube to minimize the heat flow. The disadvantage of this construction resembling a pendulum is the low eigenfrequency. Figure 3.16 shows the oscillating behavior of this system. Having an extremely high quality factor the helium tank is resonating for several minutes after being excited. Its resonant frequency of about 2.5 Hz was close to the oscillation frequency.
CHAPTER 3. INSTRUMENTAL DEVELOPMENT

Figure 3.15: Cryostat stiffening. (1) filling tube of the helium tank; (2) stiffening parts. They are rigidly coupled to the radiation shields but have sliding contacts at the outmost ends to avoid mechanical stress.

Figure 3.16: Cryostat stiffening: oscillation. Once excited the undamped cryostat is oscillating for >6 min whereas the modified version is damped within 10-20 s.
of the building. Furthermore the damping system (see fig. 3.11) is only little effective at these frequencies. To avoid the coupling of low frequency noise, the properties of the oscillating system had to be changed by stiffening of the inner parts between the flange holding the helium cooling stage and the helium tank itself.

Due to the extreme temperature range of 4 K up to 420 K occurring this stiffening had to be build in a way avoiding strain because of thermal changes. Furthermore it has to be stiff enough to damp the oscillations. Testing different variations of modifications have shown, that the best properties are achieved by three straight columns as shown in figure 3.15. This columns consist of stainless steel tubes connected to the top flange as well as to every radiation shield.

The strain decoupling is achieved by using modified banana plugs made of copper beryllium connecting the uppermost and the lowermost stiffening tube to the flange respectively helium tank. These modifications result in a higher resonant frequency of about 10 Hz as well as a higher damping and thus lower quality factor in figure 3.16. The increased heat flow through this additional parts did not change the He consumption of the cryostat significantly. After the modifications the 10 l last for more than 90 hours, whereas the 46 l liquid nitrogen last for 70 hours.
3.3.3 Damping issues

As one measures elongations in the sub-Ångstrom range, a major task of setting up a scanning probe microscope is to protect it from external sources of vibration. This can partially be achieved by a rigid construction of the instrument itself (high eigenfrequencies). Nevertheless, an unrealistic high resonant frequency in the high kilohertz range would be needed to avoid most of the mechanical perturbances [45]. A realistic approach is to target a resonant frequency of about 1 kHz. Low frequency noise can be filtered out by using a damping system. Mechanical oscillations due to acoustic noise coupling has been minimized by placing the whole UHV setup into a sound-proof chamber.

Each damping system has its particular characteristic with a typical transfer curve (fig. 3.17) [46]. Working quite well in the high frequency range, all damping systems normally have a limited performance in the frequency range of several Hertz. Furthermore, all passive damping systems have a resonant frequency where they are less effective or, even worse, are amplifying the oscillations. If one cascades several damping stages one has to take care that these frequencies are shifted against each other to avoid coupling.

![Figure 3.17: Mechanical damping: Theoretical transmission coefficient $T(f)$.
(1) Ideal damped oscillator with resonance at 10 Hz; (2) two serial oscillators with resonance frequencies of 10 Hz respectively 15 Hz.](image-url)
In the present setup a three stage damping system has been chosen (see fig. 3.18). The stage consists of an active damping system [48]. It is situated between the floor and an optical table. Not activated, this systems works like a normal passive damping. Once activated it additionally actively damps the oscillations especially in the low frequency range as can be seen in graph 3.19. The second stage is a usual passive damping stage [47] which is lifting the whole chamber with pressurized air. The third passive damping system is only damping the inner part of the He-cryostat.

To test and improve the damping system we performed measurements of the acceleration caused by the floor motion with mechanical sensors [48]. The acceleration signal has been recorded and fourier transformed. The averaging of 64 curves for each graph and a prompt measurement of all data guarantees the comparability of the different graphs in figure 3.19.

The first attempt showed a coupling of the last two stages causing an amplification of noise in the range of approx. 125-150 Hz. Changing the resonant frequency of the last damping stage by adding some masse to the stage removed this problem. As a result the vibrational acceleration reaching the STM is damped by more than 30 dB for all frequencies.
Figure 3.19: Mechanical damping: frequency power spectra of the acceleration (logarithmic scale). Each damping stage reduces the signal. The two different measurements of the last passive stage show an unwanted resonance surge at approx. 130 Hz which can be avoided via changing the last stages resonance frequency with additional weight.
3.4 Scanning probe control unit

The electronic control system is a vital part of any scanning probe since it controls all major parts of the instrument. On the one hand, the control unit has to fulfill various requirements in order to enable the microscope to acquire data in a proper way. On the other hand a suitable software has to provide an user interface which controls all important parameters.

The hardware can be divided into several basic units: the completely analog parts controlling for example the tip-sample distance, the computer controlled units for I/O-purposes and additional interfaces like high voltage amplifiers and filters.

The connection to the computer is realized by two interface boards. A combined analog/digital interface, the National Instruments IO card NI PCI 6052E [49], offers two 16-bit digital-analog converters and 8 analog-digital converters with 16-bit resolution. The second board, a NI-PCI DIO 96 card [49], provides 96 digital signal lines partially used for signal lines and a parallel bus providing data for the external 16-bit digital/analog-boards.

The external DA-boards driven by the parallel bus generate the signals needed for the piezo which are the (x,y)-scanning motion as well as an offset value for the z-signal (see chapter 3.4.1).

The analog signals generated by the PCI 6052E card are used as current setpoint and bias voltage respectively.

The signal lines are used for several functions. Two signals are used as remote lines for the z-coarse approach motor defining the direction and status of the motor. Two more lines control the feedback control circuit to retract the tip from the surface of the sample and to open the feedback-loop to keep the z-position of the tip constant. One further signal is used to synchronize the oscilloscope with the scanning motion.

In order to minimize high frequency noise all analog signals coming from or going to the computer are amplified and filtered using low-pass filters.

The most vital part of any scanning probe microscope is the feedback loop. It keeps the tip sample distance at a preset value by controlling the absolute position of the tip in the z-direction. Commonly the feedback control circuit is called ”feedback loop”, but in fact the whole instrument has to be included to the circuit sketched red in figure 3.20. It consists of the instrument itself, the I/V-converter, the feedback control circuit, one high voltage amplifier and several low-pass filters. In order to avoid interferences like high frequency glitches caused by DAC-steps this part of the electronics consists of analog electronics only. This realization allows a regulation of the tip sample distance without
Figure 3.20: Sketch of electronics: green: digital signal (motor signals and bus), blue: recorded signals, red: feedback-loop.
any computer support.

The feedback-loop maintains a constant current according to the chosen setpoint by employing a proportional-integrator architecture. At the input, the absolute value of the current is formed to make the feedback and the setpoint independent of the bias voltage and the logarithm of the current is derived in an analog circuit. This serves to linearize the exponential dependence of the current on the distance and hence linearizes the feedback-loop.

All signals driving the piezos are amplified by low-noise high voltage amplifiers providing an output voltage range of ±220 V. As the scanning piezo was chosen to have a large scanning range its sensitivity is quite high. This results in a higher sensitivity to the electronic noise, too. Therefore, one has to take care, that the voltage steps generated by the DA-converters result in reasonable steps in x and y at the piezo. To adjust this step size to suitable values the output is scaled down again with voltage dividers if necessary.

Data acquisition is done by using four of the IO-boards analog-digital-converters. The signals read in are the z-voltage, representing the tip height, the voltage representing the tunneling current and the two channels of the lock-in amplifier. Combining these signals with the tip position one can get all the data needed.
3.4.1 Plane substraction circuit

One drawback of any analog/digital converter is the limited resolution. Having a resolution of 16 bit for an analog signal of ±10 V (corresponding to a z-range of 660 nm) results in a voltage resolution of about 0.3 mV (respectively a z-resolution of about 10 pm). As one normally investigates structures with height differences of several monolayers the full voltage respectively z-range is not needed. Therefore it is possible to increase the resolution by restricting the sampled voltage to smaller ranges. One possibility to do this is a virtual shift of the z-signal to get rid of offset values. This can be done by adding a constant voltage generated by an external D/A-converter to the z-signal like shown for one forward/backward scanline in figure 3.21.

![Figure 3.21: Sketch of typical scan lines of a tilted sample with correction: a) simple offset compensation b) plane substraction.](image)

Generally the sample is not only shifted by a constant value, but it is tilted to some extend because of mechanical inaccuracies of the sample holder. While scanning the surface the tilt results in a big background signal with a small “parasitic” signal on top. Therefore a more sophisticated way of limiting the voltage range is to subtract a tilted plane of the shape

\[ \Delta z = A \cdot V_x + B \cdot V_y + C \]  

where \( V_x \) and \( V_y \) are the voltages for scanning in x and y direction supplied by the DA-converter boards. \( A \) and \( B \) have to vary about from negative to positive values to be able to compensate all possible slopes, \( C \) is a constant voltage also of both polarities compensating offsets. If the \( \Delta z \) signal is added to the z-signal obtained by the feedback loop, and the surface scanned is virtually flatened while the scanpiezo still gets the full
z-signal needed. The acquisition hardware has to sample the reduced voltage range only, the feedback loop does not have to deal any more with the tilt of the sample.

![Figure 3.22: Plane substraction circuit drawing.](image)

The realization of an according circuit is shown in fig. 3.22. It is a fully analog circuit generating the signal

\[
\Delta V_z = \frac{R_{13}R_{12}}{R_{14}} \left( \frac{1}{R_5} \frac{1 - \frac{R_3R_5}{R_1R_5}}{1 + \frac{R_3R_5}{R_1R_5}} U_x + \frac{1}{R_{10}} \frac{1 - \frac{R_7R_8}{R_6R_8}}{1 + \frac{R_7R_8}{R_6R_8}} U_y + \frac{15V}{R_{11}} (1 - 2\alpha) \right)
\]  

(3.3)

as well as the inverted signal for monitoring purposes. The different \( R_i \) are resistors; \( P \) (with position \( 0 \leq \alpha \leq 1 \)), \( R_2 \) and \( R_7 \) are potentiometers to tune the parameters \( C \), \( B \) and \( A \). Resistors have been chosen in a way that a tilt of about 25% of the maximum z-range is accessible.
3.5 Setup testing

To test the stability and performance of the STM setup described in the previous sections and to obtain a reliable piezo calibration a number of experiments on copper surfaces were performed reproducing known results found in literature. As a side effect of these experiments the quality and cleanliness of the Cu(111) and Cu(110) substrates used for the growth of ultrathin KCl layers described in chapter 5 was checked.

All single crystals used within this work were obtained by Mateck [50]. They were cleaned by a standard cleaning procedure in UHV consisting of ion sputtering and subsequent annealing cycles. After sputtering the sample for 15 minutes with an Ar$^+$ ion current of 18 $\mu$A (background Ar-pressure $5 \cdot 10^{-6}$ mbar) the samples were generally annealed for 1-2 minutes at 800 K (Cu(111)) respectively 770 K (Cu(110)) to cure sputter induced surface defects. However, when the crystals were used for the first time a new surface layer of lower defect concentration was produced. The procedure used for this purpose consists of performing a sequence of sputter and annealing cycles starting at an increased annealing temperature and slowly decreasing the temperature with each cycle.

After further sample treatment, for example dosing some gas or depositing substances, the crystal is transferred to the SPM. Due to the background pressure of $1 \cdot 10^{-10}$ mbar in the analysis-chamber the sample can be used for more than one week without considerable surface degradation by adsorbates.
Table 3.1: Piezo calibration parameters. The values for 4K are determined by measurements. Room temperature values are calculated according to the suppliers guidelines. As expected from other instruments, the values for low temperatures are by a factor of four smaller than the room temperature values.

### 3.5.1 Piezo calibration

The scanning movement is done with a scanpiezo. Due to the piezoelectric effect this element translates an applied voltage to an elongation as has been described in chapter 3.1.1. This elongation depends on temperature as shown in table 3.1.

