TEMPLATED GROWTH AND PROPERTIES OF IRON NANOWIRES:
ANISOTROPIC ELECTRON STATES OF THE QUASI 1D COPPER SUBSTRATE, AND MORPHOLOGICAL AND MAGNETIC PROPERTIES OF THE IRON ADSORBATE.

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Abstract

Low dimensional and nano-scale material systems display quantum behavior due to the confinement in one or more dimensions of the electron states. The goal of nanoscience is to understand and exploit such behavior. Reaching such goal implies growing or fabricating nano-scale systems with atomic precision, not achievable by statistical top down methods. Self-organized and self-assembled systems on single crystal surfaces are prototypical atomically precise systems since they can be reduced to 1 (quantum wire) or 0 (quantum dot) dimension, maintaining the atomic precision of crystal.

The surface reconstruction of stepped surfaces, induced by locally selective chemical reactions, is exploited in the present work to produce: a) a quasi 1D stripes array of single crystal terraces that can be studied both by local probes to establish the morphology and the local density of states as well as by means of extended electronic structure techniques to probe the anisotropic confinement of the electronic states; b) to provide chemically selective substrates for the growth of atomically precise quasi 1D metallic wires.

This work presents a study on the morphology and on the electronic states of the Cu(332) surface as selectively oxidized to form a quasi 1D terraced surface. This surface provides then a template for the growth of 1D iron wires. The oxygen exposition of vicinal Cu(n,n,n-1) surfaces induces a reconstruction of stripes, parallel to the step edges, consisting of alternating uncontaminated Cu(111) terraces and Cu(110)-O(2x1) facets. We show that the control of the surface synthesis conditions, i.e. oxygen dose and substrate temperature, allows to tailor the periodicity of the reconstruction from 3 to 10 nm on the same primitive vicinal surface. The structural characterization of the surfaces was accomplished by means of Low Energy Electron Diffraction (LEED) and Scanning Tunneling Microscopy (STM) with atomic resolution, in ultra-high vacuum.

The Angular Resolved Photoemission (ARPES) data, obtained with polarized synchrotron radiation at the APE-INFM beamline at Elettra, show important changes in the Cu(111) L-gap surface states as a function of stripe width (reconstruction periodicity) due to quantum confinement: the surface state in the oxygen treated Cu(332) is confined in the (111) terraces and displays a large asymmetry with respect to the terrace axes. The Cu surface state of the clean Cu(332) surface is little perturbed by the monoatomic steps, and behaves as an average-surface-like electron state. The surface state of the oxygen treated surface is, on the other hand, characteristic of a quasi 1D terraces system, and display anisotropic dispersion with clear evidence of quantum confinement in the direction of the terrace width.

The growth of iron on the O/Cu(332) nanostructured surface is ruled by the affinity for the oxygen-induced (110) facets that run parallel to the Cu(111) terraces. Well ordered Fe nanowires can be produced on such facets even at room temperature (RT). Such ultrathin 1D iron nanowires have been characterized by X-ray absorption spectroscopy (XAS), by magneto-optic Kerr effect (in situ) and by X-ray magnetic circular dichroism, by using circularly polarized radiation from the APE-High Energy beamline at Elettra.
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CHAPTER 1: INTRODUCTION

The study of the electronic and magnetic behavior of systems with the quantum-confined electrons is of great importance in the understanding of fundamental concepts in condensed matter physics and for its technical application. The experimental study of such system became possible thanks to the improvements of the techniques of obtaining nano-scale structures. For example, the development of the molecular beam epitaxy (MBE) in the early 70's allowed the stacking of ultrathin films of different materials (heterostructure) with monolayer precision. The energy potential at films interfaces (heterojunctions) leads to an electron confinement, allowing the experimental study of quantum well and 2-D electron gas. Ever since the electron transport and photoluminescence of different heterostructures; like Si/Ge, GaAs/AlGaAs and GaAsP/InGaAs; were exhaustedly studied, and nowadays find application in devices as HEMT's (High Electron Mobility Transistor) and the quantum well based lasers.

The study of quantum wires (1-D ) and quantum dots(0-D) systems followed in the middle 80s. The quantum dots, in particular, have their electrons confined to discrete energies similar an electron in atom [1]. This caused the arising of the expectation for the possibility to create a macroscopic “artificial atom” and assembled them in artificial solids. From the technological point of view, the quantum dots, having a sharp density of states (DOS), could be employed in lasers resulting in a narrow spectrum width. In addition, the laser wavelength could be easily tuned with the dot's size [2]. The quantum wires are used to investigate
interesting electron interaction properties of the one-dimensional systems. In one-dimensional metal, the behavior of the electrons cannot be explained by the quasi-particle Fermi-liquid theory; the Peierls instability leads to a charge-spin separation and the system is better described by the Thommagar-Luttinger liquid model. This model predicts the vanishing of Fermi Edge and the appearance of charge and spin-density waves, and the enhancement of electron-electron interaction [3]. Some of the Luttinger liquid characteristic has been already observed in the carbon nanotube [4]. The study of magnetic properties in one-dimensional or quasi-one-dimensional systems is also an active field of research today.

There are two basic approaches to create structures with small dimensional in a controlled manner; the 'top-down' and the 'bottom-up' method. In the 'top-down' method, the structure or pattern is imposed to the substrate. The lithography techniques and the microcontact print are kinds of top-down method. The 'bottom-up' is a more recent approach method, in which the pattern emerges from the assembly of the atomic or molecular constituents into an organized surface structures through a self-ordering process. The bottom-up methods allow to create patterns with features sizes 1 to 20 nm with a good reproducibility at long range [5], this resolution limit is not achievable by any of the present top-down methods. For instance, at the beginning, quantum wires and quantum dots were producing using lateral lithographic of heterojunctions[1,2]. The usual lithographic techniques can produce lateral confinement as small as 100 nm. Recently, the electron-beam lithography has achieved the resolution of 15 nm [6], however the throughput is so slow that the patterning of large areas is unfeasible. In contrast, the bottom-up techniques allow the growth in large areas of nanodots with size of tens of nm [5] and one-dimensional system compounded of monoatomic-wires [7].
Chapter 1

Figure 1.1 - Two approaches to control matter at the nanoscale. For top-down fabrication, methods such as lithography, writing or stamping are used to define the desired features. The bottom-up techniques make use of self processes for ordering of supramolecular or solid-state architectures from the atomic to the mesosopic scale. Shown from the top are an electron microscopy image of a nanomechanical electrometer obtained by electron-beam lithography, a single carbon nanotube connecting two electrodes, a regular metal-organic nanoporous network integrating iron atoms and functional molecules (image adapted from [5]).

The bottom-up strategies is founded in the self-ordering process. The conceptualization of the self-ordering process has been in debate in the last years [8, 9]. The terms “self-assemble” and “self-organization” has been used in similar but slight different ways in the biology, chemistry, physics and sociology [8]. In physics, specially in surface science, it is suitable to define three self-ordering process on thermodynamic basis; namely, 'self-assembly', 'self-organization' and 'self-organized growth' [5]:

• The self-assembly process is the spontaneous association and structural order due the specific interactions among the individual components. It is a process that leads the system to its thermodynamic equilibrium. A example of self-assembled systems is
the growth of quantum dots by means of a lattice-mismatched heteroepitaxial growth; the strain produced by the buffer layer induces the spontaneous formation of 3D islands in the wet layer. In the heterostructure InAs/GaAs the nanodots size ranges from 20-50 nm [5]. Other examples are the faceting of vicinal surfaces and the surface reconstruction induced by adsorbates.

• The self-organization implies to a non-equilibrium process, usually driven by some external energy supply. The system ordering can not be attributed to the properties of its individual components, but it emerges from a collective (and usually complex) nonlinear interaction among the multiple components and without any explicit external control or guiding template. The classical example, from the sociobiology, is the collective intelligence in insects colonies [10]. In physics, we can quote the “convection cell phenomena” from the fluid dynamics; that is, the circular flow path of a fluid subdue a temperature gradient [New Physics book 1989]. The growth of the carbon nanotube, which is undertaken in non-equilibrium regime, is another important example [11].

• In the self-organized growth the interplay between the mesoscale force field and the kinetic energy of atoms play the main role. During the growth, the ratio (Deposition Rate/Diffusion) have to be chosen such that the deposited atom can probe a select number of sites, finding a local-minimum that leading the system to a desirable structure. The self-organized growth can therefore be carried out near or far to the thermodynamics equilibrium. It includes the growth on a templated surfaces which
provide either an anisotropic nucleation potential or a chemical selectiveness of the adsorbates. An example of self-organized growth is the lateral ordering and vertical alignment of the stacks of quantum-dots layer: the strain caused by the buried dots of one layer induced a nucleation potential in adjacent layer leading to the alignment of dots.

The self organized growth is so far the most used method to grow nanowires. An usual approach is the growth using a vicinal surface as template. The vicinal surfaces can presents a very ordered stepped surface, as we'll see in chapter 2. The basic idea is that the atoms at step edge are more reactive than those in terrace plane. This leads to a decoration of the adsorbate along the step edges resulting in a nanowire formation. The growth of one-dimensional iron films using the vicinal surfaces of appropriate substrates has been reported by many authors. Shen et al [12] studied the iron growth on a vicinal Cu(111), with average step size of 10 nm. The deposition of iron at 273K in such substrate produces isolated iron wires up to 1.4ML equivalent thickness of deposit. Similarly to the growth on flat Cu surfaces a transition from pseudomorphic distorted fcc to bcc phase is observed when the deposited thickness reaches 2.3 ML equivalent. This transformation is simultaneous to a reorientation transition of the magnetization that switches from perpendicular to in-plane. Guo et al [13] produced Fe monoatomic rows in a vicinal Cu(111), with average periodicity of 3nm, depositing iron at 120K. Shiraki [7] et al managed to produce monoatomic rows at RT depositing iron on Au(445), which has 3nm step size.
In this work we used a self-assembly process in order to reach the one-dimensional confinement of the electron states at vicinal copper surface and afterward use this self-assembled system as a template for a self-organized growth of iron nanowires. Our self-assembled system consists in an oxygen-induce faceted Cu(332) vicinal surface. It was previously demonstrated that the oxygen exposition of vicinal Cu(n,n,n-1) surfaces induces a reconstruction of stripes consisting of alternating Cu(111) and Cu(110) facets [14]. We show that the control of oxygen dose and temperature allows tailoring stable and reproducible reconstruction of 3, 7 and 10 nm of periodicity.

The Angular Resolved Photoemission (ARPES) data shows important changes in the Cu(111) L-gap surface states as a function of stripe width (reconstruction periodicity) due to quantum confinement: the surface state in the oxygen treated Cu(332) (OCu(332)) is confined in the (111) terraces and displays a large asymmetry with respect to the terrace axes. The Cu surface state of the clean Cu(332) surface is little perturbed by the
monoatomic steps potential, which can be modeled by the penning potential, and behaves as an average-surface-like electron state. The surface states of the oxygen treated surface are, on the other hand, characteristic of a quasi 1D terraces system, and display anisotropic dispersion with clear evidence of quantum confinement in the direction of the terrace width. Similar behavior has been measured for clean (111) vicinal gold with lower miscut angle [15]. In that case, the effect is ascribed to an enhancement of the effective step potential felt by the surface electron due a opening of the bulk projection band gap at small miscut angles. That is, at small miscut angles, the surface state behaves like a Schottky surface state, having lower penetration in the bulk and therefore, more sensible to the surface potential. In the Cu(332) surfaces the gap is completely shrink and the surface electrons behaves like a surface resonance, having part of its electronic density in the bulk, and therefore less sensitive to the step potential. However, even at smaller miscut angles, the stepped copper doesn't produce the same degree of quantization observed in the stepped gold[15], what indicates that the step potential is not as strong as it is in the gold. In our experiment, the enhancement of confinement can be attributed to the substitution of the step potential by a OCu(110) facet. Moreover, the photoemission linewidth analyses suggest that the surface state in the OCu(332), in contrast with Cu(332), doesn't behave as surface resonance, despite of the overall surface angle is still the same. We present also a Scanning Tunneling Microscopy (STM) study of the self-organized growth of Fe nanowire using the OCu(332) as template. We show that the iron grows preferentially on the (110) facets forming nanowires. The MOKE and XMCD show that the wires are magnetic with easy axis perpendicular to the surface.
In chapter two, we discuss the electronic properties of the vicinal surface, its potential as template for self-organized growth; and present some electronic and magnetic properties of one-dimensional systems from the literature.

In chapter three, we present the experimental techniques used in this work; namely: STM/STS, ARPES, Low Energy Electron Diffraction (LEED), XMCD and MOKE;

The chapter four describes the instrumentations used on APE beamline facility at ELETTRA where the complete set of measurements has been performed taking advantage of the interconnected system of UHV chambers.

In chapter five, we present the oxidation procedures of the Cu(332) and the structural characterization of the reconstruction by means of STM and LEED techniques.
In chapter six, we present the results obtained by the ARPES measurement, we show the evolution of the L-Gap surface state from the Cu(332) to the OCu(332), and discuss some theoretical aspects.

In chapter seven, we demonstrate the using of the OCu(332) as a template for growth of iron nanowires and present some MOKE and XMCD data.

A final chapter summarizes the conclusions and points the contributions of this thesis.

References:


CHAPTER 2

Surface States in Vicinal Copper (111)

2.1 Vicinal Surfaces

2.2 Surface State

2.3 Surface States in Vicinal (111) Surfaces
Chapter 2 – Surface States in Vicinal Copper (111)

This chapter presents some basic concepts discussed in this thesis. We deal with vicinal surfaces and surface states. The chapter summarizes a work published by Mugarza and Ortega [1], where these authors have grouped several studies with gold and copper vicinal surfaces.

2.1- Vicinal Surfaces

The vicinal surfaces are produced when a crystal is cut with a small angle deviation from the low Miller-index plane (i.e. (100),(111),(110)...). The results is either a facet or stepped surface, where the terrace has the direction of the low index plane.

![Geometric parameters for a vicinal surface](image)

**Figure 2.1** - (a) Geometric parameters for a vicinal surface: step array periodicity $d$, the terrace width $L$, the step height $h$ and the miscut angle $\alpha$. (b) Top (up) and side (down) view of the vicinal (111) surface. Steps running in opposite directions display different minifacets.

The most important geometric parameters are shown in the figure 2.1-a. The optical surface is defined as the macroscopic average surface, i.e. the plane defining an angle $\alpha$ with the low-index plane, and it is represented by dashed lines.

The vicinal (111) noble metal surfaces with the miscut angle perpendicular to the [-1-10] direction and towards either the [-1-12] or [11-2] direction leads to straight steps by reducing kink formation. The vicinals originating from this cut display two types of different minifacets at steps, as can be seen in figure 2.1-b. In the [-1-12] direction, the minifacets...
are \{100\}-like, while in the opposite direction, i.e. \{11-2\}, the steps are \{111\}-like. The terrace width is slightly different for \{100\}- or \{111\}-like vicinals. Assuming periodic monatomic step arrays, terraces will contain \(m + 2/3\) atomic rows for \{100\}-type steps, and \(m + 1/3\) for \{111\}-type steps, where \(m\) is an integer number.

The terrace width distribution is usually narrow for larger miscut angles. Such homogeneity in size can be ascribed to the repulsive character of the potential step edges, which get closer in higher miscut angles, and, as we will see later, to the higher terrace-terrace coupling of electronic states.

### 2.2 - Surface State

*The abrupt change of the periodic potential caused by the surface creates new electronic states. The states created at surface that cannot propagate inside the crystal are called surface states. The surface states originate in the energy gaps of bulk band structure projected on the surface plane.*

![Figure 2.2. Potential and wavefunctions for the surface in Cu(111). Surface electrons are trapped between the vacuum barrier (image potential) and the crystal gap.](image)

If one considers an infinite periodic crystal, the electronic wave functions assume the form of the well know Bloch functions:

\[
\psi_k(\vec{r}) = u_k(\vec{r})e^{i\vec{k} \cdot \vec{r}} \quad (2.1)
\]
The imposing of an infinite periodic boundary condition (Bron-Von Karman) restricts the values of \( k \) to be real. In the presence of the surface, however, the symmetry is broken; it leads to additional solutions for the Schrödinger equation, which can be written in the form of (2.1) but with a complex perpendicular component of \( k \); 
\[ k = k_R + i k_I. \]
The imaginary part of \( k \) is responsible for the exponential decay of the wave functions outside of the crystal \((z<0)\). Some of these additional states, resulted from the confinement between the crystal energy band gap and the vacuum barrier, present also a decay inside of the crystal \((z>0)\), and are consequently confined at surface. These states are known as \textit{surface states} and assume, inside the crystal, the following form:

\[ \psi_k(r) = u_{k||}(r_{||}) e^{k_{||}r_{||}} e^{-k_I r_{\perp}} \]  

(2.2)

Due to the missing of periodicity in the perpendicular direction, one can not assign a discrete value for \( k_{\perp} \), but a range of values spanning continuously along the perpendicular direction in the k-space \([2]\), in an analogy with the rods in Ewald construction known from the LEED theory (Chapter 3-Fig. 3.2). It is important to realize that a true surface state can not be degenerate with any bulk state. It means that for the existence of a surface state with a momentum \( k_{||} \) and energy \( E(k) \), there can not be any bulk state with the same energy and \( k_{||}^{\text{bulk}} = k_{||} \) for any value of \( k_{\perp}^{\text{bulk}} \). If there was such bulk state, the surface state could couple to it and penetrate infinitely into the bulk, unless that bulk state has a symmetry that does not allow the couple with the surface state. A state originated in the surface that is coupled with the bulk state is not called surface state any more, but a surface resonance. In other words; the surface states originate at energy band gaps of the bulk band structure projected on the surface.

