Atomic and electronic structure of bulk intermetallic and heteroepitaxially grown surface alloys

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ATOMIC AND ELECTRONIC STRUCTURE OF BULK INTERMETALLIC AND HETEROEPITAXIALLY GROWN SURFACE ALLOYS

A Dissertation
Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Physics and Astronomy

by
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Dedication

This dissertation is dedicated to my wife, Funda Kizilkaya, and our son, Ekrem Eren, for their endless support and love.
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After 4 years of research at the Center for Advanced Microstructures and Devices (CAMD), I would like to wholeheartedly and gratefully acknowledge following people for their contribution to this dissertation that could not be possible to finish without their help and support.

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Abstract

It has been well documented that the surfaces of solids may differ from their bulk counterpart. The symmetry that a bulk possesses is broken at the surface. Due to this broken symmetry in the reduced dimension of the surface, the energetic of the surface also differs from the bulk counterpart. Reconstruction, charge redistribution, and surface alloying are phenomena that minimize the surface free energy.

Surface properties of scientifically and technologically important bimetallic systems are the main focus of this dissertation. Specifically, surfaces of bulk alloy or heteroepitaxially grown metal-on-metal systems have been investigated primarily with two indispensable surface techniques, scanning tunneling microscopy and angle-resolved photoemission spectroscopy, which reveal the atomic and electronic structure of bimetallic systems, respectively.

In the first system detailed herein, the surfaces of the ordered intermetallic alloy FeAl(110) exhibit surface segregation, which changes the Al concentration in the near surface region. The segregation and corresponding concentration change of Al induces a reconstruction on the surface as a function of annealing temperatures. The increased Al concentration gives rise to stronger Al and Fe interaction and results in hybridization of the Al-\(sp\) and Fe-\(d\). Moreover, the oxide that forms on this surface is a homogeneous ultrathin alumina film. Because of the nanometer thickness, this thin film displays a two dimensional electronic structure. It is concluded that an even mix of octahedrally and tetrahedrally coordinated Al ions in the zigzag-stripe thin-film alumina structure is formed, which has been under scientific debate for many years.
The atomic and electronic structure of Ag on Cu(110) and on Cu(100) systems has also been studied. These bimetallic systems form a surface confined alloying at the initial stages of growth and an overlayer phase as the Ag concentration increases in order to relieve the strain caused by Ag atoms, which have larger atomic size than Cu atoms. Electronically, bulk like energy distribution of the states indicates stronger interaction of Ag and Cu in the surface alloy phases than the overlayer phase, which displays only a two dimensional structure.
Chapter 1

Introduction

Comprised of two differing metals, a bimetallic surface is a reduced dimensional, 2 dimensional (2D) world in which the physical and chemical properties can be radically different from either of each constituent metal surface or of their bulk counterparts. The basic and practical importance of bimetallic surfaces is the profound impact of these materials on surface related phenomena such as catalysis, corrosion, and electrochemistry. In order to predict and control these phenomena, studies to probe and understand the structural, electronic, and chemical properties of bimetallic surfaces, on a fundamental level, have become a major technological and scientific goal over the last decades. It is well acknowledged that bimetallic surfaces exhibit remarkably different chemical and catalytic properties than the corresponding pure metal surfaces. A small alteration of the structure and the composition of bimetallic surfaces may drastically enhance or diminish the properties aforementioned.

Bimetallic surfaces are produced in various ways. In addition to cutting/cleaving bulk alloys along high-symmetry crystallographic directions, bimetallic surfaces may be grown via heteroepitaxial metal-on-metal growth methods. This latter approach entails depositing, typically through molecular beam techniques, one metal onto another metal
surface (i.e. heteroepitaxial growth) and allowing for the intermixing of two species on the surface. This intermixing of two metals is termed *surface alloying* and it deviates from the well-known three simple growth models named for their original investigators: layer by layer or Frank van der Merwe (FM) growth [1], three dimensional or Volmer Weber (VW) growth [2], and layer by layer growth followed by island formation or Stranski Krastranov (SK) growth [3]. The quantity which determines the growth mode is given by Young’s equation [4]

\[ \Delta \gamma = \gamma_a + \gamma_i - \gamma_s, \]  

where \( \gamma_a \) and \( \gamma_s \) are the surface free energies of the adlayer and substrate respectively, and \( \gamma_i \) is the interfacial free energy, which is generally unknown.

In the case of heteroepitaxial growth, if the adlayer and the substrate are miscible in the bulk, the intermixing or alloying is also expected at the surface. These metals, which intermix in the bulk phase, form stable bulk alloys and possess a negative enthalpy of mixing. There have been numerous studies that confirm this growth mode, for instance, Ag/Pt(111) [5] and Pd/Cu(100) [6]. Surprisingly, it has been shown in several studies that surface alloying (2D) may also occur for metals which are immiscible in the bulk (3D) and whose enthalpy of bulk mixing is high and positive [7]. The growth of Au on Ni(110) is a remarkable example of this [8,9]. The initial stages of Au growth on Ni(110) result in a 2D surface alloy phase which has no 3D bulk analog.

In this dissertation, we focus on elucidating the novel properties of different bimetallic alloy surfaces. In the case of bulk alloys, we investigate the clean and
oxidized surfaces of FeAl(110), a technologically important intermetallic bulk alloy. In addition, the bimetallic properties of two heteroepitaxially grown, bulk immiscible surface alloy systems are investigated. Specifically, the initial surface alloy growth stages of Ag on Cu(110) and Ag on Cu(100) in the submonolayer region are experimentally probed. The overall focus is to correlate the resultant geometric/atomic and the electronic structure of these unique bimetallic surfaces. In order to do this, various experimental probes are employed. Two primary experimental tools are scanning tunneling microscopy (STM), which is a powerful technique used to atomically resolve the images of surfaces, and angle-resolved photoemission spectroscopy (ARPES), which reveals the electronic structure of bimetallic surfaces.

Specifically, the underlying focus of this thesis research is driven by the successful inquiry to questions such as:

- How do we judiciously prepare reduced dimensional bimetallic surfaces?
- How do we probe and characterize the unique structural and electronic properties of these surfaces as a function of temperature, coverage, and other parameters?
- In the case of surfaces of bulk bimetallic alloys (i.e. FeAl), what is the driving force behind the ensuing surface atomic and morphological properties? How does surface stress/strain and near-surface composition dictate the resultant atomic structure? How do 2D surface binary phase diagrams differ from the bulk counterparts? How do the novel atomic properties and composition at the surface modify the electronic structure? How can we understand the observed surface electronic band structure in terms of the bonding at the surface?
• What is the atomic and electronic structure of an ultra-thin oxide grown on a bimetallic surface? How do the properties of such a nano-oxide compare with the corresponding bulk oxide?

• In the case of heteroexpitaxially grown surface confined alloys, what are the driving forces to form surface alloys? How do temperature and coverage modify the atomic structures? Does that determined dimensionality of the electronic structure correlate with the observed atomic structure?

As will be presented in more detail in subsequent chapters, in attempt to answer some of these questions we have focused on examining a few select systems. In what follows is introduction of what systems have been studied and correspondingly, what results have been determined.

FeAl(110) is an intermetallic alloy like NiAl(110), which is very stable and terminates with bulk structure. However, in previous studies conducting low energy electron diffraction and auger electron spectroscopy techniques [10,11], it has been revealed that the surface of FeAl(110) is not bulk terminated. The Al concentration in the near surface region depleted by preferential sputtering and subsequent annealing does not restore the bulk termination. In fact, the surface of FeAl(110) reconstructs into different phases as a function of annealing temperatures. However, the detailed atomic and electronic structure of phases formed on the surface has not been explored to this date. Motivated by this, we have investigated the atomic and electronic structure of FeAl(110). In addition, the oxidation behavior of the FeAl(110) surface has also been studied. A uniform and homogeneous thin film is formed only by heating the substrate during oxygen exposure at and above 850 °C. A new oxide phase which structurally has no bulk
counterpart is observed. ARPES measurements also show that this thin film has a well
defined band structure only in the surface plane.

Since the surface energy of Ag (1.3 J/m²) is smaller than Cu (1.5 J/m²), the
propensity for Ag island formation on the Cu(110) and on Cu(100) surfaces is expected.
However, STM results reveal that at submonolayer coverages, a surface alloying is
formed by exchanging Ag atoms with Cu atoms located at the topmost layer of the
substrate. It has been noted that Ag atoms substitutionally alloy into the Cu surface layer
to reduce the surface stress and to increase the effective coordination of the Cu atoms.
The increased coverages of Ag, however, induces a strain field, which is energetically
unfavorable and leads to an alloy-dealloy transition by replacing incorporated Ag atoms
out of the surface layer. In this phase, Ag atoms form dimer and trimer chains on the
Cu(110) surface and Ag(111) patches on the Cu(100) surface. The electronic
dimensionality of the surface alloyed and dealloyed Ag atoms has been studied with
ARPES.

The outline of this dissertation is as follows. This first chapter provides an
overview and motivation of this thesis study. The following chapter contains a
description of the experimental techniques employed; specifically, the theory and
physical operation of underlying the key techniques, STM and ARPES, which have been
used throughout this research. Chapters three through five contain the core of the
experimental results. Background, experimental data, and discussion of the experiments
on clean and oxidized surfaces of FeAl(110) is found in chapter three and four,
respectively. The results and discussions for surface confined surface alloys (Ag/Cu(110)
and Ag/Cu(100)) are presented in chapter five. Finally, chapter six provides a summary of the dissertation findings.

1.1 References


4. T. Young, Philos. Trans. 95, 65 (1805).


Chapter 2

Experimental Procedures

2.1 Introduction

This chapter will describe the experimental methods used for the research presented in this dissertation. Most notably, STM and ARPES are the two indispensable techniques mainly used through the entire research. Even though both techniques are electron based probes, the former primarily reveals morphological features and the latter elucidates the electronic structure of the surfaces of interests. All surface/thin film measurements were carried out in ultrahigh vacuum (UHV) chambers, which were typically maintained in the range of $10^{-10} - 10^{-11}$ Torr. As is well known, an UHV chamber is essential for keeping the contamination of the surface to a minimum. The homemade Aarhus STM located at Center for Advanced Microstructure and Devices (CAMD) was employed for STM measurements, and a plane grating monochromator (PGM) and 6m-toroidal grating monochromator (6m-TGM) located at the CAMD synchrotron radiation facility, were used in the photoemission experiments. A small hemispherical analyzer on the PGM endstation and a large HA150 hemispherical analyzer on the 6m-TGM beamline endstation were used to collect and analyze the photoelectrons excited from the surface of the sample probed. The description of the UHV chambers (endstations) used for the
present study and the procedures to acquire UHV have been described in detail elsewhere [1,2].

2.2 Scanning Tunneling Microscopy (STM)

2.2.1 Basics of the Operation

The scanning tunneling microscope was invented in the early eighties by Binning and Rohrer at the IBM research laboratory in Zurich [3,4]. Binning and Rohrer received the Nobel Prize in physics in 1986 for this achievement. Even though the STM images the surface in real space, it is not a true microscope. It does not give a direct image of the surfaces under investigation. It is a spectroscopic tool that probes the local electron density. The STM yields information about the density of filled and empty states below and above the Fermi level. The lack of elemental/chemical specificity of the imaged atoms is the most notable limitation of the STM.

The principle and operation of the STM are astonishingly simple. A sharp conducting tip, typically made of W or Pt/Ir wire, is brought into close enough proximity (~5 Å) with a conducting surface that an overlap occurs between the wavefunction of the tip and the atoms at the surface of the sample. When applying a bias voltage, ranging from a few millivolts to a few volts between the tip and sample, no current would flow in a classical picture due to the vacuum gap; however, electrons tunnel through the potential barrier in the quantum mechanical tunneling picture and give rise to a small tunnel current on the order of 1-10 nA. Depending on the polarity of the bias voltage, the electrons can tunnel from the tip to the sample or vice versa. The operative principle is shown in fig. 2.1. The scanning movements depend on the piezo tube, also called a scanner tube. The inside and outside of the tube are comprised of silver electrodes. The
outside electrode is cut symmetrically into four sections. By applying a positive voltage to one electrode and a negative to the one on the opposite side, one side will expand and the other side will contract.

Fig. 2.1. The schematic shows the basic operation principle of the STM (from Ref. [5]).

This causes the scanner tube to bend and makes the $x$ and $y$ raster scan with four electrodes. The $z$ motion is manipulated by applying a voltage to the inner electrode. The preset value of the tunnel current, typically 0.5-5 nA, is chosen and the actual tunnel current is compared with the preset current. To compensate for the difference in current, a voltage proportional to the difference is applied to the $z$ voltage enabling a feedback circuit in the constant current mode. The actual current is normalized as the distance between the tip and sample changes across the corrugated surface. The $z$ voltage is
recorded as a function of the lateral position of the tip during the raster scan and this provides the map of the surface topography. Normally, the constant current mode is used, and quick response feedback is implemented. The other mode used for imaging is the constant height mode, wherein the tunneling current is recorded while the tip and the sample distance is kept constant. In this mode a slow response feedback loop is used to maintain a constant time averaged current.

One of the prerequisites to obtain atomically resolved STM images is to make a sharp tip. Chemical etching is used to fabricate a sharp tip. The following is a short summary of how such a tip is made. A tungsten wire of 4mm diameter is submerged ~1 mm in the middle of the Pt ring that placed in the top of solution 2-4 Normal NaOH solution. A constant voltage of 10 V is applied between the wire and the tip to electrochemically etch it away. The initial current of 15 mA reduces to 5 mA through the etching process. The bottom part of the wire submerged into the solution breaks down and forms the sharp tip as displayed in Fig. 2.2. The voltage is turned off to avoid further etching.

![Fig. 2.2. Scanning electron microscope image of a W tip after electrochemically etched.](image)
2.2.2 STM Theory

The theoretical approach to STM is a formidable task due to complexities in characterization of the tip and sample wave function, description of the tunneling potential and determination of the strong interaction of the tip and sample. The interaction results from close proximity of the sample and the tip. Another difficulty is the unknown shape and chemical composition of the tip which may change during the scanning. A reasonably complete explanation of the STM was achieved on the basis of Tersoff-Hamann theory [6,7]. This theory is based on the perturbative transfer Hamiltonian, originally proposed by Bardeen, where the tip and sample are treated as two independent wavefunctions [8]. Fig. 2.3 shows wavefunctions of the sample ($\Psi_\nu$) and the tip ($\Psi_\mu$) which decay into the classically forbidden region of potential barrier.

Fig. 2.3. The wavefunctions tip and the sample decay exponentially into potential barrier between the tip and the sample.
The time dependent Schrödinger equation for $\Psi$, which is a time dependent linear combination of two time independent wavefunctions ($\Psi_v$, $\Psi_\mu$), is used to express the matrix element $M$ as

$$M_{\mu\nu} = \frac{\hbar^2}{2m} \int_{S_0} d\vec{S} \cdot \left( \Psi_{\mu}^* \nabla \Psi_v - \Psi_v^* \nabla \Psi_{\mu} \right).$$  \hspace{1cm} (2.1)$$

$S_0$, the area in which integral is calculated, lies over the tunnel barrier region. By applying Fermi’s golden rule, the tunnel current can be found and reads

$$I_t = \frac{2\pi e}{\hbar} \sum_{\nu,\mu} f(E_v) \left[ 1 - f(E_v + eV_t) \right] |M_{\mu\nu}|^2 \delta(E_\mu - E_v),$$  \hspace{1cm} (2.2)$$

where $f(E)$ is the Fermi-Dirac function [9]. The delta function reflects that the electron does not lose energy during the tunneling, and the Fermi-Dirac function designates a tunneling from a filled state to an empty state. In order to calculate the matrix element, Tersoff and Hamann used 2D Bloch expansion of the wavefunction. The $s$-wave is chosen for the wavefunction form of the tip. Under these assumptions the tunneling current can be written as

$$I \propto VR^2 \exp\left(-\frac{8m\phi}{\hbar^2 z}\right) \rho_s(r, E_t),$$  \hspace{1cm} (2.3)$$
where

\[ \rho_s(r_t, E_F) \equiv \sum |\Psi(r_t)|^2 \delta(E_c - E_F), \tag{2.4} \]

\( \varphi \) and \( R \) denote the effective local barrier height (work function) and the radius of the curvature of the tip apex in (2.3). \( \rho_s \) is the local density of the sample surface at the Fermi level evaluated at a position right above the surface in the center of the tip, \( r_t \). The equation (2.3) reveals that the STM images are the contour map of the surface LDOS at \( E_F \). If typical values are inserted into this equation, a change in the tip and the surface distance by 1 Å will vary the magnitude of the tunnel current by a factor of ten. Furthermore, this demonstrates that the outermost tip atom dominates the entire electron tunneling process. The corrugation of the LDOS reflects the geometric structure of the surface since for metals the LDOS spatially follows the positions of the individual atoms. The application of the Tersoff Hamann theory is limited to low bias voltage. With higher bias voltages, the STM image is interpreted as the integrated LDOS of the surface atoms between \( E_F \) and \( E_F \pm V \). Depending on the polarity of the bias voltage the filled or empty states of the sample are determined as sketched in Fig. 2.4. As the bias voltage increases, more states are involved in the tunneling.

\[ \text{Fig. 2.4. The energy diagram of tunnel junction between the tip and sample.} \]
2.2.3 The Aarhus STM

In the past, the biggest challenge to implementing STM was to bring tip and sample into close proximity (~10Å) and control them to obtain reasonable tunneling current. With today advancements, this challenge has been virtually overcome. The Aarhus STM used in this study is shown in Fig. 2.5. It is a very stable and compact ultra high vacuum STM based on the scanner tube and inchworm design. The small size of the STM and rigid mounting of the crystal diminish the demand of external damping. The sample is placed on a tantalum plate and clamped to the STM house with two springs. In the case at hand, a tip is made of tungsten wire, and as detailed above, is electrochemically etched. The tip holder is glued to the scanner tube and holds the tip

![Fig.2.5. A cross sectional view of the Aarhus STM. (1) Al cradle, (2) top plate, (3) springs (4) sample and sample holder, (5) quartz ball, (6) scanner piezo tube, (7) STM housing, (8) ceramic rod, (9) ceramic disc, (10) inchworm piezo tube (11) zener diode, (12) spring, (13) cold finger, (14) LN₂ feedthrough (from Ref. [5]).]
with a spring load. Three quartz balls provide electrical and thermal insulation of the STM from the top plate to keep the thermal drift as small as possible. The bias voltage is applied to the top plate. Since the plate is mounted on the Al cradle and holds the sample, the Al cradle is also at the bias voltage. The scanner tube is made of piezoelectric material and coated with silver electrodes inside and outside. The outer electrode is divided into four electrodes in equal size along the tube axis. The z movement is controlled by applying a voltage to the inner electrode. The deflection is achieved for raster scanning by applying voltages to opposite electrodes which stretch and shorten the tube. The scanner tube is glued onto a ceramic rod, called the inchworm. This rod is placed into another piezo tube for coarse approach. The piezo tube is connected to the STM housing with a ceramic disc. The outer electrode of the inchworm is divided into three parts, while the undivided inner electrode is kept at ground potential. The upper and lower electrodes clamp and unclamp the rod by applying a negative or positive voltage, respectively, while the center electrode expands and contracts for movement toward or away from the sample in an “inchworm” like mode. The STM is housed in an Al cradle which due to its high heat capacity, acts as a cooling reservoir. The sample can be cooled down to 120 K by passing liquid nitrogen through a tube in the Al cradle locking mechanism. The STM can be kept at room temperature during cooling with a 75 V zener diode which is placed right under the STM house. The Al cradle is suspended by three springs with a low resonance frequency (~2-4 Hz) which damps high frequency vibrations. Due to the compact size of the STM, the mechanical resonance frequency is high (~2 kHz). The resonance frequency of the ceramic rod and the scanner tube is even higher (~8 kHz) and requires no further vibrational damping. All electrodes are
controlled by high voltage, low noise amplifiers with a voltage range of ± 200V. These
voltages are controlled by 16-bit Digital to Analog converters (DAC) performed in the
range of ± 5V. DAC also governs the bias voltage on the sample and the set point for
tunnel current.