The piezo sensitivity can be calibrated for the different temperatures from known surface properties. In principle there are three different parameters which have to be determined: x, y and z. However, due to the symmetry of the setup one can expect the value for x and y to be equal.

The z calibration can easily be obtained from the topographies of the clean surface, either form a line scan or with a more accurate estimation of the error from histograms of topographies shown in figure 3.23. From the analysis of such data one obtains the z calibration at low temperature shown in table 3.1 and the noise level of ±7 pm of the tip sample distance.

Calibration of the lateral parameter is not so easy to perform. The LDOS corrugation especially of the (111) surfaces is in the range of the above noise level. Most experiments demonstrating atomic resolution of these surfaces rely on strong tip-sample interactions and sometimes on the presence of an adsorbate between tip and sample. At a later stage atomic resolution was obtained on a Cu(110) sample with a few percent of a monolayer of KCl. However even if atomic resolution is not available, a reliable calibration can be obtained on the two surfaces by two methods described in the following.

The methods involve measuring lateral distances on the surface on the order of several nanometers. These larger distances also allow to estimate the non-linearity of the piezo movement observed for higher applied voltages i.e. large scan ranges.

The first example is oxygen on the Cu(110)-surface forming an O(2x1) reconstruction.

For the sample preparation one first has to clean the crystal as described above. After the cleaning cycles the crystal has to be heated to a temperature of 630 K. Keeping this

<table>
<thead>
<tr>
<th>Parameter</th>
<th>d(4K)(Å/V)</th>
<th>d(RT)(Å/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x, y</td>
<td>210.30 ± 20</td>
<td>879.8</td>
</tr>
<tr>
<td>z</td>
<td>30 ± 3</td>
<td>116.8</td>
</tr>
</tbody>
</table>
temperature constant the sample is exposed to oxygen at a pressure of $2.1 \cdot 10^{-9}$ mbar for 30 s. Finally the sample is annealed in vacuum for 5 minutes at the same temperature.

Performing this measurement one typically gets structures like shown in figure 3.24 [51,52].

The lines are formed by alternating oxygen and copper atoms along the [001] direction. The distance between the single rows is defined by $a_{Cu} = 3.62 \text{Å}$. As it is only possible to image one type of atoms, depending on the dip configuration either the oxygen or the copper atoms, one finds a distance $1/2\sqrt{2}a = 2.56 \text{Å}$ for the protrusions on the line. As a side effect the growth direction of the oxygen-stripes allows to determine the crystallographic orientation of the $Cu(110)$. However, the sample holder is not restricted to an exact orientation to the scanpiezo and can be rotated by $\pm 20^\circ$. Therefore the crystals orientation is slightly different for each sample preparation and thus sample transfer.

The second method used for calibration was the surface state on the $Cu(111)$ surface. This state resides within the energy gap at L and therefore as a two dimensional character. Within the "Nearly-free-electron" model (NFE-model), it can be described as a 2-D free electron gas with the dispersion relation

$$k(E) = \sqrt{\frac{2m^*}{\hbar^2}(E - E_0)}$$  \hspace{1cm} (3.4)

with the effective electron mass $m^* = 0.38 \cdot m_e$ and the surface state onset $E_0 = 0.44 \text{eV}$ [19,53,54].

Figure 3.25 shows a representative set of measurements. The topography shows a $Cu(111)$ surface with several straight steps that were created by indenting the tip. On the terraces one can see the LDOS variation of the surface state as a small corrugation.
Figure 3.24: $O(2\times1) - Cu(110)$ reconstruction. Upper image: 50x25 nm$^2$ overview; lower image: zoom to the center 10x5 nm$^2$; sketch: model [52]. Empty circles: $Cu(110)$, shaded circles: Cu atom, filled circles: oxygen atom. The topography of the lower image has been filtered using median filters; 0.5 V, 1 nA.
CHAPTER 3. INSTRUMENTAL DEVELOPMENT

Figure 3.25: Cu(111): surface state. Left: topography 50x50 nm$^2$, 0.1 V, 0.2 nA; middle: according dI/dV-map; right: FFT of dI/dV-map 20x20 nm$^{-2}$.

This can be seen better in the dI/dV map which is directly proportional to the LDOS. The surface state is fully isotropic with respect to the surface plane. Therefore the fourier transformation of the measured dI/dV is a circle. This fact can be used to cross check the x and y-calibration of the piezo independently. The dispersion relation obtained by the fourier transformation for different energies is shown in figure 3.26. From the comparison with the known dispersion relation the calibration factors were found to be consistent with those obtained on the Cu(110). Table 3.1 gives an average value of all calibrations experiments.
Figure 3.26: Cu(111): surface state dispersion relation. Squares: STM data, black line: NFE-theory with $m_{\text{eff}} = 0.38 \cdot m_e$, $E_0 = 0.44$ eV.
3.5.2 Spectroscopy

In the previous section spectroscopy with the system was already demonstrated. Besides the lateral investigation of the surface state LDOS it is also possible to investigate its dependence on energy. The ultimate goal of any instrument built for spectroscopic measurement is to achieve an energetic resolution which is only limited by the sample's thermal state. In the case of the present instrument this limit should be lower than 1 meV.

A spectroscopic feature suitable to proof the instrument’s capability is the onset of the Cu(111) surface state. This onset has been widely studied with different experimental techniques like STM [55] and Photoemission Spectroscopy (PES) [?]. The mechanisms leading to the present line width has been studied theoretically and is well understood [57].

Due to the instrument’s stability the surface state onset is visible in both the $I(V)$ and $dI/dV$ curve. In the $I(V)$ it shows up as a slope change. For temperatures comparable to the present case a linewidth of approx. 30 meV has been reported. Using the same analysis method as Kliewer [55] et al. as shown in figure 3.27 this linewidth $\Delta E$ has been reproduced.
Chapter 4

Thin insulating layers

The industrially most important insulator/conductor heterostructure is undoubtedly SiO$_2$ on Si. Modern electronics is based on the properties of this system. Fulfilling Moore’s law the complexity of the devices has steadily increased and as a consequence, the size of the single building blocks, i.e. on chip transistors or capacitors, has shrunken. Thus the insulating layers included in device technology has also been scaled down. The ongoing miniaturization already has reached the nanometer scale, i.e. where the oxide layer is only a few monolayers thick [1]. At these dimensions the insulating properties break down due to imperfections or simply due to the tunneling effect. This is one aspect of the motivation to study ultrathin layers of insulators. But insulating layers are also necessary for future applications in molecular electronics or catalysis hence a thorough understanding is necessary. Efforts in this direction are reflected in the variety of literature available in this field (see for example the review article [58]).

Most techniques to study surfaces like scanning electron microscopy, low energy electron diffraction (LEED) or photoemission have difficulties to cope with from the insulating properties which trap charges on the surface. A technique widely used for investigations at the 10 nm scale is the scanning force microscope. The technique is not restricted to conducting surfaces and thus seems to be the ideal tool for morphological studies. However it also suffers from the insulating properties of the films of interest as electrostatic forces due to trapped charges have to be compensated [59]. Furthermore, AFM is limited to the investigation of topographic and mechanical properties and normally does not have access to electronic properties. Clearly a combination of both STM and AFM as is foreseen with the developed instrument could provide a maximum of information.

In the following chapters STM and STS measurements are discussed that provide atomic scale resolution of the morphology and the electronic structure of the sample.
STM is suitable especially for ultrathin layers of insulating materials as they are are on the one hand side thick enough to show to some extent insulating properties and on the other hand thin enough to allow the electrons to tunnel through the thin layer.

There is a variety of different systems in this area that have been studied in literature. This ranges from in situ grown oxides like $\text{Al}_2\text{O}_3$ on $\text{NiAl}(110)$ [60]; $\text{V}_2\text{O}_y$ on $\text{Cu}_3\text{Au}(100)$ [61]; $\text{MgO}$ on $\text{Ag}(100)$ [62–65] and other substrates like $\text{Fe}(100)$, $\text{Mo}(100)$; $\text{CoO}$ on $\text{Ag}(100)$ [66, 67], $\text{BN}$ films or grids on transition metals [68–71] up to ionic films like alkali halides on many different substrates. Examples for such systems are: $\text{LiF}$ on $\text{Ag}(111)$ [72]; $\text{LiCl}$ on $\text{Cu}(100)$ [73] and $\text{Au}(111)$ [74–76]; $\text{NaCl}$ on $\text{Ag}(100)$ [77], $\text{Al}(100)$ [79], $\text{Cu}(100)$ [78], $\text{Al}(111)$ [79], $\text{Cu}(111)$ [80–84], $\text{Cu}(211)$ [85], $\text{Cu}(311)$ [86, 87], $\text{Cu}(531)$ [88] and $\text{Ge}(100)$ [89–91]; $\text{KCl}$ on $\text{Au}(111)$ [74–76], $\text{Ag}(110)$ [92–96] and $\text{Ge}(100)$ [91]; $\text{RbCl}$ on $\text{Au}(111)$ [74, 76] and other salts like $\text{CaF}_2$ and $\text{BaF}_2$ on $\text{Si}(111)$ [97].

All systems mentioned above have their individual advantages and disadvantages. Films can often be easily prepared by oxidation of the substrate as e.g. in the case of $\text{SiO}$ on $\text{Si}$ or $\text{Al}_2\text{O}_3$ on $\text{NiAl}(110)$. But the heterostructure often suffers from the different lattice constants of oxide and metallic substrate. As a consequence they in general have a complicated crystallographic structure. Another example, the $\text{MgO}$, can exhibit very nice islands growth [62–64], but the growth parameters have to be adjusted to a high accuracy, which seems to make transfer from one experimental setup to the other difficult [65]. The $\text{BN}$ films created by decomposition of $\text{B}_6\text{N}_6$ on transition metals are easily prepared with uniform thickness as their growth stop after the first monolayer is closed [68–71]. There are, however, inherent problems with the stability of the precursor molecule used for the preparation [69].

A promising family of insulating layers which is suitable for systematic investigations are the alkali halides. As they have certain disadvantages like being soluble in water they will not have technical impact, but due to their properties they can serve as examples for insulating layers in surface science. Being the prototype for this material class the sodium chloride is the by far best characterized system on a manifold of surfaces [74–90]. It provides simple and straightforward sample preparation for the different substrates. On most surfaces it grows as in a carpet like mode as (100) facets.

As insulating material $\text{KCl}$ was chosen which is related to the $\text{NaCl}$. By the standpoint of scanning probe microscopy it is an almost uncharacterized system. As it has a similar crystal structure as the sodium chloride, it is likely that some of the properties known from the sodium chloride will be valid for this system too. Contrary to the sodium chloride the ionic diameters of potassium and chloride are nearly the same as they both
are isoelectronic to argon. The latter gives the chance to compare the influence of thin

$KCl$ layers with the influence of argon layers $[53,54]$ on surface properties.

Among the different possible substrates we have chosen the copper (111) and (110)
surfaces. The $Cu(111)$ surface has proven to be a suitable substrate for $NaCl$ and thus is
a perfect candidate for analog investigations with $KCl$. It provides a well characterized
surface state which interacts with adsorbates. Furthermore this surface state is a perfect
reference for spectroscopic measurements.

The second surface chosen is the $Cu(110)$. It provides only a 2-fold symmetry in
comparison with the 3-fold symmetry of $Cu(111)$. Furthermore it is a more open surface
with higher corrugation. Both gives hope to a higher interacting strength leading to one
dimensional structures like known form the oxygen stripes $[51,52]$. 
Chapter 5

Morphology of KCl on Cu(110) and Cu(111)

In this chapter the growth of thin KCl films on Cu(111) and Cu(110) is presented. It is shown that their properties are affected by the properties of the different copper surfaces used.