In (111) noble metals surfaces, the projection of the s, p-bands near the Fermi level leaves a gap at the center of the surface Brillouin zone (SBZ), as shown in figure 2.3-b. The figure displays a cut of the bulk Fermi surface (Fig. 2.3-a), in the direction perpendicular to the surface, where we can see the s, p-band gap arising from the L-neck projection at \( \Gamma \), i.e. at the center of the SBZ. In the figure 2.3-c we see the 2D bulk band projection over the whole SBZ. The Fermi surface of the surface state appears as a black ring centred in the
gap, as expected for a 2D state with isotropic and parabolic dispersion. Note that the ring was not present in the bulk Fermi surface because it is a state originated in the surface. The (111) noble metal surfaces has been extensively studied in the past[4-6], displaying free-electron-like isotropic behaviour parallel to the surface and around $\Gamma$:

Figure 2.3- (a) Copper Fermi surface (b)vertical cut ([111], [11-2]) of the Fermi surface, note the gap in the center of the SBZ. (c) Projection of the bulk states at Fermi Surface on the (111) plane SBZ. The Fermi surface of the surface state is seen as black ring in the center of gap.

2.3 - Surface States in Vicinal (111) Surfaces

By changing the miscut angle the band structure projection in the SBZ have to be rotate. This is schematically depicted for different miscuts in figure 2.4. Along this plane, regions of the SBZ where bulk bands are projected from both sides of the BZ are marked in dark grey, whereas regions with projection only from half of the BZ are marked in light gray. The L-point projection marks the edge of the SBZ at $\pm \pi/d$.

Figure 2.4- Bulk band projection at $E = E_F$ onto vicinal surfaces with small and high miscut angles. Dark-grey zones are the regions where bands are projected from both sides of the BZ, whereas light-grey zones present projection only from half a side. For $3.5^\circ$, the $\Gamma$ gap that supports the L-neck surface state is still present. For $11^\circ$ miscut there are bulk states projected over the entire SBZ and only surface resonances can exist.
We see that by increasing the miscut angle the $L$ gap shrinks and eventually vanishes. The critical miscut for closing the gap is obtained as $\alpha_c = \tan^{-1}(k_{\text{neck}}/k_L)$, where $k_{\text{neck}}$ is the radius of the neck and $k_L$ is the distance $L$. For Cu, $k_{\text{neck}} = 0.19$ and $0.26 \text{ Å}^{-1}$ for the band bottom and $E_F$ respectively, leading to a closing angle ranges of $\alpha_c \sim 7.2^\circ - 9.8^\circ$. Strictly speaking, surface states can only exist in the presence of a gap; thus the peaks observed for miscut angles bigger than $\alpha_c$ will be surface resonances. The increasing overlap with bulk states decreases the photohole lifetime what is manifested in the surface state photoemission peak width. Thus surface resonances are effectively found deeper in the bulk, and hence less affected by the step potential. In the direction perpendicular to the surface, the electrostatic potential, induced by the dipole-like charge-density formation at the step edge, diminishes rapidly, decreasing to $\sim 50\%$ for 2 Å inside the bulk [3].

![Figure 2.5 - Kronig–Penney potential mimicking the potential array formed by the step superlattice.](image)

The potential produced by the steps edge can be modeled using the Kronig-Penney (KP) model. The step lattice can be viewed as a periodic array of potential barriers, as described in figure 2.5. The barrier is given by $U_0 \delta(x)$. As for any other periodic potential, the KP model gives bands and forbidden gaps as solutions of the energy dispersion. The figure 2.6 shows different dispersions with the increasing of the barrier height. For a potential consisting of a periodic array of $\delta$ functions the dispersion relation takes the following form[1]:

$$E(k_x) = E_0 + \frac{\hbar^2}{2m^*} \left( \frac{1}{d} \right)^2 \left( \cos[(\mathcal{T}(E,U_{\text{ob}}) \cos k_x d) - \phi] \right)^2$$

where $|\mathcal{T}(E,U_{\text{ob}})|$ is the modulus of the transmission coefficient and $\phi$ the phase:

$$|T|^2 = \frac{1}{1 + (q_0/q)^2} \quad ; \quad \phi = -\tan(q_0/q)$$

$2-6$
and

\[ q_0 = \frac{m^*}{\hbar^2} U_0 b \quad q = \frac{2m^*}{\hbar^2} \left( E - E_0 \right) \]

Figure 2.6- KP bands for increasing potential barrier. (a) U0b = 0, free-electron parabola. (b) Finite potential barrier. The band splits into superlattice subbands which are zone folded by the reciprocal superlattice vector \( gn = \frac{2\pi}{d} \). (c) Infinite potential barrier. The subbands become flat levels. The levels are centred at \( k = \frac{n}{d} \cdot N \) (except \( N = 1 \)). The free-electron parabola is plotted in (b) and (c) in red.

**Terrace versus average-surface character**

For vicinal samples with small miscut, where the opening of the gap allows the existence of a true surface state, the potential at the steps edges is more effective than in the case of the surface resonance. The surface states present a terrace character in the sense that the overlap the wavefunction from different terraces is small. In such case the \( k_\perp \) of the surface states are spanned in the direction normal to the terrace, resulting in a decay in this direction (Fig 2.7-a). With the increasing of the miscut angle and consequently closing of the L-gap, the original surface states become surface resonances leading to a reducing of the effective potential, as discussed previously. A low step potential results in a terrace-to-terrace coupling, increasing the surface band dispersion. Such states have a average-surface character, since the surface states “feel” an average surface potential and its \( k_\perp \) is spanned in the direction normal to the optical plane of the surface and present a decay in this direction (Fig. 2.7-b).
Figure 2.7 - Schematic of the wavefunction for terrace (a) and average-surface modulation (b). The wavefunction decay is perpendicular to the terraces (optical plane) in the terrace (average-surface) modulation.

References:


CHAPTER 3

Experimental Techniques

3.1 Low Energy Electron Diffraction (LEED)

3.2 Scanning Tunneling Microscopy (STM)

3.3 Angle Resolved Photoemission Spectroscopic (ARPES)

3.4 Magneto-optic Kerr Effect (MOKE)

3.5 X-ray Absorption (XAS) and X-ray Magnetic Circular Dichroism (XMCD)
Chapter 3 – Experimental Techniques

This chapter describes the experimental techniques used in this work. We explain first some basic features of the LEED; and then we follow with a description of the STM technique, where we detail our procedure of tip producing. Afterward we present the ARPES and discuss some important aspects for this thesis. We finish presenting two techniques for magnetic characterization: the MOKE and synchrotron technique XMCD.

3.1- Low Energy Electron Diffraction (LEED)

The LEED is the most used technique to check the medium and long range crystallographic quality of surface. A monochromatic beam of electrons with a primary energy usually variable between 10 and 100 eV is incident on the surface and is elastically backscattered, giving rise to diffraction spots that are imaged on a phosphorous screen[1].

This energy range is particularly suited to surface studies since it corresponds to the lowest values of the quasi-universal curve for the mean free path of electrons in solid (see Fig. 3.1);

![Figure 3.1. The mean free path as a function of the kinetic energy of the electrons:[2] the scattered measured points represent different crossed materials.](image)

The diffraction pattern is simply explained by the Bragg equation. In analogy with the treatment of X-ray interferences in bulk crystals, each spot at fluorescent screen is a result of an interference maximum in a direction perpendicular to a set of periodic scattering lines on the surface. This approach forms the basis of the geometrical theory of diffraction, which easily provides the geometry of the unit cell - the diffraction pattern corresponds
essentially to the surface reciprocal lattice - but does not explicitly carry information on the location of the atoms within this unit: this further information requires a detailed measurement of the diffracted intensities and a more thorough description of the scattering process using the so-called dynamic theory of diffraction, which takes into account relevant effects as the multiple-scattering events due to the ‘strong’ interaction of low energy electrons with matter [1].

The condition for the occurrence of an elastic Bragg spot is that the scattering vector \( \mathbf{K} \) must have the component parallel to the surface equal to a vector \( \mathbf{G}_\parallel \) of the 2D surface reciprocal lattice, that is

\[
\mathbf{K}_\parallel = \mathbf{k}'_\parallel - \mathbf{k}_\parallel = \mathbf{G}_\parallel \quad (3.1)
\]

where \( \mathbf{k} \) and \( \mathbf{k}' \) are the wave vectors of the incident and backscattered electron.

The possible elastically scattered beams (\( \mathbf{k}' \)) can be obtained by the following construction illustrated in Fig. 3.2. According to the experimental geometry the wave vector \( \mathbf{k} \) of the primary beam is positioned with its end at the (0, 0) reciprocal lattice point and a sphere is constructed around its starting point: the condition \( \mathbf{K}_\parallel = \mathbf{G}_\parallel \) is so fulfilled for every point at which the sphere crosses a “reciprocal lattice rod”. Collecting the elastically scattered electrons under these conditions, we obtain a pattern corresponding to the projection of the surface reciprocal lattice.

**Figure 3.2.** Ewald construction for elastic scattering on a 2D surface lattice. The corresponding 2D reciprocal lattice points \( (h, k) \) are plotted on a cut transversal to \( ky \) (on the left) and \( kz \) (on the right)

The classification of surface structures follows a nomenclature where the relation between the surface lattice (basis vectors \( \mathbf{b}_1 \) and \( \mathbf{b}_2 \)) and the bulk lattice (basis vectors \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \)) is...
expressed by the ratios of the basis vectors (and the angle of rotation between the two lattices, if any), i.e., \( m \times n \) with 
\[
m = \frac{|b_1|}{|a_1|} \quad \text{and} \quad n = \frac{|b_2|}{|a_2|}.
\]

**Setup**

The essential elements of a LEED system are an electron gun for producing a sufficiently parallel and mono-energetic electron beam with energies typically varying between 30 and 300 eV and a detection system for the elastically scattered electrons. A typical LEED system is exhibited in Fig. 3.3. A heated cathode emits electrons that are focused and accelerated to the desired energy before leaving the last aperture which is usually at the same potential of the sample; the same is true for the last hemispherical transparent grid, thus a field-free space is established between the sample and the display system through which the electrons travel to the surface and back after scattering. The fluorescent screen (collector) has to be biased positively (3 to 5kV) in order to accelerate the slow electrons against the fluorescence screen which is usually transparent from its backside. A second grid (suppressor) is at a negative potential whose magnitude is slightly smaller than the primary electron energy in order to repel the inelastically scattered electrons which would produce an isotropic background reducing the pattern contrast at screen.

![Figure 3.3](image_url)

*Figure 3.3. Schematic of four-grid LEED optics for electron diffraction experiments.*
3.2- Scanning Tunneling Microscopy (STM)

The STM is a revolutionary technique that allows the visualization of individual atoms on a surface. It is one of the pillars of the development in nanoscience in the last years. Briefly, the STM technique consists in the scanning of a surface by a sharp metallic tip and the reconstruction of the three-dimensional topography of the electronic density of such surface, by mean of the measure of the tunneling current between tip and surface.

**Figure 3.4** - (a) Diagram of tip and sample surfaces. The wave function in both surfaces shows an exponential decay outside. (b) If the sample surface and tip are placed closed enough, the overlapping of the wave functions tails allows the electron tunneling through the barrier. The voltage determines the sense of current. $\Phi$ is the work function.

In the STM, the tip is approximated to the sample surface of some micrometers thanks to piezoelectric actuator system controlled by feedback current loop. In this condition, the vacuum implies a very narrow potential barrier between the tip and surface, narrow enough to allow a measurable tunneling of the current from the tip (surface) to surface (tip) for a positive (negative) bias (see Fig 3.4).

The tunneling transmission probability $T(d,V,E)$ and consequently the tunneling current ($I_{\text{tun}}$) are strongly dependent on the distance $d$ between sample and tip. For a trapezoidal barrier the tunneling transmission probability is given within WKB (Wentzel–Kramers-Brillouin) approximation as [3]:

$$T(d,V,E) \approx \exp\left(-2d\left[\frac{2m}{\hbar^2}(\phi + eV/2 - (E - E_p))^{1/2}\right]\right) \quad (3.2)$$

where $\phi = (\phi_s + \phi_t)/2$ is the average of sample $\phi_s$ and tip $\phi_t$ work functions, and $E$ is the electron energy. $E_p = \hbar^2 k_p^2 / 2m$ are the component of electron energy parallel to the junction interface, and $k_p$ is its corresponding electron momentum. However the electrons
with momentum parallel component, $k_p$, different from zero is usually neglected due to the smaller contribution of such states for the tunneling current [4].

The $I_{tun}$ has also dependence with the convolution of the LDOS of tip, $\rho_t$, with the LDOS in the surface, $\rho_s$, assigned by a specific the sample bias.

$$J(d, V) = A \int_{-\infty}^{\infty} T(d, V, E) \rho_t(E) \rho_s(E-eV)[f(E-eV)-f(E)] dE \quad (3.3)$$

There are two operation modes in STM: the constant current mode and the constant height mode (Fig 3.5). In the constant current mode, the tunneling current is set as a parameter and the feedback distance controller change the tip height in order to keep constant the current while the sample is scanned. The tip height is changed by the modulation of the voltage applied longitudinally on tip's piezoelectric crystal. This voltage signal is recorded simultaneously with the $X$, $Y$ scanning position, resulting in a topographic image. In the constant height mode, on the other hand, the height is passed as parameter, and the tunneling current is recorded as sample is scanned. The advantage of the constant height mode is that the interpretation by means of STM simulated image (usually calculate by DFT) is easier. On the other hand, the probability to crash the tip against the surface is higher, since the feedback circuit is off.

**Fig 3.5** - (a) Typical STM system: tip distance depends on the tunneling current and it is controlled by the feedback circuit (represented by the gray rectangular box). (b) The two STM operation modes. (Figure from http://www.iap.tuwien.ac.at/)

3-6
Tip Preparation

The preparation of a sharp and stable tip is essential to obtain high-quality STM images. The process consists of two steps: ex-situ electro-chemical etching and the in-situ annealing and sputtering.

Electron-chemical etching

In our experiments, the material used for a tip was a tungsten wire of 0.38 mm diameter and the etching solution is a NaOH solution. A 7mm long tungsten wire is spot-welded in the tip holder and positioned vertically at the center of a gold ring (Fig. 3.6). The set is then immersed for a very short time in the solution in order to form a thin liquid film at gold ring. The successive step is the application of an electrical potential in the tip in respect to the ring, usually about 5 V. This potential will drive the corrosion of the wire through the enhancement of the reaction with the OH- ions, present in the solution with tungsten atoms. The electrochemical redox reaction can be described by the following overall equation:

\[
W(s) + 2OH^- + 2H2O \leftrightarrow WO_4^{2-} + 3H_2 (↑);
\]  

(3.4)

In an aqueous solution, the \(WO_4^{2-}\) anion dissolves and forms pertungstic acid (\(H_2WO_5H_2O\) or \(WO_3H_2O_2H_2O\)). In practice, the reaction is much more complicated, as intermediate oxidizing steps occur [5]. The etching reaction is initiated when the applied potential exceeds 1.43 V.

![Figure 3.6- Electro-chemical etching of the tungsten wire. Note the solution liquid film in the gold ring.](image)

The etching produces a “neck” in the wire at the region of contact with the film, the neck increases progressively, thinning the wire until the dropping of the bottom part. The top
part along with the tip-holder is then inserted in UHV chamber for the degassing.

There are some practical problems in the production of the tip: Depending on the solution concentration, the total corrosion time ranges from 15 to 40 minutes, but the film in the ring brakes in intervals from 1 to 2 minutes, requiring several immersions in the liquid solution. Sometimes, the resulting film touches the wire at a different position from the previous immersion. It produces a wider neck, resulting, at the end of process, a long thin tip, which is less stable during the STM scanning. Another problem is the over-etching: after the dropping of the bottom part of the wire the tip is ready, any additional etching will quickly remove the top atoms on the end part, blunting the tip and reducing its resolution. For this reason is necessary cut the current immediately after the dropping of the bottom part.

In order to minimize such problems, we designed a system that allows the etching of the tip in a controlled and reproducible way. The device allows the automatically immersion of the ring once the film is broken in a reproducible way; and the immediately cut off of current once the etching process is finished (about 10 ms), which allows the using of higher solution concentration (7 M in our case) and consequently reducing the total time of the etching.