2.3 Angle-Resolved Photoelectron Spectroscopy (ARPES)

2.3.1 ARPES Theory

Angle-resolved photoemission spectroscopy is a widely used technique which
provides essential information about the electronic structure of solids and their surfaces.
Photoelectron spectroscopy, also known as photoemission, investigates the occupied
electronic states of solids.

In 1887, Wilhelm Hallwachs showed that negative particles are emitted from
various metal surfaces when similarly illuminated. In 1905, Albert Einstein explained the
photoelectric effect and proposed Planck’s quantum hypothesis. The photoelectric
phenomenon was described in a simple form: a photon of $h\nu$ absorbed by an electron
excites the photoelectron to free space with kinetic energy. The photoelectron loses an
amount of energy known as work function. Einstein’s photoelectric equation is
expressed as

$$E_k = h\omega - E_b - \phi,$$  \hspace{1cm} (2.5)

where $E_b$ is the binding energy of the electrons in the solid. Hydrogen lamps separated
with LiF windows for energies below 11.8 eV were initially used as a light source. Later,
with the development of windowless He lamp sources, emissions at 21.2 and 40.8 eV
were utilized for photoelectron spectroscopy. Today, the advanced properties of
synchrotron light sources provide tunable energy to probe the electronic structure of solids in detail.

In the photoemission process, the emitted electrons are collected by an analyzer and produce an energy distribution curve (EDC). The EDC comprises both primary photoelectrons that do not confront an inelastic collision and a background from secondary photoelectrons that confront inelastic collision one or more times. The occupied electronic structure of solids includes valence electrons (hybridized orbitals) and core level states (atomic like orbitals). The valence band reveals bonding nature, and core levels provide information on elemental/chemical identification. The description of the photoemission process is displayed in figure 2.6.

Fig. 2.6. Schematic of the photoemission process illustrates excitation of a core electron.
Photoemission is the only experimental method which reveals the absolute binding energy of the electrons in solids. Due to energy range of ultraviolet light (10-1000eV), the mean free path, that is a measure of escape depth of electrons without suffering inelastic scattering, is very limited. As seen from fig. 2.7, the mean free path is between 5-20 Å for photoemission spectroscopy energy range, which makes this technique very surface sensitive.

The theoretical formalism of photoemission spectroscopy is also a formidable task due to involvement of many body problem. Several models have been proposed to explain the process. Among them, a three-step model developed by Berghund and Spicer [10] is often used to interpret the photoemission spectra. This method is simpler and
more instructive than the one-step process which deals with an electron removed from an
occupied state within the solid and collected at the detector. However, in the three-step
theoretical approach, the photoemission process is separated into three independent
stages [11]. The three steps as shown in figure 2.8 consist of (1) optical excitation of an
electron from an initial state into a final electron state inside the crystal (2) the
propagation of the electron to the surface, and (3) the emission of the electron from the
solid to the vacuum.

Fig. 2.8. Schematic of the three-step model for photoemission spectroscopy (from Ref.
[11]).
In the first step the optical excitation indicates an interband transition between the states of the same wave vector $k$ in the reduced zone scheme, see Fig. 2.9. The internal energy distribution of the photoexcited electrons is

$$N_{\text{in}}(E, \hbar \omega) \propto \sum_{f,i} d^3k |M_{ji}|^2 \delta(E_f(k) - E_i(k) - \hbar \omega) \delta(E - E_f(k)), \quad (2.6)$$

where $E_f$ and $E_i$ are the energies of the final band state $|f, k\rangle$ and initial band state $|i, k\rangle$, respectively. $E$ in the equation (2.6) denotes the final kinetic energy. $|M_{ji}|^2$ is the
transition probability for optical excitation between the initial and final state and is given by Fermi’s golden rule

\[
|M_\beta|^2 = \frac{2\pi}{\hbar} \left| \langle f, \vec{k} | H^\text{int} | i, \vec{k} \rangle \right|^2 \delta(E_f - E_i - \hbar\omega).
\]  

(2.7)

The perturbation operator (interaction Hamiltonian) between an electron and electromagnetic radiation with the vector potential \( \vec{A} \) is given by

\[
H^\text{int} \propto \frac{e}{m} \vec{A} \cdot \vec{p}.
\]  

(2.8)

The second step is the propagation of the electron to the surface. A large number of electrons suffer inelastic scattering, mainly from electron-electron interaction, and lose part of their final energies. These electrons form a continuous low-energy background in the photoemission spectroscopy and lose the information of their initial energies in the solid. The probability that an electron reaches the surface without undergoing an inelastic scattering process is described by the mean free path \( \lambda \). As mentioned before, the small range of mean free path of an electron (5-20 Å) in UV-VUV photoemission spectroscopy makes this technique very surface sensitive. The propagation to the surface is characterized by the transport probability \( D(E, \mathbf{k}) \) which is proportional to the mean free path.

In the third step photoelectrons are transmitted to the vacuum through the surface. Those electrons for which the normal component of the kinetic energy is higher than the
surface potential barrier, \( V_0 \), can escape into the vacuum and those whose energies are not sufficient are reflected back into the crystal. \( V_0 \) is also called inner potential and is determined by \( E_0 + \phi \) where \( E_0 \) is the bottom of the valence band as shown in Fig. 2.10. Therefore in order to escape to the vacuum photoelectron must have the energy

\[
\left( \frac{\hbar^2}{2m} \right) \vec{k}_{\perp}^2 \geq E_{\text{vac}} - E_0
\]  

(2.9)

where \( \vec{k}_{\perp} \) is the normal component of the wavevector of the photoelectron.

Fig. 2.10. The electrons travel in a potential of \( V_0 \) inside the crystal.

Fig. 2.10 also shows that the wave vector of the electron in the vacuum is determined by the intersection of a free electron parabola with its zero in the vacuum.
level and the final state energy $E_f$. Due to transitional symmetry parallel to the surface, the parallel component of the wavevector is conserved

$$\vec{p}_\parallel = \vec{k}_\parallel^{\text{ext}} = \vec{k}_\parallel^{\text{int}} + \vec{G}_\parallel,$$  (2.10)

where $\vec{p}$ is the momentum of the photoelectron in vacuum, $\vec{k}_\parallel^{\text{int}}$ and $\vec{k}_\parallel^{\text{ext}}$ are the parallel components of the wavevector inside and outside the crystal, and $\vec{G}_\parallel$ is the parallel component of the reciprocal lattice vector. Since the surface breaks the symmetry, the wavevector component perpendicular to the surface is not conserved. The potential barrier decreases the kinetic energy of the photoelectron escaping from the surface. The perpendicular component of the wavevector of the photoelectron is determined by the energy conservation

$$E_{\text{kin}} = \left(\frac{\hbar^2}{2m}\right)(\vec{p}_\perp^2 + \vec{K}_\perp^2) = \left(\frac{\hbar^2}{2m}\right)(k_{\perp}^{\text{ext}}^2 + k_{\perp}^{\text{int}}^2) = E_f - E_{\text{vac}}.$$  (2.11)

With consideration of equation (2.5), the parallel component of the wavevector exterior to the crystal can be given by

$$k_{\parallel}^{\text{ext}} = \sqrt{\frac{2m}{\hbar^2}} \sqrt{\hbar \omega - E_k - \phi \sin \theta} = \sqrt{\frac{2m}{\hbar^2}} E_{\text{kin}} \sin \theta$$  (2.12)
where $\theta$ is the emission angle between the normal of the sample surface and the analyzer. Due to inner surface potential, $k_\perp$ is not conserved; however, the external component of the wavevector can be determined by energy conservation in the equation (2.11)

$$k_{\perp}^{\text{ext}} = \sqrt{\frac{2m}{\hbar^2} E_{\text{kin}}^2 - k_{\parallel}^{\text{ext}}^2} = \sqrt{\frac{2m}{\hbar^2} E_{\text{kin}}^2 \cos \theta}.$$ (2.13)

In brevity, the third step can be described by a transmission rate of $T(E,k)$ as long as $k_{\perp}^{\text{ext}} > 0$.

Combining the description for each step, the final form for the energy distribution of the photoelectrons is given by

$$N(E, k_\parallel, \hbar \omega) \propto \sum_f \int d^3 k |M_{fi}|^2 D(E_f, \bar{k}) \Gamma(E_f, k_\parallel) \times \delta(E_f - E_i, \hbar \omega) \delta(E - E_f, \bar{k}) \delta(k_\parallel + G_\parallel - k_{\perp}^{\text{ext}}).$$ (2.14)

The simplification of the final state as a free electron like within the model reveals a good estimation to describe the band structure of the crystal.

### 2.3.2 Dipole Selection Rules

Dipole selection rules are implemented to identify possible transitions between the electron energy bands. Bands in the crystal and the electric dipole operator exhibit distinct symmetry. Since the photocurrent depends on the matrix element

$$|M_{fi}| = \frac{2\pi}{\hbar} \left\langle f, \bar{k} | \frac{e}{m} \vec{A} \cdot \vec{p} | i, \bar{k} \right\rangle,$$ (2.15)
by considering special geometries of the experiment, selection rules can be used to reduce the number of transitions and make more tractable the observance of the initial states. The polarized light which excites the electron and the detection direction of the analyzer which collects the emitted electron may lie in the mirror plane of the crystal. The initial electronic states can be odd (anti-symmetric) or even (symmetric) with respect to reflection in the mirror plane of the sample. They retain or reverse their sign upon reflection. Therefore, the last term, initial electronic state, in the matrix element of the equation (2.15) is sample dependent. On the other hand, the final electronic state and dipole operator in the matrix element is fixed by geometry. The final state wave function must always be even; otherwise the analyzer, located in the mirror plane, would see a node of the emitted electron. In order to detect a photoemission signal the matrix element should be non-zero and this is satisfied in the following symmetries,

\[
|M_{\beta}| = \frac{2\pi}{\hbar} \left( \frac{f, \bar{k}}{e m \tilde{A} \cdot \tilde{p}} \right) \left\{ \begin{array}{c}
\langle + | + | + \rangle \\
\langle + | - | - \rangle
\end{array} \right\}
\]

Therefore, the appropriate choice of the geometry reveals important information about the symmetry character of the bulk, the surface states and also the molecular orbitals of adsorbates.

The bulk and surface Brillouin zones of the Cu(110) and Cu(100) used in the investigation of the surface confined alloy experiments in this study are shown in Fig. 2.11(a) and (b). In addition, the Brillouin zones of the FeAl(110) conducted to elucidate the segregation phenomenon, which occurs in the near surface region, are displayed in Fig. 2.12. The selection rules depending on the geometries of the parameters are given in
the text of the corresponding chapters. In normal emission, photoelectrons are collected with the analyzer normal to the surface, and initial states along the bulk symmetry line.
are probed by varying the photon energy. Since the parallel component of the wavevector is zero, the final state lies in a high symmetry direction of the bulk. For Cu(110) and FeAl(110) the principal direction is $\Sigma$ and for Cu(100) it is $\Delta$ line.

2.4. Photoemission Spectroscopy System

The plane grating monochromator (PGM) and 6-meter toroidal grating monochromator (6-m TGM) were used in order to monochromize and focus the incident beam onto the sample in the UHV chambers. The radiation is provided to these beamlines from the 1.3-1.5 GeV electron storage ring at CAMD. Electrons are injected into the storage ring from a 200 MeV linear accelerator. The typical beam current is
around 100 mA at 1.3 GeV and slightly lower for 1.5 GeV. The main layout of the CAMD storage ring, eight bending magnets, 7 T wiggler and the beamlines are shown in Fig. 2.13. As the electrons pass through the bending magnet, a very intense radiation is emitted in a continuous spectrum. The synchrotron radiation intensity is approximately $10^6$ higher than conventional sources.

2.4.1 PGM Beamline and CAMD Analyzer

The PGM beamline was used to monochromize and focus the radiation onto the sample, and the CAMD analyzer (hemispherical analyzer) was employed to measure the
energy of the photoelectron ejected from the surface of the sample. These two systems were utilized for Ag/Cu(110) experiments. The detailed description of the beamline is given elsewhere [12]. The photon range of PGM is 30-1000 eV and the measured resolving power is 800 between 200-1000 eV. The measured beamline flux normalized to 100 mA ring current for high and for low energy grating is shown in fig. 2.14.

![Figure 2.14](image)

Fig. 2.14 The plot of the measured PGM beamline photon flux for high energy grating with 1220 grooves/mm and for low energy grating for 360 grooves/mm as a function of photon energy.

Besides two gratings, the optical elements of the beamline include five mirrors, and the entrance and exit slits. Table 2.1 illustrates the parameter of the optical components in the beamline, and Fig. 2.15 shows the schematic of the PGM beamline. The entrance slit keeps the energy resolution independent of source size and stability and the exit slit makes the beamline operate with high resolution. Decreasing the exit slit width supplies a
higher resolution at the expense of lower intensity. The PGM will be upgraded to a variable line spacing plane grating to increase the resolution in the near future.

Table 2.1. Parameters of the optical components of the PGM beamline

<table>
<thead>
<tr>
<th>Component</th>
<th>Size (mm)</th>
<th>Radius (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1 Cylinder</td>
<td>330×30</td>
<td>193</td>
</tr>
<tr>
<td>M2 Cylinder</td>
<td>330×30</td>
<td>103125</td>
</tr>
<tr>
<td>M3 Plane</td>
<td>120×30</td>
<td>∞</td>
</tr>
<tr>
<td>PG Plane</td>
<td>110×30</td>
<td>∞</td>
</tr>
<tr>
<td>M4 Sphere</td>
<td>250×30</td>
<td>288120</td>
</tr>
<tr>
<td>M5 Toroid</td>
<td>100×30</td>
<td>4000052.3</td>
</tr>
</tbody>
</table>

Fig. 2.15. Schematic of the PGM beamline and incorporated optical elements (from Ref. [12]).
Photoelectrons emitted from the sample were collected with the hemispherical energy analyzer (CAMD analyzer), shown in Fig. 2.16. The CAMD hemispherical analyzer employs constant pass energy and operates with a series of electrostatic lenses (L1-L5). The electrostatic lenses collect electrons and transmit them to the analyzer entrance slit; they also decelerate or accelerate the electrons to the chosen pass energy of the hemisphere. The analyzer chooses the electron kinetic energy of interest and passes these electrons through the exit slit to the electron analyzer detector. Pulses are collected here and amplified using commercial electronics. The angular motion of the analyzer is functioned by a drive mechanism which consists of two rotary motion feedthroughs. These feedthroughs are coupled to each other as the azimuthal drive located on the polar drive and they accomplish any polar and azimuthal angles needed for photoemission measurements.

Fig.2.16. The schematic of the CAMD hemispherical electron energy analyzer (from Ref. [13]).
2.4.2 6-m TGM Beamline and HA150 Analyzer

6-m TGM was relocated from the National Synchotron Light Source (NSLS) at Brookhaven National Laboratory to CAMD in 1996. The layout of the beamline and the optical elements are shown in Fig. 2.17. Optical elements contain plane (M1), bendable float glass cylinder (M2), spherical (M3), and elliptical (M4) mirrors. The TGM monochromator incorporates three gratings; low (288 lines/mm), medium (822 lines/mm) and high energy (2400 lines/mm) gratings. The details of the optical elements are given in Table 2.2. The distance between the entrance slit and the exit slit is 6 meters. Fig. 2.18 shows the measured beamline flux based on silicon photodiode at the target point normalized to 100 mA ring current. The operating range of the TGM is 15-200 eV with a maximum resolving power of 2000.

Fig. 2.17. Schematic of the 6-m TGM beamline (a) top (b) side view.
Table 2.2. Parameters of the optical components of the PGM beamline (from Ref. [2])

<table>
<thead>
<tr>
<th>Optical Element</th>
<th>Type</th>
<th>Radius of Curvature (mm)</th>
<th>Pole Distance from Source (mm)</th>
<th>Deflection Angle (deg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₁</td>
<td>Plane Mirror</td>
<td>—</td>
<td>2650</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Gold:Copper</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>80 x 400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M₂</td>
<td>Bendable Cylindrical Mirror</td>
<td>Variable</td>
<td>4050</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Gold:Glass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 x 1400</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M₃</td>
<td>Spherical Mirror</td>
<td>3995.73</td>
<td>8000</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>Gold:Copper</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>60 x 360</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Entrance Slit</td>
<td>Adjustable Jaws (0.025 - 1.00) x 15</td>
<td></td>
<td>11,500</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>toroidal Grating</td>
<td></td>
<td>11,430 - 11,550</td>
<td></td>
</tr>
<tr>
<td>G₁</td>
<td>~288 lines/mm</td>
<td>R=19246</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G₂</td>
<td>~822 lines/mm</td>
<td>ρ=470.5</td>
<td>13,611</td>
<td>20</td>
</tr>
<tr>
<td>G₃</td>
<td>~2400 lines/mm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gold:Glass</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>45 x 125</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exit Slit</td>
<td>Adjustable Jaws</td>
<td>17,500</td>
<td></td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>(0.05 - 1.00) x 15</td>
<td>17,000 - 17,650</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M₄</td>
<td>Elliptical Mirror</td>
<td>a=1600.0</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Gold:Copper</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>40 x 250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Target</td>
<td></td>
<td>20,699</td>
<td></td>
<td>—</td>
</tr>
</tbody>
</table>

A large HA150 hemispherical analyzer was employed to collect the photoemission data for the clean and oxidized surfaces of the FeAl(110) single crystal. The schematic diagram of the energy analyzer is shown in Fig. 2.19. The analyzer has a mean radius of 150 mm. Since the analyzer is fixed, angle dependent photoemission measurements were accomplished by rotating the sample. The HA150 hemispherical analyzer control electronics operates a series of electrostatic lenses (L1-L4) to collect and transmit the photoelectrons.
Fig. 2.18. The plot of the measured photon flux for the 6m-TGM beamline [from Ref. [2]].

Fig. 2.19. Schematic of the HA150 hemispherical electron energy analyzer (from Ref. [2]).
2.5 References


Chapter 3

Surface Reconstruction of FeAl(110)

3.1 Introduction

The physical and chemical properties of the intermetallic alloys in high technology applications such as corrosion resistance, oxidation, and catalytic activity depend on the structure and the composition of the surface layer. By changing the stoichiometry of the alloy, a new material can be readily developed and the new structure of the alloy can show unprecedented physical and chemical properties. In order to modify these properties, a detailed understanding of the atomic and the electronic structure of metal alloys is required.

Particularly, transition metal aluminides, e.g. NiAl, CoAl, and FeAl, have attracted considerable interest due to their unique properties such as high melting points, enhanced corrosion resistance, relatively low density, and utility as soft magnetic materials [1-4]. These transition metal aluminides are ordered intermetallic alloys. In contrast to random alloys wherein one of the alloy constituents preferentially diffuses to the surface selvage region at elevated temperatures, ordered intermetallic alloys typically have the same atomic composition (stoichiometry) on the surface as in the bulk due to their strongly attractive chemical bonding between the bimetallic species of the alloy.
These interactions hamper the diffusivity and give rise to a terminated surface with bulk stoichiometry composition. However, the chemical bonding trends between the early transition metals (TiAl, VAl) and the late transition metal alloys (FeAl, NiAl) show different characteristics [5]. For early transition metal alloys, the bonding is dominated by strong directional interaction between the nearest transition metal neighbors. For the case of late transition metal alloys, charge transfer from Al to the transition metal, and hybridization between Al $sp$ and transition metal $d$-states play essential roles in bonding. These differences in bonding give rise to an $fcc$ based crystal structure for early transition metal alloys and a $bcc$ based crystal structure for late transition metal alloys.