The copper (110) surface shown in figure 5.2 shows two different prominent directions: the close packet direction [011] where the copper forms “chains”, and the [001] direction perpendicular to the chains. The surface is 2-fold symmetric.

In contrast to the (110) surface the (111)-surface has a six-fold symmetric structure in the first layer. The dense packing of surface atoms gives rise to a higher mobility of adsorbates.

Potassium chloride has the same crystallographic structure as sodium chloride which is the rocksalt structure shown in figure 5.1, but with different lattice constants of $a_{KCl,\text{bulk}}(298\,\text{K}) = 6.29\,\text{Å}$ [99] and $a_{NaCl,\text{bulk}}(298\,\text{K}) = 5.64\,\text{Å}$ [98]. The lattice constants decrease with decreasing temperature: at 0 K an extrapolation gives $a_{KCl,\text{bulk}}(0\,\text{K}) = 6.25\,\text{Å}$ respectively $a_{NaCl,\text{bulk}}(0\,\text{K}) = 5.6\,\text{Å}$.

The three low index surfaces of the rocksalt structure show different properties. The (100) surface and cleavage plane is the most stable one. Besides a hexagonal low temperature phase [77] it is the only surface of closed films reported for NaCl on metallic substrates. It consists of alternating positive and negative ions in a quadratic lattice as shown in figure 5.2. The nearest neighbor distance of equal ions is $a_{\text{surface}} = \frac{1}{2}\sqrt{2} \cdot a_{\text{bulk}}$. The (110) surface shows alternating lines of different ions which is less favorable from an energetic point of view. The last low index surface, the (111)-facet, consists of stacked layers of planes with one kind of ions each. Although this surface is less favorable compared to the (100) surface it has been predicted for thin layers
by theory [109,110] and observed for thin magnesium oxide films on Ag(111) of up to several monolayers [111].

The preparation of thin layers of the chosen material KCl is straightforward. After cleaning and annealing of the substrate as described in chapter 3.5.1 the material is deposited by thermal evaporation of KCl from a fused silica crucible situated in a home build Knudsen cell. At a temperature of approx. 640 K, which is well below the melting temperature at normal conditions of 1050 K, the material sublimes giving a deposition rate of about 0.1 monolayers per minute. This low deposition rate is due to the small KCl source installed in the evaporator and a large distance of evaporator and sample. The chambers background pressure during the deposition is of the order of $5 \times 10^{-10}$ mbar. Higher temperatures lead to much higher growth rates due to the increasing vapor pressure shown in figure 5.3. At the low temperatures used for the deposition process one expects the salt to sublimate as molecules [101]. Higher temperatures first lead to evaporation of clusters and later to dissociation into ions. The sample temperature is kept constant during deposition. Afterwards the sample is kept at this temperature for several minutes to anneal the salt layer. When cooled down to room temperature the sample has been transferred to the instrument.
Figure 5.2: Surfaces lattices. Left image: $Cu(111)$ surface; Middle image: $Cu(110)$ surface; Right image: KCl(100) surface with surface lattice unit cell, circles: $K^+$, dots: $Cl^-$. 

Figure 5.3: KCl vapor pressure: The potassium chloride shows a significant vapor pressure far below its melting point. Data from [102].
5.1 Potassium chloride on Cu(110)

The Cu(110) has a rectangular unit cell whereas the KCl(100) surface has a square lattice which due to its lattice parameters should lead to an incommensurate growth.

The growth of potassium chloride on Cu(110) depends on a variety of parameters. The parameters changed within this studies are the sample temperature during deposition and the amount material deposited.

Figure 5.4 shows the topography of the surface with a small amount of salt deposited at room temperature. The salt decorates the step edges where it appears as bright rims. Higher sample temperature during the deposition leads to the situation shown in figure 5.4 b). The step edges are straight and show kinks with distinct angles. Both is indicating a high mobility of the salt molecules on Cu(110) at room temperature and above. Furthermore it clearly shows the modification of step edges by the salt.

At a higher coverage the salt starts to form large islands. Figure 5.5 shows a typical topography for this situation. Additionally to the step decoration large island of two different types are visible. Due to their step heights they can be attributed to mono- and bilayers of salt. The periodicity of the structures is approx. 2 nm for both modifications.

Increasing the temperature up to 370 K during deposition leads to more clear step
5.1. POTASSIUM CHLORIDE ON Cu(110)

Figure 5.5: KCl on Cu(110): step decoration and islands. Island (I): bilayer crystallite at the image center. Island(II): monolayer of salt. Deposition at RT. 200x100 nm², 0.1 V, 0.6 nA.

modifications. Furthermore the monolayer becomes less prominent and the topography is dominated by bilayer islands.

In contrast to the case of NaCl or KCl on Cu(111) or MgO on Ag(100) [62] and similar surfaces the salt appears as a visible structure in the STM for all bias voltages which does not allow to “see” the copper surface underneath. This is in contrast to MgO on Ag(100) where it is even possible to achieve atomic resolution on the underlying substrate [62].

5.1.1 Islands type I: KCl - Bilayer

The first and most prominent appearance of the KCL islands consists of stripes parallel to the closed packed [110] direction of Cu(110). The stripes themselves are not smooth, but they show a periodic modulation along the [110] direction of the copper in the topographic measurement. These islands are normally connected to at least one step edge. They start on step edges or grow along step edges as shown in figure 5.5.

The crystallites formed prefer to grow along the [110] direction of the copper surface. They tend to form facets ending parallel to the [111], [111] or equivalent directions of the copper surface.

Two main kinds of defects can be distinguished: straight lines and meandering curves. The straight lines mostly appear as long lines parallel to the KCl-stripes. The lines prefer to start at free island edges, i.e. not form a copper step and can jump
perpendicular from one corrugation line to a neighboring one. They can travel through the whole crystallite or end somewhere inside the island as can be seen in figures 5.6 and 5.7 marked as (1).

The second type marked as (2) shows much less corrugation. Similar to the other defects they start at the borders of crystallites and can travel through the whole islands. These lines consist of small line segments situated on top of the salt stripes. Each of these segments has the width of the salt line and the length of the modulation of the stripes. Possible variants to connect this segments are either along the salt stripes or perpendicular to the stripes. The latter results in a “jump” of the defect line from one salt stripe to a neighboring one.

Figure 5.7 shows a closer look to this kind of defects and unmasks them as phase domain boundaries. The two white lines are situated in the gaps of the main corrugation of the two sides of the boundary. They are shifted by about 0.5 nm. Most probably they can be ascribed to defects in the salt lattice itself as will be described below.

A characteristic property of the crystallites of modification I is their voltage dependence of the step height shown in figure 5.8. The step height clearly increases with the bias voltage and reaches a plateau at around 2.6 V. This can be attributed to an electronic effect: As the tunneling current depends on the LDOS of the sample this height change is originated in a electronic state caused by the salt layer.
5.1. POTASSIUM CHLORIDE ON CU(110)

Figure 5.7: KCl on Cu(110): Different kind of defects: straight deep lines (1) and fuzzy lines (2). Left image: 100x100 nm$^2$, 0.1 V, 0.6 nA; right image: The shift indicated by the fuzzy defect lines is lightened up with two white lines. Deposition at 370 K, 38x38 nm$^2$, 0.1 V, 0.38 nA.

Figure 5.8: KCl on Cu(110): KCl - Bilayer. The measured apparent stepheight is changing with the bias voltage applied.
The step-like features on the salt islands as can be seen in figure 5.6 (marker (3)) suggests to be steps between one layer and the next layer of salt. However the height difference is equivalent to the copper step height and the apparent step height does not change with the applied voltage. Other measurements show structures which are suggesting triple or even thicker layers. In this case the step heights are again equivalent to the copper step height. If these structures would be salt multilayers, one would expect changing step height for each additional layer as has been observed for other systems like $NaCl$ on $Al_{99}Ni_{1}(111)$ [79] or $MgO$ on $Ag(100)$ [63]. Therefore in figure 5.6 there are only single bilayers of salt. As a consequence, the copper surface is restructured during the growth. Remarkably the salt layers investigated always appear as free-standing islands with a positive step height and not as holes. This behavior is known from the $NaCl$ layers too and has been explained by the changed tunneling conditions [80], whereas for for example $CoO$ on $Ag(100)$ systems hole-like features are known [66].

A second hint that the islands consist of one salt bi-layer only observed can be seen in figures 5.5 and 5.11. If an island passes from one terrace to another, the corrugation will have a phase shift such that the maxima on the upper terraces layer is situated on the minima of the lower terraces layer. This is quite obvious if the copper-steps are perpendicular to the salt stripes. But this also holds for salt islands which are spread over a copper step edge along the salt stripes. Obviously there must be an interaction of substrate and salt layer providing the information to the respective terrace.

Atomic resolution has been achieved on $KCl$-bilayers on $Cu(110)$ as shown in figure 5.9. The salt shows a cubic structure with a lattice constant of around 0.5 nm, the salt stripes are along the close packed direction of the copper. The measured distance corresponds to the lattice parameter of the $KCl(100)$ surface shown in figure 5.2. Obviously this is only true if one assumes that only one type of atoms is visible. Studies on $NaCl$ on $Cu(111)$ [80] as well as $Al(111)$, $Al_{99}Cu_{1}(100)$ and (111) [79] show that the atoms visible are the chlorine atoms. In the latter case the chlorine atoms have been identified by theoretical calculations which explain the STM topography by the hybridization of the copper states with the negative chlorine ions. Being alkali chlorides with ”neighboring” alkali elements, both $NaCl$ and $KCl$ are analog systems. This suggests that this behavior is true for the $KCl$ too. NEXAFS studies of $KCl$ on $Cu(111)$ [103] show a state which is interpreted as a chlorine induced state.

Combining this information it is possible to propose a model for the observed $KCl$ layers. This model explains the corrugation as a Moiré effect and does does not take surfacelayer stress into account. The salt layer is assumed to show a carpet like growth mode which is well known for other systems like $NaCl$ on $Cu(111)$ or $MgO$ on $Ag(100)$. 
5.1. POTASSIUM CHLORIDE ON CU(110)

Figure 5.9: KCl at Cu(110): atomic resolution of KCl layer with defect causing a corrugation shift marked by a white arrow. Left: topography, Right: dI/dV-map. Deposition at 270 K, 15x15 nm², -0.1 V, 0.55 nA.

Figure 5.10: Model of KCl on Cu(110). Left sketch: perpendicular to stripes, right sketch: along stripes. Only chlorine ions of the second KCl are shown to illustrate the Moiré pattern. Open circles: Chlorine-ions; closed circles: copper atoms.

The in-island corrugation observed can be ascribed to the gradual hybridization of the chlorine ions with the copper surface. This hybridization will depend on the position of the ions on the copper surface and thus will produce a Moiré pattern as sketched in figure 5.10.
Using the lattice constant of copper along the Cu[001] (3.615 Å) and assuming the KCl lattice along the KCl[011] direction to be 4.42 Å one gets a Moriée pattern with a fraction of 4 Cl-ions to 5 copper rows with a mismatch of less than 2%. This value corresponds to a periodicity of approx. 18 Å which is in good agreement to the 19 Å measured.

A second behavior explained by this model is the corrugation observed along the stripes also with a measured periodicity of around 18 Å. In this case, 4 Cl-ions are corresponding to 7 copper atoms with a mismatch of less than 1% giving a theoretical wavelength of approx. 17.7 Å. As the hybridization change in this case is smoother due to the higher copper density, the lower contrast along the salt stripes is explained too.

This proposed model also explains the observed “phase shift” of the stripes at step edges. Subsequent copper layers are placed in such a way, that atoms of the second layer are situated in the hollow sites of the first one. As the salt layer is only weakly affected by the substrate, its atomic structure and thus the absolute position of its ions will not be changed by this fact. Nevertheless, their relative position to the copper structure will be different: salt ions which would be placed on top of copper atoms on the first layer will be situated on the hollow sites of the second layer. Thus the contrast is changed by half a wavelength as can be seen in figure 5.11.