Figure 3.7 - Apparatus for the tip electro-etching: Two current loops are simultaneously measured. The $I_{\text{etching}}$ current loop pass through the gold ring and is proportional to the etching efficiency. When the solution film at the gold ring brakes, the $I_{\text{etching}}$ goes to zero and the container lift is promptly set in motion for a new immersion. Alternatively, the user can set a limit current $I_{\text{lim}}$ with a value somewhat higher than zero in order to trigger the immersion a moment before the film broken. The $I_{\text{drop}}$ current loop pass through the solution in the container, once the bottom part of the tip drop, $I_{\text{drop}}$ goes to zero and the Current Sensor acts on the switch interrupting the current and signing the end of process.
In situ Annealing and Sputtering

After degas, the tip is annealing by electron bombardment: a filament placed in front of the tip at a very short distance, in such a way that the current flow through the thinnest end part of the tip of the filament. The tip is bias at 500 V and the with the an emission current of 5mA. The electrons are majority attracted to the end part of the tip due the higher electrical field in sharp points, it creates a current density high enough to produce a temperature of 2000° in few seconds. Such temperature is necessary to remove the layer of tungsten oxide from the tip. Afterward the tip is argon-sputtering at 1KV during 20 minutes. The sputtering has to be done frontally in other to increasing the sharpness of the tip.
3.3- Angle Resolved Photoemission Spectroscopic (ARPES)

The ARPES experiment consists in the measuring of the velocity angular distribution of the electrons emitted from a sample when it is illuminated by a light with specific energy. The ARPES allows one to get information about the energy, symmetry and dispersion of the electronic states. In the electron photoemission phenomena (or photoelectric effect) an electron is emitted from the matter, with the kinetic energy $E_{\text{kin}}$, after the absorption of a photon with energy $\hbar \nu$. The energy balance is given by:

$$E_{\text{kin}} = \hbar \nu - \Phi - E_b$$  \hspace{1cm} (3.5)

where $\Phi$ is the metal work function, and $E_b$ is the electron binding energy. A photoemission spectrum is measured counting the emitted electrons as function of $E_{\text{kin}}$ for a sample illuminated with a fixed photon energy. Inverting the relation (3.5) one obtains a set of $E_b$ peaks that corresponds to the electronic energy levels in the solid (Fig. 3.8).

![Figure 3.8 - Energetics of the photoemission process.](image)

The ARPES shows its potential in the study of valence bands, where one finds higher electron energy dispersion. For the study of valence band the usual photon energy ranges from 10 to 100 eV. This energy range allows a reasonable angular resolution, as showed by equation (3.6), and produces photoelectrons with mean free path from 5 to 10 Å (see Fig.3.1), what makes the ARPES a surface sensitive technique. Notwithstanding the ARPES is also used to study the bulk states: It is well know that, in a solid, the atomic
position has very small modification for the first layers in relation to the bulk, consequently, with exception of the very first layer, the atoms close to the surface keeps almost the same electronic properties of the bulk atoms.

In the standard ARPES experiment, the $E_{\text{kin}}$ is measured using an energy analyzer (or electron spectrometer), which collected the photoelectrons and, by means of electric fields, allows the passage of electrons having an narrow kinetic energy range around $E_{\text{kin}}$ to the detector (usually a electron multiplier).

The main characteristic of the photoemission that allows the ARPES experiment is the conservation of the photoelectron momentum parallel to the surface, $\vec{k}_{\parallel}^{\text{initial}} = \vec{k}_{\parallel}^{\text{final}}$. Thanks to this, the parallel electron dispersion can be assigned to the parallel component of the photoemitted electron momentum $\vec{p}_\parallel$ and consequently to the emission angle:

$$\hbar k_{\parallel}^{\text{initial}} = \sqrt{2mE_{\text{kin}}} \sin \theta$$  \hspace{1cm} (3.6)

In the ARPES measurement the sample is positioned such that the Electron Analyzer scan the kinetic energy measuring the photoemission spectrum $p(E_{\text{kin}})$ in a specific direction defined by the polar and azimuthal angle $(\theta, \varphi)$, as depicted in Figure 3.9. Once the spectrum is acquired, the sample is rotated and a new direction is scanned, so that one obtains the total parallel dispersion of the electronic states. This procedures is referred as the EDC (energy-distribution curve) mode.
Photoemission line shape

The photoemission consists in the optical excitation between the ground to the final state (system plus photoelectron). The transition probability $w_{fi}$ can be approximated by the Fermi’s golden rule.

$$w_{fi} = \frac{2\pi}{\hbar}|M_{fi}|^2 \delta(E_f^N - E_i^N - \hbar \nu) \quad (3.8)$$

in which $M_{fi}$ is a Hamiltonian matrix element in the N-electrons state base;

$$M_{fi} = \langle \psi_f^N | H_{int} | \psi_i^N \rangle \quad (3.9)$$

and the interaction $H_{int}$ is treated as perturbation given by

$$H_{int} = -\frac{e}{mc} \mathbf{A} \cdot \mathbf{p} \quad (3.10)$$

where $p$ is the electronic momentum operator and $A$ is the electromagnet vector potential. This approximation is known as electrical dipole interaction. The momentum conservation is implicit in the $M_{fi}$. In order to calculate $M_{fi}$ let us defined the initial and final state as

$$\psi_i^{(N)} = \alpha \Phi(k_i) \psi_i^{(N-1)} \quad (3.11)$$

$$\psi_f^{(N)} = \alpha \Phi_f(E_{kin}(k_f)) \sum_s \psi_f^{(N-1)} \quad (3.12)$$

where $\alpha$ is an antisymmetric operator that properly antisymmetrizes the N-electron wave function so that the Pauli principle is satisfied. $\Phi(k)$ is the one-electron wave function of the state from which the electron is photoemitted and $\Phi_f(k_f)$ is the photoemitted electron wave function; $\psi_i^{(N-1)}$ and $\psi_f^{(N-1)}$ are the remaining (N-1) electrons wave function before and after the photoemission. The subindex $s$ stands for any possible state that the initial $\psi_i^{(N-1)}$ can assume after the interaction with the remaining hole.

The photoemission current $I$ is proportional to the transition probability $w_{fi}$ and consequently to the $M_{fi}$:

$$M_{fi} = \langle \psi_f^N | H_{int} | \psi_i^N \rangle = \langle \Phi_{f,Ekin} | H_{int} | \Phi_i(k) \rangle \sum_s \langle \psi_f^{(N-1)} | \psi_i^{(N-1)} \rangle \quad (3.13)$$

The first term on the right side is the coupling of the one-electron initial and final state caused by the photon interaction; the second term measure the overlap of the $|N-1>$ final state with the $|N-1>$ ground state, giving the line shape of the photoemission peak. We defined it as spectral function $A(k,E)$:

$$A(k,E) = \sum_s |\langle \psi_f^{(N-1)} | \psi_i^{(N-1)} \rangle|^2 \quad (3.14)$$
If we assume no electron-electron interaction, one has $\psi_{f,s}^{(N-1)} = \psi_{i}^{(N-1)}$ (frozen-orbital approximation) and the spectral function is reduced to:

$$A(k, E) = \frac{1}{\pi} \delta(E - E^0(k))$$  \hspace{1cm} (3.15)

If we switch on the electron-electron interaction, this can be taken into account in the photoemission by adding to the single-particle electron energy $E^0(k)$, so-called self-energy $\Sigma(k, E)$ (provided perturbation theory is valid) [6]:

$$\Sigma(k, E) = \text{Re} \Sigma + i \text{Im} \Sigma,$$ yielding for the spectral function:

$$A(k, E) = \frac{1}{\pi} \frac{i \text{Im} \Sigma}{(E - E^0(k) - \text{Re} \Sigma)^2 + (\text{Im} \Sigma)^2}$$  \hspace{1cm} (3.16)

Providing that the self-energy varies slowly with energy and momentum the spectral function gives a Lorentzian shape centered in the energy $(E^0(k) + \text{Re} \Sigma)$ with a linewidth $\Gamma_h = 2 \text{Im} \Sigma$. The imaginary part of the self-energy represents the lifetime of the excited hole and therefore one can associated it to part of the intrinsic linewidth of the photoemission peak. Another part is given by the damping of electron final state caused by the symmetry broken at surface. Such damping is the responsible for a relaxation of the $k_{\perp}$ conservation resulting in an additional broadening of photoemission energy peak; and can be modelled by adding an imaginary part to the final state momentum $k_{\perp}^f$. The resulting cross section is [7]

$$\sigma \propto \frac{1}{a_{\perp}(k_{\perp}^i - \text{Re} k_{\perp}^f)^2 + (a_{\perp} \text{Im} k_{\perp}^f)^2}$$  \hspace{1cm} (3.17)

That is a Lorentzian centered at $k_{\perp}^i$ with a width given by $\text{Im} k_{\perp}^f$. This “uncertain” in the $k_{\perp}$ produces the extra peak linewidth:

$$\Gamma_e = 2 \hbar |v_{e,\perp}| \text{Im} k_{\perp}^f$$  \hspace{1cm} (3.18)

where $v_{e,\perp}$ is perpendicular component of the group velocity of the final state. The total intrinsic linewidth for normal emission is approximately

$$\Gamma_{\text{intr}}(9=0) = \frac{\Gamma_h + \Gamma_e |v_{h,\perp}/v_{e,\perp}|}{1 - |v_{h,\perp}/v_{e,\perp}|}$$  \hspace{1cm} (3.19)

where $v_{h,\perp}$ is the perpendicular component of the group velocity of the initial state. The group velocity is a measures the dispersiveness of the band. The case that the initial state is from a flat band we have $v_{h}=0$, and the $\Gamma_{\text{intr}}=\Gamma_h$. It holds for surface states or two- and one dimensional electronic states. Therefore, in these low dimensional systems one does
have the possibility to **measure the imaginary part of the self-energy directly.**

The extrinsic part of the broadness is mainly result of the photon linewidth, analyzer resolution and the thermal effects.

### Symmetry Selection Rules

A direct consequence the electrical dipole interaction is the parity selection of the initial state. The $H_{\text{int}}$ has a odd symmetry and therefore couples states with opposite parities. However, if we define the parity to be related only to the mirror symmetry of the scattering plane, $H_{\text{int}}$ is **odd** for p-plane polarization and **even** for s-polarization: Taking the plane-yz in figure 3.2 as scattering plane, one obtains:

- $H^p_{\text{int}}(-x, y, z) = H^p_{\text{int}}(x, y, z)$ (even)
- $H^s_{\text{int}}(-x, y, z) = -H^s_{\text{int}}(x, y, z)$ (odd)

If the emission direction lies in the scattering plane, the final one-electron state wavefunction, $\Phi_f(k_f)$, is **even** with respect to the symmetry operation of the scattering mirror plane [6]. Consequently, neglecting spin-orbital interaction, the p-polarization can probe only the initial even states, $\phi_i(-x, y, z) = \phi_i(x, y, z)$, and the s-polarization, the odd states, $\phi_i(-x, y, z) = -\phi_i(x, y, z)$. Remember that odd and even symmetries are in respect to the mirror symmetry of the scattering plane.

### Free-Electron Final-State Model and

**momentum conservation in vicinal surfaces**

Assuming that the final state is a free-electron, the dispersion relation is:

$$E_f = \left(\frac{\hbar^2}{2m^*}\right)(k + G)^2 - |E_0|$$  \hspace{1cm} (3.20)

where $m^*$ is the effective mass, and the energies are measured with respect to the Fermi energy. The $E_0$ is the band bottom of the final electron dispersion and is given by $|E_0| = V_0 - E_v$. The $E_v$ is the vacuum energy and $V_0$ is the inner potential, which is adjusted in such a way that the agreement between experimental and theoretical band structure for the occupied states is optimal.

Due the missing of the perpendicular periodicity is not possible to know the perpendicular component of the crystalline momentum of initial state. Anyway, keeping the approximation
of free-electron final state we can model the potential at surface as a step potential that acts only in the perpendicular component of $k$, resulting in the relation:

$$\hbar k_{\perp}^{\text{final}} = \hbar k_{\perp}^{\text{initial}} - \sqrt{2mV_0}$$  \hfill (3.21)

The momentum conservation using this relation is depicted in Figure 3.10. Disregarding the non rigorousness of such approximation, it is useful tool to understand the relationship between the angular distribution and the electronic dispersion.

![Figure 3.10 - Momentum conservation in photoemission process in the free-electron final state model. The parallel component of the photoemitted electron is equal to the initial state, whereas the perpendicular component is equal to the initial state subtracted of ($K_{\perp}$)$_{\text{min}}$.](image)

The photoemitted electron conserves the component of momentum parallel to the optical plane. In vicinal surfaces the optical plane is tilted in relation to the terraces by an angle $\theta$. A specific state probe from a flat surface (in the terrace direction) at angle $\theta_1$ from the surface normal can be also probe from a vicinal surface at angle $\theta_2$ from this surface normal(Fig. 3.11). The difference $\theta_1 - \theta_2$, however, can be different from $\theta$. It happens because the refraction is different for each plane and it is a function of the kinetic energy, and consequently of the incident photon energy.
Figure 3.11 - Extended zone scheme of the ΓXWK mirror plane in the bulk Brillouin zone of copper. The relative orientation of the flat (100) and vicinal (610) surfaces is indicated, the angle between the two surfaces is θ = 9.5. Using the free electron final state approximation, the probed state (represented by square) is measured at different angles from the two surfaces; (110) and (610). The dashed lines show additional step-induced umklapp $k_\parallel + g$. In this relation $g = 2\pi/d$ where $d$ is the translation vector between neighbouring steps.

In photoemission, the final state can be scattering by the periodic superstructure of the steps, adding in the parallel component of moment, $k_\parallel$, multiples of vector $g = 2\pi/d$, where $d$ is the periodicity of steps. Such effect is referred in literature as umklapp scattering. In figure 3.11 we see dashed lines point to the umklapp directions, $k_\parallel + g$. The open triangles represent states that may be measured at angle $\theta_1$ due to the umklapp scattering, altering the original peak intensity of the photoemission. However, Matzdorf and Goldmann [8] concluded that the umklapp scattering of bulk states can be neglected.
3.4 - Magneto-optic Kerr Effect (MOKE)

The rotation of the polarization plane of a light reflected by polished electromagnetic pole was discovered in 1898 by John Kerr and since the phenomena is known as the magneto-optic Kerr effect (MOKE). Though a phenomenological description of these effects was quickly achieved within Maxwell’s electromagnetic theory a correct microscopic theory of magneto-optic effect in a quantum mechanical framework was proposed only in 1955[9].

In a standard MOKE experiment, the magnetic state of the sample is studied by the measuring of polarization or intensity change of the reflected polarized light; such change is, in first approximation, proportional to the magnetization of the sample. Unfortunately it is almost impossible to extract the absolute value of the magnetization and the Kerr effect is used mainly to record its relative variations under the application of an external magnetic field, generating a hysteresis loops. The Kerr effect is also detectable in ultrathin magnetic films. The study of the ultrathin iron films on gold, using this technique, started in 1985 under the acronym of SMOKE which stands for surface magneto-optic Kerr effect [10]. Due to the relative high probing depth (about 20nm for visible light) the Keer intensity depends linearly on the film thickness, at least for films smaller than 10 ML.

![Faraday and Kerr effect](image)

**Figure 3.12** - In the magneto-optic Kerr and Faraday effects transitions occur between filled and unfilled electronic band states through linearly polarized light: the right and left circularly polarized components may be absorbed differently and the emitted (reflected or transmitted) radiation will then reflect this imbalance.
Microscopically, the coupling between the electrical field of the light and the electron spin within a magnetic medium occurs through spin-orbit interaction. The figure 3.12 depicts the transition in the Kerr effect. Different from the x-ray techniques, as will see later, the light in a Kerr experiment excites the valence band electrons to the conduction band.

Macroscopically, magneto-optics effects arises from the antisymmetry in the off-diagonal elements in the dielectric tensor, in presence of a magnetic field. It implies in a non vanish off-diagonal components in the reflectivity tensor and a modulation of its diagonal components. The reflected and incident light can be related through the reflectivity tensor as

\[
\begin{bmatrix}
E_s' \\
E_p'
\end{bmatrix} =
\begin{bmatrix}
r_{ss} & r_{sp} \\
r_{ps} & r_{pp}
\end{bmatrix}
\begin{bmatrix}
E_s \\
E_p
\end{bmatrix}
\]

(3.22)

Where the electric field is decoupled in p-plane and s-plane polarization. The s, p and d orientation are depicted in Fig. 3.6. Depending on the relative orientation of the magnetization compared to the light incidence plane (scattering plane) and the surface plane, one distinguishes the polar, longitudinal and transverse (or equatorial) Kerr effect (Fig. 3.13)
Transverse Kerr geometry

In transverse Kerr effect, the magnetization lies in the film plane perpendicularly to the scattering plane [Fig. 3.14(c)]. Describing the interaction between electromagnetic wave and matter as a classical oscillatory motion of electrons, one concludes that, in this geometry, the magnetic vector perturbs only the components of electrons motion that is parallel to the scattering plane. Such perturbation can be modelled as an equivalent electrical field $E'_d$, along the $d$ axis (see Fig. 3.13), that is given by:

$$E'_d = a \cdot (M \times E_p) \quad (3.23)$$

Where $a$ is a complex number constant that carries the dielectric and permeability properties of the material; $E_p$ is the component of the light parallel to the scattering plane (see Fig. 3.13) and $M$ is the magnetization vector. The vector $E'_d$ is always parallel to the scattering plane; it doesn't add to the off-diagonal components of the reflectivity and neither affect the $r_{ss}$ component. The component $r_{pp}$, on the other hand, in first order, gets modified as:

$$r_{pp} = r_{pp0} + \frac{E'_d \cdot \hat{d}}{E_p} \left( \frac{2 \eta_1 \eta_2}{\eta_1 \cos \theta_2 + \eta_2 \cos \theta_1} \right) \cos \theta_1 \sin \theta_2 \quad (3.24)$$

where $r_{pp0}$ is the ordinary reflectivity in the absence of $M$; and $\eta$ is the refractive index.