Among the late transition metal alloys, the most investigated intermetallic alloy is the ordered NiAl metal alloy; moreover, the most intensely studied surface of this alloy is the (110) surface, which is the close-packed surface of the $bcc$ lattice. In terms of the crystal structure, NiAl has one of the simplest structures among intermetallic alloys. Two simple cubic lattices of Ni and Al interpenetrate and form a CsCl structure which retains a $bcc$ lattice. As compared to Ni or Al, NiAl has a higher melting point, and its high heat of formation makes the alloy very stable at room temperature. Most interestingly, both LEED-$IV$ and medium energy ion scattering revealed that the surface exhibits a rippled relaxation as Al atoms are “pulled out” of the surface by 0.2 Å and Ni atoms are moved inwards by 0.12 Å with respect to their bulk position [6,7]. Electronically, due to charge transfer from Al, the Ni $d$-band is filled. Moreover, surface states, measured experimentally by ARPES, exist in the bulk band gap and have been explained theoretically with pseudopotential total energy calculations [8]. It is proposed that the
electronic density due to these surface states is the origin of the electron standing waves which have been observed even at room temperature by STM [9,10].

It is well known that surfaces of solids can differ significantly from the bulk in regard to the atomic and electronic structure. In addition to the geometrical reordering in the surface, metal alloy surfaces can exhibit a deviation in chemical composition. Surface atoms may have chemically different atomic neighbors compared to those in the bulk and this leads to a chemical reordering in the surface. When the chemical reordering is not stoichiometric (not preserving the quantity of constituents present in the bulk) due to segregation of one of the constituents to the surface, new ordered/disordered phases emerge in the surface/surface selvage. This leads to a “surface” phase diagram which can be radically different from its bulk phase diagram counterpart. However, as mentioned above, the ordered intermetallic alloys are expected to be bulk terminated due to the strong interaction between the different atoms. NiAl is the most notable example of this phenomenon. Another transition metal alloy, CoAl(110), also possesses a bulk terminated surface which has been investigated by Blum et al. employing LEED experiments with computational calculations using Tensor LEED approach [11]. The surface rippling (i.e. periodic relaxation normal to the surface) also was observed on the CoAl(110) surface as the Al plane of atoms protrudes 0.18 Å with respect to Co plane of atoms. Like these other late transition metal aluminides, FeAl(110) also crystallizes in the CsCl structure. Surprisingly, it has been reported by Graupner et al. [12,13] that, in contrast to NiAl(110) surface, FeAl(110) does not follow the trend of NiAl and CoAl.

LEED and AES results of Graupner [12,13] indicate that the surface of FeAl(110) does not show a structure and composition expected from a simple bulk termination of
the surface. As in NiAl(110), the surface cleaning is performed by sputtering, and this process results in a depletion of Al in the surface region. However, unlike the NiAl(110) case, subsequent annealing after sputtering does not restore the surface to its bulk stoichiometry, and indeed, Al preferentially segregates to the near surface region. This surface segregation leads to the development of a sequence of different atomic structures, or superstructures, as a function of annealing temperatures. Annealing to 400 °C reveals a (2x1) structure. Higher annealing produces an incommensurate superstructure. In the temperature range of 600-800 °C, LEED shows a severe streaking along the [1\bar{1}0] direction of the substrate. Above the annealing temperature of 800 °C, the incommensurate superstructure reappears in the LEED pattern. It is astonishing that over the entire annealing temperature ranges, this previous study did not observe a (1x1) diffraction pattern with LEED, to correspond to a bulk terminated (110) surface. With this finding, Graupner et. al. disproved the previous LEED study of Gleason et. al. [14], where a bulk terminated surface of FeAl(110) was found due to an observation of (1x1) diffraction pattern. Moreover, in addition to the (110) surface, previous LEED studies have shown that other low index and vicinal surfaces of FeAl also exhibit surface segregation and geometrically and chemically different structures on the surface [13,15].

In catalysis, the local geometric and electronic structure of a surface must be characterized to determine the active sites of the alloy. In the local picture, wherein each individual atom carries its identity at the surface, and the non-local picture, wherein the surface electronic structure is modified due to alloying mechanism, elucidation of the valence band electrons is vitally needed to understand the physical and chemical properties of the alloy. Previous studies based on LEED and AES have yielded only a
qualitative picture of this surface. This calls upon further studies using other techniques to obtain the local ordering and composition on the atomic level with the electronic structure which drastically affects the gas adsorption and heterogeneous catalysis phenomena. STM and ARPES techniques have proven to be indispensable for revealing the atomic and electronic structure of the metal alloy. In this chapter, the results of STM and ARPES measurements, which determine the atomic and electronic structure of the phases that develop on the surface of FeAl(110) due to Al segregation, will be presented and discussed.

3.2 Experimental Procedures

The STM experiments in this and the next chapter were started at Oak Ridge National Laboratory, employing an Omicron room temperature Scanning Probe Microscope. A variable temperature STM made by the STM group at the University of Aarhus in Denmark was used to complete the studies at the Center for Advanced Microstructures and Devices at Louisiana State University. Both measurements were conducted in ultrahigh vacuum surface science chambers, equipped with LEED, a cylindrical mirror analyzer and a quadrupole mass spectrometer. Atomic resolution could be obtained on a routine basis with these microscopes. The FeAl single crystal was grown at the Max Plank Institut fur Eisenforschung in Germany. The lattice constant was determined with X-ray diffraction as $a = 2.903 \, \text{Å}$ corresponding to a constituency of Fe$_{0.53}$Al$_{0.47}$ [16]. This composition of the constituents prevents the phase transition, seen at 50-50% of the bulk alloy, between FeAl and FeAl$_2$ structures at low temperatures [17]. The sample was cut by spark erosion and aligned to $\pm 0.3^\circ$ using Laue diffraction. The (110) oriented surface was mechanically polished using carborundum followed by 1 $\mu$m
alumina powder. The sample was mounted on a Ta sample platen with a K-type thermocouple attached to determine the sample temperature for STM study. For ARPES measurements, the sample was placed on a 2 cm² Ta sheet with two W wire passed through the sides of the crystal for a resistive heating. The ARPES data were conducted at the Center for Advanced Microstructures and Devices, using the end station on the 6-meter-Toroidal Grating Monochromator beamline. The normal emission measurements were taken with a $s+p$-polarized light directed at 45° incident angle. The FeAl(110) crystal was rotated in the plane of incidence for ARPES measurements since the 6-meter TGM beamline analyzer, VSW HA150, is fixed. The substrate was cleaned by repeated cycles of sputtering at room temperature (Ne⁺ ions, 1 keV, 20µA). The surface cleanliness was checked with the sharp LEED diffraction spots and photoemission spectra of clean FeAl(110) surface.

3.3 Results and Discussion

3.3.1 Atomic Structure of FeAl(110)

FeAl crystallizes, like NiAl, in the CsCl structure. Two interpenetrating simple cubic sublattices of Fe and Al form a bcc lattice. As drawn in Fig. 3.1 the truncated bulk (110) surface comprises the composite layers of Al and Fe parallel to the surface. The chains of Fe and Al atoms are coplanar and alternate with each other.

As mentioned before, the LEED study by Davis and Noonan [6] found that the NiAl(110) surface is bulk terminated with a large rippled relaxation. Ni atoms are contracted towards the bulk by 6% and Al atoms are expanded away from the bulk by 4.6% of the ideal interlayer distances. These results were also confirmed with medium-energy ion scattering experiment. The driving mechanism behind the rippling
mechanism is explained in several theoretical papers [18,19]. The charge distribution in the surface region is different from the bulk. The charge distribution around the Al atoms is modified considerably. Initially, the corrugated surface charge is smoothed in order to reduce the surface tension. Then, the Al atoms in the topmost layer move outwards, that is towards to vacuum region allowing more space to the compressed sp-electrons. Since

![Diagram of FeAl crystal](image)

**Fig.3.1.** The models illustrate the (110) plane of bcc lattice of FeAl crystal.

a Ni atom has nearly 10 d-electrons which strongly localize in the core region, the relaxation of Ni atoms results from the electrostatic interaction with the redistributed sp electrons. Due to migration of the released sp-electrons from the Al sites in the [001] directed Ni-Ni bridge (see Fig. 3.1), there is an increased charge in this region, which, in turn, increases an interaction around the Ni sites. The d-electrons localized in the bridge region feel a strong repulsive force which pushes them down to the bulk. The corresponding deeper layer relaxation is smaller compared to the topmost layer. The bulk structure is restored within the several layers.
In comparison to the theoretically and experimentally well-investigated NiAl(110) surface, the FeAl(110) surface has only been probed by AES and LEED experiments [12,13]. Interestingly, although it is expected to be similar to the surface of NiAl(110), the bulk terminated surface was not observed. The preferentially sputtering results in a depletion of Al in the near surface region and the annealing of this surface leads to diffusion of Al atoms from the bulk to the surface selvage. From the AES measurements, the Al concentration in the near surface region was calculated as a function of annealing temperatures and is shown in Fig. 3.2. The near surface Al concentration was derived from the Auger peak intensities (Fe: 47 eV, Al: 68 eV). The estimated electron depth of 4.2 Å for the Auger electrons was used in the calculation. As seen in the left side of the plot at room temperature, the depletion of Al right after sputtering gives rise to an Fe$_{59}$Al$_{41}$ stoichiometry in the near surface region. However, this attenuated Al

![Fig. 3.2. AES results of near surface Al concentration as a function of annealing temperatures of FeAl(110). The uncertainty is included with dotted line (from Ref. [14]).](image-url)
stoichiometry is lifted as the annealing temperatures is increased and Al diffuses from the bulk into the surface region. Two plateaus evolved in the data at 400 °C and above 600 °C and a transition region is observed between the annealing temperatures 600-800 °C. LEED reveals different superstructure spots as the annealing temperature increases. The first ordered superstructure that was reported is a (2x1) structure. LEED shows this superstructure at 400 °C. Previous studies [12,15] have proposed that this structure on the FeAl(110) is similar to the proposed reconstructed subsurface of FeAl(100) that develops at this temperature region. It is found that the metastable c(2x2) phase on the FeAl(100) surface at 400 °C leads to a bulk terminated surface at temperatures higher than 600 °C. For the c(2x2) surface, AES revealed an average 0.55 Al concentration in the near surface region, and an Al terminated surface was obtained by LEED IV analysis. As sketched in Fig. 3.3, the subsurface region also reconstructs and forms an Fe₃Al

![Fig. 3.3. Schematic view of the Al terminated surface of FeAl(100). The subsurface reconstructs and forms Fe₃Al metastable film. Unit cell of Fe₃Al is shown with dashed line.](image-url)
metastable interfacial film on the bulk FeAl. This reconstructed subsurface region is an interface to the bulk and is capped with the Al layer. Since the lattice constant between the Fe<sub>3</sub>Al and FeAl differs by only 0.5%, the interfacial Fe<sub>3</sub>Al slab may simply accommodate nearly pseudomorphically on top of the bulk FeAl. The top layer is chemically homogeneous, and this homogeneity is the reason for the fact that there is no rippling at this layer. However, it is clearly seen that the next nearest neighbor atoms in the first and third layers are chemically different and this causes the buckling in the third layer. This buckling exists in the fifth layer and decays for deeper layers [15]. From the best theory-experiment fit, it is proposed that the Fe<sub>3</sub>Al thickness on top of the FeAl bulk vertically consists of at least 6 layers. This implies that the stable interfacial layers are formed at around 400 °C. A clear picture is given in the bulk phase diagram of the FeAl shown in Fig. 3.4 [20].

![Bulk phase diagram of FeAl](image)

Fig. 3.4. The bulk phase diagram of FeAl shows several stable structures depending on the temperatures and concentration.
In the bulk phase diagram of the FeAl compound shown in Fig. 3.4, three stable phases occur for Al concentration lower than 50%. At low Al concentration the A2 phase is formed with Al and Fe randomly occupying the bcc lattice sites satisfying the actual stoichiometry. For temperature less than 600°C and Al concentration around 25%, DO₃ (Fe₃Al) structure dominates. For higher Al concentrations the B2 structure (CsCl) prevails in the bulk phase diagram. In the case of the FeAl(100) surface, wherein the surface is capped with the Al layer, the surface Al atomic concentration was calculated to be 0.32. This AES result coincides with the bulk phase diagram outcome of the Fe₃Al concentration at 400 °C. The question arising here is that, like the FeAl(100) subsurface, does the FeAl(110) develop a new chemical structure in the subsurface region at this temperature range?

In previous studies, Graupner et. al. assumed a comparable Fe₃Al formation for the (110) subsurface of FeAl, similar to the FeAl(100) subsurface reconstruction. However, the stoichiometry of the top layer, which reconstructs to a (2x1) structure, could not be reconciled with the theoretical fitting procedures. They claimed that the inhomogeneity precluded a reasonable fit. Clearly, they leave a quite controversial description of the structure of the FeAl(110) surface regarding the temperature range around 400 °C. In the present study the STM, LEED and ARPES measurements show that the surface has a bulk termination at this temperature. All assessments made by previous studies for this temperature are ruled out within this study. Furthermore, the preliminary LEED study by Gleason and Strongin on this surface also supports the bulk termination with their observation of a (1x1) diffraction pattern [14].
The STM image in Fig. 3.5(a) was acquired after the sample was annealed to 400 °C. The rectangular unit cell drawn with the solid line matches the unit cell of the

Fig.3.5. (a) STM image (47x47 Å², Iᵣ=3.96 nA, Vᵣ=331 mV) of bulk terminated surface (inset; fourier transform of the image) and (b) the ball model.
FeAl(110) surface (see the ball model in fig. 3.5(b)). The (1x1) LEED pattern, the inset displayed in fig. 3.5(a), also confirms the bulk termination on the surface. In addition, evidence will show that the electronic structure of this phase supports the STM and LEED results. Fig. 3.5(a) shows some vacancy hole-like defect sites (see arrows in the image) which are believed to be due to low initial Al concentration in the near surface region. However, if the larger STM derived morphology of this surface is imaged as in the Fig. 3.6, the number of defect sites is observed to be very small. This image shows that at this annealing temperature FeAl(110) has a well-ordered surface. In contrast to the previous predictions, no inhomogeneity or the existence of an incommensurate structure on an Fe$_3$Al subsurface [21] has been observed.

![STM image of (150x150 Å$^2$, I$_t$=1.83 nA, V$_t$=954 mV) bulk terminated FeAl(110) surface. It reveals very small defect sites on the surface.](image)

Fig. 3.6. STM image of (150x150 Å$^2$, I$_t$=1.83 nA, V$_t$=954 mV) bulk terminated FeAl(110) surface. It reveals very small defect sites on the surface.
STM is a very powerful technique to study the properties of solid surfaces. However, it does not reveal the chemical contrast between the different atom species for compound surfaces except for the cases wherein large differences in atom sizes exist. Therefore, the chemical identity of the atoms in fig. 3.5(a) and 3.6 is not known. On the one hand, since the LDOS of Fe-3d (in the surface plane) in the vicinity of the Fermi level is higher (see fig. 3.15), one may think that the Fe is preferentially imaged. On the other hand, the localized nature of the Fe d-states decays rapidly away from the surface in contrast to the delocalized nature of the Al sp-states. Therefore, the LDOS from the Al sp-states contribute predominantly to STM images. In accordance, Hansen et al. used a theoretical approach to elucidate “the imaged atoms” with STM on NiAl (110) surface [9]. Fig. 3.7(a) and (b) show gray scale representations of the state density

![Image](image.png)

Fig. 3.7. Gray scale representation of the state density (a) parallel to the surface calculated at the surface and (b) 2 Å above the surface (from Ref. [9]).
of NiAl(110) constituents parallel to the surface. The LDOS contour plot in 3.7(a) shows Ni d character at the surface. However, at a plane 2 Å above the surface, the more extended/delocalized sp states dominate the contour plot. Besides, the simulated STM images generated using the Tersoff-Hamann theory, reveal the imaged atoms as Al atoms. However, it is not stated in the previous study that the surface morphology also can affect the STM imaging. Since the Al atoms are pulled outward and Ni atoms pushed towards the bulk, Al atoms are positioned higher than Ni atoms, therefore, their sp states may tunnel more efficiently. In the present study, the localized nature of the Al sp states is assumed to also dominate the STM image. However, to elucidate the accurate identity of the imaged atoms, further theoretical studies are needed.

In the temperature range of 400-600 °C, a significant rise in the AES Al signal (Fig. 3.2) indicates a higher Al segregation to the near surface region. Higher Al concentration leads to an incommensurate structure on the surface. Fig. 3.8(a) and 3.8(b) show the LEED and the schematic patterns. LEED studies reveal superstructure diffraction spots due to the formation of an incommensurate superstructure. From LEED, it is known that the atomic structure of this phase is commensurate in the [1 1 0] direction and incommensurate along the [001] direction of the FeAl (110) surface. Experimentally, the near-surface concentration of this incommensurate superstructure is measured to be 0.55 (see Fig. 3.2), which corresponds to a 60% Al concentration in the first layer of the alloy surface when integrated mean-free paths are included [12,13]. This concentration approaches FeAl2 stoichiometry on the topmost surface layer. LEIS results [13] reveal the presence of Al and Fe on the topmost layer and 0.55 Al concentration, which shows good agreement with AES results. The STM image in Fig. 3.8(c) shows a quasi
hexagonal overlayer from this high-temperature incommensurate phase. The atoms imaged in STM are believed to be from the LDOS of Fe atoms for reasons detailed below.

Fig. 3.8. (a) LEED pattern and (b) the schematic model of the incommensurate phase of FeAl(110). (c) STM image (50x50 Å², 4.69 nA, 151 mV) shows a quasihexagonal arrangement of an overlayer.
The atomically resolved STM image (Fig.3.8(c)) shows that the structure of this phase has a local order. However, larger STM images indicate that the surface does not have a long range order. Defect sites and disorder are clearly visible in Fig. 3.9. With streaks along the [1\bar{1}0] direction of the FeAl(110), the LEED pattern of this phase also indicates that this phase has a lateral disorder. Due to the large number of defect sites and the unknown identity of the atoms imaged, it is difficult to extract more information on the surface structure.

![STM image](image)

Fig. 3.9. STM image (70x70 Å², Iₜ=0.96 nA, Vₜ=52.5 mV) shows defect sites and disordered surface at 550 °C.

It is believed that Al segregation induces a strain field (thermally) in the surface region. In order to relieve the strain field, the surface reconstructs at higher annealing temperatures. In the range of annealing temperature 600-800 °C, strong streaking along the [1\bar{1}0] direction appears on the LEED pattern, shown in the inset in Fig. 3.10(a). The
streaking indicates that a disordered structure forms along $[1\bar{1}0]$ direction. The incommensurate spots in the LEED pattern disappear at this phase. The STM image in

Fig.3.10. (a) STM image of FeAl(110) (200x200 Å$^2$, $I_t=3.33$ nA, $V_t=-0.01$ mV) shows a missing row like reconstruction (see arrows). (b) STM image (500x500 Å$^2$, $I_t=0.75$ nA, $V_t=-0.07$ mV) reveals a long range order missing rows.
Fig. 3.10(a) confirms the reconstruction, revealing a missing-row-like superstructure along the [001] direction. The presumed missing-row structure possesses a long range order as displayed in the STM image in Fig. 3.10(b). A variation in the distances between adjacent missing rows is observed; however, the average distance is 25 Å. The cross section line (not shown here) indicates that the missing atoms in the rows are restricted to only the topmost layer, and the width of the rows corresponds to one and in some rows three atoms. Fig. 3.11 (a) and (b) illustrates the structural model of this phase.

Fig. 3.11. The models show (a) top and (b) side view of the missing row reconstructed phase.

At temperatures above 800 °C a structural transition from the streaky phase to an incommensurate phase occurs. The same LEED pattern in Fig. 3.8(a) is observed for this phase as well. AES gives a 0.58 Al concentration in the near surface region with concentration relation $c_{Fe}+c_{Al}=1$. This result gives rise to the topmost concentration of Al to be $0.67\pm0.06$, corresponding to FeAl$_2$ stoichiometry (i.e. 66%) assuming the
segregated Al is confined to the topmost layer. XRD measurements yield a result of Fe$_{0.35}$Al$_{0.65}$ stoichiometry for the first layer composition [22], which is in good agreement with the AES result.