5.1.2 Islands type II: Monolayers of KCl

The second type of islands shows a similar structure as the first one. They are identified as monolayers in the following. Upon annealing at 400 K monolayer islands are converted into bilayers. In contrast to the first modification it shows stripes along the Cu[111], Cu[1\overline{1}1] directions. Islands often are situated at facets of bilayer crystallites as can be seen in figure 5.12.

Having a closer look to the structure of this modification one can see that the broad stripes consist of two parallel separate stripes which are separated by a small gap. A typical line section is shown in figure 5.15.

Similar to the other island type this island shows a strong voltage dependence of the step height plotted in figure 5.13 which can be explained in the same way as for the KCl bilayers. At voltages of approx. 2.6 V, which corresponds to the salt state mentioned above, the corrugation disappears and the islands appear as flat patches. For lower voltages as well as negative energies the corrugation is visible.

As one observes a smaller workfunction on the the salt layers compared to the pristine copper surface (see sect. 6.2), the electronic wavefunctions are expected to have a longer decay length into the vacuum than on the salt. Hence the measured stepheights will be
Figure 5.11: Model of KCl on Cu(110)-steps. Left image: topography of an island grown over several steps and "second-layer"-like structure down left. The lines on one terrace are shifted like explained in the text. Deposition at 270 K, 50x50 nm$^2$, 0.1 V, 0.22 nA. Right image: line cut along the line marked in the left image and according layer model. Black dots: Cu, open circles: Cl-ions, only the upper layer of the bilayer is sketched.

Figure 5.12: KCl on Cu(110): Monolayers. The small island is connected to the large patch of bilayers. Deposition at 270 K. 25x25 nm$^2$, 0.1 V, 0.22 nA.
CHAPTER 5. MORPHOLOGY OF KCL ON CU(110) AND CU(111)

Figure 5.13: KCl on Cu(110) monolayers: Step height and corrugation. Left: topography at 0.1 V (upper image) and 2.75 V (lower image), deposited at 270 K, 0.66 nA, 20x40 nm². The high-voltage image does not show any strip structure, defects are still visible. Right: step height (squares) and corrugation (dots) as function of bias voltage. The height shows a similar behavior as known from the bilayers. The corrugation vanishes at approx. 2.6 V which is an electronic effect.

Figure 5.14: KCl on Cu(110): Monolayers with defects. Defects are visible at all tunneling biases. They are located at the center of the doublelines and appear as small dips like the one marked in both measurements. Deposition at 270 K. Left: 0.2 V, right: 2.9 V, 0.57 nA.
5.1. POTASSIUM CHLORIDE ON CU(110)

Figure 5.15: KCl on Cu(110): Monolayer line section. The graph shows an average line section perpendicular to the corrugation lines. Additional to the main structure one can see that the stripes have a dip at their center. 0.1 V, 0.57 nA.

larger than the “real” heights. For voltages of approx. 3 V the step heights in the present case is ca. 3.4 Å whereas the geometrical step height of monolayers extracted from the crystallographic structure of KCl is 3.1 Å. Hence one can attribute this structures to monolayers of KCl. The structures described in the previous sections have the double height for low as well as high voltages (fig. 5.8), therefore they were identified as bilayers.

Defects seem to be concentrated on the middle of the double lines. At this position they appear as small holes which extend perpendicular to the stripes as marked in figure 5.14. These defects are visible for any voltage in the range of ±4 V. Most probably they are defects in the salt lattice or contaminants which prefer to sit in the small gaps. Atomic resolution has not been achieved on this structure, therefore it is not possible to model the structure.

STM is limited to structural information about the topmost layers. As shown it is possible to model the observed structures to some extend. Further structural data by other techniques like LEED and theoretical support would be needed to fully clarify the structural properties.
Figure 5.16: KCl on Cu(111): growth at low coverage and adsorbates. KCl layer is marked with arrows. Left: 100x100 nm$^2$, 0.2 V, 75 pA; Right: 50x50 nm$^2$, 2.6 V, 75 pA. Deposited at 270 K.

5.2 Potassium chloride on Cu(111)

As seen in the previous section KCl on Cu(110) appears corrugated in STM images (and consequently has a lateral variation of its electronic properties) due to the interaction with the substrate. However the proposed model is based on a geometrical flat (i.e. carpet like) layer on KCl. Work on NaCl films showed that on Cu(111) the salt layers appear without lateral variation of electronic properties. In this section the analogous system KCl on Cu(111) is investigated.

Figure 5.16 shows less than a monolayer potassium chloride grown at room temperature. Contrary to the case KCl on Cu(110) discussed in chapter 5.1, there is no step modification. The growth mode is a step flow mode. The salt growth starts at the step edges and forms a homogenous monolayer. Sometimes the surface is not as uniform as the pure monolayer but shows some protrusions which may be adsorbates or imperfections in the film.

Apparent step heights as function of bias voltage yield a similar behavior to the energy dependence observed for KCl on Cu(110) (see fig. 5.17). According to the discussion in the case of Cu(111), the apparent step height of approx. 8 Å suggests the structures observed to be doublelayers of salt which is in agreement with experiments of NaCl on Cu(111) [80]. Furthermore there is a major change in the height of the defects as shown in graph 5.17. Being nearly invisible at lower voltages, they show up at higher voltages. Remarkably they disappear at approx. 3.5 V, a behavior which is the
opposite of the monolayers of $KCl$ on $Cu(110)$. The protrusion are sitting on positions of a quadratic lattice with a lattice constant of about 5 Å corresponding to the surface lattice of $KCl(100)$. Most probably they are potassium chloride molecules which are not yet incorporated to the salt layer or represent a starting second layer.

For higher coverage full layer growth has been achieved. In this case all salt molecules are build into the salt layer and the salt can only be distinguished from the copper substrate by its electronic properties discussed later.

Atomic resolution was achieved on this layers as can be seen in figure 5.18. This result again shows the quadratic surface lattice of $KCl(100)$ as in the case of $Cu(100)$ but with a uniform layer thickness.

Figure 5.17: KCl on Cu(111): step height and defects. Left: topography 7.5x7.5 nm$^2$, 82 pA, upper image 0.2 V, lower image 2.6 V, deposition at 270 K. Right: Apparent heights: Squares: KCl step height, dots: the defect height vanishes at approx. 3.5 V due to an electronic effect.
Figure 5.18: KCl on Cu(111): atomic resolution. Deposition at 270 K, 33.4x20.1 nm$^2$, 0.1 V, 85 pA.
Chapter 6

Electronic structure

The power of the The scanning tunneling microscope consists to a great extent in the ability to give information about the electronic structure of conducting surfaces. To obtain this information one uses the scanning tunneling spectroscopy outlined in chapter 2.1.1.

In the case of thin insulating layers like the KCl layers discussed in the previous chapter, this technique gives valuable insight into the properties of an insulator at the atomic limit. Especially the question of electronic states within the salt layer can be investigated. Furthermore, one expects a reasonable band gap within the salt layer similar to other systems investigated so far (e.g.: [62,63,77,79,80]). As the salt layer is in contact with the metal surface this band gap will be different from the band gap of 8.4 eV [105] known from the bulk material.

On the other hand defects can influence the electronic properties of the salt layer. Using the STM ability to spatially resolve the LDOS it is possible to learn about the nature and behavior of the defects. As the final goal is to use the salt layer as a spacer layer for molecules, it is a vital task to characterize the electronic structure and to know the influence of possible defect structures.

Potassium chloride has been characterized in the previous chapter concerning growth and morphology. As it provides different structures on the two substrates Cu(111) and Cu(110) used it is an ideal playground for investigations of the changed interaction of molecules on the clean copper surfaces in comparison to the salt covered substrates if their electronic structures are known, too.
6.1 Bandgap determination

When applying STS to an unknown system one has to carefully assess its limitations. Besides technical challenges in terms of instruments stability, electronics and software, there are some inherent complications of this technique.

One problem is, that the signal obtained is a convolution of the density of states of tip and sample. The usual assumption is to approximate the LDOS of the tip to be constant in the range studied. This implies that the dI/dV curves are only containing information about the sample. In reality the situation is more complicated and one will rarely find the constant-tip-LDOS conditions when investigating large voltage ranges as in this sections. One has to take care that the tip is suitable in this sense and does not show any additional structure because of i.e. adsorbed molecules. Having a "good" tip, i.e. somehow microscopically prepared, for spectroscopy is a way to simplify the LDOS of the tip.

A simple way to assess the tip properties is to have a known structure as reference. An example is the the Cu(111) surface with its well characterized surface state onset as shown in figure 3.27. For all measurement presented such checks have been performed. Some of the experiments have been repeated with both platinum-iridium tips and tungsten tips and show that the results obtained do not depend on the tip material.

The current of the tunneling gap is dominated by the electrons at the Fermi energy of the negative electrode. Therefore at positive bias voltages the energy dependence of the LDOS of the tip is less dominant and one is probing the empty states of the sample. In the case of negative bias voltages the situation is inverse, the LDOS of the sample is scanning the unoccupied LDOS of the tip. For small voltages this problem can still be neglected, but for larger voltages one has to take possible tip-effects into account.

Depending on the energy range different variants of the STS-technique can be used. For small energy ranges the most common option is to perform the measurements with a fixed tip-sample distance as described in chapter 2.1.1. This boundary condition simplifies the interpretation for the data obtained at small energies. If sweeping over larger voltage ranges the exponential characteristic of the tunneling contact becomes dominating. This leads to the technical problem of the limited dynamic range of the current and the lock-in amplifier: It is only possible to resolve data in a certain current range. Using a large bias voltage range and thus tunneling current will lead to either a resolution problem in the range of low currents (which basically will be read as zero) or a voltage overflow for the exponential tails as demonstrated in figure 6.1.

If it is still possible to find suitable lock-in parameters one has to take into account
6.1. BANDGAP DETERMINATION

Figure 6.1: $dI/dV$ on KCl on Cu(110), one monolayer raw data. All three curves are taken at the same position but with adjusted parameters in dependence of the scanning range. For smaller voltage ranges and thus lower current ranges the spectroscopic resolution increases. The feature at ca. -1 V (marked with arrow) is interpreted as copper state (see page 71).

1: $V_{Bias}$: 3 V, I: 0.5 nA, Lock-In-sensitivity: 1 V, Lock-In-modulation: 15 mV;
2: $V_{Bias}$: 2 V, I: 1 nA, Lock-In-sensitivity: 0.3 V, Lock-In-modulation: 20 mV;
3: $V_{Bias}$: 1 V, I: 1 nA, Lock-Insensitivity: 0.3 V, Lock-In-modulation: 20 mV.

that the approximation of small voltages done to interpret the $dI/dV$-signal is not any more valid and the signal will not proportional the LDOS. A possible way to circumvent is a rescaling of the $dI/dV$-curves as proposed by Feenstra and other authors [17, 46, 106–108] especially in the context of determining the bandgap of semiconductors.

The idea is to normalize the differential conductance with respect to total conductivity: $(dI/dV)/(I/V) = d(lnI)/d(lnV)$. Using equ. 2.5 the differential conductance can be expressed by:

$$\frac{dI}{dV} \propto e\rho_s(eV)T(eV, eV) + e \int_0^{eV} \rho(E) \frac{d}{d(eV)} [T(E, eV)] dE \quad (6.1)$$
(dI/dV)/(I/V) then can be expressed as

\[
\frac{dI/dV}{I/V} \propto \frac{e\rho_s(eV) + e \int_0^{eV} \frac{\rho(E)}{T(E, eV)} \frac{d}{dE} [T(E, eV)] dE}{\frac{1}{eV} \int_0^{eV} \rho_s(E) T(E, eV) dE}
\]  \hspace{1cm} (6.2)

In this equation T(E,eV) and T(eV,eV) only appear as ratios. Thus their exponential behavior will cancel out to first order. The first term in equ. 6.2 can be interpreted as the normalized LDOS. The second term is a background caused by the change of the tunneling barrier with the electrical field between tip and sample. Note, that the tip LDOS is assumed to be constant at all energies.