Summarizing, if the incidence light is p-polarized, the reflection in the transverse geometry does not rotate the polarization but alters the intensity and the phase of light. No effect is observed for an incident s-polarized light and a small effect is present for a normal incidence (second order effect).

Polar Kerr geometry

In Polar Kerr effect, the magnetization vector is normal to the interface. Unlike the transverse geometry, the magnetic field vector lie in the scattering plane, it induces an additional electric polarization along the vector $s$ for p-polarized light and with components along $p$ and $d$ for a s-polarized light. It results in the coupling of the s and p–polarized waves, changing in magnitude and phase of the off-diagonal components of the reflectivity tensor; $r_{sp}$ and $r_{ps}$. The reflected light is elliptically polarized with the major axis rotated with respect to linear polarized incident light. The effect is maximized when the incident light is normal to the surface, i.e. parallel to $M$: Considering for instance a light polarized
along \( p \), the electrons motion will be deviated by \( M \) to the \( d-s \) plane, maximizing the transfer of part of the \( p \)-wave energy to the \( s \)-wave. The measurement of Keer rotation consists in the measure of the relation of the intensities \( E_s/E_p \).

**Summarizing, the reflection in the polar geometry does rotate the light polarization, the effect is observed for \( p \) and \( s \)-polarization and is maximum at normal incidence.**

**Longitudinal Keer geometry**

In the longitudinal configuration, \( M \) lies along the intersection of the interface and plane of incidence. Likewise the polar geometry, the \( M \) field changes the phase and magnitude of diagonal and off-diagonal reflectivity components, producing a elliptical polarization and rotation of the polarization of the reflected light. At normal incidence the geometry is reduced to the transverse one, and, therefore no Kerr effect can be measured.

![Figure 3.14](image-url)

**Figure 3.14.** The three MOKE geometries: polar (a), longitudinal (b) and transverse (c) magneto-optic Kerr effect. \( E \) denotes the incident polarization vector, \( N \) the regular component of the reflected light and \( R \) denotes the perpendicular part of the Kerr amplitude after reflection.
Setup:
The MOKE setup (see Fig. 3.15) mainly consists of three components: a light source to illuminate the sample, an electromagnet to apply a magnetic field to the sample and a photodiode detector to measure the reflected intensity of light.

Figure 3.15 Scheme of MOKE apparatus.
3.5 X-ray Absorption (XAS) and X-ray Magnetic Circular Dichroism (XMCD)

The XAS technique consists in the analysis of the line shape of the light absorption spectra in the X-ray energy range, such range can be covered by a synchrotron light source. Photons in this energy range cause excitations of localized 2p core level electrons into empty 3d final states in transition metals like Mn, Fe, Co, Ni, Cu.

The absorption spectra line presents a characteristic jump when the probing photon energy matches the energy difference between the 2p core level and the first unoccupied state above the Fermi energy. These jumps is called L edges, and its energy position (binding energy) is specific for each element (Fig. 3.16). The intensity of this transition and the line shape of the absorption is strongly influenced by the chemical environment and magnetic order of each species.

![Absorption spectra](http://www-ssrl.slac.stanford.edu)

**Figure 3.16 – Element Specificity of the XAS technique** [http://www-ssrl.slac.stanford.edu].

The absorption measurement can be done directly by the measure of the transmission light (Fig 3.17 - a) or indirectly either by the measure of the emitted photon (photon yield) due the excited electron decay (Fig 3.17 b) or by counting the ejected electrons (electron yield) by Auger process, trigged by the decay of the core hole created by the probing photon, and the secondary electrons, resulted from the secondaries scattering of the excited electron. The electron yield method is so far the easiest way to measure the absorption, it can be measured by an ampermeter connected between sample and ground as depicted in figure 3.17-c, or by a collector electromagnetic lens system with gain in spatial resolution. The figure 3.18 shows the Auger process in detail. The current measure by the ampermeter in the electron yield method is a sum of the direct photoemission plus
Figure 3.17 – Methods of obtaining x-ray absorption signal. (a) Transmission method measures the relation between the transmission ($I_t$) and initial photon intensity ($I_0$). (b) The fluorescence yield method measures the photon released from the relaxation of a atom excited by $I_0$. (c) Electron yield method measures the number of electrons emitted by Auger process.

Figure 3.18 – XAS photon absorption and electron emission process. Panel 1, absorption of photon/creation of core hole; panel 2, decay of core hole; panel 3, escape of high-energy (Auger) electron or low-energy electron cascade; panel 4, energy distribution of electrons contributing to total-electron-yield signal. [12]

the Auger and the secondary Auger electrons, the XAS signal is proportional only to these
two last. In the measure using the collector lens the entrance energy is set to at the secondary electrons, which has the most intense peak (Fig. 3.18-4).

The XMCD technique consists in to measure the difference between two XAS spectra acquired with circularly polarized light of opposite helicity. The measure usually is done in presence of a magnetic field to probe the magnetic ordering. The case of L2,3 edges of 3d metals (2p → 3d) is of particular interest because the final state probed by the transition are the 3d energy states, which determine the ferromagnetic properties of these metals.

The qualitative understanding of the XMCD phenomena is easier achieved by the use of the atomic model, which is sometimes called configuration picture. Let us first review some concepts of atomic angular momentum. For light atoms (Z<30) one can use the LS-coupling approach:

\[
L = \sum_{i} l_i \quad ; \quad S = \sum_{i} s_i \quad ; \quad J = L + S \quad (3.25)
\]

The \(l_i\) and \(s_i\) are the orbital and the spin quantum number of the ith electron. \(L\) is the total orbital angular momentum; \(S\) the total spin momentum. \(L\) and \(S\) combine to form the total angular moment \(J\). The z-projection \(m_j\) can assume the values \(m_J = j, j-1, \ldots, -j\), where \(j\), the total angular momenta quantum number, represents the maximum value of z-component. The Fig. 3.19 shows a example of LS-coupling.

\[\text{Figure 3.19 – LS-coupling between } L \text{ (l=1) and } S \text{ (s=1/2). Note that this coupling can produces two different vectors } J: j=1+1/2 \text{ and } j=1-1/2.\]

As a consequence of the electron-dipole interaction between light and matter, the electronic transition obeys the follow selection rules concerning the angular momenta:

\[\Delta J = 0, \pm 1 \quad ; \quad \Delta m_J = \sigma \quad ; \quad \Delta L = \pm 1 \quad (3.26)\]
where $\Delta J$, $\Delta m_J$, and $\Delta L$ is the change of total angular momentum, the angular quantum number and the total orbital angular momentum; and $\sigma$ stands for the elicity of light in $\hbar$ units: $\sigma=\pm 1$ corresponds to left (right) handed circularly polarized light and $q = 0$ corresponds to linearly polarized light. The circular dichroism is a consequence of the selection rules (3.26) and the unbalanced number of electrons with a specific spin state.

In a ferromagnet, the net magnetization is caused by the fact that the total energy is lowered when neighbouring spins are aligned parallel (exchange energy). For this reason electronic states with a particular $m_J$, for example corresponding to a spin down configuration, are preferentially occupied. This is illustrated in the figure 3.20, we see the transition $2p^63d^9 \rightarrow 2p^53d^{10}$ in which the total angular momenta change $(L=2, S=1/2) \rightarrow (L=1, S=1/2)$ is represented by the atomic states $^2D \rightarrow ^2P$.

![Total Magnetization](image)

**Transition rules:**

- $\Delta S = 0$
- $\Delta L = \pm 1$
- $\Delta J = 0, \pm 1$

**Fig. 3.20** - Possible optical transitions from a 2D state to a 2 P. The s initial total angular momenta $L=1$ and total spin momenta $S=1/2$. The net magnetization is given by the majority spin down states is represented by $^{32}P$.
thicker lines mj states. The XMCD spectra (at bottom-left) is the difference between the absorption spectra (adapted from [13])

The light gray areas represent the probability of an electron to populate the corresponding mj level in the ground state. The probability is inverted with respect to mj between the 2D_{5/2} and 2D_{3/2} state, because the spin-orbit coupling is opposite in these two states.

The total L_{2,3} absorption intensity for either left or right circular polarization can be obtained by adding the possible transitions weighted with the occupation of the particular sub level that has been excited. In a metallic 3d ferromagnet the mj sub levels are only separated by a few meV and therefore the different transitions are usually not resolved in an XAS experiment. Therefore the absorption peak L_{2,3} is simply the sum of all mj contributions.

![Image of XAS and XMCD spectra of Fe at the L2,3 edges. The XMCD spectra is the difference between the XAS spectra: I↑↑ - I↓↓](image)

**Figure 3.21** – XAS and XMCD spectra of Fe at the L2,3 edges. The XMCD spectra is the difference between the XAS spectra: I↑↑ - I↓↓

The orbital and spin contribution to magnetism can be calculated as [14]:

\[
m_{orb} = -\frac{4}{3} \frac{1}{P \cdot \cos \phi} \frac{A_{ML3} + A_{ML2}}{A_{iso}} \left( 10 - n_{3d} \right)
\]

\[
m_{spin} = \frac{2}{P \cdot \cos \phi} \frac{A_{ML3} - 2A_{ML2}}{A_{sum}} \left( 10 - n_{3d} \right) \left( 1 + \frac{7}{2} \left\langle T_z \right\rangle \right)^{-\frac{3}{2}}
\]

where the \( A_{MLx} \) is the area correspondent to the hatched area in the fig. 3.21; the value n3d is the number of electrons occupying the 3d levels, typically a fractional number. \( \left\langle T_z \right\rangle \) is the expectation value of the magnetic quadrupole, for cubic symmetry this value is very
small and the last term in (3.28) is usually omitted.

References:


CHAPTER 4

Experimental Setup

4.1 Synchrotron Radiation Source

4.2 APE beamline at Elettra Synchrotron
   4.2.1. The Low Energy chamber
   4.2.2. The High Energy chamber
   4.2.3. The STM chamber
   4.2.4. The KERR (Preparation) chamber
Chapter 4 - Experimental Setup

All the experiments were as carried out in the APE (Advanced Photoemission Experiments) laboratory of synchrotron light facility of ELETTRA. In this chapter, it will be presented an overview about synchrotron light and the description of the apparatus available in the APE laboratory.

4.1 - Synchrotron Radiation Source

In the 40s and 50s, many particle accelerators were constructed in order to study the nuclear and elemental particle physics. In a synchrotron accelerator, the accelerated charged particles are confined in circular orbitals by magnetic fields. Those accelerators were used in subatomic collision experiments, in which a particle has to be accelerated up to velocities close to light velocity. In this process, the principal cause of energy loss is the electromagnetic radiation that is produced when the particle trajectory is deflected; the bremsstrahlung effect.

Soon the scientists noticed that a smoothness and continuity of the spectrum of such electromagnetic radiation, which covers the energies from the infrared to the X-ray. The synchrotron radiation attracted many material scientists that developed different kinds of spectroscopic techniques. In that time, the work that used the synchrotron radiation was considered a secondary work in comparison to the high energy collision experiments. The first synchrotron constructed specifically for light experiments was the Tantalus, in Wisconsin (1968). From 70s the synchrotron technology changes from the minimization of synchrotron radiation, which privileges the high energy subatomic experiments, to maximization of such radiation for the use in material science. Today the majority of the synchrotrons is dedicated to spectroscopic experiments, these synchrotrons can be classified in first, second and third generation.

In the first generation synchrotrons, the light is collected from a device called “bending magnet”. The bending magnet produces a simple constant magnetic field perpendicular to the orbit plane, used for deviating the electrons. The radiation emitted from the electrons in
such device presents a continuous spectrum and is linearly polarized in the plane of the orbit and partially circularly polarized above and below the orbit plane with opposite phase. We can consider as first generation synchrotron those ones where the light experiments are realized along with the colliding-beam experiments.

The second generation synchrotrons use insertion devices called “wigglers” and “undulators” to increase the light intensity. The wigglers are composed of a series of strong magnets one after another with alternating magnetic fields. Those magnetic fields are used to obtain the electron trajectories to “wiggle” inside this device, then producing the radiation with an intensity $2N$ times larger than that of an equivalent bending magnet, $N$ is the number of magnet periods. Because the magnetic fields are “strong”, the radiation emitted at every curve is summed incoherently then producing photons with spectra similar to those of bending magnets and linearly polarized radiation only in the plane of the orbit. The undulator operation is similar to wiggler, except that in the later the radiation is taken only from the peak part of the trajectory amplitude, whereas the undulator uses the radiation from the whole electron trajectory. The undulators are usually longer (more dipoles) and have weaker magnetic fields, such that radiation sums coherently. The intensity is $N^2$ that of the equivalent bending magnet. The polarization can be tuned and the energy spectrum is not continuous, but characterized by a series of spectral lines due to the interference: the fundamental and the (odd) harmonics. Despite the discrete spectrum, the energy can be tuned varying the undulator gap: the aperture between the magnets. The wigglers and undulators are called insertion devices because they are

![Figure 4.1: Wiggler. The wavelength distribution of the emitted light is a function of the gap $g$ between the dipoles. The period and phase molds the focus and polarization of the light beam.(from http://www-project.slac.stanford.edu/)](http://www-project.slac.stanford.edu/)
placed in one of the generally empty straight sections that connects the curved arcs, where the bending magnets are set.

The third generation synchrotrons are characterized by still higher light intensity and better energy resolution. The higher intensity was mostly obtained by the optimization of the insertion devices that became also longer. Efforts to reduce the emittance angle and improve the collimation permitted the use of longer monochromator mirrors, resulting in an energy resolution of the order of meV. The synchrotron light facility Elettra is an example of third generation synchrotron.

**Figure 4.2.** Layout of a storage ring. The inner booster ring provides accelerated electrons. In the left-bottom panel a zoom of a period of the storage ring indicating the position of the main constituent devices, between which the bending magnets.
4.2 - APE beamline at Elettra Synchrotron

The beamlines are the laboratories attached to the storage ring where the light is collected, conditioned and led to the experimental chambers. The APE beamline is constituted by two branches; the High-Energy (HE) and Low-Energy (LE) branch, each one using the radiation from different undulators. The HE branch works with photon energy ranging from 200 to 1600eV used for absorption and core-level photoemission experiments. The LE branch has been built for ARPES experiments and works with photon energies ranging from 10eV to 150eV. There are two extra chambers: Keer and the STM chambers. The Kerr chamber is used for sample preparation and measurement of Magneto-Optical Kerr Effect (MOKE). Scanning Tunnel Microscopy (STM) at room temperature is available in the STM-chamber.

All the chambers are interconnected through UHV transfer chambers. The figure 4.3 shows the layout of the APE beamline. Two photon beams coming from their respective undulators (not show in the picture) arrive in the pre-focus mirrors forming an angle of 2mrad to each other. The beams are deviated to the HE and LE branch, where they are monochromatized and refocused onto a 150x75 micrometer spot on the sample surface in the HE and LE chambers. The HE branch monochromator operates in the 200-1600 eV energy range by means of three different grating of 900, 1400 and 1800 lines/mm, each on dedicated at a different energy range. The LE branch monochromator operates 10-140 eV also using three different variable spacing grating; 700, 1200 and 1600 lines/mm.

![Figure 4.3 – Layout of APE beamline](image-url)
4.2.1 - The Low Energy Chamber

The Low Energy (LE) chamber is dedicated to valence band photoemission experiments. It is kept in Ultra High Vacuum (UHV) by two turbo pumps, one ionic pump and a Ti sublimation pump. The base pressure is around 1E-10 mbar, but when the system is cooled, the pressure can reach values lower than 5E-11 mbar. The chamber is equipped an ion gun, used with Ar to ion sputter the sample surface and with a LEED apparatus, which permits one to check the crystalline quality of the sample surface. Extra flanges are available on the chamber walls to install metal or molecular evaporators and to mount the quartz microbalance for evaporator calibration.

The photoemission intensities and directions in the ARPES experiment are measured using a dispersive sector electron energy analyzer Scienta SES2002. The SES-2002 collects electrons in a 14° × 0.5° solid angle. The electron detector has an angular acceptance of 14° window with more than 100 angular channels. The angle between analyzer inlet and the photon beam line is fixed at 45°. The nominal angular resolution is 0.2°. The energy resolution, in the best case, is 2meV.