The details of the atomic structure of this incommensurate phase are seen in the STM image in Fig.3.12(a). A quasi-hexagonal arrangement of atoms is atomically resolved in the image. The structural model of the ordered quasi-hexagonal overlayer which has a unit mesh containing two Al and one Fe atoms is displayed in Fig. 3.12(b). The hexagon mesh drawn with a solid line in the ball model implies that observed atoms are Fe, surrounded by six Al atoms. The unit mesh, shown with dash line adopting 1:2 ratio of Fe:Al, confirms the FeAl$_2$ stoichiometry. This proposed model, also supported by X-ray reflectivity measurement [22], presumes a surface relaxation normal to surface, similar to the NiAl(110) surface, but with a reverse relaxation in which Fe protrudes from the surface plane. Thus our STM measurements confirm the previous sketched model determined from previous LEED and XRD studies for the incommensurate phase. The measured distance of 8.22 Å between two successive Fe atoms in [1T0] direction of substrate confirms that this phase is commensurate with the underlying lattice in this direction; however, the periodicity along [001] direction (4.2 Å) indicates that it is incommensurate with the underlying substrate (2.9 Å) along this direction. The equilibrium with the bulk reveals FeAl$_2$ stoichiometry on the surface.

A qualitative explanation of the Al segregation can be given in the context of the broken bond model. When the bonds between the neighbor atoms are broken at the surface of a crystal, the resulting increase in energy can be minimized if the species with the lower bond strength enrich the surface. Therefore, this model predicts Al segregation
Fig. 3.12. (a) STM image \((150\times150 \, \text{Å}^2, \, I_t=5.41 \, \text{nA}, \, V_t=30.2 \, \text{mV})\) of FeAl(110) surface after annealing to 850 °C. (b) Ball model displays Fe atoms surrounded by six Al atoms and a unit cell of FeAl\(_2\) stoichiometry.
due to its lower heat of vaporization compared to transition metals, which in general have 20-30% higher heat of vaporization than that of Al [23]. Similarly, the segregation phenomenon which is the interchange of the constituents of the alloy is energetically more favorable for the alloy composition which has lower heat of formation. This free enthalpy of formation is lower for FeAl (25.1 kJmol⁻¹) compared to that of NiAl (72 kJmol⁻¹) and CoAl (54.2 kJmol⁻¹) [16,25]. Therefore, the driving force to lower the surface free energy through Al segregation is more favorable for FeAl than NiAl and CoAl transition metal alloy.

3.3.2 Electronic Structure of FeAl(110)

The physical and chemical properties of the transition metal aluminides are governed by the interaction between Al sp and transition metal d-bands. Changing the Al concentration affects the chemical bonding and results in differences in hybridization between the sp and d-bands. The charge transfer increases as the Al concentration increases in the alloy. This phenomenon occurs on the late transition metal aluminides. For early transition metal aluminides the directional bonding asserted by the transition metals dominates the structural stabilities.

It has been reported by Caskey et. al. that various physical properties show drastic changes in going from NiAl to FeAl [25]. The electronic heat capacity increases by a factor of 4.3, the electrical resistivity by a factor of 10.2 at 4.2 K, and thermopower by a factor of 3.5 at 4.2 K. These contrasts are related to the difference in the electronic structure of the NiAl and FeAl. The density of states of the FeAl at the Fermi level is four times larger than that for NiAl.
In addition to the atomic structure, the electronic structure of the NiAl(110) surface has also been the focus of many experimental and theoretical investigations. In the bulk, the self-consistent energy band structure has been calculated by Nagel et. al. using the APW scheme in the local density approximation [26]. Thirteen valence electrons fill six initial states and partially occupy the seventh band. The lowest band, which has the highest binding energy, is made up of the $s$-states of Al metal. Al $p$ and Ni $d$-bands dominate the electronic band structure at lower binding energies. Ni-bands are located between the 1-4 eV binding energy range and characterized as having minimal dispersion. The top of the $d$-band of the NiAl is located at 1.5 eV which indicates a total $d$-band filling of this transition metal alloy. Kang and Mele reported that the redistribution of $sp$ electrons around the Al atoms in the topmost layer and the localized surface states play an effective role in surface rippling [18].

The bulk and surface electronic structures of the NiAl(110) surface were measured by Liu et. al. with ARPES spectroscopy [8]. They showed that the surface also has a filled $d$-band, similar to the bulk. Experimental measurements showed a very good agreement with the theoretical results except for the position of the surface states. The discrepancy with the theory was attributed to self-energy effects near the surface.

It has been shown that the ordered intermetallic alloy FeAl is nonmagnetic down to 1 K [25]. In contrast to the experimental finding of a nonmagnetic state of FeAl, all electronic structure calculations reveal a ferromagnetic ground state for FeAl and yield a magnetic moment of $\sim0.7 \mu_B$ at the Fe site [27,28]. In a recent work of Mohn et. al. the electronic structure was calculated with full potential linear augmented plane wave method in the WIEN97 code [29]. They concluded that Local Density Approximation
(LDA) is not sufficient to describe the localized electron behavior. Therefore, the LDA has been extended to the Local Density Approximation with Hubbard U (LDA+U). The LDA+U calculation revealed a nonmagnetic state for $U \geq 3.7$ eV. The two symmetry components of the d bands, Fe-$t_{2g}$ ($\Sigma_4$) and Fe-$e_g$ ($\Sigma_3, \Sigma_2$), are affected differently with this consideration. It gives rise to a smaller energy difference between the Al-$p$ and Fe-$t_{2g}$. Consequently, the Fermi level is pushed toward the unoccupied $e_g$ states and the DOS at Fermi level become small enough to fulfill the Stoner criterion where $U, \rho(E_F) > 1$ for spontaneous ferromagnetism.

In order to have a reference for the experimental results discussed here, the calculated density of states and band structure using self consistent scalar relativistic tight-binding (TB)-LMTO method in the atomic sphere approximation based on the density functional theory by Das et. al. is displayed in Fig. 3.13 (a) and (b), respectively [30]. The bands of bulk FeAl(110) along the high symmetry direction $\Gamma \rightarrow M$ are labeled.

Fig.2.12 shows the bulk brillouin zone in relation with surface brillouin zone. In normal emission from FeAl(110), the states having $\Sigma$ symmetry along the $\Gamma M$ symmetry line are probed. The $\Sigma_1$ band in the calculated band structure along this line is $s$-like. The next $\Sigma_1$ band is a mixture of $s$ and $d$-states. The bands from the Fermi level to 2.75 eV comprise mostly Fe $d$-bands. The initial states $\Sigma_1, \Sigma_3,$ and $\Sigma_4$ exhibit dipole allowed symmetries; however, $\Sigma_2$ band is dipole forbidden. The initial states are identified by implementing the polarization of the light and symmetry of the crystal. $\Sigma_3$ and $\Sigma_4$ initial states are excited with $s$-polarized light with the vector potential kept along the [001] and [1$\bar{1}$0] direction, respectively. The $\Sigma_1$ band is probed with $p$-polarized light in both of the
Fig. 3.13. (a) Total (diamond symbol) and Al (cross symbol) density of states and (b) bulk bands of FeAl (from Ref. [30]). The bands probed with normal emission for (110) surface of FeAl are labeled.
mirror planes of the FeAl(110). The normal emission EDCs were taken with $s+p$ polarization in the present study. The EDCs shown in Fig. 3.14 were measured after annealing the clean surface to 400 °C and correspond to a surface atomic structure equivalent to the bulk terminated surface discussed above. The EDCs were collected at a photon energy of 56 eV. These transitions were taken at normal emission with the photons incident at a 45° angle. Two symmetry conditions are evaluated with the vector

![Graph](image)

Fig. 3.14. EDCs of clean FeAl(110) after annealing to 400 °C for both symmetry direction of the FeAl(110). The normal emission and 45° incident angle are implemented.
potential aligned along either the [001] or the [1\bar{1}0] direction. Implementing dipole selection rules the peak that appears at 0.2 eV is identified as $\Sigma_3$ state. The other sharp peak located at 1.8 eV is characterized as $\Sigma_4$ state, which has an allowed transition with the vector potential perpendicular to [001] direction of the substrate. The shoulder at 1.5 eV and broad peak at 8 eV are attributed to be $\Sigma_1$ states. Figure 3.14 indicates that the states near Fermi level are governed by the Fe $d$-states. Comparing these states with the bulk band calculation in Fig. 3.13 shows a good agreement considering a free electron final state for a photon energy of 56 eV.

In order to reveal the variations in the valence band structure of the FeAl(110) due to increased Al concentration in the near surface region, and also to elucidate information for the surface slab structure under the topmost layer, EDCs were measured at room temperature after annealing to temperatures of 400 °C and 850 °C. The EDCs, as a function of the photon energy, are shown in fig. 3.15 (a) and (b) for bulk terminated and incommensurate surfaces, respectively. The change seen in the figure is the increased density of the states near the Fermi edge for the incommensurate surface shown in fig. 3.15(b). Apart from this finding, the EDCs for bulk terminated and incommensurate phase surfaces show very similar dispersion behavior (see $\Sigma_4$ state dispersion). This indicates that the underlying surface slab for two surfaces possesses nearly the same composition and structure. Based on this, the assessment of Graupner for Fe$_3$Al slab under the outmost layer like the c(2x2) reconstructed surface of FeAl(100) can be ruled out in the present case. Electronically and geometrically, neither ARPES nor the STM and LEED results supports the Fe$_3$Al slab under the bulk terminated surface. The actual stoichiometry of the slab layers can not be determined by the surface techniques used in
this study and needs the corroboration of the techniques that will give rise to stoichiometry of the slab layers such as LEED-IV.

Fig 3.15. EDCs of (a) bulk terminated and (b) incommensurate clean surfaces collected at normal emission and within the geometry of $A_{\perp}[001]$. 

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This study and needs the corroboration of the techniques that will give rise to stoichiometry of the slab layers such as LEED-IV.

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Fig 3.15. EDCs of (a) bulk terminated and (b) incommensurate clean surfaces collected at normal emission and within the geometry of $A_{\perp}[001]$. 

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This study and needs the corroboration of the techniques that will give rise to stoichiometry of the slab layers such as LEED-IV.

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Fig 3.15. EDCs of (a) bulk terminated and (b) incommensurate clean surfaces collected at normal emission and within the geometry of $A_{\perp}[001]$. 

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This study and needs the corroboration of the techniques that will give rise to stoichiometry of the slab layers such as LEED-IV.

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Fig 3.15. EDCs of (a) bulk terminated and (b) incommensurate clean surfaces collected at normal emission and within the geometry of $A_{\perp}[001]$. 

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This study and needs the corroboration of the techniques that will give rise to stoichiometry of the slab layers such as LEED-IV.

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Fig 3.15. EDCs of (a) bulk terminated and (b) incommensurate clean surfaces collected at normal emission and within the geometry of $A_{\perp}[001]$. 

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This study and needs the corroboration of the techniques that will give rise to stoichiometry of the slab layers such as LEED-IV.
The increased Al concentration on the surface after annealing at higher temperatures modifies the surface potential. This modification is expected to cause increased hybridization between the Fe $d$ and Al $p$-states. It is pointed out in the previous studies that Fe-$e_g$ orbitals provide bonding between the Fe atoms and Fe-$t_{2g}$ orbitals bond to the Al atoms [28,29]. Therefore, it makes sense that in the hybridization scenario between the Al and Fe atoms, the Fe $d$-bands which are close to Fermi level and possess the $t_{2g}$ symmetry should be affected. The photoemission spectra in Fig. 3.16 compare the bulk terminated surface with the incommensurate surface after annealing the crystal to

![Graph](image)

Fig. 3.16. EDCs of clean FeAl(110) for bulk terminated (400 °C) and incommensurate surface (850 °C) collected at normal emission and A[001] geometry. Incommensurate phase exhibits a $\Sigma_3$ derived new state labeled S.
850 °C for a photon energy 56 eV. The major difference between the two spectra is the appearance of a new feature near the Fermi level (~0.3 eV) on the incommensurate phase photoemission spectrum. It is believed that the feature labeled S is the consequence of the hybridization of the Fe $d$-band with the Al $p$-band. The S feature appeared at the same position with $\Sigma_3$ state which is dipole forbidden in this geometry ($A\perp[001]$). Therefore, this state is an induced state due to hybridization phenomenon, and the reduction of the symmetry resulting from the reconstruction and the modified surface charge density. It is presumed to be emission from Al $p$ admixed with the symmetry forbidden $\Sigma_3$-state. For the other symmetry direction of the surface ($A\perp[\overline{1}0]$), the existence of the hybridization and its effect on the $\Sigma_3$ state is shown in Fig. 3.17. The

![Graph showing EDCs of clean FeAl(110) for bulk terminated (400 °C) and incommensurate surface (850 °C) collected at normal emission and $A\perp[\overline{1}0]$ geometry.]

Fig.3.17. EDCs of clean FeAl(110) for bulk terminated (400 °C) and incommensurate surface (850 °C) collected at normal emission and $A\perp[\overline{1}0]$ geometry.
figure shows two photoemission spectra for bulk terminated and incommensurate phase surfaces at a photon energy of 80 eV. The distinctive features are the diminished intensity of the $\Sigma_1$ state at 1.25 eV and intensified peak feature of the $\Sigma_3$ state at 0.6 eV on the photoemission spectrum of the incommensurate phase compared to photoemission spectrum of the bulk terminated surface.

In order to profile the increased concentration of Al in the near surface region, the shallow core level photoemission spectra of the Al-$2p$ and Fe-$3p$ were measured with the normal emission and $60^\circ$ emission angle. Fig. 3.18(a) and (b) show the photoemission spectra for Al-$2p$ core level.
spectra of Al-2p measured at normal and 60° emission angle, more sensitive due to smaller electron mean free path, for bulk terminated and incommensurate surfaces, respectively. For bulk terminated surface (Fig. 3.18(a)) the intensity of Al-2p spectrum taken at 60° emission angle is smaller than that taken at normal emission. However, for the incommensurate surface the photoemission spectra of Al-2p show the opposite behavior. The Al-2p intensity is more enhanced with the 60° emission angle. The higher intensity ratio of Al-2p to Fe-3p for the incommensurate phase spectra is also obtained. These findings indicate that the surface of the FeAl(110) at elevated temperatures is dominated by Al atoms and confirm the surface segregation which supports the STM results presented in the atomic structure of this chapter.

3.4 Conclusion

The geometric and electronic structure of FeAl(110) intermetallic alloy has been investigated by STM and ARPES. Preferential sputtering results in Al depletion in the near surface region and subsequent annealing promotes surface segregation of Al and leads to new reconstructed phases on the surface. In contrast to previous AES and LEED which rule out bulk terminated surface, our STM and LEED results reveal a bulk terminated surface after annealing the surface to 400°C. At temperature ranges 400-600 °C and above 800 °C, an incommensurate phase develops. The incommensurate diffraction pattern and the STM results reveal a lattice match only along the [1$ar{1}$0] direction of the substrate. The STM data are consistent with a superstructure composed of a quasihexagonal form of Fe atoms surrounded by six Al atoms. The AES and STM are consistent with the stoichiometry of the topmost layer to be FeAl$_2$. Due to long range order, the elevated temperature incommensurate phase is found to be the stable phase.
The diffraction pattern of the incommensurate phase is replaced by a strongly streaked pattern along the \([1\bar{1}0]\) direction after annealing the sample to temperatures of 600-800 °C. At this stage STM reveals a missing-row-like reconstruction which provides a relief of the strain induced with Al segregation to the surface. The ARPES measurements confirm the Al segregation with increased DOS at the near Fermi level. The increased density of state near Fermi level is believed to be due to hybridization between the Fe \(d\)-band and Al \(p\)-band and derived from \(\Sigma_3\) bulk state. Increased intensity of Al-2\(p\) core level for incommensurate phase with the higher emission angle becomes another proof for the Al diffusion to the near surface region.

3.5 References


Chapter 4

Aluminum Oxide Thin Film on FeAl(110)

4.1 Introduction

Despite years of studies, the complex physical and electronic structure of metal oxides, their charging problems, difficulty in producing high quality surfaces, and poor electrical and thermal conductivities have left an incomplete understanding of their fundamental properties [1-3]. Due to their technological applications, for instance in catalysts, microelectronics, and metal-ceramic based sensors, this fundamental level of understanding is essential. Among the oxides, alumina has received much attention due to its desirable physical and chemical properties.

Alumina occurs in several phases, and, in fact, all involve a close packed oxygen sub-lattice. The differences in occupancy of tetrahedral or/and octahedral coordination determine the crystal phase of alumina. Besides the thermodynamically stable alpha-alumina phase, there are many metastable phases (transition aluminas); gamma, delta, theta, kappa, chi, eta, and rho. These phases are derived by dehydration of various aluminum hydroxides. Among them, gibbsite, an aluminum-trihydroxide –Al(OH)$_3$– and boehmite, an aluminum oxidehydroxide –AlO(OH)– are the most important ones [4]. The dehydration is employed by heating the aluminum hydroxide in UHV or in air.
$\alpha$-$\text{Al}_2\text{O}_3$ is the final product of both gibbsite and boehmite upon heating to above 1100 °C in air. $\gamma$-$\text{Al}_2\text{O}_3$, a unique material in the respect that it is widely used in catalysis and adsorbents, is produced by heating boehmite to 450 °C in air [5]. In contrast to $\alpha$-$\text{Al}_2\text{O}_3$, it contains water and a surface rich with hydroxyl groups. The last alumina to be mentioned here is $\kappa$-alumina, formed from gibbsite after annealing to 950 °C in air. Even though the bulk structures of $\alpha$-$\text{Al}_2\text{O}_3$ stable phase and $\gamma$-$\text{Al}_2\text{O}_3$ and $\kappa$-$\text{Al}_2\text{O}_3$ metastable phases have been revealed by X-ray crystallography, the difficulty in preparing well-defined surfaces without hydrogen impurities leaves questions as to the detailed nature of the surface structure. For instance, preferentially sputtering and charging problems are the main obstacles to clean the surface. In addition, the impossibility of cleaving along all possible orientations and the likelihood of creating point defects that are not easily eliminated by annealing are additional challenges for preparing a clean crystal surface. However, aluminum oxide thin films have been used as model system to study the surface properties of bulk oxides. Thin films can be prepared on appropriate substrates, and can be “conductive” due to their ultrathin dimensions. This allows electrons to tunnel through oxide films, and enables the study of their surface properties without charging using techniques like STM which require a conducting substrate.

Thin oxide films grown on NiAl alloys have been the subject of many studies focused on characterizing their resulting geometric and electronic structure. This has particular importance in technological applications such as corrosion protection at high temperatures for coatings like those on turbine blades in jet engines, and providing an appropriate representation of model catalyst supports. At low oxygen pressure and high temperatures, different phases of well ordered thin $\text{Al}_2\text{O}_3$ films have been formed on
Ni$_3$Al (111) [6,7], NiAl (111) [8,9] and NiAl (110) [10,11]. X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) studies have demonstrated that a well ordered 5 Å thick $\gamma$-Al$_2$O$_3$ film is produced on NiAl(110) after dosing 1200L of O$_2$ at elevated temperatures and annealing to 850-950 °C for a short time. Two layers of oxygen and aluminum ions were found in the epitaxially grown ultrathin oxide. High-resolution electron energy-loss spectroscopy experiments [HREELS] have confirmed that this oxide has $\gamma$-Al$_2$O$_3$ -like rather than $\alpha$-Al$_2$O$_3$ -like structure, and is terminated with a hexagonal arrangement of oxygen ions [11]. It has been suggested that Al$_2$O$_3$/NiAl(110) consists of a mixture of octahedral and tetrahedral Al ions similar to $\gamma$-Al$_2$O$_3$ structure. Due to the symmetry of the substrate, two domains of oxide have been reported in accordance with STM images and LEED patterns [10,11].