To increase the dynamic range of the measurement, the large currents at high voltages have to be avoided. Thus curves have to be recorded while changing the tip-sample distance. This can be done for example by ramping the z-distance by a defined curve as described in [46].

The method used in this work is to measure dI/dV curves for large voltage ranges is to keep the feedback loop closed and thus keeping the current constant. In this case one records additionally to the dI/dV(V)-curves the tip sample distance z(V). In principle it is possible to rescale the dI/dV curves obtained in this way to corresponding curves at a fixed distance. This method is commonly used for measuring states at an energy range comparable to the work functions. The image states discussed in detail in chapter 6.2 are an example. To avoid tip crashes at 0V bias voltage this techniques requires to record data for positive and negative biases separately.

For small voltages \( V \ll \phi \) the z(V) curves can be calculated by equation 2.1 in chapter 2.1.1. For larger energies the changes in the transmission coefficient due to the bias voltage have to be taken into account.

Figure 6.2 shows the processed and unprocessed data obtained for different samples. Rescaling the data with equation 6.2 leads to a signal proportional to the LDOS. This process eliminates the artefacts caused by the exponential behavior observed for high voltages in the case of fixed tip sample distance and low voltages in the case of closed feedback loop. Furthermore it lights up the “true” features of the data recorded like the peak at position (1) which later will be discussed in detail. The disadvantage of the rescaling process can be seen in this figure too: if the fraction I/V tends to be zero the LDOS-calculations is causing physically impossible LDOS data in this range. If this artefact for example visible at the arrows (3) position occurs, the the according data points have to be removed form the plots.

Regarding the case of KCl on Cu(110) one gets for a large voltage range scan with fixed tip sample distances typically spectroscopic curves like shown in figures 6.2
6.1. BANDGAP DETERMINATION

Figure 6.2: dI/dV raw data and calculated LDOS: spectra taken on Cu(110) with (1) and without(2) a bilayer of KCl. Both dI/dV-curves show the exponential tail at positive voltages. If rescaled as described in the text this behavior is suppressed and but the peak in (1) remains. At ca. -1 V the calculated LDOS-data (3) shows the artefact caused by small currents described in the text. Settings: V_{Bias}: 3.1 V, I: 0.3 nA.

and 6.3. Obviously the salt layer suppresses the LDOS features observed for the clean copper surface.

Nevertheless, this LDOS is still “shining through” the salt as can be seen in figure 6.4. The right graph shows the LDOS structure of pristine copper. On the negative side two features are visible: a peak at approx. -0.5 V which can be related to the surface state onset of Cu(111), and a peak at -1 V. This structure is still visible if the copper surface is covered with a KCl-layer, but their intensity is strongly decreased. To first order this decrease in intensity can be explained with the exponential decay of the electronic states combined with the larger tip-copper distance caused by the salt spacing layer.

On the negative energy range one can observe a feature at ca. -4.2 V. It is extremely difficult to get stable tunneling conditions for these energies. Therefore the -4.2 V feature is to some extend a preliminary estimate of the position of the valence band edge. Together with the 2.4 V peak at positive energies one obtains a band gap of at least 6.6 eV.

The property of being transparent for the underlying copper substrate can be supported by another method, too. Figure 6.5 shows the topography and dI/dV maps of a KCl island with two monolayers thickness. The salt being clearly identifiable in the topographic image does not appear in the dI/dV map showing the LDOS distribution.
CHAPTER 6. ELECTRONIC STRUCTURE

Figure 6.3: $dI/dV$ on bilayer of KCl on Cu(110). Left graph: Curve (1) is taken on an island of KCl on Cu(110). Curve (2) is the Cu(110) reference curve taken with the same parameters as (1). Settings: $V_{\text{Bias}}$: 3.1 V, I: 0.25 nA; Right graph: bilayer of KCl on Cu(110). The Settings are changed to resolve the shoulder at -4.2 V. At this conditions the 2.4 V peak is not visible due dynamic range problems. Settings: $V_{\text{Bias}}$: 3.8 V, I: 0.5 nA.

at 0.1 V. Besides some topographic artefacts, the contrast does rather show the same behavior as on the copper terraces. Again, this is a clear hint to the band gap of the salt layer and the copper states shining through the island. At a higher energy which is above the 2.4 V of the peak observed, the salt layer island shows up in the $dI/dV$ map indicating that new electronic states are accessible in this range. The states at high positive bias will be discussed in section 6.2.

Having a closer look to both $dI/dV$ maps some details are important. In the case of band gap energies some structures show up as white dots or rings in the salt layers indicating a dominating LDOS at this position. As the remaining parts of the salt islands remain invisible, they can be identified as irregularities of the salt structure. This will be discussed in more detail in chapter 6.4.

At the higher voltage of 3 V one accesses salt states. They start to become visible at voltages of approx. 2.5 V which corresponds to the salt feature as well as the increase in apparent step height observed. For higher voltages they are still visible and the contrast becomes even clearer. The structures visible are on one hand concentrated to the top of the salt stripes. On the other hand the second modulation along the lines discussed in chapter 5.1 now clearly shows up in the LDOS reinforcing the assumption that the apparent salt structure is due to an electronic Moirée pattern discussed in chapter 5.1.1.
6.1. BANDGAP DETERMINATION

Figure 6.4: 2ML KCl on Cu(110). Left figure: Figure 6.1 reduced to ± 2 V. Right figure: STS measured on pristine Cu(110) $V_{Bias}$: 2.1 V, I: 0.3 nA, same Lock-In settings as for figure 6.1. The copper features marked or visible in both cases.

To conclude, the bandgap of $\geq 6.6$ eV observed qualifies the KCl layers as insulators in the sense discussed above. Nevertheless, the electronic states of the underlying copper are still accessible in the vacuum regime and guarantee stable tunneling conditions within the bandgap.

Figure 6.5: KCl on Cu(110). Left image: topography at 0.1 V, middle image: dI/dV at 0.1 V, right image: dI/dV map at 3 V, 51.2x51.2 nm$^2$, 0.77 nA, 3 V.
6.2 Imagestates on pristine and potassium covered copper

At a first glance the peak observed at 2.4 V on the KCl layer may be related with the imagestates which occur in front of conducting surfaces, a metal induced gap state or a quantum well in the salt layer. Nevertheless, this peak can be traced back to an intrinsic salt state.

Imagestates are many-electron effects as the potential felt by an electron near the surface is created by the induced polarization of the metal. This collective behavior can however be mapped onto the concept of an induced image-charge in the metal and a corresponding resulting one-electron potential as described in standard text-books. As a result of the effective one-electron potential bound states are found on all metal surfaces with energies close to the vacuum level of the metal. A simple formula for the first \( n=1 \) and subsequent higher images states is given by \([112,113]\):

\[
E_n = -0.85eV \left( n + a \right)^2
\]  

where the parameter \(a\) accounts for the remaining influence of the crystal potential.

A suitable model for the calculation of this states has been developed by Chulkov et al. \([114, 115]\). The idea of this model reducing the problem to one dimension is to describe the surface properties with a phenomenological potential including the bulk as well as the vacuum part of the crystal. The full model potential is shown in figure 6.6. It is continuously differentiable and its four free parameters are adjusted to reproduce experimental or theoretical data on surface and image potential states.

Measuring the image states with STM complicates the situation \([116]\). Additionally to the image potential outside the crystal the tip-sample field has to be taken into account. Assuming this field to be linear close to surface results in an additional term for \( V(z) \):

\[
V^*(z) = V(z) + \frac{U_{Bias}}{z_{eff}} \ast (z - z_{im})
\]

with the effective tip sample distance \( z_{eff} \), the position of the image charge \( z_{im} \) and \( z \) outside the crystal. This results in a Stark shift of the image states towards higher energies. As the tip sample distance \( z_{eff} \) depends on the tunneling conditions, the image states position can shift to some extend.

The energy range which has to be observed is rather large. Hence it is not possible to measure the typical state sequences of image states with STS at a fixed tip sample
6.2. IMAGESTATES ON PRISTINE AND POTASSIUM COVERED COPPER

Figure 6.6: Imagestates: Chulkov-potential and Imagestates. The position of atomic layers are marked with lines. Left image: potential; right image: imagestates for different $n$. From Ref. [115].

In principle there are two equivalent techniques which can be used for this purpose. The method used by for example Wahl et al. [116] is to record the tip sample distance as a function of the bias voltage. If a new image state becomes available with higher voltages the current will increase at fixed sample distance and thus the tip sample distance has to increase at fixed current. As a result one gets a staircase like $z(V)$ dependence as shown in figure 6.7 for the case of Cu(110). A second method is to record the $dI/dV$-signal at a variable distance and fixed current. As these two techniques require the same tunneling conditions it is possible to record both data sets at the same time.

The characteristic image state series shows for $n \geq 2$, which corresponds to $V > 5$ V, steadily decreasing peak intensities. This known behavior is due to the higher energy and the lower lifetime in the band. The first peak, which actually appears as double peak, has a lower intensity. A comparison with the projected Cu(110) bandstructure shows that this peak is close to Cu(110) band gap of 4.5 V to 5.5 V [117] and thus will have a different interaction with the copper bulk electrons. Hence one can not expect this peak to have an intensity which is fitting to this series as e.g. the state $n = 2$ on the clean Cu(110) is situated inside a copper band.

This measurement done on the salt doublelayer on Cu(110) results in the curves shown in figure 6.8. The first Cu(110), peak at ca. 3 V, marked with KCl, corresponds to the salt peak at 2.4 V observed earlier. Due to the variable tip sample distance its position is shifted to higher energies.

At a first glance the first peak could be attributed to the first imagestate too. Ac-
Figure 6.7: Imagestates on Cu(110). Left: z(V) measurement. Right: simultaneous dI/dV measurement. The imagestates are marked with arrows.

Figure 6.8: Imagestates on Cu(110) and 2ML KCl on Cu(110). The corresponding image-states have the same label. The salt feature is marked mit "KCl". The KCl-curve is shifted in the y-direction to clarify the diagram. Grey box: Cu(110) bandgap.
6.2. IMAGESTATES ON PRISTINE AND POTASSIUM COVERED COPPER

<table>
<thead>
<tr>
<th>State</th>
<th>$E$/eV: KCl on Cu(110)</th>
<th>$E$/eV: Cu(110)</th>
<th>$\Delta E$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4.1</td>
<td>4.5</td>
<td>0.4</td>
</tr>
<tr>
<td></td>
<td>4.7</td>
<td>4.9</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>5.4</td>
<td>5.8</td>
<td>0.4</td>
</tr>
<tr>
<td>3</td>
<td>6.3</td>
<td>6.7</td>
<td>0.4</td>
</tr>
<tr>
<td>4</td>
<td>7</td>
<td>7.4</td>
<td>0.4</td>
</tr>
<tr>
<td>5</td>
<td>7.7</td>
<td>8</td>
<td>0.3</td>
</tr>
<tr>
<td>6</td>
<td>8.3</td>
<td>8.5</td>
<td>0.2</td>
</tr>
<tr>
<td>7</td>
<td>8.8</td>
<td>9</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Table 6.1: Energies of the different states of KCl on Cu(110). "KCl" is the salt state, $n = 1..7$ are imagestates.

According to tab. 6.1 this means a shift of ca. 1.9 V compared to clean Cu(110). Due to this large shift, this state can be excluded from the imagestate series as will be discussed in the following.