At the APE beamline the scattering plane coincides with the horizontal plane which contains the storage ring electron orbit. The manipulator rotation angles are determined with respect to the scattering plane: polar angle $\theta$ is the angle between the sample normal and the electron analyzer axis. When $\theta=0°$ the surface is perpendicular to the analyzer axis, the so-called “normal emission condition”, and the electrons are collected in the $-7°<\theta<+7°$ angular region. In order to extend the measurement region the polar angle is turned, for example to a value $\theta_i$, and the electrons are collected in the $\theta_i-7°<\theta<\theta_i+7°$ region. The other angular degree of freedom is the azimuthal angle $\Phi$, the rotation of the sample about the surface normal. The chamber has two interchangeable manipulators: the RIAL© and the Irchel. The RIAL manipulator can be cooled with liquid helium reaching 12 Kelvin, and is designed to use the APE standard sample holder (Fig 4.4-b), allowing the sample transferring through all the APE chambers. In the Irchel manipulator, the changing of polar and azimuthal angle are computer automatized with the accuracy of 0.5°, what is suitable for Fermi surface mapping experiment. The lowest temperature is 80 kelvin, using liquid helium. The design of sample holder is completely different from the APE standard (Fig 4.4-a), what requires some kind of tricky adapter to transfer the sample.
through the different chambers.

![Sample holders](image)

**Figure 4.4** – Sample holders used for Irchel manipulator (a) and the APE standard sample holder (b).

### 4.2.2 - The High Energy chamber

The HE chamber is dedicated to absorption core level photoemission experiments. The chamber is kept in Ultra High Vacuum (UHV) by an ionic pump and a Ti gathering pump. The usual pressure is around $3 \times 10^{-10}$ mbar, but when the system is cooled, the pressure can reach values lower than $5 \times 10^{-11}$ mbar.

The chamber is equipped with a position controlled manipulator with 0.01 mm of spatial resolution that allows the automation of the sample mapping. The spot size on the sample, after the refocusing of the toroidal mirror, was about 200x100 $\mu$m (horizontal x vertical) in our experiments. The manipulator can change only the polar angle, the azimuthal angle is fixed. A small coil, which fixed position in reference to sample, is used to magnetize the sample in the XMCD measurement.

The photoemission intensities in the XPS are measured with a hemispherical electron energy analyzer (Omicron EA 125). The analyzer inlet is centered at 45° from the photon beam line. The best achievable instrumental resolution is about 10 meV. For absorption experiments we can measure in total electron yield mode by monitoring the sample current extracted from the ground and read by a Kethley picoampermeter, or in partial electron yield mode by means of an in situ channel electron multiplier operated alternatively in current or pulse counting mode. A photodiode detector or in alternative a semi-transparent molybdenum mesh is used to measure the intensity of the beam entering the HE end station which is used to normalize the recorded spectra.
4.2.3 - The STM Chamber

The STM chamber is a small chamber designed for STM measurements in RT. It is kept in 1x10^-10 mbar by one ion pump (mechanical pumps would produce a prohibitive level of noise for STM using). The chamber has a stage where the STM tip is fixed and where the sample plus sample holder are placed for the scanning. The sample is positioned in front of the tip pushed by a fork wobble-stick, the final approach, which set the sample at tunneling distance from the tip, is done by an inertial sliding system performed by a piezoelectric set below the stage platform. All the stage is hung by a system of 4 springs; the oscillatory shear vibration is damped by a magnetic eddy-current system.

Figure 4.5- The interior of the STM chamber.
4.2.4 - The KERR (Preparation) Chamber

The sample preparation is carried out in the KEER chamber. The chamber is equipped with an ion-gun, used for back-sputtering; and a copper heating stage, used for annealing when a precise temperature control is required. The heating is done by electron-bombardment from a tungsten filament placed behind of the stage, and the temperature is measured by mean of tungsten-rhenium thermocouple (Wre3/WRe25); the maximum temperature is 650°C. For higher temperatures the annealing can be done directly at the molybdenum manipulator by electron bombardment; the maximum temperature is about 1000°C. The temperature measurement, however, done by thermocouple, is not precise in this manipulator. In any case, for temperatures above 400°C, it is possible to use an electronic pyrometer for temperature calibration.

For the surface characterization, it is available LEED/Auger instrumentation: LEED apparatus is a rear-view 4-grid SPECTALEED optics by Omicron, with the EG&G lock-in amplifier for Auger spectroscopy; the size of the electron beam on the sample is less than 300 μm. This chamber also has a set of flanges that allow the installation of up to three different evaporators. There is a retractable water cooled quartz microbalance for the evaporation flux calibration and a molybdenum mask, used for the growth of wedge films.

The MOKE experiment is performed using a set of four fixed coils: Three coils are assigned to measure the polar, longitudinal and transversal KEER effect, with maximum field of 500 Oe. The fourth one is assigned only to polar KERR, with the maximum field of 1500 Oe. The laser diode (ILEE LDA-2000 model: λ = 675 nm, P < 40 mW) plus the focussing lens system are mount externally on two view-port flanges. A Glan-Thompson prism polarizer is used to polarize the incoming light in p-polarization, and the other Glan-Thompson prism polarizer, out of phase 90° to the first one, is used to measure the polarization rotation caused by the KERR effect. A photodiode provides a photocurrent proportional to the intensity of the reflected light: the current is converted to voltage and amplified. Computer controlled hysteresis loops are taken by setting the coil current and reading the MOKE signal via an ADC converter. To improve the signal to noise ratio, several hysteresis curves are taken and averaged.
The Kerr Manipulator

The KEER chamber has a manipulator that allows the positioning of the sample for the different procedures available in the chamber. The manipulator arm has an 'L' shape, with a liquid nitrogen cryostat on the top end. We have designed improvements that allowed the freedom at polar angle, which is important for grazing sputtering; and the increasing of thermal contact between the sample holder and the colder finger (Fig 4.6).

![Figure 4.6 – The Keer manipulator, front(a) and side (b) view. The rotation and the lock system are handled by screw-driver stick.](image)

4-10
CHAPTER 5

Structural Characterization of the oxidized Cu(332)

5.1 Oxygen-induced Surface Faceting in Vicinal Copper

5.2 Experimental Details

5.3 Cu(332) Surface Oxidation and Morphological Analysis
Chapter 5 - Structural Characterization of the oxidized Cu(332)

In this chapter we will describe the substrate cleaning procedure and the preparation of the oxidized Cu(332) surface as well as its characterization by LEED and STM in ultra-high vacuum.

5.1 - Oxygen-induced Surface Faceting in Vicinal Copper

The oxygen exposition of vicinal Cu(n,n,n-1) surfaces induces the formation of (110) facets in the surface, where the oxygen gets adsorbed in a (2X1) superstructure [1]. The oxidized surface consists of alternating Cu(111) terraces and Cu(110)-O(2x1) facets (Fig 5.1). The average size of the (110) facets determines the periodicity of the overall reconstruction. In our study, we found that the reconstruction periodicity can be tailored by the exposure condition. We expose the clean Cu(332) surface to oxygen gas with pressures ranging from 5e-8 to 2e-7 mbar at different substrate temperatures, following by 10 min of annealing. The control of the (110) facets size and consequently the reconstruction periodicity is very sensitive to the exposure and annealing temperature.

Figure 5.1- Geometry of the oxygen-induced reconstruction: the blue facets represents the (110) planes where the oxygen atoms (blue balls) are adsorbed, the red lines represents the (111) terraces. The structure periodicity is given by the distance $a$.

The geometry of the reconstruction is explained in figure 5.1, from where we obtain the following relations:

$$d_{110} = 0.30 \cdot a \quad d_{111} = 0.74 \cdot a$$
\[
\frac{d_{110}}{d_{110} + d_{111}} = 0.29
\]

Later we will see that the STM images show the presence of a monoatomic step with adsorbed oxygen at edge between the (110) and (111) facet. But by now, let us neglect this in order to facilitate the following discussion.

In the adsorption of oxygen on a flat Cu(110), the molecular oxygen from the gas phase dissociates at the surface and combines with the Cu adatoms forming Cu-O-Cu atomic chains, which grows along the [100] direction.

Let us make a rough estimate of the gain in energy of the reconstructed Cu(332) surface. Considering the reconstructed vicinal surface as series of alternating Cu(111) and Cu(110)-facets (without O-Cu chains), we can use the values of the surface energy \( \gamma \) of the Cu(111), 1.31 J/m\(^2\), and Cu(110) 1.53 J/m\(^2\), both calculated by DFT (see Appendix A.), in order to have an estimate of the average surface energy in the reconstructed Cu(332):

\[
\gamma_{\text{Cu}(332)}^{\text{rec}} = d_{110} \cdot \gamma_{\text{Cu}(110)} + d_{111} \cdot \gamma_{\text{Cu}(111)} = 1.43 \text{ J/m}^2
\]

where we have taken into account the surface area increasing of 4%. This value should be compare to the surface energy of Cu(332), \( \gamma_{\text{Cu}(332)} = 1.46 \text{ J/m}^2 \), what means that the faceted surface would be the stable configuration, at least at 0K. The same conclusion holds for several vicinal metals [7]. However, the surface faceting does not happen at finite temperatures thanks to the contribution of the steps edge for the reducing of the free energy, \( \gamma \), by means of the increasing of entropy, S. The total energy \( E_{\text{surf}} \) of a surface is:

\[
E_{\text{surf}} = TS - PV + \mu N + \gamma A
\]

resulting in

\[
\gamma = \frac{1}{A} \left( E_{\text{surf}} - TS + PV - \mu N \right)
\]
There are two sources for the increasing of $S$: the step meandering over surface and the thermal vibrations of the vicinal surfaces. The second source is the most important; the reduced coordination of the step atoms on a vicinal surface makes the average vibration amplitude of the edge atoms significantly higher than the vibration amplitude on low-index surfaces [7]. As a consequence, the excess vibrational entropy of a vicinal surface is higher than that of the corresponding low-index facet combination, which is enough to stabilize the stepped surface and avoids the faceting.

In our system, we believe that the two forms of contribution for entropy are inhibited by oxygen adsorption. As will see later, the oxygen has an energetically stable position at the four-fold coordinated site at step edge (see Appendix A). We suggest that the adsorption occurs first in such sites, what would inhibit the meandering of edge atoms and also change the vibrational properties of the vicinal structure, reducing the contribution for the surface entropy. The reduction of entropy would favour the faceting of the surface. Moreover, the formation of the (110) facets allows the assembling of the Cu-O chains, which contributes drastically with the reduction of the total energy. Lier et al. [5] calculated that the gain in energy for (2x1) oxygen reconstruction in the flat Cu(110) is -5.28 eV for O-Cu-O chain.
5.2 – Experimental Details

The Cu(332) surface is vicinal to the Cu(111) forming 10.0° and exhibits monoatomic steps with (11-1) microfacets and (111) terraces. According to the hard-ball model the terraces consist of 5 1/3 atomic rows (l=1.2 nm).

The sample was a single crystal with nominal miscut of 10°, characterized by X-ray diffraction. The clean surface was obtained in UHV (p<1e-10 mbar) by repeated cycles of Ar-ion sputtering at 650 eV and annealing at 500°C followed by slowly cooling to RT. The surface order was checked in situ by LEED and STM (Fig. 5.2).

![Figure 5.2 – LEED (a) and STM (b) image of the clean Cu(332). In (a) the relation a/b ~ 5.5; the inset image in (b) shows the step in atomic resolution. The electron energy in (a) is 72 eV and the STM images were acquired with $I_{\text{set}}=1\text{nA}$; and $V_{\text{bias}}=-1.0 \text{ V}$ for the large image and $V_{\text{bias}}=-4 \text{ mV}$ for the inset image.](image)

The LEED show a hexagonal pattern composed by sharp spots as expected for a clean and well ordered surface. The splittings in the [11-2] direction are caused by an additional diffraction at the periodic monoatomic steps. The ratio between a split and the spots distance along the [112] direction, a/b, multiplied by the interatomic distance in the plane results in a periodicity of 1.2 nm for the steps (see Fig. 5.2-a). The same periodicity was found as average periodicity in the STM (Fig. 5.2-b).
5.3 – Cu(332) Surface Oxidation and Morphological Analysis

The oxygen exposure was carried out by the backfilling for the preparation chamber to pressures from 5x10-8 to 2x10-7 mbar. High purity Oxygen (Messer Grisheim – 99.998% purity) was admitted in the UHV chamber from a calibrated sapphire leak valve operated manually.

![STM images](image)

**Figure 5.3** - STM topographic images of the (a) 4nmOCu332, periodicity=3.8 Å; (b) 6nmOCu332 and (c) 10nmOCu332. A high resolution image is shown as a inset in (a). In all the images the sample voltage was -1.45 V and the tunneling current amounted to 0.3 – 0.8 nA. The period size distribution is shown below the STM images.

We optimized experimentally the exposure parameters for three ranges of periodicity showed in table1. For the structural analyses, we prepared the surface with three different reconstruction periodicities. In order to simplify the discussion, the reconstructions are labelled according to the periodicity of stripes as 4nmOCu(332), 3.7 nm average periodicity; 6nmOCu(332), 5.7 average periodicity and 10nmOCu(332), 9.7 average periodicity. The STM images of the three surfaces can be seen in fig. 5.3.
Table 1. Dependence of the reconstruction periodicity with the exposure parameters.

<table>
<thead>
<tr>
<th>Periodicity average</th>
<th>3-4 nm</th>
<th>5-7 nm</th>
<th>10 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exposure</td>
<td>O₂ Pressure (mbar)</td>
<td>5E-8</td>
<td>1E-7</td>
</tr>
<tr>
<td></td>
<td>Time (min)</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Temperature</td>
<td></td>
<td>100°C</td>
</tr>
<tr>
<td>Annealing</td>
<td></td>
<td></td>
<td>100°C</td>
</tr>
</tbody>
</table>

The line scans placed as a inset images in Fig 5.3-b,c show clearly the (110) facet (positive slope) and (111) terrace (negative slope), the angle measured between the two slopes ranges from 28 to 35°, depending on the tip condition.

The observed LEED patterns of the oxidized Cu(332) present a hexagonal pattern, from the (111) terraces, plus a rectangular pattern, attributed to the (110) facets; as show in Fig. 5.4-a,b. The splitting of the hexagonal pattern along [112] direction is clearly observed in sample 4nmOCu332 (Fig.5.4-b). Selecting the primary electron energy of the beam such to avoid interference from the rectangular pattern (not shown), the ratio between a split and the spots distance along the [112] direction give us a periodicity of 3.7 nm for the stripes. The rectangular pattern from the 4nm sample is composed of fainter and more elongated spots (Fig 5.4-a) than those from 6nm one (Fig. 5.4-b). We ascribe this effect to the smaller size of (110) facets in the first case. Changing the polar angle of the manipulator, we could find the gamma specular reflection of the rectangular pattern facet at angle 35° from [111] (Fig5.4-c), in good agreement with the expected angle between (111) and (110) plane, 35.26°.
Figure. 5.4 - LEED image for the (a) 4nmOCu332, (b) and (c) 6nmOCu332. In (a) and (b), the hexagonal dashed line depicts the pattern of the (111) terrace. In (c), the LEED was taken at [110] direction. The ratio $a/b\sim\sqrt{2}$ of the rectangular pattern indicates a (2x1) superstructure on the Cu(110) facet. The electron energy is 70 eV for (a) and (b), and 92eV for (c). In (a) the contrast was locally enhanced at the (110) spots.

The ratio between the sides of the rectangular pattern in the LEED of (110) facet (Fig 5.4-c) and the comparison with the hexagonal pattern indicates a periodicity of 5.1 and 3.6 Å along [-110] and [001] directions, which is compatible with a (2x1) reconstruction on the Cu(110) facets surface.
The high resolution STM images (Fig. 5.5) reveal the presence of the O (2x1) reconstruction on the (110) facet. The Fig. 5.5-a shows O-Cu chains as bright stripes, which are equally spaced by 5.3 Å along the [-110] direction. Additionally, above the stripes, we observe a extra row of bright spots, also spaced by 5.3 Å but shifted of 1.27 Å from the O-Cu chains in the [-110] direction. The line scan along the O-Cu chain (Fig. 5.5-b), [001] direction, suggests a presence of a monoatomic step between the (110) and (111) facet, where the extra row is ascribed to the oxygen atoms on four-fold hollow site (or close to this position) on the step.
edge, as illustrated by the hard-ball model in (Fig 5.5-c). A similar geometry has been reported for the oxidized Cu(211) [4]. In addition, first principle calculation shows that the O atom is very stable in a position close to the fourfold hollow site [5].