As mentioned in the previous chapter, FeAl is also an ordered transition metal alloy, like NiAl, and crystallizes in the same CsCl-type crystal structure. To date, there is only preliminary Auger Electron Spectroscopy (AES), LEED and XPS studies of oxide films on FeAl(110) [12], in contrast to the well investigated oxidation behavior of NiAl(110). Graupner et al. reported that oxygen dosing at room temperature leads to the formation of amorphous Al$_2$O$_3$. However, elevated temperature oxidation results in a well-ordered oxide film with a thickness of 6 Å. LEED patterns for similarly oxidized NiAl (110) are also observed for FeAl (110), and preliminary XPS results indicate that Al is the only metallic constituent in the oxide film, indicating formation of Al$_2$O$_3$ [12]. Yet, the detailed atomic and electronic structure of the oxide film has not been explored. In the present chapter, we present a detailed investigation of the nucleation, growth and
atomic structure of this thin oxide film. The structure of the substrate-oxide interface and the coordination of ions in oxide film grown on FeAl (110) by means of STM will be discussed, and measurements and results on the electronic nature and dimensionality by ARPES will be presented.

4.2 Experimental Procedures

The preliminary STM experiments were conducted at Oak Ridge National Laboratory using an Omicron room temperature Scanning Probe Microscope, followed up by work completed at the Center for Advanced Microstructures and Devices at Louisiana State University, using a variable temperature STM. This microscope, described in detail in chapter 2, was made by the STM group at the University of Aarhus in Denmark. Both measurements were performed in ultrahigh vacuum surface science chambers, equipped with LEED, a cylindrical mirror analyzer and a quadrupole mass spectrometer. The FeAl single crystal used for the experiments described in chapter three has been used in this study as well. The sample was mounted on a Ta sample platen with a K-type thermocouple used to determine the sample temperature for STM study, and the sample was placed on a 2 cm² Ta sheet with two W wires passing through the sides of the crystal for a resistive heating for the ARPES measurements. The substrate was cleaned by repeated cycles of sputtering at room temperature (Ne⁺ ions, 1 keV, 20 µA), followed by e-beam annealing to 850 °C in the STM case and resistive heating for the ARPES studies. The ARPES data were conducted at the Center for Advanced Microstructures and Devices, using the end station on the 6-meter-Toroidal Grating Monochromator (TGM) beamline. S⁺p-polarized light was used with a 45° incident angle for normal emission measurements. Since the VSW HA150 hemispherical electron energy analyzer
on the endstation of the 6-meter TGM beamline is fixed, the FeAl(110) crystal was rotated for ARUPS measurements. The oxygen coverages were calibrated with STM and corresponding LEED observations. The Al₂O₃ film was prepared by dosing the sample with oxygen at 850 °C and consequently annealing for a short time at this temperature.

4.3 Results and Discussion

4.3.1 Atomic Structure of Al₂O₃/FeAl(110)

As outlined in the previous chapter employing LEED and AES measurements, it has been reported that, in stark contrast to NiAl surfaces, low index and vicinal surfaces of FeAl are often reconstructed [13,14]. Preferential sputtering reduces the aluminum concentration on the surface and sequential annealing drives aluminum back to the surface selvage. FeAl (110) shows different superstructures upon annealing to different temperature ranges. Annealed to 400 °C, unreconstructed bulk-terminated surfaces are observed. Between the temperature ranges of 400-600 °C and 800-1000 °C, an incommensurate hexagonal FeAl₂ overlayer is obtained. At annealing temperatures of 600-800 °C, STM images reveal a long-range, missing row reconstruction parallel to the [001] direction of the FeAl(110) substrate.

STM results from the incommensurate phase, obtained by annealing in the temperature range of 800-900 °C, atomically resolved the quasi-hexagonal arrangement of atoms on the clean surface, as shown in Fig. 3.8. As mentioned before, this is the most stable phase of the clean surface, corresponding to an FeAl₂ stoichiometry assuming the segregated Al is confined to the topmost layer. The structural model is an ordered quasi-hexagonal overlayer which has a unit mesh containing two Al and one Fe atoms. The details of the atomic structure of this incommensurate phase seen in the STM image in
Fig. 3.8(a) has been sketched with a hardball model in Fig. 3.8(b). This phase serves a template for the oxide thin film since it grows homogenously and uniformly only at the temperature range in which clean incommensurate phase occurs on the oxygen-free surface.

It has been reported that the oxidation of FeAl(110) can result in three different phases [12]. Since the enthalpy of formation of Al$_2$O$_3$ ($\Delta H_f = -1676$ kJ/mol) is lower than Fe based oxides (Fe$_2$O$_3$=-826 kJ/mol, FeO=-278 kJ/mol, Fe$_3$O$_4$=-1118.4 kJ/mol) [15], it is thermodynamically more favorable that aluminum is preferentially oxidized on the FeAl(110) surface, forming Al$_2$O$_3$. From previously reported LEED studies [12], three structural phases have been observed for oxide formation on FeAl(110). Amorphous Al$_2$O$_3$ forms at temperatures up to 500 °C but it forms a phase with a streaked LEED pattern in the 500-700 °C temperature range. A well ordered film can be produced only at and above 850 °C. During the initial stages of oxidation, LEED spots due to the incommensurate superstructure are still visible in the LEED pattern. This implies that the oxide film grows via island formation. Higher exposure of oxygen (1000L O$_2$ at 850 °C) results in the disappearance of the incommensurate diffraction spots, which indicates that the interfacial layer between the oxide thin film and substrate does not maintain its reconstructed structure. Indeed, XPS results [12] imply that the presence of a smaller metallic Al 2$p$ peak, in addition to the major one, is indicative of Al atoms between the oxide and the substrate. The main spots in the LEED pattern demonstrate that the overlayer is a very thin film of aluminum oxide.

The ultrathin aluminum oxide film that grows on reconstructed FeAl(110) after exposing 1000L O$_2$ at 850 °C is displayed in Fig. 4.1. STM images of this ordered oxide
film were recorded after the sample was recooled to room temperature. The large area STM scan (700x700 Å²) shows a regular and nearly hexagonal superstructure pattern. The image was obtained at a sample bias voltage of -1.25 V acquiring electrons from occupied states of the oxide film to unoccupied tip states, while the tunneling current was kept at -0.7 nA. The spot spot distance of the superstructure is measured to be 19 Å. This saturation coverage (1000L O₂) of STM image shows that the thin alumina has a flat and homogeneous morphology. However, there is a small lateral disorder exhibited perpendicular to the [001] direction. LEED confirms this disorder with streaking along the [110] direction. Two rotational domains are expected due to the two fold symmetry of the substrate, which are observed in the STM study of Al₂O₃/NiAl(110) [11]. Notwithstanding, in the present study STM results reveal only one domain as in the case of the alumina thin film study on Ni₃Al(111) [7]. The unit cell of the oxide film (18.6x19.4 Å), shown by a solid line, is much larger than that of the substrate (2.9x4.1 Å). The unit mesh is rotated by 30° with respect to the [110] direction of the substrate. The corrugation height is measured to be 0.55±0.05 Å. This large corrugation reflects both the local variation of the electronic structure and a variation in the structural morphology.

In a recent paper [16] reported by Magtoto et al., STM induced nanoscale “void” formation was revealed at the interface between an Al₂O₃ oxide film and a Ni₃Al(111) substrate. In the present study this type of void formation is also imaged. However, in contrast to the Ni₃Al(111) case, in which voids were formed by voltage pulses to increasingly high voltages, here the voids were found to occur after applying a constant voltage. The STM image in Fig. 4.2 exhibits homogeneous oxide film terraces separated
by a step edge. Two voids labeled A and B are observed in the oxide film and they are imaged as depressions. A cross section line in Fig. 4.2 indicates that voids are formed in

![STM image](image)

Fig. 4.1. STM image (70x70 nm², Vₛ = -1.25 V, Iₜ = -0.7 nA) of oxidized FeAl(110) surface. The surface exposed to 1000 L of O₂ at 850 °C. Unit mesh of oxide structure (18.6x19.6 Å) is shown with solid line.

oxide layers. The void labeled A has a 38 Å width and is 2.25 Å deep. The second void is deeper (4 Å) and wider (80 Å) than the first one. The line scan in fig. 4.2 signifies that since the void depth is limited to the oxide film, there is no collapse of the oxide layer resulting from void growth in the metal itself. The depth of the hole (4 Å) is quite similar to the thickness (6 Å) of this oxide film determined by LEED studies [12]. However, due to electronic effects the measured depth of the void may not provide an accurate measure of the thickness of the oxide film. It has been reported that moving an STM tip from a
Fig. 4.2. STM image (69x100 nm², $V_s = -1.25$ V, $I_t = 0.17$ nA) shows a step edge and two void formation labeled A and B. Line scan below the image demonstrates a step edge height of 8 Å and a void formation of 4 Å depth and 80 Å across.

A hole to the oxide gives a strong change in the tunneling current [17,18]. The measurements of height level across the void and oxide film as changing bias voltages revealed height variations. At a bias voltage of -4.8 V no height variations were observed; however, with the positive polarity the height variations were noticed [17]. In the present case, tunneling with different parameters did not show any noticeable height variations. In the STM image (Fig. 4.2), a step edge which separates homogeneous films has a height of 8 Å. This height is not considered to be the actual thickness of oxide film. The STM images of clean FeAl(110) surface reveal 2-8 Å step heights. However, the depth of the void can be due to the oxide film. The void depth is measured to be 4 Å and is quite similar to the thickness of 6 Å extracted from previous LEED studies [12].
A lack of long range order is observed for subsaturation coverages of oxygen at 850 °C. Exposing the surface to 125 L oxygen results in a structurally different morphology as shown in Fig. 4.3. This subsaturation coverages result in a local order with a larger spot spot distance (~32 Å). Since the oxide film has only a local order, it is difficult to determine the detailed atomic structure of the film. However, LEED indicates that in addition to the oxide superstructure spots, incommensurate diffraction spots that arise from the clean reconstructed FeAl(110) surface are concurrently observed. This suggests that some part of the clean FeAl(110) surface is not yet fully oxidized and remains in the reconstructed metallic phase. However, the LEED pattern for saturation coverage displays only spots from the oxide film. The disappearance of incommensurate spots for higher coverages indicates that the interfacial layer between the oxide and the substrate does not preserve its reconstructed phase. Also, it implies that the oxide film wets the FeAl(110) substrate homogeneously at saturation coverage. As will be shown in the electronic structure studies of the thin oxide film, shallow core level photoemission spectroscopy also substantiates this finding. The presence of a small peak in addition to the main oxide peak is consistent with the existence of Al atoms located between the oxide film and the substrate.

In order to investigate the influence of the oxide electronic structure on STM images, images were acquired with a variety of bias conditions, including polarity switching. Fig. 4.4 shows an STM image that was recorded at +3 V bias voltage which has a reverse tunneling polarity compared to the data in Fig. 4.1 and 4.3. Reversing the
Fig. 4.3. A subsaturation coverage of oxygen (125 L) gives a local order with a larger unit cell compared to saturation coverage (72x72 nm$^2$, $V_s = -0.4$ V, $I_t = -3.69$ nA).

Fig. 4.4. STM image (50x50 nm$^2$, $V_s = -3.02$ V, $I_t = -1.04$ nA) reveals electronic structure effect, displaying a line pattern with positive polarity.
sample bias voltage probes a different electronic configuration and reveals different morphology. Fig. 4.4 exhibits a line pattern of oxide structure with a periodicity of 30 Å. The lines are rotated 40° with respect to the [001] direction of the underlying substrate. The structural change observed with opposite polarity is assumed to be produced by electronic band structure effects of the oxide film. It is well acknowledged that employing different bias voltages may result in tunneling into different density of states and these states may have drastically different symmetry. Here, the positive polarity used in Fig. 4.4 reveals the morphology resulting from the unoccupied states whose symmetry may differ from the occupied state symmetry and gives rise to the observed structural differences. A similar line pattern was also reported in the STM/AFM studies of Al₂O₃/NiAl(110) [19]. Therefore, it is proposed that the difference in the local electronic structure and symmetry of the unoccupied and occupied states of the alumina film is the apparent reason for the observed morphological differences.

In previous studies on Al₂O₃/NiAl(110) [11,18], it was argued that due to the wide band gap of the oxide (8 eV), STM images obtained by tunneling in this gap show the topography of the oxide-metal interface, and the topography of the oxide surface is only possible at higher voltages. However, it has been found in this study that this conclusion is controversial and we believe that tunneling with voltages in the band gap may reveal more information on the oxide structure due to a finite thickness of the oxide film. A recent theoretical discussion by Jennison et al. [20] asserted that the local density of states (LDOS) of aluminum and oxygen have a finite value in the bulk band gap, where they are expected to diminish to zero. They come to this conclusion due to distinctive film thickness and the expected quantum mechanical mixing in the non-bulk
like chemical environment of the oxide layers. In the following, the experimental evidence to support Jennison’s theoretical argument will be presented. The Al₂O₃ thin film investigated here has electronic states in the band gap, and it is proposed that the new phase found here may result from an alternate arrangement of Al ions in the oxide film.

The structure of γ-Al₂O₃ and κ-Al₂O₃ has been a matter of discussion for nearly two decades. The debate over γ-Al₂O₃, whose structure is described as a defective cubic spinel, mainly originates from the location of vacancies required for charge balance in the defect structure. Most of the experimental studies argue that a small number of cations occupy tetrahedral sites, whereas the normal preference for Al ions is considered to be in octahedral sites. However, a recent study of transmission electron diffraction [21] has came to an opposite finding, indicating that all tetrahedral sites are occupied by cations and vacancies are found at the octahedral sites. In short, Al ions occupy both octahedral and tetrahedral positions but the relative occupancy in each position is a matter of debate.

The lack of good crystallinity and impure phases has resulted in debate over the κ-Al₂O₃ structure for years. The position of Al ions has also been a question for decades and still awaits an answer. Although previous work concluded that a hexagonal structure existed for this phase, XRD studies by Liu and Skogsmo have revealed that an orthorhombic crystal structure is the correct answer [22]. Gross and Mayer reported both octahedral and tetrahedral occupancy of Al ions by high resolution electron microscopy and XRD [23]. Remarkably, theoretical studies based on the density functional calculations [24] found that ¼ of the Al ions occupy tetrahedral interstitial sites and ¾ occupy octahedral
sites. All of the results mentioned above are controversial findings regarding the bulk structure of these oxides.

Previous experimental studies reject $\alpha$-$\text{Al}_2\text{O}_3$ as the phase that forms on NiAl(110) [10,11]. Indeed, they have claimed that the thin film has a $\gamma$-$\text{Al}_2\text{O}_3$ structure. However, theoretical studies of alumina films on Al(111) and Ru(0001) asserted that the alumina films most closely resemble the $\kappa$-phase of bulk alumina. No reports, however, are available to date on the STM atomic-scale characterization of the coordination of Al ions in an oxide film. Motivated by this, our STM study was conducted to elucidate the atomic structure of the thin film $\text{Al}_2\text{O}_3$ structure on FeAl(110) and to give information on its electronic structure. The results presented here provide substantial evidence in support of the proposed electronic structure of an ultrathin film of $\text{Al}_2\text{O}_3$ based on the theoretical calculations performed by Jennison et al. [20]. Ab initio calculations performed on 5 Å $\text{Al}_2\text{O}_3$ films, simulated on Al(111), Mo(110) and Ru(001) substrates, have demonstrated that the tetrahedrally coordinated $\text{Al}^{3+}$ ions are located nearly in the same plane as the oxygen ions for electroneutrality. These calculations asserted that two oxide layers and a chemisorbed oxygen layer without vacancies characterize the surface structure with the lowest energy. Even though the occupied density of states of the bulk oxide begins at about 4 eV below the Fermi energy, the calculated LDOS of aluminum and oxygen for two clean oxide layers are located in the bulk band gap of oxide. Due to this LDOS of surface atoms located within the bulk gap, at small tunnel voltages, the observation of the thin film oxide structure becomes possible.

Considering a larger unit cell in a recent study [25], Jennison et al. showed the propensity of the surface to consist of an even mix of tetrahedral and octahedral site Al
cations as the lowest-energy stable film. The resulting structure is an alternating zigzag structure of tetrahedral and octahedral Al ions with an increase in the interlayer Al-Al spacing. They also found a structure consisting of alternating stripes, but due to the decrease in the Al-Al separation resulting in higher energy, this structure was not energetically favored.

In Fig. 4.5a, a well ordered structure consisting of a zigzag and stripe structure alternating with every two atoms along the [001] direction of the substrate is clearly observed. We propose that Al ions are coplanar with oxygen atoms and produce this structure in agreement with the theoretical calculations. The top part of our ball model in Fig.4.5b depicts this structure, and the bottom part shows the pure octahedral arrangement of Al ions allowing one to compare unit cells. Relative to the unit cell of bulk Al₂O₃, the structure suggested by these STM measurements indicates a large unit cell of (4x2). This structure is both spatially and rotationally consistent with the superstructure form of the oxide film displayed in Fig. 4.1. Occupancy of cations in octahedral and tetrahedral sites is consistent with theoretical findings. The STM results show an equal number of Al ions in tetrahedral and octahedral sites. However, the large Al-Al lateral separation is inconsistent with pure Al₂O₃ stoichiometry and symmetry. Since atomically resolved images that determine quantitative vacancy ratios of the outmost layer could not be acquired, this model is only tentative and requires theoretical input. The reason that atomically resolved images could not be acquired may result from the relatively small density of states of the oxygen ions. Notwithstanding, the STM images recorded in the bulk band gap imply that the thin oxide film has a LDOS due to the arrangement of cations and the finite thickness of the film. As seen in Figure 4.5, the
Fig. 4.5. (a) STM image (20x20 nm$^2$, $V_s = -1.9$, $I_t = -2.54$) reveals zigzag-stripe structure along the [001] direction of the underlying FeAl(110). (b) Ball model shows zigzag-stripe compare to unit cells.
oxide structure does not resemble the $\gamma$-Al$_2$O$_3$ structure. However, the structural model proposed by Jennison indeed shows similarities to the STM data in the present case. In the LDA calculations, the relative energies of the Al$_2$O$_3$ unit cell of zig-zag and stripe structures with an even mix of octahedral and tetrahedral Al ions are considerably smaller than structures which are purely tetrahedral or octahedral Al ions. In that report, an energetic preference for zigzag structure over stripe structure was found to be due to the spatial position of the Al ions. Another type of structure which exhibits a mixing of zig-zag and stripe structure with the same ratio of occupancies of tetrahedral and octahedral Al cations was proposed but due to the reduced Al-Al averaged separation this structure has a higher energy than the zig-zag structure. The energetically favorable zig-zag pattern resembles the A plane of $\kappa$-Al$_2$O$_3$ which is depicted in Fig. 4.6. $\kappa$-Al$_2$O$_3$ has A-B-A-C bulk stacking of O layers and the A plane has an even mix of octahedral and tetrahedral Al cations in alternating zig-zag rows. Although there are similarities between the kappa phase of alumina and the oxide film on FeAl(110), the oxide structure

![Fig. 4.6. Schematic drawing of the A plane of the kappa alumina structure. Octahedral atoms are black and tetrahedral ones are in gray color.](image-url)
proposed here is a new phase. In the following, studies of the electronic structure of the thin oxide film on FeAl(110) using angle resolved photoemission will be discussed.

4.3.2 Electronic Structure of Al₂O₃/FeAl(110)

Studies of the atomic structure of the thin oxide films on Ni based transition metal aluminides have drawn much more attention than the studies of their electronic structures. The first detailed electronic structure study to elucidate the dimensionality and the nature of the Al₂O₃/NiAl(110) system was reported by Jaeger et al, using XPS and ARPES [10]. XPS measurements revealed that exposing the clean surface to oxygen at elevated temperatures chemically affects Al atoms and not Ni. This conclusion was also confirmed by their EELS results, which revealed three features in the Al₂O₃/NiAl(110) system and only two features for NiO. This assessment was also made based on the AES results of Isern and Castro [26]. They reported that the Al-LMM transition exhibits the Al⁴⁺ lineshape of bulk Al₂O₃. No Ni involvement in the oxide film was reported. However, the XPS results found higher binding energy features in the oxide overlayer on NiAl(110) and suggested that both tetrahedrally and octahedrally coordinated Al ions were in the oxide film. The s and p-polarized data identified five different oxygen induced features in the ARPES measurements, and a well defined band structure parallel to the surface, only, was observed.