Regarding the present case it is obvious that a salt layer in front of the metallic substrate complicates the situation as it will influence the electrical fields included.

The simplest way to include the influence of the salt layer is to ignore the additional layer itself and only include the workfunction change caused by the ionic layer. The field interacting with the electrons is the energy difference of the vacuum energies. Thus the effective field which has to be taken into account for the image state measurement consists of workfunction change and bias voltage as sketched in figure 6.9.

To be able to guess the magnitude of the according energy shift one has to know the shift of the workfunction. In principle there are different techniques available to determine the workfunction like the field emission microscope ultraviolet photoelectron spectroscopy (UPS). Kelvin force microscopy is able to measure the local change in workfunction on the micrometer scale [74, 75].

The normal way to measure local changes of the workfunction by STM is acquiring $I(z)$ curves and using equ. 2.7 to calculate the effective local barrier height. This barrier contains the workfunctions of both tip and sample. As the tip preparation includes controlled tip crashes one can expect the tip vicinity to consist of the same material as the sample. Using this simplification it is possible to directly extract the substrates workfunction from the $I(z)$ curves. Knowing this parameter, the surface modified by salt layers can be treated in a similar way but using the measured value as one of the
CHAPTER 6. ELECTRONIC STRUCTURE

Figure 6.9: Workfunction change in the tunneling barrier. Left image: same workfunction for both tip and sample. Right image: sample workfunction lowered by $\Delta \Phi$. $E_F$: Fermi energy, $E_{Vac}$: vacuum energy, $\Delta \Phi$: workfunction change, $V_{Bias}$ applied bias voltage. Grey boxes: conduction bands.

two workfunctions.

The curves shown in figure 6.10 measured on copper respective salt show typical results for this technique, in this case for a large current range of two orders of magnitude. Using a semi-logarithmic plot the values needed can be directly extracted by a linear fit. This values obtained for the actual case can be transformed into a workfunction of approx. 3.37 eV for the $Cu(110)$ surface without salt. Assuming the tip to be a copper tip results in a workfunction of 1.72 eV for the KCl island and thus a workfunction change of about -1.65 eV.

A second approach used by Repp et al. [80] is to rescale the data to the $Cu(110)$ workfunction. The effective tunneling barrier has been lowered by approx. 14.4%. This corresponds to a workfunction change of approx. 21%. Using the copper’s work function of 4.48 eV [118] this yields an workfunction change of -0.95 eV. Measurements of NaCl on $Cu(111)$ lead to a workfunction change of approx. -1 eV [80].

Whereas the latter value quite close to similar measurements performed with Kelvin force microscopy and UPS on KCl layers on $Au(111)$ which give values of -707 meV [75] resp. -909 meV [74], the first first estimation is a factor 1.5 too large.

The model used for equ. 6.10 is using a homogenous tunneling gap to derive an effective tunneling barrier as has been shown in chapter 2.1.1. The additional layer changes the tip-sample field distribution and the image potential both. Thus the approximations are not valid for this case and it is not surprising that the definite calculation of workfunctions fails. Nevertheless this measurements give the same order of magnitude
and direction of the workfunction difference.

In the case of Cu(100) a field change of about 4 V is changing the first image states energy by only about 0.5 V as can be seen in figure 6.11 [116]. For different metallic substrates one can expect similar behavior too. Thus, as the workfunction change of the KCl on Cu(110) system is only in the order of 1 V, it can be excluded that the first peak could be an image state peak shifted by a workfunction change only.

A second way to include the salt layer is not only to take the workfunction change into account but the salt layer itself, too. A possible approach is to treat the layer as a dielectric layer. This implies that the salt layer is described within the concepts of continuous materials. While it may be questionable to use this attempt at the atomic scale it has been shown by experiments with noble gas layers to give reasonable results. Neglecting further the samples crystallographic structure, this simplification leads to the so called “Cole”-Potential [120–124] shown in image 6.12 which reduces the bulk states to a step function. Poles at the surfaces have to be avoided by an cut-off energy at the metal surface and interpolation between two point on both sides of the dielectric-
Figure 6.11: Calculation (dotted lines) of the energies of the image-potential states in the electric field of the STM tip as a function of the applied voltage. Each of the dotted lines corresponds to one particular state ($n = 1$ to 4) calculated for a tip-sample distance including the variable tip sample distance. Full circles are plotted at the voltages where the steps in the $z(V)$ curve appear.[116]

vacuum interface. In the case of noble gas layers the offset $E_A$ is the electron affinity of the atoms. In the case of $KCl$ corresponding data is not available. As the electron affinity is the energy gain of an electron added to the noble gas atom one can take it as a rough estimation the lower edge of the conducting band. Nevertheless it is possible to use this value as a rough assumption. Assuming the 2.4 V peak to be the lower band-edge of $KCl$ one gets a value of approx. $E_F+2.4$ eV for the lower conduction band edge corresponding to the value of $E_F+2.5$ eV was used for the system $NaCl$ on $Cu(111)$ by Repp et. al. [80]. If the 2.4 eV peak were a shifted image state or a quantum well state, $E_A$ must be lower in order to explain this in the framework of the Cole-potential. As tunneling through the salt should be enhanced by the conduction band stated at $E_A$, one would certainly be able to observe them in the $dI/dV$ spectra. Therefore if the 2.4 eV state is not a state within the salt layer, it can only be the conduction band-edge. This is consistent with the analysis proposed by Repp et al. for the similar state at 2.5 V for the case of $NaCl$ on $Cu(111)$ [80].

A consequence of this description is, that the wave function of the imagestates are shifted away from the copper surface. At the same time the energies will shift to lower binding energies which is consistent with the numbering in figure 6.8. In the case of the isoelectronic argon on $Cu(100)$ the downshifts observed and theoretically explained with the Cole potential presented above are in the range of 0.1 eV to 0.3 eV for 1 ML to
Figure 6.12: Cole potential: “Dielectric continuum model for physisorbed multilayers on a metal surface. Thick full line: Modified image potential $V(z)$. In classical electrostatics, the modified image potential has divergences at the metaldielectric and dielectricvacuum interfaces. Thick dashed lines: The divergences are removed by a cutoff ($E_{\text{cut}}$) at the metaldielectric interface and a linear interpolation over a range $b$ at the dielectricvacuum interface.” [126]
Again, this defect can not explain the KCl peak as a shifted imagesate. This is still true if one combines both workfunction change and dielectric layer. Nevertheless it is easily possible to explain the shift of the remaining peaks classifying them as imagestates.

A further possibility for this state would be a metal induced gap state (MIGS) [103, 104]. MIGS are concentrated at the insulator-metal interface and decay into the vacuum. Nevertheless they can reach several nanometers into the vacuum. The atomic resolution observed on NaCl has been attributed to them as they are stronger at the chlorine ions [79,103,104]. A second example for these states is the interface state observed for MgO on Ag(100) with a energy of approx. 1.7 eV [58]. There the intensity decreases for thicker insulating films.

Such states have not been observed in STS for the KCl systems. Furthermore, as MIGS are interface states, one should expect a decreasing stepheight for each additional layer of salt. In contrast to other systems like MgO on Ag(100) [58] or NaCl on Al(111) [79] this has not been observed for the present system too: the previously described doublelayers are nearly twice as high as the monolayers. Combining this information one can exclude the interface state, too.

A last possible origin would be a quantum well state inside the salt layer. In this case one would expect an energy shift with changing layer thickness. As this shift was not observed for mono- and bilayers on Cu(110), quantum well states have to be excluded.

As a result, the state has to be attributed to the salt layer itself. It could be a molecular state which is the first stage of the conduction band edge. Nevertheless, theoretical support is needed to finally clarify the origin of this state.

Similar to the case of potassium chloride on Cu(110) this states can be observed for the Cu(111) surface as shown in figure 6.13. In contrast to the Cu(110), in this case all peaks of the imagestate series show an decreasing intensity. This is due to different projected band structure of Cu(111) which does not show a gap in the range observed [117]. The same line of argument discussed for the Cu(110) is true for this case. The first state is situated at 2.9 V, which is nearly the same position as for state on the Cu(110). This similarity can be an indication that the geometric structure and hence the overlap of molecular KCl orbitals within the layer is the same for the two systems.
Figure 6.13: Image states on KCl on Cu(111). The first image states are marked with n=1..4, the salt features is marked with KCl. Parameters: V_{Bias}: 0.1 V, I: 0.2 nA.
6.3 KCl on Cu(111) interface state

Depending on the tunneling conditions, i.e. bias voltage, tunneling current and tip configuration, it is possible to access the salt states and get molecular resolution as shown for the cases of KCl on Cu(111) and Cu(110). On the other hand one can in the case of KCl on Cu(111) also observe standing wave like structures shown in figure 6.15. Similar to structures observed for the clean copper surface the standing waves show up in both the topography and dI/dV-maps. As one does not expect any state within the bandgap of the salt layer and as there is a similar state in the NaCl on Cu(111) system [80,81], this structure can be attributed to an interface state at the interface of KCl and copper which is derived form the surface state of Cu(111). The standing waves can be seen at any position close to scattering centers like step edges or point defects. The best possibility to extract the information about the dispersion relation $E(k)$ of the state is to record dI/dV maps at constant energies. Similar to the procedure shown in chapter 3.5.1 the dispersion relation figure 6.15 can be extracted from the data using Fourier-transformation.

In comparison to the clean copper surface, the main difference between both curves is a shift in the surface state onset energy. This energy is shifted from 440 meV to 410 meV. The effective mass is slightly lowered form $m^* = 0.38m_e$ to $m^* = 0.37m_e$.

One reason for choosing the KCl as an adsorbate was the possibility to compare the results obtained with a non-ionic systems which has to some degree a similar electronic structure. Such a system is Ar on Cu(111) which like other noble gas layers on metal surfaces has been studied with a variety of techniques [53,54,121–124,126–128]. Argon
should be the closest non-ionic overlayer system as both, the $K^+$ and the $Cl^-$ ion have the electronic configuration of Argon which is $[Ne]3s^23p^6$. In comparison to this, smaller sodium ion has the electronic configuration of neon leading to a comparison of $NaCl$ to argon and neon.

The argon overlayer modifies also the $Cu(111)$ surface state. We therefore have the following results concerning the modification of the surface state by the overlayers of $KCl$, $NaCl$, Ar, Kr and Xe as shown in table 6.2.

One sees that the effective mass of the state is almost unchanged by the above overlayers. The striking difference between the ionic systems $NaCl$ and $KCl$ is the shift of the state.

In contrast to the $NaCl$ the $KCl$ behaves more like a noble gas layer in sense of energy shift. As there is no data of $Ne$ on $Cu(111)$ available, one can only make a qualitative comparison in this case: Going form xenon to argon the surface state onset is shifting to lower energies while the effective mass is slightly increasing. Therefore if $NaCl$ on $Cu(111)$ were similar to $Ne$ on $Cu(111)$, one would expect an even smaller surface state onset shift which is in clear contradiction to the much higher shift observed.

The onset shift of $NaCl$ on $Cu(111)$ was attributed to the dielectric behavior of the salt in sense of the cole potential which was described in chapter 6.2 [80]. In this case
**Table 6.2:** Onset energies and effective masses the Cu(111) surface state and interface states.