An atom placed in different sites usually exhibits different local density of states (LDOS) which determines the bias dependence of the STM tunnelling current in that site position. Figure 5.6 shows that the bright spots row, attributed by us to the oxygen on four-fold hollow site, has higher intensity at small negative bias voltage, in which the tunnelling current probes occupied states near to the Fermi energy; whereas the O-Cu chains feature is more intense at higher negative bias, between -1.0 and -1.5 V. In order to explain the bias dependence we evaluated the projected density of states (pDOS) for the O atom in both sites performing first-principles calculation with the Quantum-Espresso package [6] (details in Appendix A).

![Figure 5.6](image)

**Figure 5.6** - STM image in different sample bias: (a) -1.48 V, (b) -0.80 V, (c) -0.47 V. The solid line rectangle indicates the O-Cu chains. The dashed line rectangle shows the position of the spots attributed to the four-fold coordinated oxygen. The images intensities were individually normalized. (d) The LDOS projection to oxygen atom in the four-fold (top) and O-Cu chain (bottom) sites. The red vertical lines mark the energies -1.48, -0.80 V and -0.47 eV.

A comparison between the pDOS of the O atom in four-fold hollow site and of the O atom in the O-Cu chain shows that the density of states is higher at energies near to the Fermi edge.
in the first case (Fig. 5.6-d). The bias dependence of the STM images in our samples is qualitatively compatible with this result.

We have measured a series of iv-curves positioning the tip over the (110) facet and (111) terrace. The typical curve for each position is shown in Figure 5.7. Through the dl/dv curves we can notice a depletion of electronic states in the (110) facet. In the next chapter we will see that the (110) facets confine efficiently, in the (111) terraces, surface states with energy close to the Fermi edge. One of the reasons for this confinement could be ascribe to the pseudo-gap in the (110) facet in the energy region where the surface state resides.

![Figure 5.7 - STS measurement. Typical iv-curve for the OCu(332). We see the iv curve for tip positioned over the Cu(111) terrace, on left panel; and positioned over the OCu(110) facet, on the right panel. The respective dV/dl curves are shown at bottom. The red (green) curve represents the bias voltage going to negative(positive) to positive (negative).]
Other Reconstruction Structure

The surface reconstruction of a specific periodicity is not stable over the annealing temperature. For example, when a sample with a periodicity of 4nm is heated over 100° C, the terrace width distribution becomes broader. At temperature higher than 260°C, the structure is completely changed from the well organized facets to a mix of facets and monoatomic steps as show in figure 5.8. The same behaviour is observed for other periodicities. The structure was not analysed in this work.

Figure 5.8 – STM topographic of OCu(332) surface annealing at 260°C : The surface
References:


CHAPTER 6

Angle-Resolved Photoemission Study of Oxidized Cu(332)

6.1 Experimental Details

6.2 Photoemission Spectra of Surface States in clean Cu(332)

6.3 Photoemission Spectra of Surface States in Oxidized Cu(332) (OCu(332))

6.4 Photoemission Angle Dependency of Bulk States in Cu(332) and OCu(332)
Chapter 6 - Angle-Resolved Photoemission Study of Oxidized Cu(332)

In this chapter we present the results obtained from the ARPES measurement. We start presenting the analyses of the L-Gap surface state of the clean Cu(332) and its modification for the oxidized surface. Finally we comment the momentum conservation of the photoemitted electrons from the bulk states. The fundamental concepts for better understanding of the results presented in this chapter can be found in *chapter 2*.

### 6.1 Experimental Details

The sample was mounted in an inclined sample holder in the way that the azimuthal axis is parallel to the [111] direction, not to [332] direction. The normal emission, $\theta=0^\circ$, is then relative to the [111] direction.

![Figure 6.1 – Geometry for the ARPES measurement](image)

Details of ARPES chamber and the further technical information of the photoemission can be found in *chapter 3* and *4*.

**Resolution**

The photoemission data presented here was acquired with the following settings: monochromator exit slit = 50 um; pass energy = 5eV; step energy = 5 or 10meV. The total energy resolution has contributions from beam and analyser resolution (instrumental resolution) and from the thermal broadening effect. The total energy resolution can be measured fitting the Fermi energy edge: The photoemission data at Fermi edge can be fitted by a convolution of the Fermi-Dirac with a Gaussian curve. The Gaussian FWHM gives the instrumental resolution. In our setup the photoemission the Fermi edge...
measured at temperature of 80K is well fitted by the Fermi-Dirac curve convolved with a Gaussian with 10meV of FWHM (Fig 6.2). Therefore the instrumental energy resolution will be considered 10meV. The broadening due a thermal effect at 80K can be approximated by $7/2k_bT = 24$meV [1]. The total resolution is then 26meV. The instrumental resolution plays no role in the data at room temperature (RT). The total broadening due thermal effect is close to $7/2k_bT \approx 100$meV.

**Figure 6.2-** Determination of the total energy resolution: Fermi edge of the Cu(332) measured at 80K.

### 6.2 – Photoemission Spectra of the clean Cu(332)

The surface of the Cu(332) is pretty stable in UHV; the surface state can be measured for even 6 hours after the preparation process which indicates a low level of surface contamination. The first photoemission measurement of bulk states was carried out with p- and s-polarization with 26 eV photon energy. The comparison with the photoemission data of Cu(111) available in the APE beamline (measured in the same condition) doesn't show clear difference for the bulk states of Cu(111) except for the photoemission angles.

**Figure 6.3 –** Photoemission at 26 eV normal to the plane (111) for the Cu(111) (a) and Cu(332) (b) and (c). Surface state is shifted in the [11-2] direction by 6.5° with respect to [332] (10°). It corresponds to $\Delta k_{||}$ of 0.26(1/A), exactly half surface Brillouin zone $\pi/d$. All three spectra were acquired at RT.
The surface state, however, is clearly modified by the steps. The parabola is shifted in k-space in the [11-2] direction by $0.26\,\text{Å}^{-1}$ with respect to [332] (Fig 6.3). It corresponds exactly the half part of the superlattice vector $g = 2\pi/d = 2\pi/12\,\text{Å} = 0.524\,\text{Å}^{-1}$ of the surface Brillouin zone (SBZ) as expected by the theory presented in Chapter 2 and as reported by other authors [1] [2]. The figure 6.4 depicted the surface state position in a spherical cut of the Fermi surface in the k-space.

In a second moment we have measured the photoemission at low temperature (80K), focusing the measurement in the surface state. With photon energy of 36 eV, we found two parabolas distanced by 10.6°, which corresponds to $0.526\,\text{Å}^{-1}$, very close to the reciprocal vector $g$, suggesting band folding by the step superlattice (Fig. 6.5). Zone-folding effects can only take place in the presence of a finite periodic potential that allows coupling from terrace to terrace.

Fitting the points close to the bottom of the surface state band (positive angles and binding energy higher than 0.25eV) with a parabolic curve, we calculated the maximum binding energy and the effective mass in that point. The maximum binding energy is $E_{\text{bCu}(332)} = 0.31\,\text{eV}$, smaller than in the flat Cu(111) surface, $E_{\text{bCu}(111)} = 0.40\,\text{eV}$. This upward energy shift indicates the electron-repulsive nature of the step potential barrier. The resulting for effective mass is $m_{\text{eff}} = 0.68m_e$, whereas in Cu(111) is $0.41m_e$. 

Figure 6.4 - The red lines are the spherical cut of the Fermi surface of Cu, illustrating the Fermi mapping of bulk states from the (332) surface with photon energy of 36 eV. (FLAN program). In the picture, the blue circle represents the surface state parabola. Note that it is centred at a distance $\pi/d$ from the k given by the [332] direction. Remembering that the reference axis in our sample is the [111], the distance between the [332] and [111] direction in k-space is calculated as $dk = \sqrt{\frac{2m}{\hbar^2}E_{\text{kin}}\sin 10°}$, the direction [332] fixes the k=0. The dashed circle represents a folding of the surface state due to the surface potential.
Figure 6.5- EDC curves for the Cu(332) along the [11-2] direction measured with photon energy of 36 eV. Surface state is shifted in the [11-2] direction by 5.3° with respect to [332] (10°). We see also the band folding of the surface state. The red circles indicates the peak energy of the Lorentzian curve which is used to fitted the measured spectra of each slice with Δθ=1° and overlap of 0.5°. The red trace is the dispersion fitting curve using the Kroning-Penney model (see text). The maximum binding energy is 0.31 eV. The data was acquired at 80 K.

The folded surface state band spectrum (negative angles) shows higher binding energy and different dispersion from the other spectrum (positive angles). Mugarza and Ortega [4] found similar behaviour to Au(223), they ascribe this effect to an artefact caused by the faintness of the photoemission signal of the folded band. However this is not the case; in our experiment both bands present a good intensity.

The dispersion can be analyzed through the 1D-Kroning-Penney:

\[ E(k_x) = E_0 + \frac{\hbar^2}{2m^*} \frac{1}{d^2} \left[ \cos(\sqrt{T(E, U_{ob})}\cos k_x d) - \phi \right]^2 \]  

(6.1)

where

\[ |T|^2 = \frac{1}{1 + (q_0/q)^2} \; ; \; \phi = -\tan(q_0/q) \]

and

\[ q_0 = \frac{m^*}{\hbar^2} U_{ob} \; \; \; q = \sqrt{\frac{2m^*}{\hbar^2} (E - E_0)} \]

We see that the equation (6.1) is recursive, since that the transmission coefficient \( T \) depends on the value \( E(k_x) \). In order to calculated the \( U_{ob} \), we evaluated the equation at \( k_x = 0 \). The input parameters are \( E(k_x=0) \), \( E_0 \), \( m^* \) and \( d \). We assumed \( E_0 \) as the maximum
binding energy of Cu(111) surface state, $E_0 = 0.40$ eV, as well the effective mass $m^* = 0.41 m_e$. The $E(k_x=0)$ will be fixed at $E_{bCu(332)} = 0.31$ eV, with $d=12$Å we obtain:

$U_o b = 1.07$ evÅ ; $|T| = 0.71$ and $\Phi = -44.54^\circ$.

Using these parameters, we plotted in the figure 6.5 the dispersion curve $E(k_x)$ as function of emission angle theta; $E(\theta(k_x))$ (the red line over the photoemission data). The curve was shifted in $\theta$ in order to match the correct photoemission angle.

The experimental linewidth of photoemission peak of Cu(332) at low temperature is higher than the flat surface at RT: FWHMCu(111)=160meV (RT), FWHMCu(332)=260meV (80K); both measure in the bottom of the parabola. Such big difference can not be ascribed only to the terrace width distribution. In fact, keeping the previously obtained value of $U_{ob}$ and plotting the dispersion from $d=10$ Å to $d=14$Å (plus and minus one atomic row at terrace), we notice a difference of only 5meV at bottom of the band. The larger linewidth of surface state of Cu(332) in literature [2] [3] is ascribed to the smaller hole lifetime. It is consistent with the linewidth expected for a surface resonance, within the framework of the theory presented in Chapter 2.

In conclusion, the Cu surface state of the Cu(332) is small perturbed by the monoatomic steps, and behaves as an average-surface-like electron state. We can point out our observations that support this behaviour:

• The higher linewidth indicates that the surface state can be better described as a surface resonance, according to the theory of bulk projection presented in the Chapter 2: The surface resonances are less sensitive to the surface potential because part of its electronic density resides deeper in the bulk.

• The effective barrier height is low enough to allow the coupling of the wave function of the subsequent terrace, which is the responsible by the zone-folding effect.

• The photoemission spectra with different photon energies show that the surface state is always centred, in k-space, at a fixed distance ($\pi/d$) from the [332] direction (see fig 6.3b and 6.5). It is characteristic of an average-surface like electron state.
6.3 – Photoemission Spectra of Oxidized Cu(332) (OCu(332))

The ARPES measurements were carried out for the oxidized Cu(332) prepared with three different procedures that we label as sample A, B and C. The surface periodicity of each sample is reported in the table 2. The sample B and C were measured by STM. The sample A was not, but the condition that sample was prepared should result in a periodicity from 3 to 4nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Periodicity-a</th>
<th>Standard Deviation- $\sigma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3 to 4 nm</td>
<td>(?)</td>
</tr>
<tr>
<td>B</td>
<td>4.4 nm</td>
<td>1.0 nm (0.23)</td>
</tr>
<tr>
<td>C</td>
<td>6.0 nm</td>
<td>1.3 nm (0.22)</td>
</tr>
</tbody>
</table>

Table 2. Samples periodicity. The periodicity and the deviation is given by analyses of STM images except for the sample A which we reported the nominal value. The values between parentheses are the relative deviation ($\sigma/a$).

The O/Cu(332) is more reactive than the clean copper; the surface state is hard visible after only 4 hours from its preparation. Concerning the surface state, the first striking difference is its position in k-space: The surface state is centred at [111] direction, $\theta=0$, independently of the photon energy (fig. 6.6 and 6.7). The same behaviour is also observed vicinal copper surface with smaller miscut angle where the surface state has terrace-modulation characteristic (see chapter 2). Another important change is in the dispersion along the direction perpendicular to the stripes: the dispersion is more flat, whereas the dispersion along the steps is still parabolic. The effective mass calculated for parallel dispersion is $m_{||}=0.40$ me, very close to the flat Cu(111). It suggests a confinement of the surface states in the [11-2] direction, in fact, the dependence of maximum binding energy on the periodicity: 0.33eV for the sample A and B, Fig 6-b, and 0.38eV for the sample C; points to a confinement of electrons in the (111) terraces.

If we consider this confinement as an infinite quantum well (QW) confinement *, we have the following equation for the energy levels:

$$E_N = E_0 - \frac{\hbar^2 \pi^2}{2m^* d^2} N^2$$  \hspace{1cm} (6.2)

where the energies are given with respect to the Fermi energy.
Figure 6.6- EDC curves for the sample A measured with 36eV photon energy. The red points indicates the center of the Lorentzian curve used to fitted the dispersion of each delta=0.2° slice. Note that dispersion in direction perpendicular to the step (left) can not be fitted by a parabola. The maximum binding energy is 0.33eV. The data was acquired at 80 K.

Let us apply the QW model to analyze the surface state dispersion of the sample A (fig.6.6): We can use the parameters of the surface state in the flat Cu(111) as the reference for the free-electron; m*= 0.41 eV and E_0=0.40 eV, and regarding the maximum binding energy measured in the sample A as the ground level, E_r=0.33(1)eV, we obtain d=3.6 nm. This value should be compared with the (111) terrace size, d_{111} (see the fig. 5.1), resulting in a periodicity of 5 nm. The periodicity is a higher than the expected for the sample A, but is reasonable; actually we can not affirm that the confinement of electrons is done efficiently at the limits of the (111) terrace.

In sample B and C was measurement the surface and the bulk states of half part of the
Brillouin zone. The statistics, however, was not as good as for the sample A due to the reduced number of sweeps. On the other hand the STM images were measured for sample B and C, which allow us to estimate the surface state peak broadening in the ARPES spectra produced by the terraces width deviation. The maximum binding energy of the surface state shows dependences with the terrace size as expected by the QW model (see figure 6.7). The bulk states show a very small difference from B to C and will be analyzed later.

Figure 6.7 – EDC curves for the sample B and C measured with 26eV photon energy. We can see a increasing of the maximum biding energy from sample B to C. The data was acquired at 80 K.

The sample B shows almost the same maximum binding energy as that for A, \( E_b = 0.32(8) \text{eV} \) and we obtain a confinement size of \( d = 3.5 \text{ nm} \) from the QW model. Using this value, one can calculated \( E_2 = 0.15 \text{ eV} \) as a second energy level, such energy is still bellow the Fermi energy and thus should be visible in the photoemission EDC (Fig. 6.7). However, according to the figure 6.8, a small variation in the terrace size produces a large variation of the \( E_2 \) energy; that is even a narrow terrace width distribution (TWD) can produce very broad peak at \( E_2 \) and \( E_3 \) level.

The figure 6.9 shows the surface state for the sample B in detail. In order to point the influence of the terrace width deviation, we plot the infinite QW theoretical dispersion for \( d = 3.5 \) and \( d = 3.5 \pm \sigma \).
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Figure 6.8 – Relation between the three first energy levels of an infinite QW and the confinement size. A variation from 3 to 4nm in the terrace size produces a variation of 45 meV in E1 (represented by the vertical blue bar) whereas produces a variation 4 times bigger in E2, 180 meV (represented by the vertical red bar). In the bottom panel, we can see the terrace width distribution for sample B and C.

Figure 6.9 - Surface state for sample B (zoomed from Fig 6.8). The black solid lines represent the expected energy levels in the QW model. The dashed lines represent the energy levels due the terrace width deviation (see the text). In the right panel, normal emission photoemission spectrum averaged over 0.5° and its fitted result with Lorentzian curve is shown.
The derivative of (6.2) allows the estimation of energy broadening of the QW levels due to a finite TWD as

$$
\Delta E = \frac{\hbar^2}{2m^*} \frac{2\pi^2}{L^3} \Delta L N^2
$$

Using this equation we obtain $\Delta E_1 = 68$ meV and $\Delta E_2 = 272$ meV for sample B and $\Delta E_1 = 21$ meV and $\Delta E_2 = 84$ meV and $\Delta E_3 = 190$ meV for sample C. In the both cases the TWD gives a substantial contribution for the broadening of first level, and makes difficult the measurement of position of levels $E_2, E_3$.