Other than the preliminary XPS studies of Graupner [12], a detailed characterization of the electronic structure of thin Al₂O₃ on FeAl(110) is still missing. Here, ARPES and XPS results are presented to elucidate the electronic structure of the thin oxide film. Fig. 4.7 shows shallow Al-2p core levels for the clean and oxidized surface at a photon energy of 150 eV in the normal emission geometry. The peak
centered at 72.5 eV is due to the metallic substrate, and the feature that appears at higher binding energy after oxidizing the surface is due to Al species in the oxide film. It is clearly seen that the metallic peak is attenuated after exposure to a saturation coverage of oxygen. Due to limited resolution of the analyzer, a curve fitting procedure was implemented to extract more detailed structure. FitXPS2, a peak fitting procedure written by Dave Adams, is used to fit experimental core-level photoemission spectra with a linear background. The line shape of each peak is a (numerical) convolution of an analytical Doniach-Sunjic line shape with a Gaussian. The curve fitting with four spin-split features is shown in Fig. 4.8. In all cases, spin split peak was constrained to have the same amplitude ratio (2:1) and spin-orbit splitting (0.4 eV). The shallow core level of
Al-2p centered at 72.5 eV of the clean and oxidized surfaces exhibits a doublet due to two spin components which are split by 0.4 eV. At saturation coverage of oxide exposure, this split is still visible. These peaks have binding energies 72.5 and 72.9 eV and labeled 1 and 2 in fig. 4.8, respectively. The two broad spin-split peaks, labeled as 5-6 and 7-8, are assigned to Al species which are tetrahedrally and octahedrally coordinated in the thin film. The weak shoulder at 73.9 is attributed to Al atoms at the interface layer between the oxide film and the substrate. The presence of this layer was affirmed in Al$_2$O$_3$/NiAl(110) [10] and O$_2$/Al(111) [27], wherein the same peak was obtained at the same binding energy observed here. As seen from fig. 4.9, the intensity variation of this peak follows the substrate intensity variation as the emission angle changes from normal
to $60^\circ$ in which the latter angle is more surface sensitive. This confirms the existence of an interfacial layer consisting of metallic Al.

![Graph showing Al-2p XP spectra](image)

**Fig. 4.9** Al-2p XP spectra taken at normal and $60^\circ$ emission angle. The attenuated intensity of the weak shoulder follows the substrate peak.

In order to prove that Al is the only constituent, XP spectra of Fe-3p core level of the clean and oxidized surfaces were measured with photon energy of 140 eV at normal emission. **Fig. 4.10** explicitly verifies that no chemical shift occurs in the core level of Fe-3p between the clean and oxidized surface. The only species that oxidizes is the Al atoms.
Fig. 4.10. XP spectra of Fe-3p do not show any chemical shift for the clean and oxidized surface on FeAl(110).

The valence bands of the thin oxide film were investigated by angle resolved photoelectron spectroscopy using $s+p$-polarized light. The incident angle of the photon beam was kept at 45° from the normal and the sample was rotated to study band dispersion in the plane of the surface (as a function of $k_\parallel$). Fig. 4.11 shows a set of EDCs for the thin oxide film grown with a saturation coverage of oxygen. The analyzer and the vector potential are held in the mirror plane along the [1\bar{1}0] direction of the substrate. Oxygen induced states are observed between 5-13 eV. Three strong emissions are clearly seen and their positions as a function of photon energies are marked with a solid line.
Fig. 4.11. EDCs of Al₂O₃/FeAl(110) collected at normal emission indicate lack of dispersion as function of photon energies.

As seen from the figure, the oxygen derived states do not show significant dispersion. This implies that these states do not have dependence on the perpendicular component of the wavevector. The lack of dispersion of the oxide structure is consistent with the limited thickness of the thin film. The peaks at -4.35 eV for the EDC of 38 eV and 15.85 eV for the EDC of 56 eV are attributed to third and second order Al-2p, respectively.
The parallel component of the wavevector was also probed by changing the detection angle at a fixed photon energy. The EDCs in fig. 4.12 were taken for \( \mathbf{A}_{\perp[001]} \) and \( \mathbf{A}_{\perp[1\bar{1}0]} \) for 76 eV photon energy. The observed strong band dispersion indicates a well defined in-plane band structure. Since no dispersion of the perpendicular wavevector is observed, it is proposed that the thin oxide film has a highly two dimensional electronic structure. Oxygen derived \( p \)-states dominate the photoemission.
spectra. The valence bands of FeAl are more attenuated at higher emission angles, which implies that oxide thin film is homogeneous and wets the underlying substrate. ARPES also confirms that Al is the only metal constituent of FeAl in the oxide film because if there were any elemental Fe in the oxide structure, the states at and near Fermi level would be intensified. However, only attenuated Fe states are observed in photoemission spectra. Moreover, previous studies on FeO and Fe$_2$O$_3$ revealed oxide states between 0 and 5 eV [28,29]. However, the attenuated states between 0-5 eV are similar to the clean FeAl photoemission spectra in present case. These features do not resemble the FeO or Fe$_2$O$_3$ electronic structure. Therefore, the elemental Fe, FeO and Fe$_2$O$_3$ are concluded to be absent in the oxide layers.

In order to judge the Jennison argument and further investigate the STM findings that the thin oxide film may have a significant local density of states within the band gap, clean FeAl(110) photoemission spectra are compared with the photoemission spectra of Al$_2$O$_3$/FeAl(110). In Fig. 4.13, the intensities of clean FeAl(110) spectra are normalized to the intensities of the substrate features in the spectra from the oxidized surface. In both geometries i.e. $\mathbf{A}_\perp[001]$ and $\mathbf{A}_\perp[\bar{1}10]$ the measurements were taken at 70 eV photon energy and normal emission. The peaks above the Fermi level for oxide film are due to second order light from the toroidal monochromator. It is clearly seen that the clean FeAl and thin oxide film photoemission spectra have the same features between 0-2 eV binding energies. However photoemission spectra show differences between 2-4 eV. A state located at 2.97 eV is found in the case of oxide thin film. This peak location corresponds to the location of the $\Sigma_1$ band in the clean FeAl(110) surface. In principle, it is expected that this state would be attenuated in a surface covered with a thin oxide film.
However, in the present case it exhibits enhanced intensity. It could be that this state actually arises from an Al-$sp$ state or an interfacial (bonding) state located between thin film of $\text{Al}_2\text{O}_3$ and FeAl(110) substrate. The close proximity of the binding energy of this state to a tunneling voltage where the STM reveals a zigzag-stripe structure of Al ions also supports the notion that this is due to Al-$sp$ state. However, as mentioned above the surface could contain O vacancies and this state may be derived from defects. It has been reported that annealing the $\text{TiO}_2$(110) surface creates point defects in the rows of bridging oxygen. This induces a defect state in the photoemission spectra at 1 eV binding

![Graphical representation of EDCs for both geometry revealing an enhanced state after oxide thin formation on the FeAl(110) surface.](image)

Fig. 4.13. The EDCs for both geometry reveal an enhanced state after oxide thin formation on the FeAl(110) surface.
energy which is within the band gap of the bulk oxide [30]. The interpretations proposed here for oxide thin film need theoretical calculations of the density of states of thin film alumina with defective and defect free surfaces to better identify the nature of the state observed in ARPES of the thin oxide film.

4.4 Conclusion

The atomic and electronic structure of thin aluminum oxide films formed on the FeAl(110) surface have been investigated by use of STM and ARPES. Upon annealing to a temperature of 850 °C, the clean surface reconstructs and develops an FeAl$_2$ structure confined to the outermost layer. A streaky phase seen in LEED pattern produced by annealing in the temperature range of 500-700 °C transforms upon the formation of a well-ordered Al$_2$O$_3$ phase at 850 °C. After exposing the surface to 1000L of oxygen (saturation coverage) a hexagonal oxide film is formed, which is consistent with previous studies on the oxidation of low index surfaces of NiAl. At this coverage, the disappearance of the incommensurate diffraction spots implies that the underlying substrate does not retain its reconstructed phase. In fact, XPS results reveal the presence of Al atoms in the interfacial layer between the substrate and oxide film. This is seen as a weak shoulder in the spectrum as previously identified for thin oxides grown on NiAl and Al(111) surfaces. Furthermore, the Al ions were imaged for the first time by STM. A zigzag-stripe structure with an even mix of octahedrally and tetrahedrally coordinated Al ions was found. XPS and ARPES reveal that Al is the only metal species in the thin oxide film. After a saturation dose of oxygen, the oxide-derived state shifts to higher binding energy with respect to the metallic Al-2p state. However, Fe-3p shallow core levels do not show any measurable shift in XPS. Furthermore, the dimensionality
behavior of the thin oxide film exhibits a highly two dimensional electronic structure. The oxide states do show strong dispersion as a function of the parallel component of the wavevector and show no dispersion along the direction perpendicular to the surface. The photoemission spectra of the clean and thin oxide film covered surfaces have also been compared. The appearance of a peak at 2.97 eV implies that the oxide Al₂O₃ film may have a different electronic structure than bulk Al₂O₃. This state is believed to be derived from the LDOS of aluminum and results from the limited thickness of the thin oxide film and the detailed nature of arrangement of Al ions. This argument needs to be corroborated by theory inputs to assure that this state is not derived as a defect state from oxygen vacancies in the surface of thin alumina.

4.5 References


Chapter 5

Surface Confined Alloys

5.1 Introduction

In previous chapters, bulk alloy surfaces of FeAl single crystals have been investigated via STM and photoemission. Another physical example of an alloy surface is a heteroepitaxially grown surface alloy, which will be the focus of this chapter. In this case, one metal (adlayer) is vapor deposited onto the surface of a different metal (substrate). This heteroepitaxial growth may result in intermixing of two species on the topmost layer of the substrate surface resulting in a surface alloy. Heteroepitaxially grown alloy surfaces (i.e. 2D alloys) are expected for metals which are miscible and form thermodynamically stable bulk alloys (i.e. 3D alloys). However, as mentioned in chapter one, it has been shown in numerous investigations that surface alloying, where the growing adlayer intermixes with the substrate at submonolayer coverages, is more prevalent than anticipated, not only for the metals which are bulk miscible, but also for the metals which possess an immiscibility gap in their bulk phase diagram [1-3]. For the Ag-Cu system, due to a large miscibility gap in the bulk phase diagram and the higher surface free energy of Cu compared to Ag, from the simple thermodynamic arguments as
sketched in chapter one, the first monolayer of Ag is expected to form a simple overlayer by wetting the Cu substrate and thereby lowering the surface free energy.

In agreement with this prediction, it is well known experimentally that Ag forms a quasi-hexagonal overlayer at a full monolayer coverage on all low index faces of Cu. In this case the hexagonal overlayers have a Ag Ag bond distance nearly equal to that of bulk Ag. Thus, the Ag hexagonal overlayer is nearly equal to the Ag(111) surface plane. On the Cu(100) surface, previous STM [4] and ARPES [5,6] studies revealed that at monolayer coverage, Ag forms a hexagonal overlayer with a c(10×2) superstructure with respect to the underlying Cu(100) substrate. Moreover, a Moiré pattern of the hexagonal overlayer of Ag on the Cu (111) surface was observed by STM [1], and a two dimensional Ag electronic structure was shown to exist based on ARPES data [7]. Previous LEED and AES studies by Taylor et al. have demonstrated the formation of a Ag(111) overlayer on Cu(110), composed of a distorted c(2×4) superstructure [8,9]. However, their findings for submonolayer coverages, where Ag atoms are believed to be confined to the troughs of the Cu substrate, have been disproved by a low temperature STM study by Sprunger and co-workers [1]. This latter study showed that despite the immiscibility of Ag in the bulk Cu and a large lattice mismatch (13%) between Ag (4.09 Å) and Cu (3.62 Å), surface alloying is a favorable mechanism at submonolayer coverages. At submonolayer coverages of Ag < 0.4 ML, a surface alloying mechanism is observed whereby Cu atoms are substitutionally replaced with Ag atoms. At the critical coverage of ~ 0.4 ML, a dealloying process emerges, raising Ag dimer and trimer zigzagging chain subunits along the [001] direction of the Cu(110), while an alloy phase of Ag-Cu remains between the chains. For higher coverages (0.6-0.9 ML) of Ag, the
zigzag chains coalesce into a broader and ordered striped structure, again along the [001] direction.

In the case of Ag/Cu(100), previous experimental studies conducted with LEED [10], EELS [11], and ARPES [5,6] revealed a c(10x2) structure upon deposition of a full monolayer of Ag on Cu(100) substrate and ruled out the possibility of a surface alloy formation within the submonolayer regime. Subsequent STM studies [4], however, have shown a surface alloy formation upon submonolayer coverages. The reason that surface alloying was not observed at room and lower temperature is due to an activation barrier higher than the available thermal energy needed to initiate the exchange mechanism. It has been shown that at saturation coverage (0.9 ML), a c(10x2) structure, lying on top of the Cu substrate, is developed at and above room temperature, and the same superstructure occurs at subsaturation coverages below 225 K [4]. The resultant surface morphology in the low coverage regime (< 0.13 ML) is the formation of a surface alloy. The Ag atoms are incorporated in the topmost Cu(100) layer, displacing Cu atoms. At higher Ag coverages (0.13-0.7 ML), a phase segregation is observed, where Ag segregates into c(10x2) patches probably due to Ag induced strain. At saturation coverage (0.9) ML, Ag atoms form an overlayer [4].

Unfortunately, there has been no corresponding electronic structure study in order to corroborate the geometrical structure revealed by STM work. This chapter, therefore, focuses on an experimental study that is aimed at elucidating the electronic dimensionality and the bonding mechanisms of the Ag on Cu(110) and Cu(100) systems. Our approach is to correlate the atomic morphology with the resultant electronic structure for the surface alloy as well as the dealloying phase in the submonolayer regime. In the
present case of Ag/Cu(110), the dimensionality of geometric and electronic structure for
three different submonolayer coverages of Ag on Cu(110) will be investigated.

What we will show is that due to compressive strain along the close-packed
direction of the (110) plane, at 0.2 ML coverage, the substituted atoms, which
preferentially align along [001] direction, reveal a two dimensional-like electronic
structure along the [001] direction and a one dimensional structure along the [1 1 0]
direction due to the weak interaction of the uncoordinated Ag atoms in this direction.
The dealloy phase occurring at 0.4 ML exhibits a three dimensional electronic structure.
At higher coverages (0.65 ML), where the dimer and trimer chains coalesce and form a
broader and more ordered striped structure, a quasi-one dimensional electronic behavior
is observed along the chains. The strong d-d interaction between the Ag atoms and
hybridization of Ag sp and Cu d-states induces a two dimensional electronic structure in
the direction perpendicular to the chains.

In addition to the above system, the electronic structure changes in the surface
alloy and dealloy phases of Ag/Cu(100) will be discussed in the last part of this chapter.
We will show the two dimensional electronic behavior of the dealloy phase (saturation
coverage) and the bounding mechanism of subsaturation coverages for the low
temperature range in which Ag patches lie on top of the substrate and for high
temperature where they lie in the surface layer. Ag-Ag, and Ag-Cu interactions will be
discussed to correlate STM images with ARPES measurements.

5.2 Experimental Procedures

The STM experiments were performed with a compact, fully automated ultrahigh
vacuum STM which is described in section 2.2.3. The ARPES data were taken at
CAMD, utilizing the PGM and the 3 meter-TGM beamlines for Ag/Cu(110) and 6-meter-TGM beamline for Ag/Cu(100) studies, also described in sections 2.4.1 and 2.4.2. Both experiments were performed in ultrahigh vacuum surface science chambers, equipped with standard surface science characterization instruments.

The Cu(110) and Cu(100) crystals were cleaned by repeated cycles of sputtering at room temperature (Ne+ ions, 1keV, 15µA), followed by annealing to 825K. The surface order and cleanliness was observed by LEED, STM, and photoemission spectra. Ag atoms deposited on the surfaces were evaporated from a resistively heated cone of W wire.

The STM images were recorded in the constant current mode and the coverages were determined by measuring the island density from the STM images. In addition LEED was used as a cross-check of the coverage. In the ARPES experiments, s+p-polarized light was used with a 45° incident angle to the surface normal. The electron analyzer was rotated in the plane of light and along the two mirror planes of the crystal to collect off-normal photoemission spectra in the Ag/Cu(110). However, since the VSW HA150 analyzer on the endstation of the 6-meter TGM beamline is fixed, the Cu(100) crystal was rotated for angle-dependent PES measurements.

5.3 Results and Discussion

5.3.1 Atomic and Electronic Structure of Ag/Cu(110)

As mentioned previously, Taylor [8,9] proposed that submonolayer coverages at room temperature lead to Ag atoms being located in the grooves along the [1\bar{1}0] direction of Cu(110), whereas, recent STM findings show that a more complicated growth mode occurs at submonolayer coverages [1]. Ag atoms at coverages of less than 0.4 ML are incorporated into the Cu(110) surface by exchanging with a surface Cu atom, thereby
forming a surface alloy. For higher coverages (>0.4 ML), a dealloy phase transition develops through the formation of [001] directed Ag chains, which coalesce at a 1.3ML and evolve into a quasi-hexagonal Ag(111) overlayer [1].

The same alloying mechanism was observed by Nielsen et al. in the STM study of Au/Ni(110) [12,13]. The Au-Ni system also exhibits a bulk miscibility gap in the phase diagram similar to Ag-Cu. It appears that despite the immiscibility factor, surface alloying is an inevitable growth mode even for metal on metal systems that possess a positive heat of bulk alloy formation. In a theoretical study by Tersoff [14], the strain effect was discussed in the formation of surface confined alloys for the elements immiscible in the bulk. It was calculated that a single Au atom which has a high elastic energy (0.45 eV) in the bulk of Ni(100) possesses much lower elastic energy (0.09 eV) if it is confined to the surface layer of Ni(100). In the presence of the surface the strain is relieved by the misfit atom and the surface alloy becomes the energetically favorable configuration.

However, a detailed understanding of the precise sequence in the bonding mechanisms between adatoms and the substrate of this system that occur during surface alloying and dealloying is clearly desirable and does not exist at present. In the following, we will present and discuss the geometrical structure results from STM and the related electronic structure measurements provided by ARPES for three different submonolayer coverages, 0.2, 0.4 and 0.65 ML of Ag on Cu(110).

i) 0.2 ML Ag Coverage

The surface free energy of Ag (1.3 J/m²) is lower than Cu (1.5 J/m²). A surface free argument proposes that Ag would grow as islands on the Cu(110) substrate (see
Chapter 1). Upon submonolayer deposition of Ag (0.2 ML) at low temperature, we find, surprisingly, that Ag atoms form a surface alloy phase, in which Ag atoms exchange with Cu atoms in the surface layer. This results in a high density of small anisotropic islands on the terraces of the substrate, aligned along the [1\bar{1}0] direction. Annealing the alloy structure to 350 K and imaging subsequently at 150 K results in the disappearance of Cu islands as a result of increased mobility and step accumulation, as depicted in Fig. 5.1(a). It is seen that incorporated Ag atoms, imaged as protrusions, are in registry with substrate lattice i.e. Cu-(1x1) symmetry. Although only reached by activation, this is apparently the lowest free energy configuration. Ag atoms exchange for Cu atoms due to their higher affinity for Cu neighbors, interacting with Ag atoms to gain extra electron density and increase their effective coordination. Fig. 5.1(a) also reveals that substituted Ag atoms preferentially align themselves along the more open [001] direction of the substrate to minimize the resultant strain energy. The strain caused by the lattice-mismatched interface is the driving force for surface alloy phenomenon. Surface alloy formation is a strain relief mechanism. The tensile stress of the clean Cu surface is relieved by the incorporation of the larger size Ag atom.