<table>
<thead>
<tr>
<th>Surface</th>
<th>$E_0$/meV (onset)</th>
<th>$m^*/m_e$</th>
<th>$\Delta E_0$/meV</th>
<th>$\Delta m^*/m_e$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(111)</td>
<td>434 ± 2</td>
<td>0.38 ± 0.01</td>
<td></td>
<td></td>
<td>[53,54]</td>
</tr>
<tr>
<td></td>
<td>450 ± 10</td>
<td>0.40 ± 0.02</td>
<td></td>
<td></td>
<td>[80]</td>
</tr>
<tr>
<td></td>
<td>440</td>
<td>0.38</td>
<td></td>
<td></td>
<td>this work</td>
</tr>
<tr>
<td>NaCl/Cu(111)</td>
<td>225 ± 10</td>
<td>0.46 ± 0.04</td>
<td>225</td>
<td>0.06</td>
<td>[80]</td>
</tr>
<tr>
<td>KCl/Cu(111)</td>
<td>410</td>
<td>0.37</td>
<td>30</td>
<td>0.04</td>
<td>this work</td>
</tr>
<tr>
<td>Ar/Cu(111)</td>
<td>376 ± 3</td>
<td>0.46 ± 0.03</td>
<td>58</td>
<td>0.03</td>
<td>[53,54]</td>
</tr>
<tr>
<td>Kr/Cu(111)</td>
<td>358 ± 2</td>
<td>0.44 ± 0.02</td>
<td>76</td>
<td>0.01</td>
<td>[53,54]</td>
</tr>
<tr>
<td>Xe/Cu(111)</td>
<td>291 ± 2</td>
<td>0.44 ± 0.02</td>
<td>148</td>
<td>0.01</td>
<td>[53,54]</td>
</tr>
</tbody>
</table>

The attractive potential in front of copper surface is shielded to some extend by the salt layer. The wave function of the electrons has the highest amplitude in this area. Thus the positive potential change will shift the electrons energy to higher values.

Transferring this model to the present case of KCl bilayers one has to take several parameters into account: the layer thickness, the electron affinity, the workfunction change, and the dielectric function. The first parameter is in both cases equivalent and thus can not explain the differences. The same is true for the electron affinity and the workfunction change.

The remaining parameter is the dielectric function. The bulk value of $\epsilon$ for KCl is 4.68 compared to 5.8 in the case of NaCl [119]. This relatively small change will probably not explain the full change in $E_0$ of the interface state. Finally one can state, that the exchange of a sodium ion by a potassium ion obviously plays a major role for the interaction of the salt layer with the interface state. Apparently the KCl layer provides some compensating influences that influence the Cu surface state similar as a vacuum layer and even less than an argon layer.
Defects on the potassium chloride layers show up in different ways. In the case of Cu(111) they show up as scattering centers for the interface state as shown in chapter 6.3. Structural defects on KCl on Cu(110) can be traced back to grain boundaries or point defects as has been done in chapter 5.1.

In the latter system one finds another kind of defects which in most cases does not appear in the topographic measurement. Nevertheless they can easily be identified in dI/dV maps. Unfortunately their appearance is heavily influenced by the tip configuration as can be seen in figure 6.16. This gives a hint to a dependence of these structures on the electric field in the tunneling junction.

Having a stable tip suitable for topographical measurements, the defects observed mostly appear as white elliptic rings at positive bias indicating an empty state. The long axis of the rings is along the stripes. In most cases the center of the rings is located on top of the salt stripes. This results in a rectangular grid of possible defect positions.
which are occupied in dependence of the amount of defects as can be seen on the right image in figure 6.16.

The rings themselves have a characteristic behavior in dependence of different parameters. Their diameter is changing for example with the bias voltage applied. Nevertheless it became obvious that the most important parameter is the field in the tunneling gap. Therefore diameter measurements in dependence of the current and fixed bias voltage as well as fixed tip-sample distance at variable bias voltage were performed.

In the case of variable current the diameters are increasing with increasing current. The changed current conditions will only change the tip-sample distance while the bias voltage is kept constant for this measurement. This change is known from the I(z) curves and thus it is possible to rescale the I-axis to a z-axis using an I(z) curve obtained for the workfunction measurements. The absolute z position will only appear as an offset and therefore is not a critical parameter. The transformation leads to the curves shown in figure 6.17. Now the ring diameter shows a clear decrease for larger distances again hinting to a dependence on the electrical field applied. For the range observed the decrease shows a linear dependence with a slope of $(3.6 \pm 0.7)$ nm/nm in the case of the long axis and $(4.22 \pm 0.65)$ nm/nm for the short axis.

As the rings obviously are of electronic character, they can be observed in the dI/dV(V) curves too. Thus it is possible to determine the diameter dependence of the bias voltage at a fixed tip-sample distance. To perform this measurement a grid
6.4. DEFECTS ON KCL ON CU(110): RING-STRUCTURES

Figure 6.18: KCl on Cu(110): “ring” structure at different voltages and fixed tip sample distance. Left images: lateral energy cut. The gray scale has been changed to improve the contrast. 3.7x3.7 nm², (upper image 1.3 V, lower image 1.0 V). Graph: diameters as function of bias voltage with linear fits. Dots: short axis; triangles: long axis. The error bar corresponds to the pixel size of the left images. The data is extracted from the ring on the top right.

of dI/dV-measurement was recorded. Figure 6.18 shows cuts at a fixed energy through this grid. The grey-scale of each point corresponds to a value of the dI/dV curve at the energy chosen, the coordinates of the points are defined by the place of the dI/dV curve used for the gray-value. Similar to the dI/dV maps, one can clearly see the ring like structures.

Again, as can be seen in the graph in figure 6.18, one gets increasing diameters for higher voltages and thus fields. The slope of the curves shown are (1.88 ± 0.09) nm/V in the case of the long axis and (1.08 ± 0.06) nm/V for the short axis.

Measurements with atomic resolution on the salt and simultaneously acquired dI/dV maps showing these defects do not show any connection between the atomic structure of the salt and the ring positions. As it is only possible to image the chlorine ions this defect can obviously not be traced back to missing chlorine anions.

Similarly looking structures have recently been observed in a more complicated system which is alkali clusters on C₆₀ on Al₂O₃ on NiAl(110) [129] and have been attributed...
to ionization effects of the impurities. Therefore adsorbates are further candidates for causing these ring like structures. Another hint is the slightly increasing amount of defects within extended measurement periods.

A rest-gas analysis show that only hydrogen is present at a significant amount. Hydrogen also would be the only adsorbate with a reasonable diffusivity at 5 K. This could explain the tendency of an increasing amount of defects. Other rest-gas molecules (CO, O₂, N₂) should stick to the surfaces of the cryostat and hence be negligible. Another possible adsorbate may be copper originating form the copper surface, which is known to be mobile during the preparation of the films (chap. 5.1). But an increase of such defects with time at a sample temperature of 5 K is not to be expected.
Chapter 7

Molecules on surfaces: Cobalt Phthalocyanine

As the STM provides the access to topographic as well as electronic information it has been used for the investigation of molecules on surfaces too. This is the first step along the route to modify molecule-surface interaction by insulating spacer layers. These investigations range from growth studies to detailed analysis of electronic states as well as inelastic tunneling processes [14]. The variety of molecules range from simple molecules like \( CO \) [130] up to big organic molecules like the lander molecules [139, 140] or the phthalocyanines [131, 132, 136, 137].

Cobalt Phthalocyanine (CoPC) is a member of the huge group of molecules sketched in figure 7.1 based on phthalocyanine \( C_{32}H_{18}N_8 \). This molecule has a ring of alternating carbon and nitrogen atoms as a central element. The ring is able to coordinate two hydrogen atoms or a metal ion with the 4 nitrogen atoms.

Inserting a metal ion, the phthalocyanine is acting as a 4-fold ligand. Since a lot of different atoms can be bound by this molecule, there is a huge variety of different modifications. The molecules are known to be extremely stable in respect to of chemical and thermal treatment and can be sublimated at reasonable temperatures. They are widely used as dyes for different purposes. Commercially important members of this family are copper and cobalt phthalocyanine.

Within this thesis CoPC was studied. Its structure is well known and documented. Multilayer growth on different materials and different phthalocyanines has been reported [131], even mixed layers of CuPC and CoPC have been studied [132].

As CoPC has a cobalt ion as a metallic center, it is a candidate for the Kondo-effect. This effect has been shown not only for single atoms but also in molecules like cobalt carbyons [116] and in other molecules [133, 134].
7.1 Cobalt phthalocyanine on Cu(110)

We studied the limit of single molecules on Cu(110) and Cu(111). The preparation is simple. First the surfaces are cleaned using the standard cleaning procedure described earlier. Afterwards the molecule is sublimated from a home build OMBE-cell where the substance is placed in fused silica crucibles to avoid contaminations from the metallic surrounding. The evaporation conditions for the measurements shown are a sublimation temperature of approx. 620 K and a evaporation time of approx. 10 minutes. During the deposition the sample was kept at room temperature.

Figure 7.2 shows a typical preparation for Cu(110). The molecules are clearly visible as cross-like structures with a length of about 1.9 nm. The centers appear as bright dots for negative voltages whereas at positive voltages the center is not enhanced which is in agreement with studies on the system CoPC on Au(111) [131]. Other studies have shown that the CuPC shows in contrast to the present case a dip at this position [132]. Therefore one can assume the molecule to keep its cobalt ion and exclude an exchange process of substrate copper atoms with the coordinated cobalt. Most of the molecules are lying on the step edge such, that only two leafs are lying on the lower copper terrace as can be seen in figure 7.3. In this case the molecules are rotated such that one loop on each terrace is placed as close as possible to the step edge. On one step edge they are all rotated into the same direction indicating an interaction to the underlying terrace structure. Alternatively they are situated at the step edges lying on the lower terrace. This step-decoration takes place in a way that the molecule is connected to the step edge via two of the four phenyl rings.

The molecules on terraces, as can be seen in the images above, clearly show the cross-like shape expected for this molecule. The bright spot in the middle can be interpreted...
7.2. COBALT PHTHALOCYANINE ON Cu(111)

An intriguing possibility to investigate molecules with the STM is to place them on an insulating spacer layer. This spacer promises a weaker coupling of the substrate and the molecule as the insulator provides a band gap. Corresponding studies show that the quenching of electronic states, which normally occurs for molecules on metallic surfaces, can be avoided and thus the molecular state becomes accessible [37,38].

As the KCl layers on Cu(111) seems to be a perfect candidate for these investigations, it is consequential to investigate first the molecule of interest on the same substrate without salt layer. The sample preparation itself is the same as used for the case of CoPC on Cu(110).

The surface itself adds some new features. On one hand the surface shows a 3-fold

Figure 7.2: CoPC on Cu(110): The molecules prefer to decorate step edges. Left: overview scan (51.2x51.2 nm², -1 V, 0.77 nA), Right: single molecule scanned at different bias voltages (upper image: -1.2 V, 0.77 nA, lower image: 1 V, 0.37 nA, 5x5 nm²). The center appears to be flat at positive voltages and shows a protrusion for negative voltages.

as the position of the cobalt atom. Two orientations which are rotated by 45° are preferred by the single molecule. As the molecule is obviously quite mobile at room temperature and likes to stick at step edges, single molecules are elements of a frozen surface gas or they are pinned by defects on the surface.
CHAPTER 7. MOLECULES ON SURFACES: COBALT PHTHALOCYANINE

Figure 7.3: CoPC on Cu(110) step decoration: The molecules decorate step edges. Upper images: CoPC either lying on step edges (marked in the right image: 25.6x25.6 nm$^2$, -1 V, 0.56 nA) or on a terrace connected with two phenyl rings to the step edges (marked in the left image: 13x13 nm$^2$, 0.1 V, 0.57 nA); Lower images: according tentative models.

symmetry in contrast to the Cu(110) surfaces 2-fold symmetry. Even more important, the Cu(111) surface possesses a surface state described in chapter 3.5.

Figure 7.6 shows the topography of a sample prepared using the recipe above. In contrast to the case of CoPC on Cu(110) the molecules are distributed equally over the whole surface. This implies two possibilities: Either the molecule is highly mobile at room temperature and the measurements show a frozen surface gas. Or the molecule
7.2. COBALT PHTHALOCYANINE ON CU(111)

Figure 7.4: CoPC on Cu(111) topography. Left image: 51.2x51.2 nm$^2$, -0.1 V, 74 pA. Right image: 7.5x7.5 nm$^2$, 0.1 V, 0.57 nA.

sticks immediately at the position where it lands on the surface during the position. As the molecules tend to be mobile at higher voltages the surface gas seems to be the more probable model.