**Figure 6.10** - The same as fig. 6.9 for sample C.

The linewidth of the first level in the two samples is smaller than the Cu(332) measured in the same condition, despite of the broader TWD of the oxidized samples. It indicates a longer hole lifetime than in Cu(332).

In conclusion, the Cu surface state for the O/Cu(332) is confinement in the (111) terrace by the O(2x1)-Cu(110) facets forming a quasi 1D system. The surface state presents a terrace character. We point out our observations that support this behaviour:

- The photoemission spectra with various photon energies show that the surface state is always centred at [111] direction (see fig 6.8b and 6.10). The dispersion along the terrace normal is characteristic of a terrace-surface like electron state.
The smaller linewidth in comparison with Cu(332) suggests a smaller interference from bulk states. It is reasonable since the perpendicular component of the surface state momentum points to the [111] direction, residing in the L-Gap. The state can be considered as a real surface state and therefore is more sensitive to the surface potential.

The change of maximum binding energy and the photoemission dispersion can be well described by the QW model. The quantization of energy levels however is not clear due the broadening caused by the TWD. The periodicity calculated with the QW model is compared with the expected one in the table 6.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Periodicity (STM)</th>
<th>Periodicity (QW model)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>~4nm(nominal)</td>
<td>5</td>
</tr>
<tr>
<td>B</td>
<td>4.4</td>
<td>5</td>
</tr>
<tr>
<td>C</td>
<td>6</td>
<td>8.5</td>
</tr>
</tbody>
</table>

*Table 6.2*- Periodicities obtained with the QW model compared with the expected periodicities. The sample A was not measured with STM.
6.4 – Photoemission angle dependency of bulk states in Cu(332) and OCu(332)

In the ARPES experiments, the emitted photoelectron conserves the momentum component parallel to the optical surface. That is, in the Cu(332), Cu(331) and Cu(610) the momentum is conserved respective to the (332)[3], (331)[5] and (610)[6] plane.

The tracking of the peak position around some specific energy from the bulk states reveals a difference in photoemission angle between the flat and the vicinal surface[5]. Such tracking is not easy since the relations between peaks intensities are dependent on the incoming photon beam angle which can not be always kept constant. The Figure 6.11 shows a comparison between energy distribution curves of Cu(111) and Cu(332). We tracked the states around 3eV and we found an angle difference of 2.7 to 3 degrees. Let us remember that all the angles are measure in reference to the [111] direction.

![Figure 6.11- Electron energy distribution curves taken from Cu(100) and Cu(332), respectively. Electron emission angles are chosen in such a way that spectra displayed side by side show emission originating from the same k-space point in the bulk Brillouin zone at initial state energies around 3 eV.](image-url)
Figure 6.12

(A) and (B) show the emission angle (degrees) and binding energy (eV) for samples C, B, and Cu(332) respectively.
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Figure 6.12 – EDC for Cu(332) and for oxidized Cu(332): sample B (4nm) and C (6nm) along the [-1-12] direction. The colored traces in (a) mark the shift between the dispersion and indicate the angle profiles in (b). The photoemission geometry is shown in (c).

After the surface oxidation of Cu(332) we would not expected a change in the refraction process of photoemission of bulk state, providing that the optical plane is still the (332). And, in fact, we did not notice any remarkable change in the photoemission peaks from the clean Cu(332) to the sample B (4nm). However, at least for small photoemission angles, we see an appreciable shift of the photoemission angle in the sample C (6nm). The difference starts with 2° and get smaller whereas the angle get higher. The figure 6.12 shows the dispersion for the Cu(332), sample B and C. The shift in dispersion is pointed with the colored line bars in 6.12-a; the correspondent spectra are shown in 6.12-b.

We suggest that the size of terrace directly influences the refraction of photoemitted electron. In the case of the sample C the momentum conservation component is almost parallel to the (111) plane due the large size of terrace. As the emission angle get close to the [110] direction (35.2°), the refraction at (110) facets becomes also important.

Figure 6.13 – Detail of the band Fermi energy crossing of sample C. There are two curves crossing the Fermi energy, theses curves are ascribed to be different refractions of the same state: one at 29.6, corresponding the bulk state refracted by the (332) optical plane; and other around 32.3 corresponding to a refraction by the (111) terrace.
Moreover, we observed in the photoemission data of the sample B and C a faint shadow of the band dispersion crossing the Fermi energy around the emission angle 30° (see Fig 6.13). We believe that this second curve, not present at clean Cu(332), is reminiscent from the (111) terrace refraction as suggested by the angle difference between the two curves.

In conclusion, for the sample C we observed two spectral intensities one from the refraction by (111) and the other from the refraction by (332). For smaller emission angle the refraction by (111) has more intensity. On the other hand for, larger emission angle, the refraction by the (332) has more intensity.

References:


* The analyzes of the dispersion though the KP model in the same way that was done for cu(332), leads to a $U_0b=70$ evA and $T=0.02$ for sample A. The system is then better described for a quantum well confinement.
CHAPTER 7

Templated growth using oxidized Cu(332)

7.1 Properties of Iron nanowires on vicinal surface

7.2 Experimental Details

7.3 Fe/Cu(332) System

7.4 Fe/ O-Cu(332) System
Chapter 7 - Templated growth using oxidized Cu(332)

This chapter describes the growth of iron nanowires on the O-Cu(332) template surfaces.

7.1 Properties of Iron nanowires on vicinal surface

According to the Heisenberg model a true one-dimensional system, presenting short-range interaction, cannot be ferromagnetic [1]. In quasi-one dimensional systems, the ferromagnetic behaviour is observed due to an induced anisotropy or due some interaction effect among the stripes of an array. An example of array interaction is the Fe/W(110) system: Elmers et al [2] grew monolayer-thick iron stripes with average width of 4.5 nm on vicinal W(110) with 9nm terrace size. The magnetization easy axis in that case is in plane and perpendicular to the stripes, the distance between the nanowires allows for a dipolar coupling resulting in ferromagnetic behaviour with a Curie temperature of $T_c = 179$K.

An interesting property of the Fe/Cu(111) system is that the iron, whose bulk crystalline structure below 1000 K is bcc, grows on the flat Cu(111) in a distorted fcc structure; γ-Fe, with fcc(111) surface, up to the 6ML, followed by a transition to the bcc structure for higher thickness; α-Fe, with bcc(110) surface in Kurdjumov-Sachs (KS) orientation [3]. The KS orientation is a special case of the one-dimensional matching between bcc(110) and fcc(111) in which one of the bcc <111> directions is parallel to one of the fcc <110> directions [3], resulting in a six possible domain orientations as depicted in Figure 7.1. The fcc-bcc transition also implies a switch of the magnetization easy axis from surface normal (fcc-[111] direction) to in-plane (bcc[001] direction). Iron growth on vicinal Cu(111) undergoes to the same bcc-fcc transition, but at lower coverages. It is explained by the preferential growth close to the step edge, which results in faster piling up of iron layers then in the case of growth on flat surfaces for equivalent “average” coverage. In this way, locally, an iron island or cluster can be thicker than 6ML and can acquire the bcc structure even if the average coverage is as small as 2ML. In the vicinal Cu(111), the formation of nanowires is usually achieved at low coverages [3,4,5,6], and therefore, presents an out of plane magnetization. The dipolar interaction between stripes, in this case, would not favour a ferromagnetic coupling. In fact, Shen et al showed the different nature of the
magnetization in iron nanowires formed by the iron deposition from 0.8 to 1.3 ML on vicinal Cu(111) with average terrace size of 10 nm (see chapter 1, Fig.1.2-b). The resulting easy magnetization axis is along the surface normal, as expected by the fcc phase, but the system, at 100K, does not present a typical ferromagnetic behaviour, showing an unstable magnetization; i.e. after the removal of the magnetic field the remaining magnetization decays to zero in a time interval of a few seconds. This behaviour is explained in terms of a short-range interacting Ising spin blocks[4]. In the same work, Shen et al, observed that the transition of fcc to bcc occurs for about 2.3 ML coverage. At this thickness the film can be considered 2D (the nanowires start to percolate at 1.4 ML). About this coverage they measured, by means of MOKE, the switch of the easy magnetic axis direction from out of plane to in-plane. In spite of the measurement of a well-defined hysteresis loop in the direction perpendicular to the steps, they could not confirm the orientation of the magnetic easy axis in plane, due to experimental setup limitations. As we will see later, we obtained similar result in the high coverage of Fe/Cu(332). Moreover our MOKE setup allows the measure of the magnetization easy axis in the bcc phase that was found to be along the [1 1 -2] direction, perpendicular to the steps.

**Figure 7.1** – Demonstration of the KS superstructure. On the left is depicted the (110) surface cell for bcc. On the right we see the 6 possible arrangements of domains in fcc (111) surface. Adapted from [3].
7.2 Experimental Details

The samples presented in this chapter were oxidized according to the procedure described in chapter 6. The magnetic measurements were carried out at different times, according to the availability of the measurement facilities. For this reason several replica samples were grown following the optimized protocol and obtaining satisfactory reproducibility of the synthesis.

The Iron deposition was performed from a water-cooled e-beam evaporation cell loaded with a 99.95 pure Fe rod. The evaporation rate was calibrated through a water cooled quartz thickness monitor alternatively put in the target position. At typical Fe evaporation rates of 0.5ML/min the pressure in the synthesis chamber raised but never exceeded $5 \times 10^{-10}$ mbar. In our calibration, one iron monolayer is equivalent to the fcc iron phase layer deposited on Cu(111); that reads 2 Å on the calibrated quartz microbalance.

7.3 Fe/Cu(332) System

The templated growth of nanowires is a self-organized process (see chapter 1). There are two important growth parameters that lead to a formation of some specific nanostructure due to kinetics: the adsorbate diffusivity $D$ and the deposition rate $F$. The ratio $D/F$ determines the average distance that an adsorbed species has to travel to meet another adsorbate, resulting in nucleation of a new aggregate or in attachment to an existing island [7].

This surface diffusion is thermally activated; that is, the adatom displacement in a specific direction should surmount barriers imposed by surface potential. At low temperatures, the $(D/F)$ ratio is small which favours the growth of metastable structures where the growth is guided by the interaction of individual adsorbate and the template surface potential (like steps, kinks or corners). The growth of iron nanowires is usually done in this regime. An interesting computational study about the kinetics of growth of iron nanowires in vicinal Cu(111) can be found in the reference[6]. Briefly, the growth of nanowires starts by nucleation close to the step-edge in the upper terrace and then extends to the lower terrace.
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The figure 7.2 shows some of our attempts to produce ordered nanowires on the Cu(332), we deposited from 0.2 ML (the limit to have one iron monoatomic row at the step-edge) to 1ML (completely covered surface) at room temperature and at the lowest then available temperature of 200°K. The growth in the submonolayer regime on Cu(332) (in the above conditions) did not lead to the formation of wires but of islands. We ascribe this to the deposition temperature that was not low enough to avoid the iron atoms steps surmounting or the diffusion along the terraces, resulting in the creation of new islands. Such behaviour appears when comparing the film of 0.2 ML grown at RT (fig. 7.2-c) and at 200K (fig. 7.2-d). In the first case, the islands extends to two or more terraces, whereas in the second case, the same amount of iron produces isolated islands on a single step. It means that 200°K was low enough to suppress the displacement of the adsorbate through the steps, but is not low enough to avoid the diffusion along the terraces. Shen et al. [3] succeed to produce nanowires at 273°K, but on terraces almost 10 times wider than those of Cu(332), that is the narrowest continuous stripe is 2nm wide (the Cu(332) has 1.2 nm terrace size). To the best of our knowledge there is no report of nanowires formation in vicinal surface with terrace as smaller as 3nm[5].

Figure 7.2 – Low coverage of Fe/Cu(332). In (a) 1 ML of iron appear to cover completely the surface, the morphology is characterized by elongated domains along the [110] direction (step parallel). At 0.6 ML (b) the iron forms elongated islands and noncontinuous stripes that occupy, in average, two terrace widths. The iron forms clusters randomly spread in the entire surface at 0.2 ML (c). The same coverage deposited at lower temperature (220K) (d) produces also clusters, but now, grouped in the adjacent steps.
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The figure 7.3 shows the deposition of 1, 2 and 6ML of iron. We found a change of morphology starting from 2 ML and probably it is associated to the fcc-bcc transition. With 6ML we see domains elongated in the <110> directions typical for the bcc domains[3,9].

Figure 7.3 – High coverage of Fe/Cu(332). In (a) 1 ML iron film follows the symmetry of the substrate. For 2ML the domains are still elongated in the [-110] (along the step) but it starts to appear an elongation also in the [01-1] direction, this trend become clear at 6ML where it is observed domains also oriented along the [-101] directions.

The MOKE measurements (Fig.7.4) show a perpendicular ([332] direction) magnetic easy axis for 2ML, and an in-plane ([11-2] direction, perpendicular to the steps) magnetic easy axis for 6ML. This behaviour can be explained if one notices that the majority of bcc domains are oriented along the step direction [-110]. The two privileged domains are the two bottom domains showed in figure 7.1. In such domains, the bcc [001], which is the magnetic easy axis of the γ-Fe phase, will be nearly aligned with the fcc [1 0 -1] and with fcc [ 0 1 -1] resulting in a net magnetization either along the [11-2] (perpendicular to steps) or [-110] (parallel to steps). A magnetic coupling between the domains would result in a magnetic easy axis along the [11-2] direction, in agreement with the MOKE measurement.
Chapter 7

7.4- Fe/ O-Cu(332) system

The iron was deposited at the rate of 0.3ML/min onto the oxidized Cu(332) surface, we observed a preferential growth on the (110) facets forming nanowires even at 300°K (Room Temperature). Figure 7.5 shows a series of STM images of Fe films deposited on the oxidized Cu(332) with 4nm periodicity; 4nmO-Cu(332). We synthesized isolated wires for coverages up to 0.35ML at RT and up to 1.0 ML at about 273°K. Actually, we believe that the disordered film obtained in growth of 1ML Fe/4nmOCu(332) at RT, showed in the figure 7.5 – b, is due to the surface heating caused by irradiation from the atomic beam source; that is, the distance between sample surface and evaporator is about 15 cm, and a longer deposition (1ML corresponds approximately to 3min) can increase the surface temperature tens of degrees when the sample is not cooled.

Due to the fact that the (110) facets surface corresponds to 29% of the total surface (see Figure 7.4- MOKE measurement for 2 and 6ML Fe/Cu(332). The magnetic field is oriented in the [332], [-110] and [11-2] respectively for the polar, longitudinal and transversal MOKE.)
chapter 5, Fig. 5.1), the deposition of 1ML of Fe, evaluated for a flat surface, corresponds to growing up to 3.3 ML if all the adsorbate concentrates on the (110) facets, assuming a sticking coefficient one. We stress that we have evidence that at least up to 0.7ML, no iron resides on the (111) terraces of the substrate. By measuring the Cu(111) L-gap surface state photoemission, discussed below, we could find that the deposition of 0.3 ML of Fe does not affect significantly the copper L-gap surface state, that indicates the lack of significant perturbation of the (111) terraces.

Figure 7.5 – STM images along with 3D rendering for 0.35 ML (a) and 1.0 ML (b) and (c) iron deposited O-Cu(332). The corrugated feature is ascribed the deposited iron. In (a) and (c) one can note that the (111) terraces are free of iron, presenting a flat smooth surface. The deposition was carried at RT for (a) and (b) and at low temperature; 273K, for (c).

Additional STM images for the 0.35ML Fe/4nmOCu(332) (fig. 7.5-a) and Fe/4nmOCu(332) (0°C) (fig. 7.5-c) are presented in the figure 7.6-a and b. In the figure 7.6-a, the line profile, along the (110) facets suggests an almost completed covered of 1 ML of iron. The features pointed by the arrows in the images (also present in fig.7.6-b) refer to a formation of 1ML deep Cu holes. This process is frequently observed when we have iron cluster near of the
step edges in vicinal Cu(111) [8]: the tensile stress caused by the iron nanostructures reduces the binding energy of the top atoms of the (111) terrace, allowed the mass transport from the eroded parts. The figure 7.6-b corresponds the 1ML Fe/4nmOCu(332). The expected coverage for (110) facet is 3.3ML, the profile line along the (110) facet shows a corrugation with the height from 1 to 2 ML. At this coverage the iron incorporated on (110) starts to move towards the lower (111) terrace, as it is shown by the 3D rendered image Fig 7.7-a.

The figure 7.6-c shows a deposition of 1.5 ML at 0°C, we see a modification of the morphology. The iron appears to cover both (110) facet and (111) terraces (Fig7-b), the line profile along the stripes shows corrugation with 2 ML and 1 ML.