Now that the geometric structure has been determined, we turn our attention to the electronic states and dimensionality associated with each structure. We use ARPES to determine the electronic dimensionality of the valence electronic states. It has already been demonstrated in the Ag/Cu(100) system [5,6] that the transition from two dimensional (~1-2 ML) to three dimensional (>3 ML) electronic structure is very accessible to ARPES within the direct transition model, which reveals the relation
Fig. 5.1. (a) STM image (6x6 nm$^2$), acquired at 150 K, of Ag on Cu(110) after deposition of 0.2 ML at 300K. Substituted Ag atoms are imaged as protrusion. (b) Hard ball model depicts preferentially alignment of Ag atoms along the [001] direction.
between the energy and the wavevector of the initial states of the photoelectrons. We will apply the same methodology to determine electronic dimensionality as well as to gain insight into the bonding behavior of the Ag $d$-bands in the different surface phases of the Ag/Cu(110) system.

The dependence or lack of dependence of the Ag $d$-bands on the perpendicular ($k_\perp$) and parallel ($k_\parallel$) components of the wave vector distinguishes the dimensionality of the valence bands. In particular, the Ag $d$-band dispersion dependence on $k_\perp$ determines two or three dimensional behavior. With the photoelectron emission along the surface normal (normal emission, $k_\parallel = 0$), the lack of dispersion of the valence bands on $k_\perp$ obtained by varying the photon energy asserts the two dimensional electronic structure. Besides being independent of $k_\perp$, the necessary condition to attain the two (one) dimensional electronic structure is the dependence (lack of dependence) of the valence bands on the $k_\parallel$ when mapping out the surface bands along the high symmetry directions in the surface Brillouin zone.

ARPES data were obtained in the following geometries. The clean Cu(110) bulk states taken at normal emission for 35-50 eV photon energies are recorded, which yield the dispersion of energy bands along the $\Gamma$-K symmetry line to determine the dependence on $k_\perp$. The energy and momentum correlation is in good agreement with previous experimental and theoretical studies [15,16]. Next, due to the $C_{2v}$ symmetry group of (110) $fcc$ surface, photoemission measurements were obtained at various emission angles, along the (001) and (110) directions, to determine the dependence of photoelectrons on $k_\parallel$. 
Using the non-relativistic selection rules, along the $\Sigma$ direction of $k$ space (see fig. 2.11(a)), the initial states of $\Sigma_1$ and $\Sigma_4$ are observable for the vector potential, $A$, parallel to the $(1\bar{1}0)$ mirror plane. Conversely, $\Sigma_1$ and $\Sigma_3$ states are observable for the vector potential, $A$, parallel to the (001) mirror plane. Figure 5.2 shows energy distribution curves taken at 45 eV in the normal emission for Cu(110), with photoemission geometries of $A_{\perp}[001]$ and $A_{\perp}[1\bar{1}0]$ respectively. All features observed are from direct transitions between the Cu bands, employing the non-relativistic selection rules mentioned above. In the $A_{\perp}[001]$ geometry, the peak centered at a binding energy $E_B = 0.45$ eV corresponds to a transition from $\Sigma_1$ character of the highly dispersive, delocalized $sp$ band. The main peak seen at a binding energy of 3.15 eV stems from $\Sigma_4$ character of the $d$-band. The forbidden transition of $\Sigma_3$ character of the $d$-band in this geometry appears at $E_B = 4$ eV in the $A_{\perp}[1\bar{1}0]$ geometry. Furthermore, the peak at binding energy of 0.55 eV possesses $\Sigma_1$ symmetry and the peak at 2.7 eV is due to surface umklapp processes involving the reciprocal lattice vector $\vec{G} = (1\bar{1}1)$.[3]

The next surface phase occurs with the deposition of 0.2 ML of Ag. Here, the appearance of the Ag $d$-bands is seen between 5.5-7 eV binding energy relative to the Fermi level (Fig 5.3(a)). The energy distribution curves (EDCs) in the figure are collected at normal emission with photon energies ranging from 35 to 50 eV. In the $A_{\perp}[1\bar{1}0]$ geometry, the Ag $d$-bands disperse to higher binding energy with increasing photon energy. This dispersion perpendicular to the surface plane indicates a strong coupling between Ag and Cu electrons i.e. a coupling of wavefunctions in the perpendicular direction to surface plane. On the other hand, Fig. 5.3(b) for the $A_{\perp}[001]$ geometry shows that the valence bands of Ag do not disperse for the same photon energy.
ranges, indicating localized states along this direction. Apparently, the preferential alignment of Ag atoms along the [001] direction results in an increased coordination and strong interaction between Ag atoms, leading to a stronger interaction with the surface and underlying Cu atoms compared to the close-packed [1 1 0] direction of the substrate.

This substantial anisotropy gives insight into the alloy bonding mechanism. In order to characterize the nature of the bonding in detail and to obtain the dimensionality behavior, the EDCs were taken along two high symmetry directions in the surface Brillouin zone, $\Gamma Y$ and $\Gamma X$. These data was taken with HA50 hemispherical analyzer, which has higher angular resolution compared to CAMD analyzer, in the 3m-TGM endstation. Fig. 5.4(a) shows that the Ag $d$-bands disperse along the $\Gamma Y$ direction, which
Fig. 5.3. EDCs of Ag/Cu(110) with coverage of 0.2 ML. (a) Dispersion with photon energies in the range of 35-50 eV for A⊥[110], (b) the lack of dispersion for the same photon energy range for A⊥[001].
corresponds to the [001] direction. The fact that Ag atoms preferentially align in this direction causes coordination and overlapping of the wavefunctions, which give rise to a two dimensional electronic structure i.e. one dimension perpendicular to the surface and the other in-plane. The EDCs taken along the \( \overline{\Gamma X} \) symmetry line of the surface Brillouin zone do not show dispersion as seen in Fig. 5.4(b) indicating a lack of coordination in the [1\( \overline{1} \)0] direction. The peaks with lower binding energy (~5 eV) at 20° and 25° mission angles are due to the clean Cu substrate. It is presumed that the localization of the \( d \)-states and the weak overlap of the 3d-orbitals of the isolated/uncoordinated Ag atoms along the close-packed direction is the reason for the observed atomic-like electronic structure behavior in this direction.

In the [001] direction, in which the substituted Ag atoms are aligned, the dispersion in the EDCs implies that there is relatively strong coupling between the electronic states of the Ag adatoms and the Bloch waves of the Cu substrate. This is likely due to hybridization between Ag \( sp \) and Cu \( d \)-states, and strong \( d-d \) interaction takes place between the Ag atoms in the surface plane. In contrast, Ag bands disperse with atomic-like behavior in the [1\( \overline{1} \)0] direction. In this regard, for this surface alloy phase, Ag atoms possess a two dimensional-like nature due to preferential alignment in the [001] direction, and a one dimensional-like behavior in the [1\( \overline{1} \)0] direction due to weak interactions between Ag atoms.

Remarkably, new features have been observed due to reduced symmetry and dimensionality at the surface region. In our previous study, Hite et al. [17] reported the existence of surface electronic resonances for submonolayer coverage of Ag on Cu(110).
Fig. 5.4 EDCs of Ag/Cu(110) with coverage of 0.2 ML. (a) Along the $\Gamma Y$ high symmetry direction in the surface Brillouin zone it indicates a two dimensional electronic structure. (b) Along the $\Gamma X$ high symmetry direction it reveals one dimensional electronic behavior.
It was asserted that they were derived from Cu bands due to hybridization of Ag $sp$ and Cu $d$-bands, and as a result of symmetry breaking in the Ag-Cu nanostructure.

**ii) 0.4ML Ag Coverage**

As the Ag coverage is increased to 0.4 ML, a new dealloy phase transition develops in the surface layer in which substituted Ag atoms are expelled from the surface layer forming dimer and trimer chains along the [001] direction of Cu(110). Apparently, the surface alloy phase becomes less energetically favorable due to the increase in compressive strain caused by the incorporation of larger Ag atoms and the dealloying relieves this strain. Fig. 5.5(a) is a STM image of this chain structure acquired at 150 K, after deposition of 0.4ML Ag at 400K. As illustrated by the ball model in Fig. 5.5(b), the dimers are connected to trimers; however, at this coverage they do not exhibit long range order. From the STM image we measure a coverage of 0.16 ML of Ag, nucleating in these [001] oriented dimer and trimer chains. The rest of the deposited Ag atoms (0.24 ML) remain within the Cu surface in the alloyed Ag-Cu phase and these are imaged as the darker protrusions in Fig. 5.5(a). A similar structure was observed in the Au/Ni(110) system [12,13]. Total energy calculations using the effective medium theory and the STM results of the Au/Ni(110) system, and as well as the present Ag/Cu(110) STM results, are consistent with nucleation of Ag (or Au) chains on top of Cu (or Ni) vacancies in the topmost substrate layer. The excessive compressive stress induced by the larger Ag atoms is relived by the formation of vacancies. In the early stage of this alloying-dealloying phase transition, the adsorbed Ag atoms nucleate on top of the vacancies with pairs of Ag atoms forming above monovacancies and trimers forming above divacancies along the [001] direction of the underlying substrate.
Fig. 5.5. (a) STM image (20x20 nm) showing initial phase of zigzag Ag chain after deposition of 0.4 ML of Ag at 400 K. The dimer and trimer subunits of chain structure are imaged bright. Small protrusion between the chains corresponds to alloyed Ag atoms. (b) Ball model showing the top and side view of the vacancy stabilized chain structure consisting of dimer and trimer subunits.
The experimental STM and Rutherford backscattering spectroscopy (RBS) studies on Au/Ni(110) [13] determined that the alloying-dealloying critical coverage is 0.45 ML. The ratio of Au adatoms in the chains and Au atoms substituted in the surface layer was determined to be 0.58±0.03 for 0.4 and higher submonolayer Au coverages. This is comparable to the 0.67 ratio found here for Ag/Cu(110).

The electronic structure for this intermediate mixed phase is given in the EDCs (Fig. 5.6), which show dispersion of Ag $d$-bands for $A\bot[1\bar{1}0]$ and $A\bot[001]$ geometries, respectively. The increased peak width and higher intensities of the Ag $d$-bands (4-7eV) are presumably due to increased coordination between Ag atoms. Comparing these EDCs with those measured for the lower coverage (0.2 ML), we note that the dispersion of the Ag $d$-bands is more enhanced for the $A\bot[001]$ geometry and diminished for the $A\bot[1\bar{1}0]$ geometry at this coverage. The dealloy phase exhibits reduced interaction between Ag and Cu along the [001] direction. However, increased coordination between Ag atoms enhances the interaction between Ag and Cu along [1\bar{1}0].

Figure 5.7(a) gives the measured EDCs as a function of the emission angle for 42eV photon energy and Fig. 5.7(b) gives the resulting band map of the Ag $d$-bands throughout the surface Brillouin zone, along the two high symmetry directions for 42 and 50 eV photon energies. Along both $\Gamma[Y]$ and $\Gamma[X]$ directions, the Ag $d$-bands exhibit dispersion. As noted from the band map, the Ag $d$-bands are more dispersive along the [001] direction, along which the Ag dimer and trimer structures are aligned, than the bands along [1\bar{1}0], where surface alloying still exists between the chain structure. In this phase, it appears that the Ag $d$-bands exhibit a three dimensional electronic structure as
the $d$-bands show dispersion as a function of $k_\perp$ and $k_\parallel$ along the [001] and [110] directions.

Fig. 5.6. EDCs of Ag/Cu(110) with a coverage of 0.4 ML showing Ag bands dispersing for the photon energy range 35-50 eV. (a) A∥[1 1 0] and (b) A∥[0 0 1] geometries.
Fig. 5.7. (a) EDCs of Ag/Cu(110) with a coverage of 0.4 ML showing Ag bands dispersion as a function of emission angle for 42 eV photon energy along ΓY. (b) Map of binding energy for two directions across the surface Brillouin zone for 42 and 50 eV photon energies depicts dispersion for two directions.
iii) 0.65 ML Ag Coverage

In the Ag coverage range of 0.6-0.9 ML, the dimer and trimer subunits of the chain structure coalesce along the [001] direction and form a long range, ordered chain structure. A (5×1) LEED pattern is in good agreement with the observed STM images shown in Fig. 5.8(a) and illustrated with the ball model in Fig 5.8(b). Equally spaced Ag chains maintain a chain to chain distance of five Cu[110] lattice spacing. The darker protrusion between the chains indicate that the Ag/Cu(110) surface alloy still exists between the chains. At this coverage, Taylor et.al.[8,9] also observed the (5×1) chain configuration in the LEED pattern, noting fifth order spots along the trough direction. They proposed that the pattern was due to uniformly spaced, non-alloyed Ag atoms in a one dimensional fifth order coincidence array in the close-packed [110] direction of Cu(110). However, our STM results have disproved Taylor’s earlier interpretation, showing the existence of Ag-Cu alloyed atoms besides de-alloyed chains at 0.65 ML coverage of Ag on Cu(110) substrate. Here, the attractive interaction between the dimers and trimers subunits overcomes the repulsive interaction between the chains, which dominates at lower coverages. At a coverage slightly higher than a monolayer (1.2 ML), we observe a simple hexagonal Ag(111) structure on the non-alloyed Cu(110) substrate. As mentioned previously, this same structure has been studied in detail on other noble metals substrates [6,7]. This analysis is therefore excluded from the present study.

The anisotropic morphology of the 0.65 ML de-alloyed phase is reflected in the electronic structure as well. Fig. 5.9(a) and 5.9(b) show EDCs of 0.65 ML of
Fig. 5.8. (a) STM image (30x30 nm$^2$) and (b) ball model showing the coalescence of the chains after deposition of 0.65 ML of Ag.
Fig. 5.9 EDCs of 0.65 ML of Ag/Cu(110) collected at normal emission for photon energies 35-50 eV. (a) $\mathbf{A} \perp [1\bar{1}0]$ geometry showing negligible dispersion indicating a one dimensional electronic structure along the Ag chains. (b) $\mathbf{A} \perp [001]$ geometry showing dispersion indicating a strong coupling between the Ag and Cu bands perpendicular to the chains.
Ag/Cu(110) measured at normal emission for a photon energy range of 35-50 eV with \( A \perp [1\overline{1}0] \) and \( A \perp [001] \) geometries, respectively. The photoemission geometry in Fig. 5.9(a) reveals the nature of the bonding along the [001] direction, in which the chains coalesce. As clearly seen from Fig. 5.9(a), the Ag \( d \)-bands do not measurably disperse. This suggests that the Ag \( d \) bands have negligible dependence on the perpendicular component of the wave vector. However, in the geometry of Fig 5.9 (b), it is clearly seen that there is a strong dependence on the perpendicular component of the wave vector. This indicates a dominant Ag-Cu interaction perpendicular to the chains between Ag and surface Cu atoms through Ag \( d \)-Cu \( sp \) hybridization.

To probe the nature and dimensionality of the states in the plane of the surface, a band map of the Ag \( d \)-bands has been plotted throughout the surface Brillouin zone (Fig. 5.10). The 42 and 50 eV photon energies have been used to probe the dependence of the states on the parallel component of the wavevector. It is interesting that the Ag \( d \)-bands show the same dispersion for the two photon energies with \( A \) along the chains and different dispersion for photon energies with \( A \) perpendicular to the chains. This implies that along the chains the states possess a one dimensional electronic structure, and in the perpendicular direction they exhibit a two dimensional electronic structure. We assume that this is a result of hybridization between the \( sp \) band of Ag atoms in the alloyed phase and the \( d \)-band of Cu atoms in the near surface region, implying a strong coupling.

**5.3.2 Atomic and Electronic Structure of Ag/Cu(100)**

We now turn our attention to the growth morphology and electronic structure of Ag on Cu(100). Substrate-adatom and adatom–adatom interactions are the two forces
Fig. 5.10. Band map of Ag $d$-bands along the high symmetry directions in the surface Brillouin zone for 42 and 50 eV confirms the lack of dependence of bands on $k_{\perp}$ along the chain and dependence of bands on $k_{\perp}$ perpendicular to the chains.

competing to dictate the resulting growth morphology. Surface alloy mechanisms in heteroepitaxial growth, mixing of deposited metals with substrate atoms in the topmost layer, overlayer structure, and wetting of the underlying substrate are all dictated by these forces. If the adatom interaction is repulsive, a stable or metastable surface alloying occurs. If the adatom interaction is attractive, island formation occurs as a phase separation as depicted in Fig. 5.11. In the case of strong adlayer and substrate atom bonding, the overlayer structure grows psedomorphically on the substrate, and if the adlayer-adlayer lateral interaction is stronger, overlayer structure adopts nearest neighbor distances that are nearly equal to their bulk counterpart.
Shapiro et al. [18] used ARPES to study substrate–overlayer interactions in the electronic structure of Ag monolayer and higher coverages on Cu(111) and Cu(100) and additional substrates. The overlayer on all these substrates exhibits a virtually identical Ag(111) structure. Nearly unstrained Ag(111) growth is observed on Cu(111), and a c(10x2) structure in a two orthogonal domain is observed for Ag on Cu(100) [18]. The Ag(111) overlayer is slightly strained in Ag/Cu(100). Except for a feature derived from indirect transition, the relative intensities and positions of the Ag bands are retained for the two low index copper surfaces. However, when the overlayer phase is compared to the surface alloy case for the same heteroepitaxial growth, the shift in binding energy is unexceptionally expected due to much stronger bonding between adatoms and the substrate. The two dimensional electronic structure of a monolayer Ag on Cu(100) has been discussed in detail by Tobin et al.[5,6]. Since the overlap between Cu(001) and Ag(111) valence bands in terms of the energy and the wavevector is relatively small, the Ag/Cu(001) system is a promising system to study the electronic structure of interfacial features. In this study, s and p-polarized photons from a gas discharged beam were
employed for photoemission experiments. The silver features around 5 eV binding energy are shifted to higher binding energy along the two high symmetry lines of surface Brillouin zone with no dispersion of states as a function of photon energies as an indication of two dimensional electronic structures. Four states were identified with HeI (21.2 eV) and NeI(16.7 eV) data. Most of these states dispersed as a function of the parallel component of wavevector and none showed any significant dispersion as function of photon energy. This latter fact indicates the independence of the states on the perpendicular component of the wavevector since the $k_\parallel$ vs $E_b$ data plotted along high symmetry lines for two different photon energies are equivalent. The polarization dependence of the Ag bands is identified simply by assuming a small spin orbit and $C_{6v}$ symmetry potential. The discrepancies between the experimental data and calculated valence bands [19] have been attained to the exclusion of substrate effect into calculation. However, dispersion of bands retained the same both experimentally and theoretically. In that study the limited interaction of the Ag 4$d$-states with the substrate was concluded. In addition to the ARPUS experiment, this hexagonal Ag(111)-like overlayer was also studied with LEED [10], EELS [11] and photoelectron diffraction techniques. In all studies, surface alloy formation was excluded. Nevertheless, in an STM study of Sprunger et al. [4], surface alloy formation was observed at submonolayer Ag coverages.

In the initial stages of growth (<0.13 ML) at room temperature and above, the Cu atoms expelled from the topmost layer and the Ag atoms substitutionally alloyed into the topmost layer, in contrast to low temperature Ag growth wherein Ag patches lie on top of the Cu(100) surface layer. At higher coverages (0.13-0.7 ML) and elevated temperatures, the Ag atoms phase separate into Ag c(10x2) patches in order to relieve compressive
strain for the same temperature ranges that surface alloy mechanism formed. The Ag patches are within the Cu surface layer. At saturation coverage (0.9 ML), a complete dealloying mechanism was revealed in corroboration with previous studies. In what follows, two coverages of Ag/Cu(100) systems will be discussed to elucidate interfacial electronic structure and the bonding mechanism between the adlayer and substrate. The motivation of this study to reveal the active Ag states which play a role in the bonding mechanism with the underlying Cu substrate. Also, the combined studies of STM and ARPES presented here allow a look into the dimensionality behavior of the Ag/Cu(100) nanostructure for 0.8 ML and 0.4 ML coverages of Ag.

i) 0.8 ML Ag Coverage

In order to minimize the problem of low barrier Ag adatom diffusion on terraces, particularly for low Ag coverages, the STM imaging was performed at low temperature, which attenuates the Ag atoms mobility. As mentioned above, the c(10x2) structure exhibits at saturation coverage (0.9 ML), at room temperature and above, and at subsaturation coverages below 225 K. Figure 5.12 shows an STM image of a 0.9 ML coverage of Ag which forms a full overlayer on the Cu(100) surface. From the measurement of step height (1.8 Å) [4], it is determined that Ag covers homogeneously the underlying Cu(100) substrate. Due to the lower surface free energy of Ag, the result is consistent with the thermodynamic prediction that Ag would wet the Cu substrate surface. It is clearly seen from the STM image that the Ag overlayer highly buckled along the [011] high symmetry direction of the Cu substrate. The STM image also indicates that when one row is protruded, the other row is depressed. The distance between Ag atoms along the [011] is equivalent to the nearest neighbor Cu-Cu distance.
Fig. 5.12. (a) Atomically resolved pseudohexagonal arrangement of c(10x2) structure (40x40 Å²) (b) Ball model of the c(10x2) overlayer. Color scale shows the height above the Cu substrate surface. Hexagonal and c(10x2) units are drawn by solid line.
(2.56Å), which indicates the pseudomorphic epitaxial Ag arrangements along this direction of the substrate. Along the Cu [011] direction, the measured distance of 25.65 Å for Ag rows, comprising 9 Ag atoms, confirms the c(10x2) structure which was investigated in the previous LEED and ARUPS studies. The Ag-Ag distance along this direction is calculated to be 2.85 Å, which is 2% smaller than the bulk nearest neighbor distance of 2.89 Å. This difference causes a contraction and reveals a slightly distorted hexagonal unit pattern as shown in the ball model. As demonstrated in the ball model, Ag atoms located at bridge sites are imaged higher and those at four fold hollow sites are imaged lower. At low temperatures and at subsaturation coverages, Ag forms this overlayer structure. No indication of surface alloy has been observed for saturation coverage at room temperature and above or for subsaturation coverages below 225 K. Since the electronic structure of the overlayer has been studied in detail in previous studies, it will be only briefly discussed here. In addition the nature of hybridization and the bonding mechanism between Ag-Ag and Ag-Cu atoms will be emphasized. In order to confirm that the Ag overlayer does not disperse with \( k_{\perp} \) and form a two dimensional electronic structure, EDCs at different photon energy have been measured. After deposition of 0.8 ML Ag on Cu(100) at low temperature (~40 K), the EDCs were collected. Two sets of data were measured such that Ag was evaporated at low temperature and ARPES was conducted. Thereafter, this phase was annealed to 440 K and subsequently recooled to 40 K wherein data were recollected. Data was acquired in normal emission geometry with photon energies ranging from 40 to 70 eV and the polarization vector in the geometry of \( \mathbf{A}_{\perp}[010] \). In figure 5.13, EDCs are shown after
this annealing process. The Cu $d$-bands are seen with binding energies 2-4 eV, and Ag $d$-bands are seen between 4-7 eV. Two features of Ag bands are identified and located at 4.95 eV and 6.1 eV. EDCs taken at low temperatures do not show any noticeable change of peak positions (see detail for Fig. 5.14). As shown with the dashed line in Fig. 5.13, it can immediately be seen that Ag $d$-bands do not disperse as a function of photon energies, which asserts the lack of dependence of state energies on $k_{\perp}$. The lack of dispersion of EDCs indicates that for this coverage, which is very close to saturation coverage (0.9 ML), Ag atoms are completely dealloyed from the topmost substrate layer and wet the underlying substrate.
The calculated phase diagram for different coverages of Ag on Cu(100) has been studied by A. Christensen et al. [20]. The hexagonal phase, formed for the coverages of Ag higher than 0.13 ML as a strain relief mechanism, is found to be the most stable phase. The mixing energy, the difference between phase-separated phase and the surface energy curve, as a function of Ag coverages revealed that c(10x2) at 0.9 ML Ag coverage is the most stable phase, exhibiting the lowest energy configuration. The other ordered phase having c(2x2) structure has not been observed with STM study due to being an energetically unstable phase, taking entropy effect into consideration.

In order to confirm that this hexagonal c(10x2) structure is the most stable phase and the overlayer is not interacting with the substrate, the low temperature measurements have also been taken and compared with those conducted after the annealing procedure. Fig. 5.14 shows EDCs acquired with both 54 and 60 eV photon energies in normal emission geometry for a 0.8 ML Ag coverage. Based on the ARPES data, there are no obvious changes in the Ag $d$-bands between the two spectra taken with different photon energies. As asserted in previous studies, a monolayer of Ag overlayer does not interact with the underlying Cu(100) substrate at low and higher temperature, and it forms a c(10x2) stable phase for wide range temperature regimes. This implies that Ag $4d$-bands are not actively involved in the bonding across the interface. In order to disclose the interaction, the work function measurements were performed by applying 10 eV bias voltage to the sample. Since the electronegativities of Ag and Cu are nearly the same [21], the charge transfer is not expected for the Ag/Cu(100) system. Fig. 5.14 (b) shows that after deposition of 0.8 ML Ag, the Cu work function decreases. The measured work function difference is 0.24 eV between clean Cu(100) and Ag/Cu(100) surfaces. This
Fig. 5.14. EDCs of 0.8 ML Ag/Cu(100) at normal emission collected at low temperature and after short annealing to 440 K.
suggests that the homogenously formed Ag overlayer induces work function change for the Cu substrate due to overlayer induced dipole moment. The fact that the change in work function is not reflected in the valence level confirms the non-interaction between the overlayer and the substrate. The discussion of the atomic and resultant electronic structure for coverages between 0.13-0.7 ML, wherein substitutionally surface alloyed Ag atoms between c(10x2) patches in the first Cu layer, is presented below.

i) 0.2-0.7 ML Ag Coverage

Previously it has been described that a Ag-c(10x2) structure forms on Cu(100) at saturation coverage at room temperature or above and at subsaturation coverages below 225 K. However, it has been shown that this structure does not exist for all subcoverages and temperatures [4]. In fact, surface alloy formation is observed at subsaturation coverages (0.13 ML) at or above 300 K, which infers that alloy formation is an activated process. The intermixing of Ag with Cu atoms in the topmost layer is not an energetically favorable mechanism as the Ag coverage is increased beyond 0.13 ML. The alloyed Ag atoms coalesce and form the c(10x2) Ag patches. However, in the region between c(10x2) Ag patches, substitutionally alloyed Ag atoms are still confined within the Cu(100) surface. This indicates that there is local coverage limit that Ag can be alloyed into the Cu surface. The STM image in Fig. 5.15 shows the 0.4 ML Ag/Cu(100) morphology after Ag was deposited at low temperature (225 K) and annealed to 440 K, and subsequently recooled to 170 K. The Ag c(10x2) islands are clearly visible in the image. The elongated direction of the Ag patches gives rise to buckling c(10x2) direction. The measured distance of Ag-c(10x2) is 20 Å wide and the measured height of the patches is only 0.3 Å. In contrast to low temperature results, the Ag patches relocate into
the Cu surface upon annealing to 440 K. The c(10x2) Ag coverage in Fig. 5.14 is found to be 0.27 ML. It is presumed that the 0.13 ML shortfall of Ag is alloyed between the c(10x2) patches. The depression in the interpatch region in the figure 5.15 corresponds to substitutionally alloyed Ag atoms in the topmost Cu(100) surface and 0.13 ML coverages. The resultant electronic structure of this phase has been investigated by use of ARPES technique. It should be noted that previous ARPES results did not probe the alloy phase. Since Ag c(10x2) patches are confined within the surface layer upon annealing to 440 K, it is expected that the Ag-Ag interaction and bonding mechanism between Ag and Cu will show different characteristics in comparison to low temperature results. Here, the electronic structure of these two phases is compared to elucidate the

Fig. 5.15 STM image acquired at 170 K after deposition of 0.4 ML Ag on Cu(100) surface. The depression between the c(10x2) structures corresponds to 0.13 ML coverage of alloyed Ag atoms.
trend in the bonding behavior between two temperature ranges. To reveal the difference in the electronic dimensionality of these phases, EDCs were measured at 40 K for the overlayer c(10x2) patches on top of the surface and for the c(10x2) patches positioned into the surface layer. Fig. 5.16 displays two EDC sets taken for the 0.5 ML Ag/Cu(100) system. After EDCs were recorded at low temperature (~40 K) shown in Fig. 5.16(a), the same system was annealed to 440 K and the EDCs in Fig. 5.16(b) were measured. The overlayer phase shows behavior identical to the surface with 0.9 ML Ag coverage. This implies that at these low coverages the electronic structure behavior is very similar to saturation coverages. Employing the same polarized light and the same crystal

![Fig. 5.16 EDCs of 0.4 ML Ag on Cu(100). The figure on the left shows low temperature and on the right subsequently annealed surfaces.](image-url)
orientation (A⊥[010]), it can be seen from the Fig. 5.16(a) that at this low temperature the Ag d-states show no dependence on the perpendicular component of the wavevector. The lack of dependence on \( k_\perp \) indicates that Ag and Cu atoms do not interact. However, in the case of the annealed surface, Fig. 5.16(a), the trend is different due to location of patches. Indeed, Ag d-bands show a small amount of dispersion for this morphology in which Ag patches are nucleated in the surface layer upon annealing. This dispersion behavior is due to Ag patches and not to the alloyed Ag atoms. The underlying reason is that the alloyed Ag atoms, not shown here, exhibit an atomic–like electronic structure with no dependence of states on \( k_\perp \) and \( k_\parallel \).

Now, consideration is given to understanding and elucidating the nature of bonding for the two cases being discussed. Fig. 5.17(a) shows EDCs corresponding to the low temperature and after annealing this phase to 440 K. It appears that annealing the Ag/Cu(100) system, which results in c(10x2) structure in the surface layer, gives rise to changes in the electronic structure of Ag d-bands. Compared to the low temperature case, the Ag peak located at 5.35 eV for photon energy of 54 eV is shifted by 0.15 eV to a higher binding energy, and the peak which appeared at 5.43 eV is shifted by 0.22 eV to a higher binding energy as well. Notwithstanding, the Ag feature at higher binding energy side (~6 eV) remains unchanged. The shift in peak position, however, reflects the difference in bonding with the underlying substrate. The interaction between Cu and Ag atoms induces a hybridization between Ag and Cu bands. The origin of hybridization stems from Ag \( sp \) and Cu \( d \)-states. Nonetheless, this assessment needs theoretical consideration and calculation to confirm. Another argument which should be considered here is the interaction of Ag-Ag atoms. The narrower feature of Ag d-bands is believed
Fig. 5.17 (a) EDCs of 0.3 ML Ag/Cu(100) at normal emission collected at low temperature and after annealing to 440 K for a short time. (b) Work function measurement marks the difference in binding for Ag/Cu(100) systems.
to be due to repulsive interaction of Ag atoms, and reduced peak intensities are due to reduced coordination between Ag atoms. The repulsive interaction is very common for adatoms confined in the topmost layer of the substrate. For the case of Ag/Cu(110) and Au/Ni(110) at all subcoverages, the interaction of Ag atoms is proposed to be repulsive and not attractive.

Additionally, the work function measurements were employed to elucidate the difference in the growth mode for these subsaturation coverages. Since the interaction between Ag and Cu atoms are not strong in the surface alloy case, it is expected that the work function would not be strongly modified from the clean Cu(100) surface. The low temperature work function measurements, shown in fig. 5.17(b), reveal that for the overlayer case the work function decreases by 0.39 eV. Annealing this phase to 440 K, whereby surface alloy mechanism and Ag patches occur in the topmost layer of Cu(100), the work function increases and acquires nearly Cu(100) clean surface work function. The work function change is related to strain effects by the lattice mismatch between Ag and Cu. The strain on Ag patches is different in the c(10x2) phase, which is on top of Cu substrate surface at low temperatures, and in the case where the c(10x2) structure lies in the topmost layer with alloyed Ag atoms located between the patches after annealing the low temperature phase to 440 K.

5.4. Conclusion

The geometric and electronic structure of the Ag d-bands in both the surface alloy and the de-alloy phase of Ag/Cu(110) and Ag/Cu(100) system have been characterized by use of STM and photoemission spectroscopy. Surface alloy formation has been observed after deposition of 0.2 ML of Ag on Cu(110). Due to preferential Ag-Ag
alignment along the [001] direction of the (110) plane of the substrate, increased coordination among Ag atoms has revealed a two dimensional-like electronic structure; however, uncoordinated Ag atoms along the close-packed direction have elucidated a one dimensional-like electronic behavior. At a critical coverage of 0.4 ML, whereby the de-alloy phase begins, a vacancy stabilized dimer and trimer structure was formed. From ARPES measurements, it has been shown that this unique and complex phase acquires a three dimensional-like electronic structure. Further coverages lead to the coalescence of the subunits of the chain structure into an ordered striped structure along the [001] direction. Electronically, these stripes exhibit a one dimensional-like nature; however, a two dimensional behavior has developed due to hybridization between Ag and Cu bands in the perpendicular direction to the chains structure.

In the case of Ag/Cu(100) nanostructure, activated surface processes have been observed. Even though at room and lower temperature surface alloy is not an energetically favorable mechanism, at elevated temperature, upon providing enough thermal energy to surpass the activation barrier, surface alloy mechanism exhibits at very low Ag coverages (<0.13 ML). Furthermore, STM results indicate that at higher coverages surface morphology strictly depends on kinetics. Between the coverages 0.13-0.7 ML, the low temperature STM measurements reveal Ag islands which form a c(10x2) structure on top of the Cu surface. However, annealing this phase for a short time to 440 K gives rise to a morphology that alloyed Ag atoms at very low coverages coalesce and form Ag patches in the topmost surface layer of the Cu substrate. What has been elucidated in this dissertation is the interaction of Ag and Cu atoms for the overlayer phase of low temperature Ag growth and Ag patches located in the topmost layer after
annealing the low temperature phase to 440 K. The interaction exist between Ag and Cu
for an annealed Ag/Cu(100) nanosystem where Ag patches placed in the surface layer of
Cu substrate. It has been shown that for this phase one of the Ag features shifts to higher
binding energy. The hybridization between Ag and Cu states gives rise to the measured
shift. However, in the low temperature Ag growth for saturation coverages proximity, no
change has been observed for Ag $d$-states, which confirms the weak-bonding interaction
between the Ag and Cu atoms. Finally, work function measurements have been taken for
these phases. The low temperature overlayer case reveals a work function reduction with
contrast to Ag patches located in the topmost layer of the substrate wherein work function
depicts a slight change compared to clean Cu(100). The driving force for work function
change is believed to stem from the differences in the strain field for particular phases
discussed here for Ag/Cu(100) systems.

**5.5 References**

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Chapter 6

Summary

In this dissertation, the atomic, electronic, and chemical structures of reduced-dimensional bimetallic systems were investigated. Specifically, the surface of the bulk intermetallic alloy FeAl(110) and the heteroepitaxially grown surface confined alloys of Ag/Cu(110) and Ag/Cu(100) were studied, primarily, with STM and ARPES. Due to the reduced dimensionality of these systems, new phases occurred in each of the bimetallic systems studied. In addition, oxide formation on FeAl(110) was probed to reveal the atomic and electronic structure of a technologically relevant ultrathin alumina film.

Surface segregation, which changes the chemical composition and the structure of the surface, was found to be a central feature in the atomic structure of the FeAl(110) surface. Preferential sputtering results in a depletion of Al in the near surface region and subsequent annealing promotes a diffusion of bulk Al atoms to the surface. Al segregation to the surface gives rise to new reconstructed phases. At 400 °C, a bulk terminated surface is obtained, in contrast to previous AES and LEED results, which ruled out the formation of a bulk terminated surface. An incommensurate structural phase occurs in the temperature ranges 400-600 °C and above 800 °C. The commensurability of this structure with the underlying lattice was determined to be along
the $[1\bar{1}0]$ direction. Based on STM data, a model has been proposed in which quasihexagonal arrangement of Fe atoms surrounded by six Al atoms and a stoichiometry consistent with FeAl$_2$ structure. This incommensurate phase at elevated temperature (850 °C) is considered to be the stable thermodynamic phase. A missing row like reconstruction occurs along the [001] direction of the substrate to relieve the strain field induced due to increased concentration of Al atoms at annealing temperatures of 600-800 °C. This reconstruction appears as strong streaks on the LEED pattern. In order to correlate the geometric structure of these phases with the electronic structure, ARPES measurements were employed. Increased DOS near the Fermi edge was observed upon annealing to 850 °C. A new feature derived from the $\Sigma_3$ bulk state appears due to hybridization between the Fe-$d$ and Al-$sp$ states. Furthermore, the increased intensity ratio of Al-2$p$ to Fe-3$p$ core levels of the incommensurate phase compared to the bulk terminated surface supports the higher Al concentration for this phase.

In addition to studying the clean surface of FeAl(110), the oxidation behavior of FeAl(110) was studied to elucidate the atomic and electronic structure of the ultrathin oxide film. A well-ordered Al$_2$O$_3$ phase is formed after exposing the surface to 1000L of oxygen at 850 °C. An Al interfacial layer between the oxide film and the substrate was also found as a weak shoulder in the XPS. Moreover, a zigzag-stripe structure of an even mix of octahedrally and tetrahedrally coordinated Al ions was imaged. Al-2$p$ is the only core level that showed a chemical shift in the XPS. A two dimensional electronic structure was found from the dispersion behavior of the electronic states. The photoemission spectra of the oxide film also showed an enhanced intensity in the band

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gap of bulk oxide. Either a sub-oxide or a defect state has been proposed as the source of this peak.

The dimensionality and bonding nature of surface confined alloys, Ag/Cu(110) and Ag/Cu(100), was investigated. At very low coverages, surface alloy formation has been observed as Ag atoms substitutionally alloyed into the Cu(110) surface layer. At low coverage, Ag bands exhibit a two dimensional-like electronic structure along the [001] direction due to increased coordination and a one dimensional-like electronic structure along the close-packed direction due to a lack of coordination between the Ag atoms. An alloy-dealloy phase transition occurs at a critical coverage of 0.4 ML. At this coverage, a complex phase of dimer and trimer chain structures, which acquire a three dimensional-like electronic structures, is formed. Increased Ag coverages result in a coalescence of these chains into an ordered striped structure. A one dimensional electronic structure along the stripe structure and a two dimensional electronic structure in the direction perpendicular to stripes was revealed.

Surface alloying is also observed on Ag/Cu(100) at very low coverages (<0.13 ML). At medium coverages (0.13-0.7 ML), dispersed Ag atoms coalesce and form Ag patches. At low temperatures, the patches form a c(10x2) structure on the top of the Cu surface, and they alloy into the Cu surface layer upon annealing. In the alloyed phase, a Ag d-band shifts toward higher binding energy compared to the overlayer phase; this is believed to be due to hybridization between Ag-sp and Cu-d states.

Finally, as introduced in Chapter 1, this dissertation has focused on elucidation atomic, electronic, and chemical structure of surfaces of bimetallic systems. As has been shown, new complex phases and properties were found to develop on the surfaces of
these systems due to the relaxation of the bulk constraints in the reduced dimension. These phases have been studied to understand the nature of bonding and the structures that form for further scientific and technological applications.
Vita

Orhan Kizilkaya was born in Izmir, Turkey, on April 20, 1971. Orhan graduated from Ege University with a Bachelor of Science degree in physics in 1993. After passing a nation-wide exam, he was awarded a scholarship from the Ministry of Education to pursue a graduate program in USA. He attended the Department of Physics and Astronomy in University of Albany at New York from 1995 to 1997, and received a Master of Science degree. He was accepted the doctoral program in the Department of Physics and Astronomy at Louisiana State University in 1997 and joined Dr. Phillip Sprunger group as a research assistant in the summer of 1999. He conducted his research at the J. Bennett Johnston, Sr., Center for Advanced Microstructures and Devices. He is married to Funda Kizilkaya, and they have a beloved son whose name is Ekrem Eren Kizilkaya. Orhan will receive his Doctor of Philosophy degree in Summer 2003.