In the case of Cu(110) the molecules showed the full symmetry expected. Deposited on the Cu(111)-surface they split up into two species: in some rarer cases the molecule still appears as symmetric crosses. In the majority of cases, the molecule appears to have a bar-like structure over the molecule connecting two opposing phenyl rings. The remaining two rings show a slightly smaller corrugation as can be seen in figure 7.4.

The surface state apparent on this surface does obviously interact with the molecules as can be seen in topography and dI/dV-map shown in figure 7.5. Electrons are scattered in a way that in general one finds a black, and thus lower, ring around the molecule in the topographic measurements.

From the investigation of quantum corals on Cu(111) surfaces [138] the theoretical treatment of scatterers on this surface for distances in the order of the surface state wavelength is known. Roughly speaking one solves the scattering problem for single impurities using the account that scattered electron waves will be scattered again at the other impurities. The impurities themselves are described as certain phase and on the other hand absorb to a certain degree electrons. Using this model one can try to imitate the molecules scattering behavior.

Experiments with this technique show, that it is not possible to model the scattered waves observed by assuming the molecule to be a four or five point scatterers with the
scattering center placed under the phenyl rings of the cross like structure respectively an additional scatterer at the center of the molecule. It appears, that the main scattering process takes place in the middle of the molecule at the position of the coordinated cobalt atom. Any further point scatterer placed symmetrically at the phenyl ring will increase the radius of the observed minimum around the molecule as can be seen in the example figure 7.6. Furthermore it will introduce additional maxima between the phenyl rings and changes the appearance of the interference pattern. This is similar to the behavior found for lander molecules on Cu(111) [141].

The fact that the main scattering center is placed in the middle of the molecule suggests that the scatterer is the cobalt ion. It is known that in the case cobalt carbonyl molecules the interaction with the substrate can give rise to the Kondo effect [116]. The CoPC therefore is a candidate for corresponding investigations.
Figure 7.6: CoPC on Cu(111) simulation. Left image: measurement (20x20 nm$^2$, 0.1 V, 85 pA), right images: simulations 10x10 nm$^2$, 0.1 V. The upper image shows a single scatterer in the middle, the lower one 5 scatterers at the middle and in the corners of the blue box (distance: 1.1 nm).
Chapter 8

Conclusion

Construction of a low-temperature scanning probe microscope

In the first part of this thesis, I presented a scanning probe microscope which was developed for low temperatures and ultra high vacuum conditions. This instrument combines high stability for topographic measurements as well as for spectroscopic modes with a modular design allowing a large variety of extensions.

Special attention has been paid to the mechanical damping of the system. This incorporated modifications on the cryostat and on the whole UHV system resulting in a system which is able to achieve atomic resolution under the constraints of the desired capabilities.

Within this work the design of the SPM and its control unit has been tested, improved and extended. In particular a fully analog electronic circuit for plane substraction has been developed and adapted to the requirements of the instrument.

Investigation of thin insulating layers at the atomic limit

Two different systems of thin insulating layers on metallic substrates have been prepared and characterized for the first time: Potassium chloride on Cu(110) as well as Cu(111). The studies incorporate both morphology and electronic properties.

In the case of KCl on Cu(110) different types of structures have been observed. At low coverage and low sample temperature the salt decorates the step edges of the substrate. At higher temperatures, the KCl forces sections of the steps to run along fixed crystallographic directions thereby changing the appearance of the steps away from their meandering behavior after the cleaning process. If the coverage is increased further, two different kinds of islands are growing in the carpet like mode: monolayers and bilayers of salt. Both types show a one-dimensional stripe pattern. In the case of
bilayers atomic resolution has been achieved. Using this information it has been possible to identify the stripe structure as a Moiré type pattern caused by a periodic variation of hybridization strength with the copper substrate. The lateral variation is due to the lattice mismatch.

The growth of the salt islands is not defect free. Thus different kinds of structural defects, grain boundaries and point defects, have been classified. A third class of defects has been found. These defects show up as rings of empty states in dI/dV maps. The diameter of the rings depends on the electrical field within the tunneling gap. It is likely that the defect is charged, but missing chlorine ions can be excluded.

$KCl$ on $Cu$(111) has been shown to grow large islands or closed layers. Similar to the bilayers on $Cu$(110) atomic resolution has been achieved. As expected the salt is growing as $KCl$(100) layers.

Both systems, $KCl$ on $Cu$(110) and $Cu$(111) are transparent for electrons tunneling within their bandgaps. In both cases it is possible to access substrate states. Due to the larger tip-metal substrate distance these states appear suppressed in dI/dV spectra. Therefore interaction of adsorbates on $KCl$ films with the metallic substrate are expected to be reduced. This qualifies the films for experiments where insulating spacer layers are needed. In the case of bilayers of $KCl$ on $Cu$(110) the bandgap is 6.5 eV or even larger.

Different electronic states have been observed for the salt islands on both substrates: image-states and a salt state. The image-states are situated in front of the surfaces and thus are influenced by the salt layers. This interaction causes an energy shift of ca. -0.5 V which can be explained by both the lowered workfunction and the dielectric properties of the salt layer.

At $E_F + 2.4$ eV a new state has been identified. Due to its energetic position it cannot be a shifted imagestate. Other possibilities as a metal induced interface state or a quantum well states caused by the salt layer have been excluded as the states energetic position and weight does not depend on the film thickness.

The $Cu$(111) surface shows a well known surface state. This state is interacting with adsorbates and forms in the case of $KCl$ on $Cu$(111) an interface state. Compared to the pristine copper surface state its energy onset is shifted by only +30 meV to 410 meV whereas the effective mass is unchanged. This shift is unexpectedly low as in the case of the related system $NaCl$ on $Cu$(111) a shift of +215 meV to 225 meV has been reported [80]. The model potential introduced by Cole [120] which was used for the $NaCl$ system in the latter case to explain the shift is obviously not able to explain the full nature of this interface state.
Finally studies of submonolayers of cobalt phthalocyanine on the two copper substrates are presented. In the case of CoPC on Cu(110) the molecule shows a high mobility at room temperature resulting in step decoration. This step decoration occurs in two different ways. The molecules can be adsorbed on the facet of the step edge and are thus connecting to both the lower and upper terrace. In this case they are rotated such, that on each terrace one phenyl ring of the molecule is connected to the step edge. As a second configuration the molecules can lie on the lower terraces with two leafs connected to the step edge.

Deposited on the Cu(111) surface, the molecules can be found on both places: on step edges as well as on terraces. On terraces are possibly be pinned by surface defects. The molecules are interacting with the Cu(111) surface state. Analyzing the scattering pattern shows, that the main scatter inside the molecule is situated at its center. This leads to the assumption that the cobalt ion is responsible for this interaction.

Outlook

The scanning probe microscope has been built in a modular way to guarantee large flexibility for the implementation of different types of measurement. Hence the next steps in instrumental development will be the implementation of the AFM-optics foreseen as well as optical components to collect light emitted from the tunneling contact. With these components further characterization of the systems presented will be possible.

The systems investigated have shown to be suitable systems for decoupling layers with respect to both, morphology and electronic structure. Hence subsequent studies with molecules on this layers are promising. Especially the molecule cobalt phthalocyanine is an interesting candidate for these studies. It has shown to interact with the substrate via the cobalt ion. This gives raise to the presumption that the cobalt atom can show collective electron effects like the Kondo effect.
Bibliography


BIBLIOGRAPHY


[21] Veeco Instruments GmbH, D-68165 Mannheim, Germany

[22] T. Murdfield Jr., Diplomarbeit, Universität Münster (1994), Germany

[23] Omicron NanoTechnology GmbH, D-65232 Taunusstein, Germany


[25] Product catalogue, PI Ceramic GmbH, D-07589 Lederhose, Germany


[27] P. Wahl, PHD thesis, Universität Konstanz (2005), Germany


[30] Nanosensors, CH-2007 Neuchatel, Switzerland

[31] Laser 2000 GmbH, D-82234 Wessling, Germany

[32] Edmund Optics Inc., D-76131 Karlsruhe, Germany

[33] Schäfter + Kirchhoff GmbH, D-22761 Hamburg, Germany

[34] Oxford Electronics Ltd, Hampshire, U.K.


BIBLIOGRAPHY


[40] VAT Deutschland GmbH, D-85630 Grasbrunn, Germany

[41] Leybold Vacuum GmbH, D-50968 Köln, Germany

[42] VAb Vakuum-Anlagenbau GmbH, D-25337 Elmshorn, Germany

[43] Varian Deutschland GmbH, D-64289 Darmstadt, Germany

[44] CryoVac GmbH & Co KG, D-53842 Troisdorf, Germany


[47] Newport GmbH, D-64291 Darmstadt, Germany

[48] HWL Scientific Instruments GmbH, D-72119 Ammerbuch, Germany

[49] National Instruments Germany GmbH, D-81369 München, Germany


[59] Clemens Barth, Dissertation, Ludwig-Maximilians-Universität München (2001), Germany


[100] Data from webelements: http://www.webelements.com

[101] Daniel Reuter, Nicola Malinowski: private communications


Acknowledgements

I would like to thank several people for their help and their contribution to this thesis. These are in particular:

Prof. Klaus Kern for giving me the opportunity to work on my Ph.D. at the Max-Planck Institute for Solid State Research, and giving me all the support needed to finish this work.

Dr. Alexander Schneider and Dr. Ralf Vogelgesang for being mentor, colleague and friend at the same time.

Prof. W.D.-Schneider, PD Dr. D. Grützmacher, and Dr. M. Wenderoth for finding time to participate on the examination.

Wolfgang Stiepany, Wolfgang Heinz, Peter Andler, and Andreas Koch for their assistance in technical design and machining as well as for solving an uncountable amount of “small” technical problems.

Members of my subgroup, Dr. Christian Ast, Dr. Lars Diekhöner, Dr. Oguzhan Gürlü, Christian Michaelis, Sören Neubeck, Robin Ohmann, Selina Olthof, Dr. Peter Wahl, Dr. Gero Wittich, and Dr. Lucia Vitali for support at any situation at any time.

My dear friends at the institute, Paolo Acosta-Diaz, Sabine Andergassen, Tilman Aßmus, Dr. Alpan Bek, Dr. Alexander Bittner, Thomas Classen, Ruben Esteban, Dr. Martin Geisler, Dr. Dominik Hoffmann, Georgios Katsaros, Dr. Mato Knez, Dr. Klaus Kuhnke, Dr. Nicola Malinowski, Dr. Martin Panthöfer, Dietmar Payer, Julius Reiss, Daniel Reuter, Dr. Daniel Rohe, Dr. Ulrich Schlicht, Thomas Weitz and all others for their collaboration, support and a very pleasant time at the institute.
ACKNOWLEDGEMENTS
Curriculum vitae

Name: Michael Vogelgesang
Date of Birth: January 28., 1975
Nationality: German

1994   Abitur at the Illtalgymnasium Illingen, Germany
1994–1995   Civilian service
1995–2000   Studies of Physics and Mathematics at the Universität des
             Saarlandes, Germany
1998   Vordiplom in Physics, Universität des Saarlandes, Germany
       Vordiplom in Mathematics, Universität des Saarlandes, Germany
2000   Diplom in Physics, Thesis: “Untersuchungen von Oberflächen
       mit dem Nadelsensor”
2001–2005   Research in the group of Prof. K. Kern at the Max-Planck-
             Institute for solid state research, Stuttgart, Germany
2005   PHD-thesis: “Ultrathin KCl films on Cu(110) and Cu(111)
       studied by low-temperature scanning tunneling microscope”