![STM images for 0.35ML (a), 1.0 ML(b) and 1.5ML (c), with the respective line scan profile on the (110) facet along the [-110] direction.](image)

Figure. 7.6 – STM images for 0.35ML (a), 1.0 ML(b) and 1.5ML (c), with the respective line scan profile on the (110) facet along the [-110] direction.
Figure 7.7- 3D rendering of the STM image of (a) 1.0 ML Fe/4nmOCu(332) and (b) 1.5ML Fe/4nmOCu(332). Note that nanowires are well isolated in (a) and appear to merge together in (b). The inset image (15x15 Å) in (a) shows the atomic resolution detail of the (111) terrace.
A fact that demonstrates the higher affinity of iron with the oxidized (110) copper facet is that the surface state present at (111) terrace is little affected by the iron deposition. The figure 7.8 shows the surface state of the oxidized Cu(332) with 6nm periodicity, analyzed in the chapter 6 under the label “sample C”. We see that the surface state is still visible after the deposition of 0.3 ML of iron. The binding energy is practically the same, but the width of the peak was significantly reduced (Fig.7.9). The explanation for this remains not clear. We have similar effect with a sample covered with 0.7ML.

![Figure 7.8](image)

**Figure 7.8** – Surface state for O-Cu(332) before (left) and after deposition of 0.3 ML of iron. The photoemission spectra were acquired with 26 eV photon energy at 80K.

Magnetic properties of nanoscale system usually are manifested at very low temperatures. We suffered for a technical limitation in our experiments that prevented us to perform MOKE experiments at low temperature. The minimum temperature available for the MOKE
was about 200K, (later we modified the manipulator as described in chapter 4). The minimum temperature achieved in the XMCD experiments was 40K by running liquid helium in the sample cryostat.

Figure 7.9 – Normal photoemission for sample C before and after 0.3ML of iron. The peak energy (xo) is almost the same. The width given by the Lorentzian fitting is 140 meV for OCu(332) and 98 meV for Fe/OCu(332).

We grew a wedge film on 4nmO-Cu(332) with the nominal range of 0.5ML to 3ML of iron in order to perform the MOKE measurements. At 200K the film shows no magnetic response for coverages thinner than 2 ML. No response was obtained also for magnetic field parallel to stripes (Longitudinal MOKE) at any coverage. The figure 7.8 shows that there is a switching of the magnetic easy axis from out of plane (Polar MOKE) to the direction perpendicular to the stripes (Transversal MOKE) around 2.3 ML.
The Fe initially grows on the Cu(110) in fcc(110) structure [9] [10], presenting sometimes (111) facets at the submonolayer regime[10]. We know from literature that at about 6 Å the film undergoes a transition to a disordered state, consisting of bcc Fe domains[10]. This explains the initial magnetic easy axis to be out of plane: as in the Fe/Cu(111) system, the magnetization is given by the fcc [111] direction of the iron film. The switching to in-plane magnetization is then ascribed to the transition to bcc Fe phase, suggesting that the domains are rotated in such way that their bcc [001] directions result in a magnetic easy axis along the [11-2] direction, likewise in the Fe/Cu(332) system.

Figure 7.10 - MOKE measure of Fe/OCu(332) at 200K. The magnetic fields are oriented in the [332] and [11-2] respectively for the polar and transversal MOKE.
The conclusion of the switching of the magnetic easy axis is also supported by the XMCD measurement in another wedge sample preparation (0.5 to 3.5 ML). The figure 7.9 shows a decay for the perpendicular magnetization for thickness higher than 1.8 ML. Such decay with the increasing of film thickness can be only explained by the switching of magnetic easy axis. The decay of magnetization for thickness smaller than 1.5 ML can be ascribed to the decreasing of Curie temperature with the reducing of the system dimension. Unfortunately the magnet available in our XMCD system can give no more than 10% of the necessary saturation field, according to the MOKE values. Therefore the XMCD results cannot be fully exploited for a quantitative analysis.

![Figure 7.11- XMCD measurement of Fe/OCu(332). (a) Typical absorption spectra for positive, M+ and negative, M-, perpendicular magnetization. (b) Difference between M+ and M- absorption spectra (dichroism) for several thickness. (c) $\Delta L_3$ Peak intensity vs thickness: The $\Delta L_3$ peak intensity is proportional to the sample magnetization [11].](image)

Figure 7.11- XMCD measurement of Fe/OCu(332). (a) Typical absorption spectra for positive, M+ and negative, M-, perpendicular magnetization. (b) Difference between M+ and M- absorption spectra (dichroism) for several thickness. (c) $\Delta L_3$ Peak intensity vs thickness: The $\Delta L_3$ peak intensity is proportional to the sample magnetization [11].
References:


CONCLUSION:

The aim of this thesis was to address the formation of metallic/magnetic nanowires on a well characterized surface template, i.e. by the “bottom-up” synthesis phenomena that can be defined self-assembly and self-organized growth. We have addressed this phenomenology by using highly surface sensitive analytical methods with atomic resolution, high energy resolution and magnetic order and magnetometry sensitivity: Scanning Tunnelling Microscopy and Spectroscopy, Angularly Resolved Photoelectron Spectroscopy (ARPES), Vectorial Magneto-Optical Kerr Effect (V-MOKE), X-ray Circular Dichroism (XMCD). All the physical probes (tips, laser and polarized synchrotron radiation from Elettra) were available in the suite of the APE instruments that form the AE beamline end station laboratory.

The primitive substrate that has been chosen for this study is the Cu(332) vicinal surface. The self-assembled surface system was synthesised by developing a preparation protocol of the O-Cu(332) system. We demonstrated that, by controlling the oxygen exposure, it is possible to reproducibly obtain a reconstruction consisting of alternated facets of Cu(111) and O(2x1)-Cu(110) with average periodicity from 3 to 10 nm, always maintaining the same average orientation of Cu(332). Such reconstruction has been reported before in the literature[1], but the tailoring of the periodicities by exposure control is an original contribution of the present thesis work. Also we report, for the first time in our knowledge, direct images of the (110) facets. We have focused on the understanding of the morphological properties of O-Cu(332) by means of LEED and STM measurements; and by comparing to atomic models. We found that the surface reconstruction is indeed composed by Cu(111) clean terraces and O(2x1)-
Cu(110), but at the edge between the two facets, we characterized a monoatomic step in which the oxygen is coordinated in the four-fold site. The adsorption of oxygen in such site in the unreconstructed Cu(332) is suggested to be the trigger of the faceting reconstruction by the decreasing of vibrational entropy energy and the consequent increasing of total surface energy of the stepped surface. With the increasing of the surface energy in stepped surface, the faceting becomes favourable.

We have performed a thorough ARPES analysis of the clean Cu(332) in order to gather a reference for the subsequent study of O-Cu(332). Our results are in agreement with similar studies found in the recent literature [2] [3][4]. The Cu(332) surface state is little perturbed by the monoatomic steps, and behaves as an average-surface-like electron state displaying energy dispersion that can be well fitted with the KP model. In our AOPRES study we exploited the tenability of the photon energy and polarization and managed to measure the folded surface state for the Cu(332). Such measurement had never been reported before. The ARPES study shows that the O-Cu(332) is a very interesting system with peculiar electron state properties: The confinement of the surface electron states in the Cu(111) terraces, imposed by the introduction of (110) facets, determines a quasi-one dimensional system. The anisotropic dispersion of the L-gap surface state and change of its binding energy as compared to the infinite (111) surface are clearly measured and can be well described by the QW model. The fact of that the surface state band is always centred in the photoemission angle \( \theta = 0 \), means that its perpendicular dispersion is along [111] direction and, therefore, has a characteristic of a 1D terrace-surface like electron state.
The peculiarity of this system, in comparison with a usual vicinal surface, is the possibility to change the terrace size without changing the overall optical plane. This feature offers an interesting tool for a technical study of the angular dependence in photoemission phenomena. We observed that, in O-Cu(332), the photoemitted electrons originated from bulk states display an intricate angular dependence. We suggest that spectral intensity has contributions from the refraction by (111) terraces plane and by the (332) optical plane, and the relative weight of these contributions is given by the terraces size.

Further analysis by STS indicate that, whilst the (111) terraces do display the expected metallic behaviour, the (110) facets display a band-gap, giving further indication that the Fermi surface electrons of the (111) terraces undergo reflection at the boundaries with the (110) facets determining a very anisotropic extended state structure. Furthermore, theoretical calculations of the electron states for O-Cu(110) were performed by using the Quantum Espresso package in order to compare the spectroscopic signals arising from the different atomic sites. A reference calculation was also performed on the flat O-Cu(110) surface in order to compare with the available literature.

The self-organized growth is represented by the templated growth of Fe on the oxidized Cu(332) surface, producing nanowires. The growth of iron at the submonolayer regime on primitive Cu(332) did not occur in shape of wires but rather 2D islands. For higher Fe coverage, our observations are in agreement with the literature reports for vicinal Cu(111)[5]. We observed, by STM, the formation of domains elongated along the substrate steps and as the thickness was increased the domains become elongated along all <110> directions in
plane. The MOKE measurement shows a transition of the magnetic easy axis from out-of-plane to in-plane in the direction perpendicular to the steps for thick films. The transition occurs along with the phase change from fcc(111) film to bcc (110) film.

The iron growth on O-Cu(332) presents a completely different phenomenology. We observed a preferential growth on the (110) facets and the formation of iron nanowires even at RT. Providing that the iron is completely incorporated by the (110) facet, as indicated directly by the STM and indirectly by the Cu L-gap surface state ARPES, the deposition of a nominal coverage 1ML of Fe on a flat surface corresponds to a 3.3ML on the O(2x1)-Cu(110) facets. The iron nanowires has the same width of the (110) facet and the same periodicity of the template. For O-Cu(332) with 4nm periodicity, we could grow nanowires up to the limit of 1ML. The magnetization response for such nanowires could not be measured due to our experimental limitations for low temperature. For films thicker then 2ML we found, by means of MOKE and XMCD measurement, that at about 2.3 ML the magnetic easy axis switches from out of plane to in-plane perpendicular to the steps. Such behaviour can be ascribed to the fcc to bcc transition.

Through the study of the systems O-Cu(332) and Fe/O-Cu(332), we have addressed and put in evidence two of the main phenomena of nanoscience: the quantum confinement of electronic states in nanopatterned systems and the self-organization phenomena in the synthesis of nanopatterned systems. Our research also demonstrates that kinetics plays a key role in the organized growth of nanostructures, but favourable conditions of growth can be
obtained in the case of the Fe/O-Cu(332) thanks to a relative higher affinity of the iron with the O(2x1)Cu(110) facet versus the (111) terraces. Understanding the different affinity for Fe adsorption on Cu modified surfaces can be a subject for further study. Furthermore, effort in the study of the template growth phenomena will help to grow nanostructures of wanted characteristics in other similar systems.

This thesis has shown that all the state of the art tools and methods of surface science and synchrotron radiation spectroscopy and magnetometry, as well as DFT calculations, represent the most advanced tool-kit for addressing and understanding the synthesis and properties of nanostructured matter.

References:


Appendix A – Quantum Espresso Calculations

The first principles calculations were used as a complementary tool for the characterization of our samples. A detailed first principles investigation is out of the scope of this thesis. The parameter optimization was inferred by the calculation made in the Cu bulk and Cu(111) slab. We mainly used as reference two works: a first principles calculation for the oxidize Cu(110) study [1] and the all-electrons DFT calculation for the vicinal surfaces [2].

Our calculations are based on DFT using plane wave basis set. For exchange correlation energy, we used the generalized gradient approach (GGA) from Perdwel et al. [3], known as PW91. The interaction between ionic cores and valence electrons is described by the Vanderbilt “ultrasoft pseudo-potential” (USPP). The 3d, 4s and 4p electrons are treated as valence electrons for copper. For oxygen, the 2s and 2p are the valence electrons. The plane wave cutoff is fixed for all calculations to 400eV. For calculation of the fractional occupancies, a smearing broadening of 0.02eV was used.

Using this parameters in the copper bulk calculation, we obtained, through total energy minimization, a value of 3.63 Å for the lattice parameter, which is < 1% larger than the experimental value; 3.615 Å. The bulk modulus was calculated in 1.5Mbar whereas the experimental value is 1.4Mbar. The calculated cohesive energy of -3.60eV is higher than experimental value; -3.50eV [5].

The surface calculations were performed using periodic slab geometry. We used 7 atomic layers and a perpendicular periodicity about 60Å for all the analyzed systems, namely Cu(111), Cu(332), Cu(332)(4fold)O and Cu(110)(2x1)O. The structures were then relaxed through BFGS quasi-Newton algorithm, keeping the central layer at fixed position, until the force in each atom was smaller than 0.5mRy/bohr. The relaxed supercells for selected structures are show in figure A.1. The distanced between the O atom and the nearest Cu atom is 1.86Å in the Cu(332) system and 1.82Å for the Cu(110)(2x1)O system. In the Cu(332), the oxygen atom relaxed to a position closer to the step edge, in a pseudo three-fold site. Similar behaviour was observed by Lien et al. [1] with O atom in the hollow site of the
Cu(110) (Fig.A.2).

Figure A.1 - Relaxed supercell used for simulation of the Cu(110)(2x1)O (a) and the Cu(332)(4fold)O. The blue and green spheres represent the Cu atom while the red spheres represent the O atom. The green spheres indicate the nearest Cu atoms for the O. In (b) the O atom relaxed from the 4 fold site (equally distanced from atom 1 and 2) to a position closer to the step edge (pseudo threefold coordinated).

The surface energy is defined as the energy per unit area needed to split an infinite crystal in two semi-infinite. It can be calculated as an excess energy $\gamma_{surf}$ given by:

$$\gamma_{surf} = \frac{1}{2A} (E_{tot}^{slab} - N_{atm} E_{tot}^{bulk}) \quad (A.1)$$

Where the $E_{tot}^{slab}$ is the total energy of the slab with $N_{atm}$, $E_{tot}^{bulk}$ is the bulk total energy and the term 2 counts the two equivalents surface of the slab. The surface energy for each studied system is then reported in table A.1. The adsorption energy, $E_{ads}$, can be calculated as the reduction energy caused by the binding of the adsorbate.

$$E_{ads} = E_{tot}^{O1slab} - E_{tot}^{slab} - E_{tot}^{O} \quad (A.2)$$

Where $E_{tot}^{O}$ is the total energy of the adsorbate, usually calculated in gas phase. For the calculation of the adsorption energy for the oxygen in Cu(332), we considered the total energy of a spin-polarized free atom. The resulting $E_{ads}$ was -4.89eV. Lien et al [1], calculated
the adsorption energy in a similar site in Cu(110) (Fig. A.2) as -4.742 eV.

Figure A.2 - Liem et al [1] found that the energetically most stable position for oxygen atom is displaced 0.86 Å from site 1 towards site 3. The adsorption energy in this site was calculated in -4.74 eV.

In order to estimate the energy gain of the (2x1)O reconstruction on Cu(110), we considered the added row (the chain Cu–O–Cu–O (see Fig A.1)) as the adsorbate. The gain of energy due absorption of each “molecule” Cu–O–Cu–O is then:

\[ E_{ads}^{CuOCuO} = E_{tot}^{OCu(110)} - E_{tot}^{Cu(110)} - E^{CuOCuO} = -4.20 \text{eV} \]

where \( E^{CuOCuO} \) was calculated not in gas phase but as a set of infinite parallel chains, keeping the periodicity of the (2x1) reconstruction in Cu(110). This choice allows to discount the energy gain due formation of bonds between oxygen and copper in the chain.

<table>
<thead>
<tr>
<th>Surface Energy (J/m²)</th>
<th>(GGA-PW91) present work</th>
<th>(GGA-PBE) All electrons [2]</th>
<th>(GGA-PW91) [1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(111)</td>
<td>1.311</td>
<td>1.317</td>
<td></td>
</tr>
<tr>
<td>Cu(110)</td>
<td>1.531</td>
<td>1.550</td>
<td>1.536</td>
</tr>
<tr>
<td>Cu(332)</td>
<td>1.459</td>
<td>1.439</td>
<td></td>
</tr>
</tbody>
</table>

Table A.1 - Surface Energies (J/m²). In our calculation, the k-points meshes were: Cu(111):(16x16); Cu(110): (16x16); Cu(332):(8x4)

The local density of states LDOS can be approached by the sum of the projection of the total electronic density in the orbitals of a selected atom (pDOS). The figure A.3 shows the pDOS for oxygen atom in the Cu(110)(2x1)O and Cu(332)(4fold)O systems. The figure A.4 shows the pDos in similar sites from the reference [1]. The LDOS near to the Fermi energy is higher for the four-fold site than for the O-Cu site. This behaviour holds also when we use a different exchange-correlation energy approximation. The figure A.5 shows the LDOS for O.
atoms in both sites, calculated using the GGA and LDA.

Figure A.3 – Projected DOS of O in the O-Cu chain on Cu(110)(2x1)O (a); and in four-fold (pseudo three-fold) site in Cu(332) (b).

Figure A.4 - Projected DOS for O atom at the pseudo-3 fold site in Cu(110) (left) ; and O atom at O-Cu chain on Cu(110)(2x1)O (right) ref. [1]
Figure A.5 – Comparison between the LDOS calculated using the GGA and LDA exchange correlation.

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References:


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Publications and Presentations:


Publications to be submitted:

