



Experimental and theoretical studies of reaction and growth of ultrathin Ni and Pd films on Al single crystal surfaces

by Vaithiyalingam Shutthanandan

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics

Montana State University

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Abstract:

Reaction and growth of ultrathin Ni and Pd films, deposited on Al(110) and Al(001) surfaces at room temperature were studied using high-energy ion scattering, x-ray photoelectron spectroscopy, and x-ray photoelectron diffraction. For Ni deposited on Al(110) surfaces, a strong Ni-Al reaction occurs at the Ni-Al interface. For the first two monolayers (ML) of deposited Ni, a NiAl-like compound is formed. The reaction continues with a different rate, forming a Ni₃Al-like compound for Ni coverages from 2 to 8 ML, at which point a Ni metal film begins to grow on the interface. However, Ni atoms deposited at 250°C on the Al(110) surface, exhibit no surface compound formation, but diffuse 400 Å deep into the Al bulk.

Interatomic potentials based on the embedded atom method are used in a Monte Carlo approach to simulate the evolution of the Ni-Al(110) interface as a function of Ni coverage. The calculated ion scattering yields and x-ray photoelectron intensities from Ni and Al atoms in these simulated interfaces are in good quantitative agreement with the experimental results. The ion scattering simulations show that a large amount of near-surface dechanneling occurs just below the Ni-Al(110) interface.

In contrast to the Al(110) room temperature results, Ni deposited on the Al(001) surface under the same experimental conditions results in the growth of metastable body-centered-cubic Ni at the interface up to 5 ML of Ni coverage in a Stranski-Krastanov growth fashion. After the bcc islands coalesce to cover the surface, a disordered Ni metal film covers the interface.

Ultrathin Pd films deposited on Al(001) surfaces exhibit strong reaction at the Pd-Al(001) interface. For the first 5 ML of deposited Pd, a PdAl-like compound is formed. After 5 ML of Pd coverage, a Pd metal film covers the reacted interface.

EXPERIMENTAL AND THEORETICAL STUDIES OF REACTION
AND GROWTH OF ULTRATHIN Ni AND Pd FILMS ON
Al SINGLE CRYSTAL SURFACES

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APPROVAL

of a thesis submitted by

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This thesis has been read by each member of the thesis committee, and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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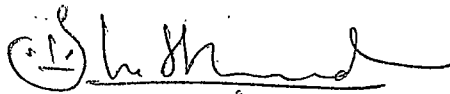
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To my wife **Janani**, whose patience, encouragement, and help have been
beyond measure and generously given....

and

To my **mother** and late **father**, who have given their unqualified love,
understanding, and support throughout my life.....

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ABSTRACT

Reaction and growth of ultrathin Ni and Pd films, deposited on Al(110) and Al(001) surfaces at room temperature were studied using high-energy ion scattering, x-ray photoelectron spectroscopy, and x-ray photoelectron diffraction. For Ni deposited on Al(110) surfaces, a *strong* Ni-Al reaction occurs at the Ni-Al interface. For the first two monolayers (ML) of deposited Ni, a NiAl-like compound is formed. The reaction continues with a different rate, forming a Ni₃Al-like compound for Ni coverages from 2 to 8 ML, at which point a Ni metal film begins to grow on the interface. However, Ni atoms deposited at 250°C on the Al(110) surface, exhibit no surface compound formation, but diffuse 400 Å deep into the Al bulk.

Interatomic potentials based on the embedded atom method are used in a Monte Carlo approach to simulate the evolution of the Ni-Al(110) interface as a function of Ni coverage. The calculated ion scattering yields and x-ray photoelectron intensities from Ni and Al atoms in these simulated interfaces are in good quantitative agreement with the experimental results. The ion scattering simulations show that a large amount of *near-surface dechanneling* occurs just below the Ni-Al(110) interface.

In contrast to the Al(110) room temperature results, Ni deposited on the Al(001) surface under the same experimental conditions results in the growth of metastable *body-centered-cubic* Ni at the interface up to 5 ML of Ni coverage in a Stranski-Krastanov growth fashion. After the *bcc* islands coalesce to cover the surface, a disordered Ni metal film covers the interface.

Ultrathin Pd films deposited on Al(001) surfaces exhibit *strong reaction* at the Pd-Al(001) interface. For the first 5 ML of deposited Pd, a PdAl-like compound is formed. After 5 ML of Pd coverage, a Pd metal film covers the reacted interface.

CHAPTER 1

INTRODUCTION

Ultrathin films of metals on metal substrates have been the subject of intense interest in recent years. In particular, a considerable amount of interest has been focused on trying to understand the interface structures and growth modes of these systems, which range from reaction¹, to island growth², to epitaxial growth³. Generally, the growth modes of vapor-deposited thin films are categorized into the following groups: (1) Frank-van der Merwe (monolayer-by-monolayer growth, FM mode), (2) Stranski-Krastanov (layer growth up to one or a few monolayers, followed by three-dimensional island growth, SK mode), (3) Volmer-Weber (formation of three-dimensional islands, VW mode), (4) Compound formation (formation of a surface alloy as a result of reaction between the adsorbate and the substrate). The driving force in these growth modes is the minimization of the total energy of the system. The total energy includes surface energy of the substrate and adsorbate, and the interfacial energy⁴. The surface energies of a particular substrate and the adsorbate can be calculated or obtained experimentally, but the interfacial energy cannot be determined easily, since strong reaction between the adsorbate and substrate can complicate the matter.

We have focused our studies on transition-metal aluminum interfaces because of their technological applications⁵ as well as the fundamental interest discussed

above. Aluminum-based transition metal alloys are important in applications for catalysis, high-temperature, low-density structural materials⁵, and metalization layers in semiconductors⁶. Also, thin films of transition metal aluminides may have different physical properties than those of the bulk material since the electronic and atomic structures in the overlayer may also be modified.

This thesis work is part of a systematic investigation to understand the fundamentals which determine the growth modes of ultrathin transition-metal films deposited on Al single-crystal substrates. In this study, we mainly concentrated on Ni and Pd ultrathin films on different Al single-crystal surfaces. A detailed description of the structures and growth modes of some other transition metal overlayers, namely Ti/Al and Fe/Al, is given elsewhere^{3,7}.

There have been numerous studies of the Ni-Al system at elevated temperature, including X-ray diffraction (XRD)⁸, photoemission spectroscopy⁹, Rutherford backscattering spectroscopy (RBS)¹⁰, ion beam mixing¹¹, transmission electron microscopy (TEM)¹², and glancing angle x-ray diffraction¹³. Of these, only the TEM work was performed on Al single-crystal surfaces. The remaining experiments were performed either on polycrystalline substrates or on bilayers of Ni and Al. Not all of the results from these experiments are in agreement, but most of them suggest that there is a strong reaction between the Ni and Al atoms, and that NiAl₃ is the first phase to form at the Ni/Al interface at elevated temperatures. For the photoemission and glancing angle x-ray experiments, room-temperature reaction was reported. Because of these conflicting observation, the Ni-Al system merits more attention.

The study of ultrathin Pd films on Al single-crystal surfaces is also very interesting since Ni and Pd have similar bulk equilibrium phase diagrams as Al¹⁴, and they belong to the same group in the periodic table. Because of these similarities, we might expect the behavior of Pd on Al single-crystal surfaces to be similar to that for the Ni-Al system. Like Ni-Al, some conflicting results have been reported for the Pd-Al system in the past^{1,15}.

In this thesis work we explored the growth and reaction of ultrathin Ni and Pd films on Al(110) and Al(001) surfaces. During the growth process the atomic and the electronic structures of the overlayer and the substrate were monitored with different surface science techniques. The experimental techniques which we used in this work are high-energy ion scattering (HEIS), x-ray photoelectron spectroscopy (XPS), and x-ray photoelectron diffraction (XPD). The HEIS and XPD techniques are primarily used to characterize the interface structure, while XPS is used to identify the chemical state of the interface. In Chapter 2, the basic theory of the aforementioned experiments are briefly reviewed. The experimental setups and procedures are discussed in detail in Chapter 3. In Chapter 5, the results of ultrathin Ni films deposited on Al(110) surfaces using HEIS and XPS are reported. The HEIS, XPS, and XPD experimental results of ultrathin Ni films on Al(001) surfaces are discussed in Chapter 6, while Pd films deposited on the Al(001) surface are discussed in Chapter 7.

The aforementioned experimental investigations are often aided by complementary theoretical work, especially in the HEIS case¹⁶. In this study we

developed a new approach to simulate our ion scattering yield and XPS intensity results. In this approach we determine the positions of the atoms as they evolve in a Monte Carlo (MC) simulation¹⁷. The interactions between the atoms are calculated using Embedded-Atom-Method (EAM) potentials¹⁸. Snapshots of the evolving interface are then generated and used to calculate the ion scattering and photoelectron yields. These simulated yields are then compared quantitatively with the experimentally observed results. The EAM potential used in these calculations and the procedures used to simulate the interface are discussed in Chapter 4. The results of the simulations of ultrathin Ni films on Al(110) surfaces are discussed together with the experimental results in Chapter 5.

Some of the acronyms that are frequently used in this thesis are listed below.

AES	Auger electron spectroscopy
EAM	Embedded atom method
FAT	Fixed-analyzer transmission
FM	Frank-van der Merwe
FWHM	Full width at half maximum
HEIS	High energy ion scattering
HA	Hemispherical analyzer
MC	Monte Carlo
MCA	Multichannel analyzer
ML	Monolayer
MCS	Multichannel scaling

PIPS	Passivated, implanted, planner silicon detector
PHA	Pulse height analysis
RBS	Rutherford backscattering spectroscopy
RGA	Residual gas analyzer
SPA	Surface peak area
SK	Stranski-Krastanov
UHV	Ultra-high vacuum
VEGAS	Ion scattering simulation program
VW	Volmer-Weber
XPS	X-ray photoelectron spectroscopy
XPD	X-ray photoelectron diffraction

CHAPTER 2

SHORT REVIEW OF THEORIESIntroduction

The experimental techniques used in this thesis work are high-energy ion scattering (HEIS), channeling and x-ray photoelectron spectroscopy (XPS). The main work has been the measurement of surface peak area (SPA) of the substrate (Al) and the adsorbate (Ni and Pd) in HEIS at different adsorbate coverages in order to investigate the reaction and growth modes of ultrathin transition metals films deposited on Al-single crystal surfaces. Furthermore, HEIS was used to measure the actual coverage of the adsorbate (Ni or Pd). In addition, XPS measurements have been performed to identify the chemical state of the reacted transition metal-Al interface during the Ni (or Pd) deposition. In this Chapter we give a short description of physical concepts and the theory behind these powerful surface science techniques. In the next chapter we will discuss the instrumentation and the experimental details of these methods.

High-energy Ion Scattering and Channeling

Rutherford backscattering spectroscopy (RBS) is a commonly used, non-destructive, surface analysis probe in modern physics¹⁹. The basic idea behind RBS is

very simple. A beam of energetic ions (He^+ , H^+) is directed at the surface of the sample. The ions interact elastically with atoms in the sample and are backscattered into a solid-state detector which counts the number of particles according to their energy. From the energy spectrum of backscattered ions we can infer considerable structural information about the sample, such as the thickness, average composition, and quality of the sample. In particular, if we align the incident ion beam along a low-index crystallographic direction in a single crystal sample, we can achieve substantial surface sensitivity, depending on the incident energy.

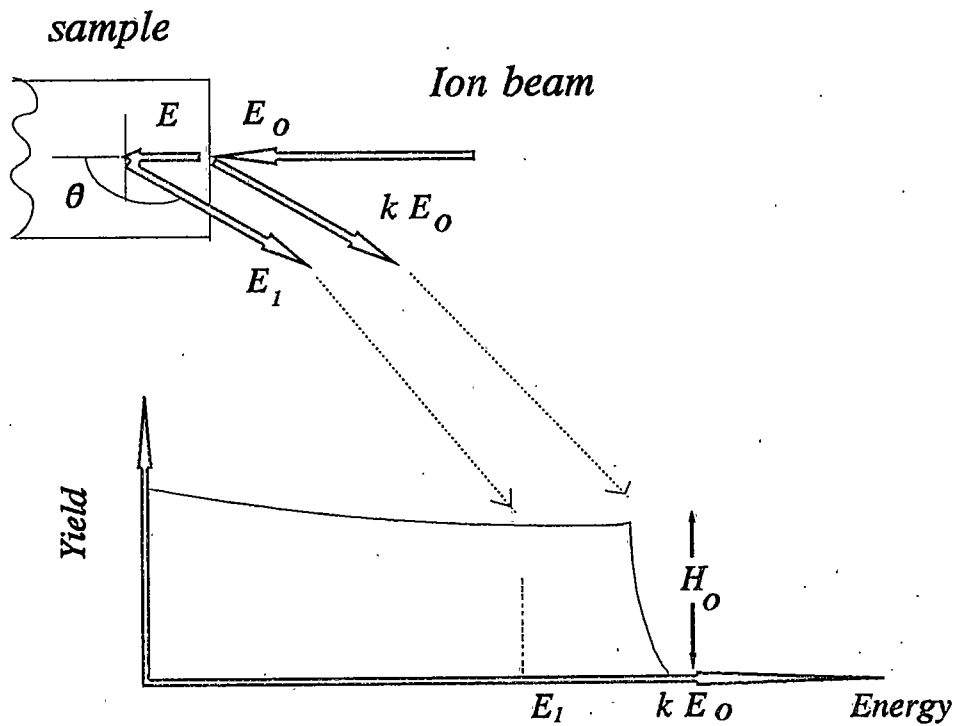


Figure 2.1: Schematic of Rutherford backscattering spectroscopy (RBS)

A typical RBS spectrum from a single-element target is shown in Figure 2.1, where the beam of energetic ions with energy E_0 , mass M_1 , and charge Z_1 strikes the sample (with atomic mass M_2 , and charge Z_2) at normal incidence, and backscattered ions are detected at a scattering angle θ . While a small fraction of the beam scatters from the surface atoms, additional scattering occurs from the atoms just below the surface. In moving through a sample before the scattering encounter, and passing back out through the sample after the scattering event, the ions continue to lose energy. The ions scattered from the surface atoms will reach the detector with energy KE_0 , where K is a constant less than unity, whereas the ions scattered from the atoms which are below the surface will give signals at energies less than KE_0 , as shown in Figure 2.1. The four basic physical properties which govern the RBS process are¹⁹: (1) *kinematic factor* K - used for mass determination, (2) *stopping cross section* - useful for depth analysis, (3) *scattering cross section* - important for quantitative analysis, (4) *energy straggling* - limits the mass and energy resolution. In the following paragraphs, we briefly describe the aforementioned concepts of RBS.

Kinematic factor K

Consider the geometry in Figure 2.1, which illustrates the scattering of energetic ions from a single-element target. The energy of the ions backscattered from the surface atoms can be related to the incident energy via the kinematic factor K , as¹⁹

$$E_s = K E_o \quad (2.1)$$

where K is given by

$$K = \left[\frac{M_1 \cos \theta + (M_2^2 - M_1^2 \sin^2 \theta)^{1/2}}{(M_1 + M_2)} \right]^2 \quad (2.2)$$

Equation 2.2 shows that the kinematic factor depends only on the masses M_1 , and M_2 , and the lab scattering angle θ .

Scattering cross section $d\sigma/d\Omega$

The probability of the scattering event to occur as illustrated in Figure 2.1 depends on the average scattering cross section (σ). The detector subtends a solid angle Ω about the scattering direction, θ . Then, for a small Ω , the average scattering cross section can be approximated being the differential scattering cross section $d\sigma/d\Omega$. Furthermore, if the interaction between the ions and the atoms is specified by the Moliere potential²⁰, then the differential scattering cross section is given by²¹

$$\frac{d\sigma}{d\Omega} = F \left[\frac{Z_1 Z_2 e^2}{2E_o \sin^2 \theta} \right]^2 \frac{\left[\left(1 - \frac{M_1}{M_2} \sin \theta \right)^2 + \cos \theta \right]^2}{\left[1 - \frac{M_1}{M_2} \sin \theta \right]^2} \quad (2.3)$$

where F is a screening correction factor

$$F = 1 - \frac{0.042 Z_1 Z_2^4}{E(keV)} \quad (2.4)$$

Stopping cross section

As we mentioned earlier, when an energetic ion passes through a solid it loses energy (dE/dx) through electronic interactions. If we consider these energy losses in the solid for the ingoing and outcoming ions, then the energy difference ΔE , between ions scattered from the surface and ions scattered at a depth x from the surface, is given by ¹⁹

$$\Delta E = x \left[\frac{K}{\cos \theta_1} \frac{dE}{dx} \Big|_{E_o} + \frac{1}{\cos \theta_2} \frac{dE}{dx} \Big|_{KE_o} \right] \quad (2.5)$$

where θ_1 is defined as the angle between the surface normal of the sample and the

direction of the incident ions, and θ_2 is defined as the angle between the normal direction and the direction of backscattered ions. For normal incidence, $\theta_1 = 0^\circ$, and $\theta_2 = 180^\circ - \theta$, where θ is the scattering angle in the laboratory. Usually, the energy loss dE/dx is related to the stopping cross section ϵ by the following Equation

$$\frac{dE}{dx} = \epsilon N \quad (2.6)$$

where N is the atomic density of the target atoms.

Using Equation 2.5 and 2.6, we can convert the energy-difference Equation into a depth Equation¹⁹, that is

$$\Delta E = N x [\epsilon] \quad (2.7)$$

with

$$[\epsilon] = \left[\frac{K}{\cos\theta_1} \epsilon(E_o) + \frac{1}{\cos\theta_2} \epsilon(KE_o) \right] \quad (2.8)$$

where $\epsilon(E_o)$ and $\epsilon(KE_o)$ are evaluated at energy E_o and KE_o , respectively.

Energy Straggling

The energy-loss process which we discussed in the previous section is subject to statistical fluctuations. As a result of these fluctuations, identical ions passing through the same distance inside the solid may have different energies as they leave from the sample. The energy loss due to this fluctuation is referred to as energy straggling¹⁹. Moreover, any uncertainty in the ion energy due to the straggling will affect the mass and depth resolution in RBS.

Quantitative analysis with RBS

Scattering Yield

In general, the ion scattering yield (Y) from a single-element target is given by¹⁹

$$Y = Q N t \frac{d\sigma}{d\Omega} \Omega \quad (2.9)$$

where

Q is the number of incident ions at the target,

N is the volume density of the target atoms,

t is the thickness of the sample,

$d\sigma/d\Omega$ is the differential scattering cross section, and

Ω is the solid angle subtended by the detector.

For the example illustrated in Figure 2.1, the ion scattering yield in the surface region is equal to the height (H_o) of the spectrum, and is given by¹⁹

$$H_o = \frac{d\sigma(E_o)}{d\Omega} \Omega Q \frac{\delta E}{[E_o]} \quad (2.10)$$

where δE is the energy loss associated with thickness t of the sample, and is typically the energy width of a single channel in the spectrum. The other parameters are the same as before.

Channeling and Shadowing

When the ion beam is well aligned with a low-index crystallographic direction of the single crystal, the ions channel through the crystal along the relatively open areas between the rows of atoms²⁰. Channeled ions do not make close-encounter collisions with the substrate target atoms. Hence the RBS yield is reduced at all depths as seen in Figure 2.2, where the aligned spectrum and the random-direction spectrum from an Al(110) crystal are shown. Roughly 95% of the incident ions are channeled through the crystal. Furthermore, shadowing of the underlying atoms by the surface atoms as shown in Figure 2.3 will reduce the RBS yield. This reduced RBS yield is referred to as aligned yield. Due to the limitations of depth resolution, the aligned yield

will show a small *surface peak* (SP), spread over the first few channels of the spectrum²⁰. If the incident ion beam is not aligned with a low-index direction, the RBS yield will be that for a random distribution of target atoms, i.e. the spectrum (Figure 2.2) will look like the one we described in Figure 2.1. The yield collected in the random direction is referred to as *the random yield*.

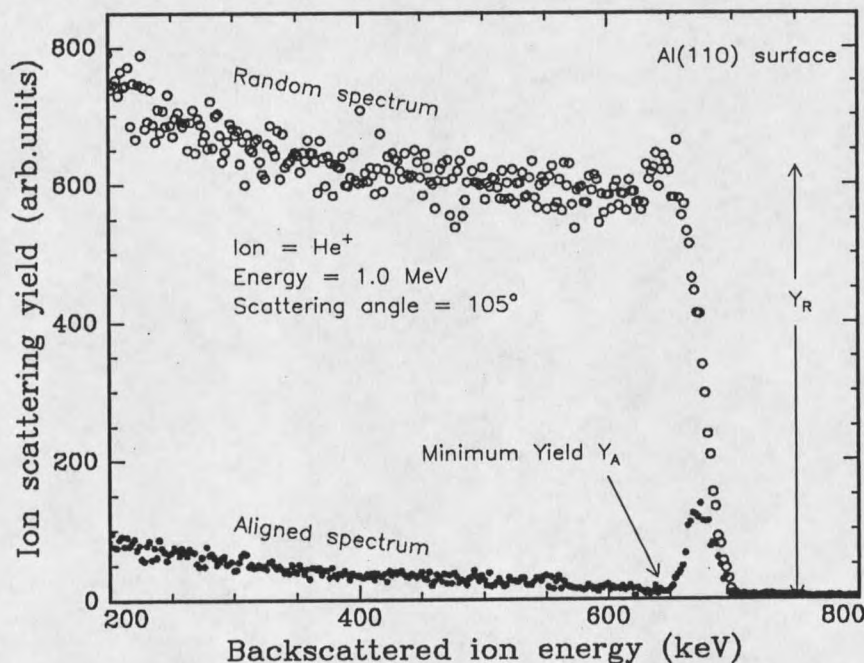


Figure 2.2 : Comparison between the channeling spectrum (closed circles) and the random spectrum (open circles) for He^+ ions backscattering from the Al(110) surface.

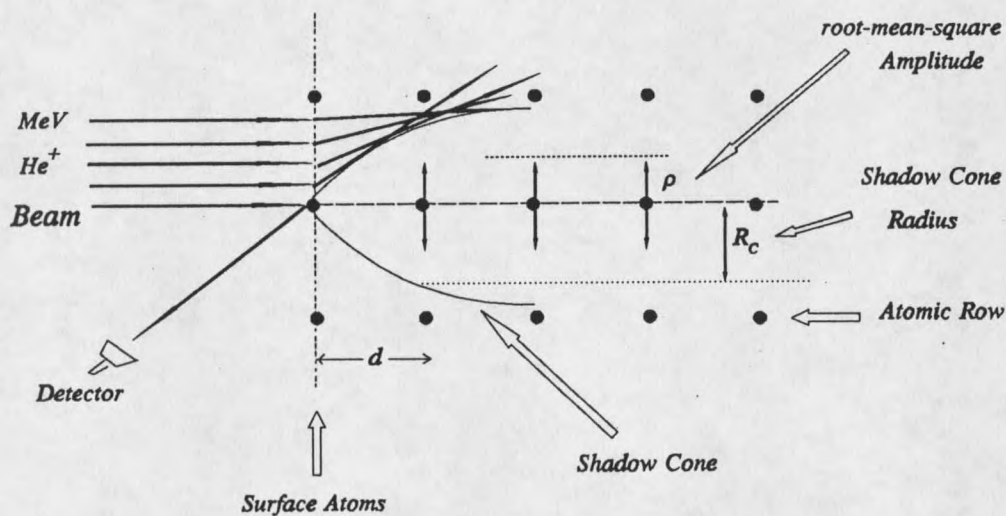


Figure 2.3 : Shadowing effect and the formation of the shadow cone in an ideal crystal.

While the surface peak is a measure of *surface order*, the minimum yield behind the surface peak (Figure 2.2) is a measure of the *bulk crystal perfection*^{19,20}. Furthermore, a measure of the channeling effect is the quantity $\chi_{\min}$, where $\chi_{\min}$ is defined as the ratio of the aligned to random yield¹⁹, ie., $\chi_{\min} = Y_A/Y_R$ (see Figure 2.2). A smaller value of $\chi_{\min}$ corresponds to better channeling. This minimum yield, $\chi_{\min}$, can be calculated from the relation¹⁹

$$\chi_{\min} \approx N d \pi (2u_1^2 + a^2) \quad (2.11)$$

where N is the atomic density, u_1 is the atomic one-dimensional vibrational amplitude, d is the interatomic distance along the row, and a is the Thomas-Fermi screening radius. Values of $\chi_{\min}$ are typically between 0.01 and 0.04.

In a channeling experiment the ions which backscatter from the first atoms in each row give rise to the surface peak observed in the energy distribution spectrum of backscattered ions (Figure 2.2), while the small-angle forward-scattered ions form a "shadow cone" with radius R_c , which extends into the solid (see Figure 2.3). For a Coulomb potential the shadow cone radius is given by²⁰

$$R_c = 2 \sqrt{\frac{Z_1 Z_2 e^2 d}{E}} \quad (2.12)$$

In Figure 2.2, the surface peak area (SPA) is a direct measure of how many surface atoms are visible to the incident ion beam. For the channeling case, the scattering yield Y in Equation 2.9 will be the surface peak area. Thus, if we know the SPA, Q , Ω and the scattering cross section, then by using Equation 2.9 we can calculate the product Nt , the *number of atoms per unit area* visible to the beam.

For a static model of an ideally terminated bulk lattice, subsequent atoms along the row and within the shadow cone do not lead to backscattered ions. However, at room temperature atoms vibrate with the two-dimensional root-mean-square

displacement, ρ , and relative to their equilibrium positions (ideal lattice positions). If these thermal displacements (ρ) are comparable to the shadow-cone radius (R_c), then subsequent atoms along the row may be found outside the shadow cone. Hence, additional backscattering occurs, leading to an increase in the surface peak area. The degree of backscattering from the underlying atoms for a given ion-target combination depends strongly on the relative magnitudes of R_c and ρ ²⁰. From Equation 2.12 we can see that R_c can be changed by changing the incident energy of the ions. Hence, with medium energy (order of keV) ions we can have a very large R_c which will cause the incident ions to probe only the first two surface layers of the crystal. This means that we can achieve a considerable amount of surface sensitivity with this channeling technique by choosing low energy ions¹. Unfortunately, with the limitation of our detection system, we cannot take advantage of this improved surface sensitivity at medium energies. However, with high energies (700-1000 keV He⁺), we can still achieve a reasonable amount of surface sensitivity. In the case of Al(110) and Al(100) with 1 MeV He ions, six to ten layers in one row will contribute to the surface peak area. Of course, the main contribution to the surface peak area will come from only the first few surface layers of the crystal.

Surface structural information from channeling

For a crystalline substrate, the combination of RBS, channeling and shadowing can provide much information about the structure of the crystal. In addition,

if we perform these experiments under UHV conditions, it is possible to explore the surface properties of the crystal, such as surface reconstruction, surface relaxation, growth of epitaxial overlayers on single crystal surfaces, and reacted overlayers on single crystal surfaces. In the following sections we will briefly discuss these properties.

Surface reconstruction

Surface atoms are well known for their behavior which is different than that for the atoms in the bulk. In some crystals the surface atoms rearrange themselves to form a different structure than that for the bulk lattice. This phenomenon is called *surface reconstruction*²². Due to this reconstruction, the atoms in the second layer, which were initially shadowed by the surface atoms, are now visible to the incident ions as seen in Figure 2.4(b). Consequently the surface peak area will increase from its ideal value. For example, the surface reconstruction of the Si(001) surface has been observed by ion channeling experiments²³. Furthermore, adsorption of a foreign species like hydrogen or oxygen can also cause the surface to reconstruct and increase the surface peak area from its value for the clean surface.

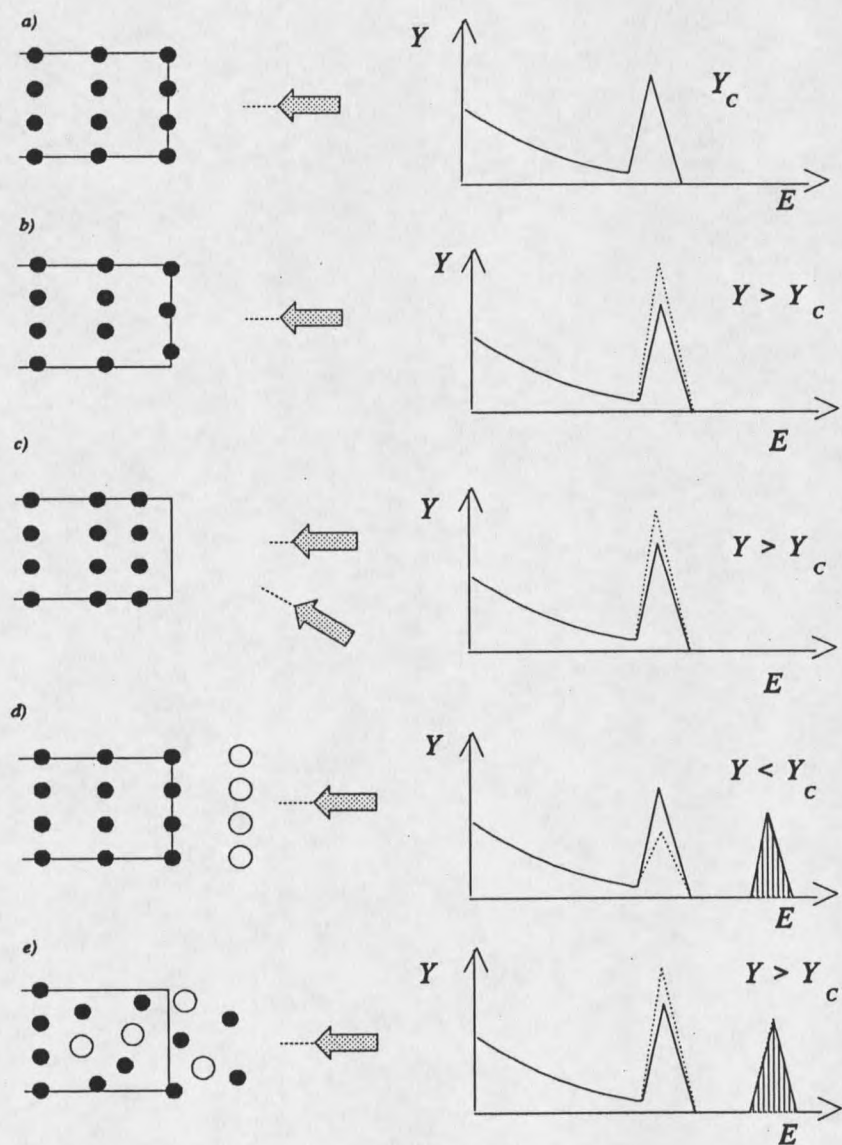


Figure 2.4 : Different uses of ion scattering spectroscopy. (a) bulk-terminated clean surface, (b) reconstructed surface, (c) relaxed surface, (d) epitaxially-ordered overlayer (e) reacted interface.

Surface relaxation

In a number of crystals, the inter-layer separation between the surface layer and the second layer differs from the bulk layer separation. This effect is called *surface relaxation*²². Sometimes, even second and third layers also show some relaxation. From Figure 2.4(c) we can see that the ions directed normal to the surface would still give the same surface peak area as for the unrelaxed clean surface since the surface atoms still shadow the next atoms in the rows. However, if we direct the ions along an off-normal direction as shown in Figure 2.4(c), the surface atoms no longer shadow the next atoms in the row, and so the surface peak area will increase. This multi-layer relaxation has been observed for the Al(110) surface²⁴.

Growth of epitaxial overlayers

With channeling techniques we can monitor the growth of overlayers on single-crystal surfaces²⁰. If heavy adsorbate (deposited) atoms grow epitaxially on the substrate surface as shown in Figure 2.4(d), ie., the adsorbate atoms are aligned with the substrate lattice rows, then these adsorbate atoms will shadow the rows of the substrate atoms. So the yield from the substrate will decrease from its clean value as seen in Figure 2.4(d). One example of an epitaxial system is Ti on Al³.

Interfacial Reaction

As in epitaxial growth, we can also monitor the progress of reaction between the overlayer (heavy) atoms and the substrate atoms with ion channeling¹. In this case, due to the interfacial reaction, adsorbate atoms will displace the surface atoms from their original position. Hence, these displaced atoms will unshadow the underlying atoms in a row as seen in Figure 2.4(e) and so the yield for the substrate will increase from its value for the clean surface as the reaction process continues. In this thesis work, we have used this technique to monitor the interfacial reaction for the Ni atoms on Al(110) and Al(100) surfaces as well as for Pd atoms on Al(100).

X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is one of the most powerful and commonly used surface science techniques^{20,25}. In this technique, the sample under investigation is excited using x-rays with photon energy $h\nu$ (radiation of Al K_{α}) as indicated in Figure 2.5. The electrons are released from their bound states with energies E_B (with respect to vacuum level) by this radiation, and the kinetic energies of the emitted electrons (usually called photoelectrons) relative to the Fermi level are given by the following Equation :

$$\overline{E}_{kin} = h\nu - E_B \quad (2.13)$$

If the photoelectrons have sufficient kinetic energy they can escape from the surface overcoming the sample work function ϕ (see Figure 2.5). The kinetic energy relative to the vacuum level is given by $\overline{E}_{kin} - e\phi$ ²⁰, or

$$E_{kin} = h\nu - E_B - e\phi \quad (2.14)$$

where E_B is now referred to the Fermi level.

A typical XPS spectrum taken over a wide range of energy is shown in Figure 2.6.

From the energetic positions, intensities, and in certain cases, the shapes of the various peaks, we can extract valuable information about the sample. Conventionally, the origin of the energy scale is taken at the Fermi level E_F of the solid (for metals), and the energetic separation of the different peaks is denoted by their binding energies E_B . For metal surfaces, the Fermi level can be easily located, since it is marked by the onset of electron emission at the higher kinetic energy or zero binding energy position in the binding energy scale as seen in the insert of Figure 2.6. As can be seen from Figure 2.6, the characteristic peaks of the XPS spectrum are superimposed on a background of secondary electrons which have undergone inelastic scattering and energy loss on their outward path in the sample²⁰.

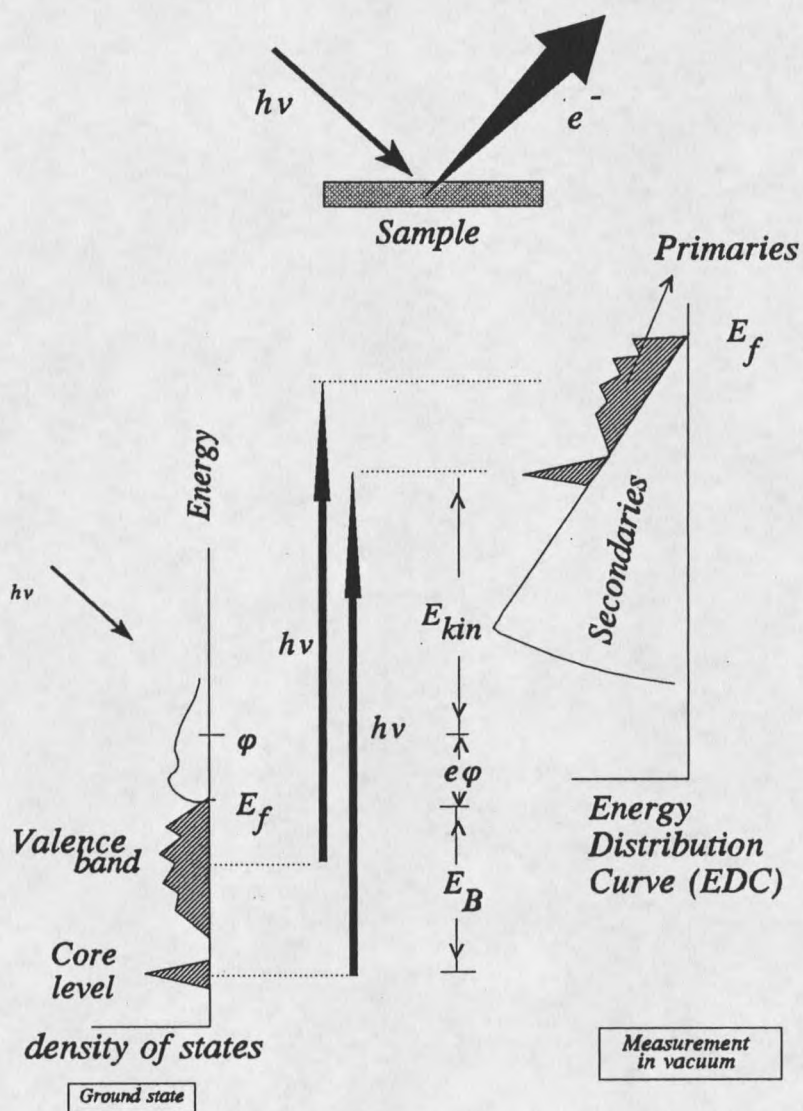


Figure 2.5 : Schematic of the energy level diagram involved in x-ray photoelectron spectroscopy (XPS).

Surface analysis with XPS

Element identification

One of the most remarkable applications of XPS is in the accurate measurement of core-level binding energies using Equation 2.14²⁵. From the XPS spectrum shown in Figure 2.6, we are able to identify the elements present in the surface region of the sample. Because the binding energies of each element are well defined and have unique values, the peak identification of the elements in XPS spectra is straightforward. Furthermore, the spin-orbit coupling which is predominant in initial-state structure, causes a characteristic splitting of the photoelectron peaks²⁵. This spin-orbit splitting can be seen in Figure 2.7, where an XPS spectrum for the Ni 2p core-level is shown. Final-state structure may arise through direct interaction of the photoelectron with other bound electrons, resulting in a discrete energy loss, and appearing as a small peak at the higher-binding-energy side as seen in Figure 2.7. These peaks, called satellites, are associated with specific core-levels. Later, we will discuss in detail the origin of these satellite peaks for Ni.

Chemical shifts

Variations in chemical environment of the atoms in some materials will significantly affect the binding energies of their core-level electrons, and cause a

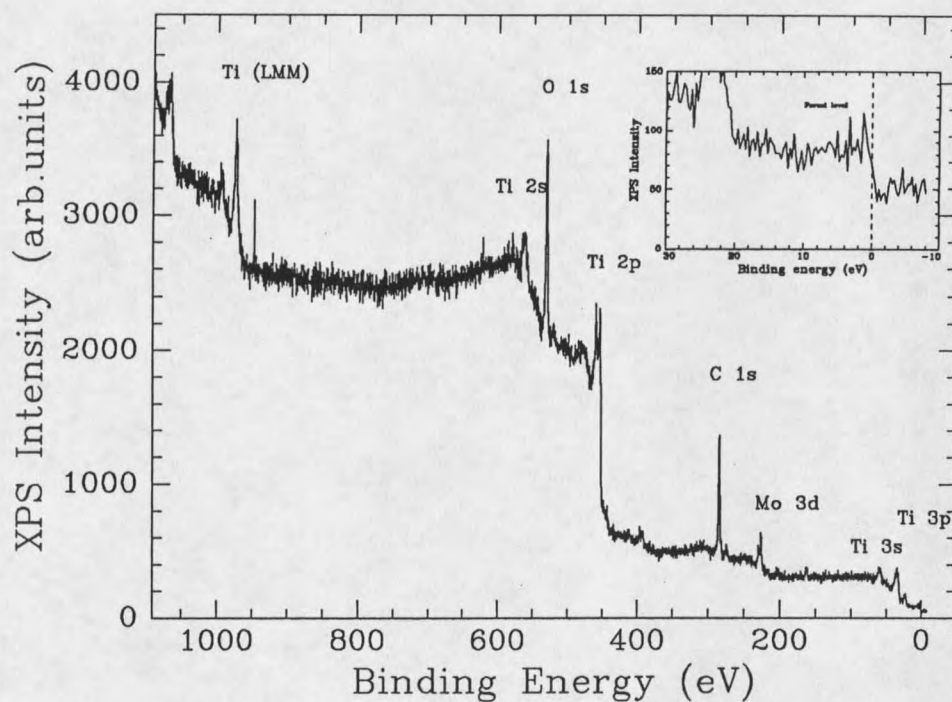


Figure 2.6 : XPS spectrum from a Ti alloy. For clarity, the region near the fermi level is shown in the insert.

detectable shift (ranging from 0.1 up to 10 eV) in the measured photoelectron energies^{20,25}. This shift is called a chemical shift. These chemical shifts can be used to identify the chemical state of the atoms in the solid, such as various states of oxidation, different phases of alloys, and chemisorption states.

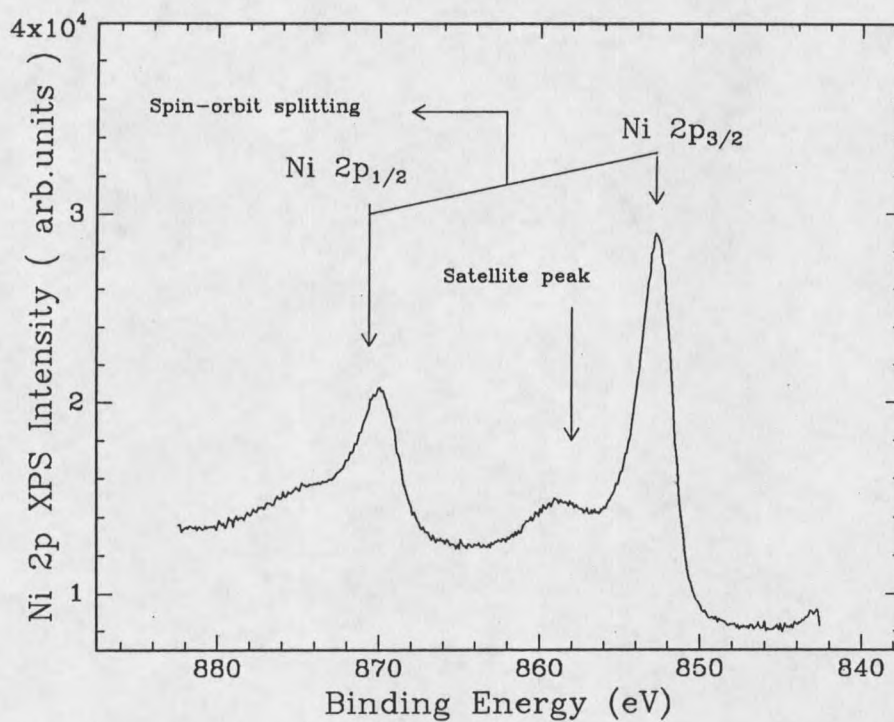


Figure 2.7 : XPS spectrum for a 12 ML Ni film deposited on the Al(110) surface. Spin-orbit splitting and the satellite peak are also shown in the figure.

Intensities and morphology

The intensities of the characteristic photoelectron peaks can be used to monitor the morphology of the overlayers deposited on solid surfaces. A photoelectron which originates at a certain depth below the surface will lose energy through inelastic

scattering events involving other electrons. Due to this energy loss, these electrons do not contribute to the characteristic photoelectron peak. Hence, the photoelectron intensity will decay exponentially as it passes through the medium. The probability of an inelastic scattering event depends primarily on the electron kinetic energy, and to a lesser extent on the material through which it is moving. The intensity of photoelectrons unscattered after traveling through a material of thickness x is given by the following Equation^{20,26}:

$$I(x) = I_o \exp \left[\frac{-x}{\lambda(E_k) \cdot \cos\theta} \right] \quad (2.15)$$

where I_o is the original photoelectron intensity, θ is the angle of emission with respect to the surface normal, and λ is the inelastic mean free path of the electrons. The intensity of a particular photopeak is usually taken as the area under that peak. But, as we can see from Figures 2.6 and 2.7, there is an uncertainty associated with calculating the area under the curve because of the spectral background. So, in order to calculate the XPS intensities, we first have to subtract the background under the peak. There are different forms by which background can be removed from the original XPS spectrum. If we know the line shape of the XPS peak, then subtraction of the background by smooth curve-fitting is straightforward. In Appendix I, the curve-fitting routines used for background subtraction, and the different line shapes of the XPS peaks in this thesis work are discussed in detail.

CHAPTER 3

EXPERIMENTAL TECHNIQUES AND PROCEDURES

Introduction

The experiments were performed in an ultrahigh vacuum (UHV) chamber which is equipped with facilities for HEIS, XPS, Ar-ion sputtering, residual gas analysis, and thin film depositions as shown in Figure 3.1 and Figure 3.2²⁷. The 2 MV Van de Graaff accelerator is connected to this chamber via a differentially pumped beam line which is also shown in Figure 3.2 and Figure 3.3²⁷. We will discuss each of the above mentioned facilities in detail.

Ultrahigh Vacuum and (UHV) Chamber

Ultrahigh vacuum

There are two main reasons why ultrahigh vacuum (UHV) environments are necessary in the surface analysis. In the first place, electrons or ions emitted from the sample should meet as few gas molecules as possible on their way to the analyzer so that

they are not scattered and thereby lost from the analysis. In other words, their mean free paths should be much greater than the dimensions of the spectrometer. Since the mean

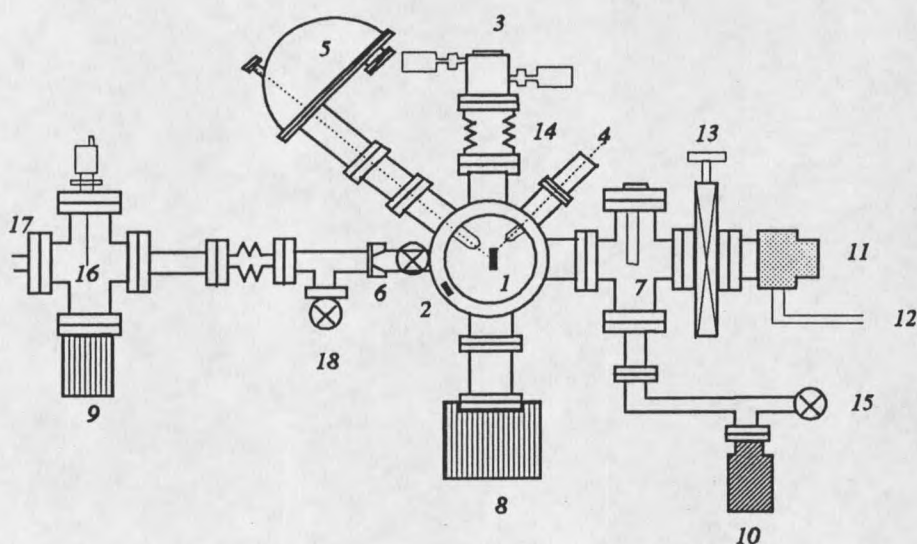


Figure 3.1 : Schematic diagram of the side view of the UHV chamber.

free path of electrons and ions in the air is very small, it is necessary to lower the vacuum of the analysis chamber in order to increase the mean free path. The second reason is to minimize the contamination of the sample. Under normal highvacuum conditions (order

of 10^{-6} Torr) a clean surface would become rapidly covered with contaminants from the residual gas atmosphere. According to the kinetic theory of gases, the arrival rate of nitrogen molecules at room temperature and at a pressure of 10^{-6} Torr would be 3×10^{14} molecules $\text{cm}^{-2} \text{s}^{-1}$. So assuming unit sticking probability and the fact that each monolayer in metals has about 10^{15} atoms cm^{-2} , it would take approximately 3 seconds to form a monolayer of nitrogen on

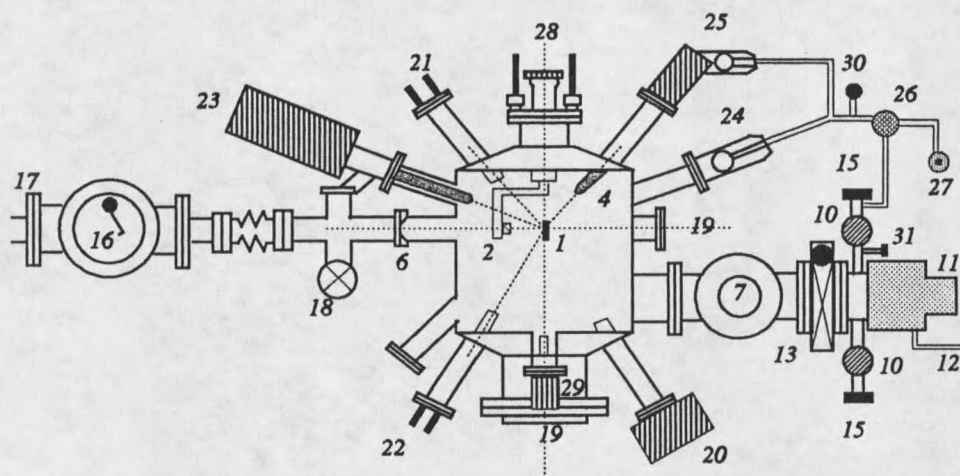


Figure 3.2 : Schematic diagram of the top view of the UHV chamber.

the metal surface²⁸. However, at pressures below 10^{-10} Torr it would take several hours.

For these reasons the ultrahigh vacuum is essential for surface work.

Ultrahigh vacuum chamber

Figures 3.1 and 3.2 are schematic drawings of the side view and the top view of the UHV chamber, respectively. The UHV chamber is fabricated from stainless steel and the inside of it is lined with mu metal to provide magnetic shielding.

All the view ports on the chamber are pointing towards the sample as shown in Figure 3.2. A pressure in the low 10^{-10} Torr (UHV) range is usually attained by using a Blazers

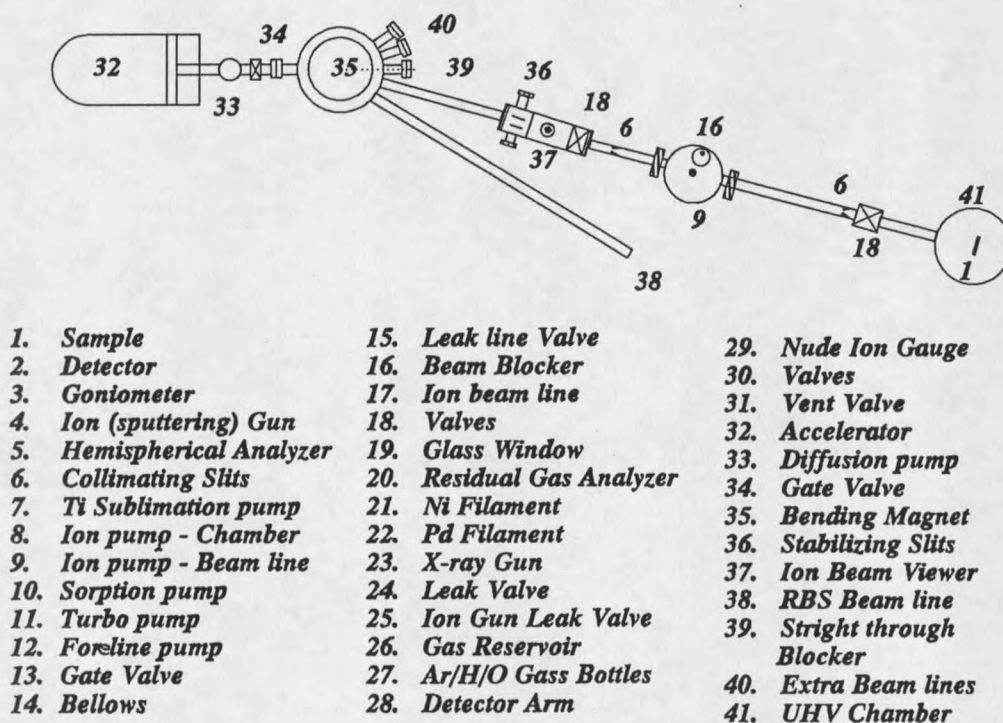


Figure 3.3 : Schematic drawing of the Van de Graaff accelerator, beam line setup, and the UHV chamber.

TPU110 *turbo-molecular pump* (11), Varian *ion getter pumps* (8,9), and the *titanium sublimation pump* (7). The UHV pumps that are mentioned above cannot be operated at atmospheric pressure, so that a *roughing pump* (12) with a foreline trap is connected to the chamber through the turbo pump for the initial evacuation of the chamber. An initial pressure of 10^{-8} Torr is attained using the *turbo* and *ion pumps*. Total pressure measurement in the chamber is made with the aid of an *ionization gauge* (29). A Dycor Electronics M100M *quadrupole residual gas analyzer (RGA)* (20) is mounted to monitor the composition of the gas present in the UHV chamber. The RGA can also be used for finding the leaks in our vacuum system using helium as a trace gas. The entire vacuum chamber and the beam line are normally baked at 150°C for one to two days to remove water vapors, oil vapors and promote outgasing of adsorbed species. During the bake out, the *sample* (1), the *ion detector* (2), and the *ion pump* (8) temperatures are continuously monitored in order to avoid any excessive heating. After the baking, a pressure of high 10^{-10} Torr is reached inside the chamber. Checking with the RGA we find that the main contribution to the total pressure is due to the residual hydrogen. Best vacuum (low 10^{-10} Torr) is achieved with a *Titanium sublimation pump (TSP)* in which a freshly evaporated Ti surface develops high pumping rates of hydrogen in the lower pressure ranges. A typical base pressure in the chamber during the experiments is around 1×10^{-10} Torr. Gases like argon, hydrogen, and oxygen are admitted to the vacuum chamber through bakeable leak valves (24, 25) which allow controlled inlet rates into UHV, directly from atmospheric pressure. These leak valves (24,25) and the gas bottles (27) are connected to the chamber through a separate vacuum system which contains two sorption pumps

(10) and a reservoir (26) as shown in Figure 3.2. The reservoir is evacuated by using the sorption pumps prior to filling with the appropriate gases.

High-energy Ion Scattering

Van de Graaff Accelerator

Figure 3.3 shows a line drawing of the Van de Graaff accelerator(32), UHV beam line(17) and the UHV chamber(41)²⁷. The high-energy ions which we used in these experiments are extracted from the Van de Graaff accelerator. The high voltage at the accelerator terminal is accomplished by means of a moving insulating belt that transports charge between ground potential and the terminal. An RF ion source is used to generate the He ions in a discharge tube. These ions are then accelerated down with an insulating column which is maintained at a pressure of 10^{-6} Torr with the help of a diffusion pump(33). To provide high-voltage insulation, the column and the high-voltage terminal are enclosed in a tank which is pressurized by CO_2 and N_2 . The discharge current (corona current) between the high-voltage terminal and a series of sharp points (corona points) is monitored and used to stabilize the terminal voltage. Typical ion energies that we can get from this accelerator range from 700 kV to 1.8 MV.

Ion beam energies

Since the $^4\text{He}^+$ ion beam from an ion source is often accompanied by some impurities, these impurity ions are also accelerated through the column. The He ions (or whatever ions we need) are separated from the impurities by using the bending magnet(35) to steer ions with the correct e/m ratio into the beam line. In addition, this bending magnet is also used to steer the ion beam into the appropriate beam lines(17,38, and 39). In order to preserve the UHV vacuum conditions in the analyzing chamber while we are running the accelerator, the beam line is differentially pumped using one ion pump(9) and two 1 mm diameter apertures(6), as shown in Figure 3.3. These apertures also serve as the collimators of the ion beam, since a well collimated ion beam is necessary in the ion channeling experiments²². Furthermore, the fluctuation in the energy (terminal voltage) can be corrected by the energy stabilizer feed back unit. After the ion beam is bent by the magnet(35), the ion beam current is monitored by two slit jaws(36), a high-energy and low-energy jaw, in the beam line. A change in the ion kinetic energy causes the ion beam to move left or right in the beam pipe. This movement of the beam will increase the current on one of the two slit jaws, depending on the direction of the movement. Then, this increase in the current is used to control the terminal voltage through the corona currents. The desired energy of the ions is usually selected from the accelerator control unit. Usually, these energies are calibrated by using nuclear reaction methods such as $^{27}\text{Al}(p,\gamma)^{28}\text{Si}$ and $^{19}\text{F}(p,\alpha)^{16}\text{O}$, since these reactions occur at well known beam energies¹⁹. These calibrations are only used as a guideline to get the desired beam

energy. However, the exact beam energy is found using the surface peak position and the random energy position of the known sample.

Ion beam detection

The backscattered ions are energy analyzed and counted using the passivated, implanted, planar silicon (PIPS) detectors(2) which are capable of detecting ions of all energies simultaneously. The principle behind this detector is that the energetic ions enter a semiconductor (Si in this case) and create electron-hole pairs over a certain length (typically 5 μm for 1 MeV ions)²⁰. If ϵ is the energy for creating an electron-hole pair and if the particle energy is E , then the number of carriers created in this process is equal to $2E/\epsilon$. These created carriers are then collected by a biased (usually with 50 Volts) gold electrode on the semiconductor surface to give an output pulse, where the strength of the pulse is proportional to the energy of the incident ion. The number of pulses at this strength gives the number of ions at that energy. Hence, the strength of the pulse and the number of carriers created with this strength will define the energy spectrum. The detector(2) is mounted 3" from the sample, and can be positioned at a desired scattering angle. In all of our channeling experiments the detector was positioned so as to give a scattering angle of 105° . The angular spread of the beam at the detector is reduced by mounting a small circular aperture of diameter 0.193" in front of the detector. The area of the aperture and the distance from the sample to the detector will define the solid angle subtended by the detector which is equal to 0.00306 steradian

in our case.

Charge integration : Total number of incident ions

For all channeling calculations, we need to know precisely, the total number of incident ions which are striking the surface during the data collection time (T_D). Usually this is done by integrating the sample current over the time T_D . The total number of incident ions (Q) on the sample, for one spectrum, is then equal to the total integrated charge divided by the charge of an ion. A typical value of Q used in these experiments is equal to 3 micro-coulombs. However, in the above mentioned current integration measurements care must be taken to suppress the secondary electrons from the sample which are induced by the incident ions, since these electrons will also contribute to the total beam current²¹. Because of their low kinetic energy (order of 100 eV), these electrons can be suppressed by biasing the sample with a 165 Volt battery as shown in Figure 3.4. Furthermore, when the sample is biased with this battery, we observed a small leakage current which is associated with the very large resistance (order of $10^5 \text{ M}\Omega$) that occurs between the sample and ground. Using a constant current source as shown in Figure 3.4, we can compensate for this leakage current. A typical ion beam current in these channeling experiments is about $1 \times 10^{-8} \text{ A}$.

Multichannel analyzer PHA and MCS modes

Data acquisition, storage and display is usually provided by a multichannel analyzer (MCA). When the backscattered He ions penetrate the PIPS detector, they produce individual charge-pulses whose amplitudes are proportional to the ion energies. These current pulses are then converted into voltage pulses by the pre-amplifier and registered in the multichannel analyzer as shown in Figure 3.4. The frequently used mode of operation of the MCA is called *pulse-height-analysis* (PHA). In this mode, the desired backscattered ion spectrum is accumulated by measuring the voltage pulse height of each signal and storing it at an appropriate channel number. That is, the x-axis of the screen is proportional to the backscattered ion energy, and the y-axis is proportional to the number of ions backscattered at that energy. The x-axis of the multichannel analyzer is routinely calibrated by using a well calibrated pulser. This is done by centering the pulser with a particular energy, e.g. 1 MeV, at a desired channel number, e.g. 1000. With these settings each channel in the MCA will correspond to 1 keV, which is the value of δE in equation 2.10. The 5.3 MeV alpha (α) particles emitted from a polonium ^{210}Po radiation source, together with the PIPS detector and the MCA, are utilized to calibrate the pulse generator. The other mode of operation for the MCA is the *multi-channel-scaling* mode. In the MCS mode, individual incoming pulses are counted for a predetermined time interval and placed in a single channel. During subsequent time intervals counting is transferred to the next channel. This mode of operation is used in the alignment of the crystal for the channeling experiments. The XPS spectrum is also collected using the

MCS mode.

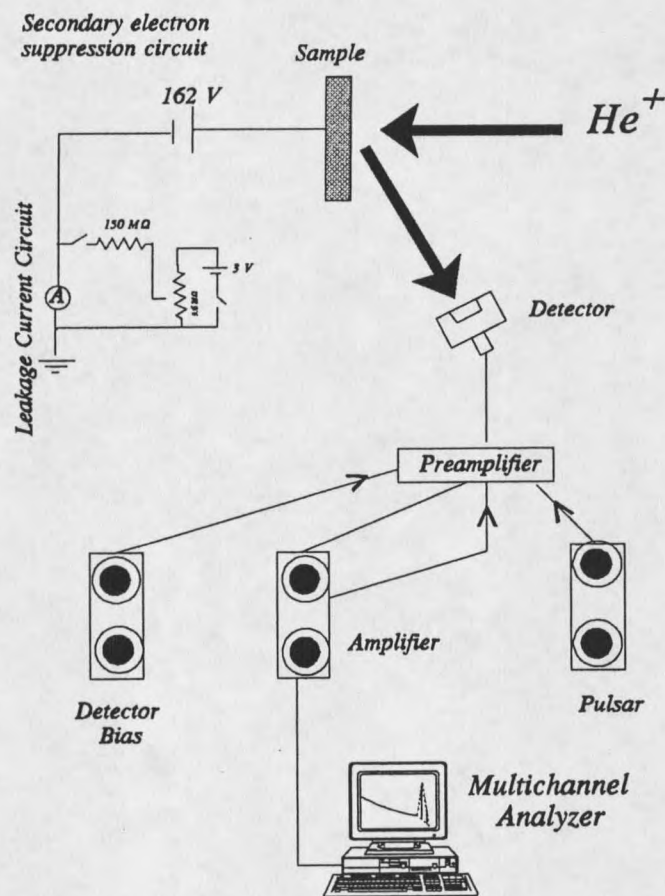


Figure 3.4 : Outline drawing of the multichannel analyzer - detector setup, secondary electron suppression circuit, and the leakage current compensation circuit.

Goniometer and sample holder:

As discussed before, channeling experiments require crystals to be oriented

with respect to the incident ion beam. In addition, we can miss the desired channeling direction if our alignment is off by a fraction of a degree²². Therefore, in order to find the channeling direction precisely and efficiently, we need to use a goniometer that has precise movements. The sample under investigation is mounted onto this

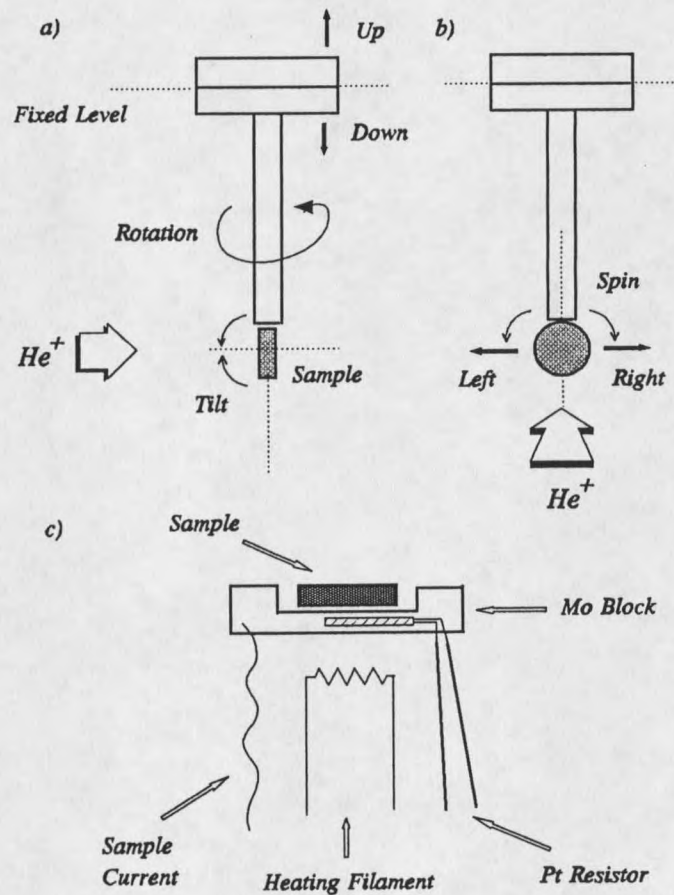


Figure 3.5 : Schematic drawing of the different motions of the goniometer (a) rotation, tilt, up, and down, (b) spin and sideways- left and right, (c) sample holder.

goniometer via the sample holder²⁷. The goniometer is capable of moving the sample in several different and independent ways as shown in Figure 3.5. The main function of the goniometer is rotating the sample around the three orthogonal axes which are important in defining the channeling direction, ie., rotation (R), tilt (T) and spin (S) about the sample normal. Two other motions of the goniometer are moving the sample up or down (Figure 3.5 a) and translating the sample sideways right or left (Figure 3.5 b) in the incident ion beam.

The sample holder which we used to mount the sample is specially designed for mounting the Al single crystals. The detailed description of this sample holder design and drawings will be discussed in Appendix II. Briefly, the sample holder consists of a molybdenum block, one tungsten filament, and a platinum resistor. The Al crystal is mounted on the Mo block and the block itself is electrically isolated from the sample holder mount by three sapphire rods. In order to measure the sample temperature, a calibrated Pt resistor is located inside the Mo block. A W filament is used to heat the sample. A schematic diagram of the sample holder and the electrical connections is shown in Figure 3.5 c.

X-ray Photoelectron Spectroscopy

The basic components of the x-ray photoelectron spectrometer are shown schematically in Figure 3.6. These are an x-ray source (23 -in Figure 3.2), an electron energy analyzer (5 -in Figure 3.1), an electron multiplier, and the sample manipulator.

As we discussed earlier, the UHV condition is an important requirement to operate the x-ray source, electron analyzer, and the electron detectors. Briefly, we will discuss these constituent parts of the XPS below.

X-ray source

Characteristic x-ray emission lines which originated from an anode bombarded by high-energy electrons (10-15 KeV) are used to excite the photoelectrons²⁰. Our XPS instrument is fitted with a twin anode x-ray source (VSW TA10) incorporating both aluminum (Al K_{α} -1486.6 eV) and magnesium (Mg K_{α} -1253.6 eV) anodes. There are two reasons to use twin anodes in XPS. One is that with the magnesium line we can achieve a better resolution than with the aluminum line. The other reason is that in any x-ray excited electron spectrum both photoelectron and Auger peaks appear, and confusion may result²⁵. The Auger electron energy is independent of the X-ray energy whereas the photoelectron energy depends on the X-ray energy through equation 2.13. Hence, the Auger peak positions (binding energies) will shift by 233 eV (ie., the difference between the Al and Mg binding energies) on switching from the Al radiation to Mg radiation whereas the photoelectron peak positions remain unchanged. Because of the high power involved in this x-ray production, it is necessary to remove the heat from the anode by water cooling. Furthermore, a small Al window is placed between the sample and the anode to prevent stray electrons from reaching the sample, to reduce the heating effect and to avoid any possible contamination originating in the source region.

Hemispherical Analyzer (HA)

The energy of the photoelectron emitted from the surface of the sample is measured with a device called a hemispherical analyzer (VSW HA100). The basic idea of operation in this analyzer is that the deflecting electrostatic fields disperse the electron at different energies so that, for any given field, only those energies in a certain narrow range are detected by the detector. The analyzer is shown schematically in Figure 3.6.

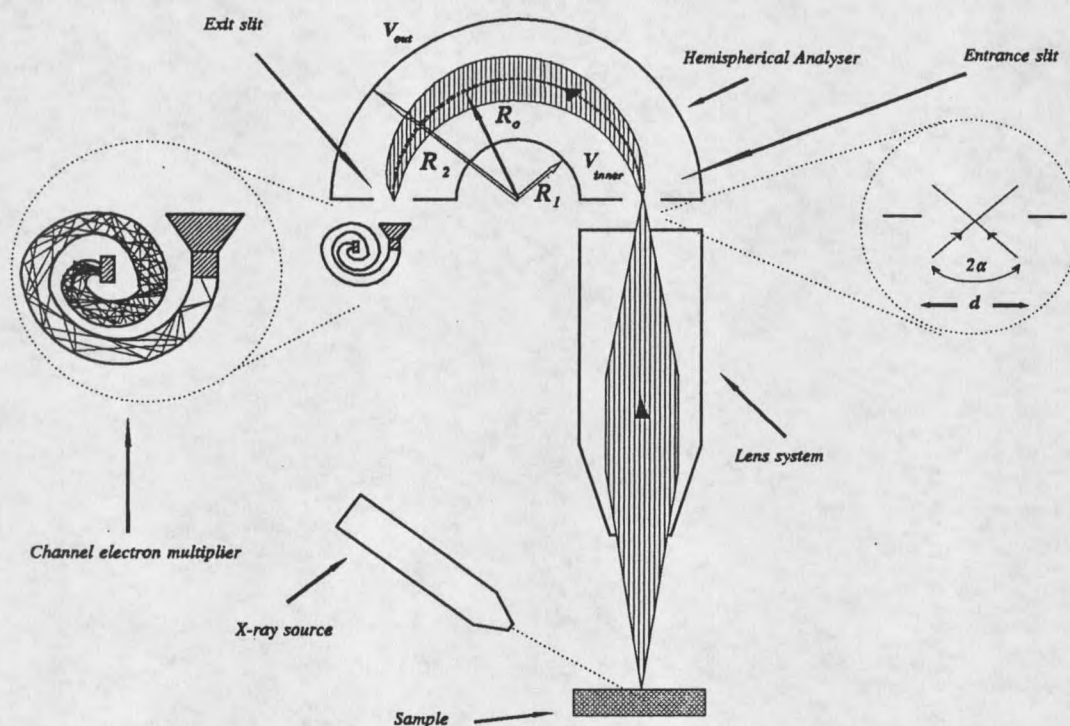


Figure 3.6 : Schematic diagram of the basic components of the x-ray photoelectron spectrometer (XPS). The insert on the right side is the exploded view of the entrance slit of the analyzer, whereas the insert on the left side is showing the exploded view of the electron multiplier and the multiplication process.

Two hemispherical surfaces of inner radius R_1 and outer radius R_2 are positioned concentrically. A potential ΔV is applied between the surfaces so that the inner and outer spheres are maintained at positive and negative voltages respectively. R_o is the median equipotential surface between the hemispheres, and the entrance and exit slits are both centered on R_o . If E is the kinetic energy of an electron travelling in an orbit of radius R_o , then the relationship between E and R_o is given by

$$e \Delta V = E \left(\frac{R_2}{R_1} - \frac{R_1}{R_2} \right) \quad (3.1)$$

Inner and outer hemispheres voltages are given by

$$V_{inner} = E_o \left(\frac{2R_o}{R_1} - 1 \right) \quad (3.2)$$

and

$$V_{outer} = E_o \left(\frac{2R_o}{R_2} - 1 \right) \quad (3.3)$$

respectively. In normal operation, the sample is maintained at ground potential and the whole analyzer floats isolated from ground. The scanning through the kinetic energy range is performed by varying the potential on which the analyzer sits. As seen in Figure 3.6, a sophisticated lens system is used to transport the ejected electrons into the HA analyzer. This lens system also changes, or retards, the electron kinetic energy incident

into the analyzer.

There are two retarding modes in which the HA can be operated. In one, the electrons are decelerated by a constant factor k from their initial kinetic energies. This mode is called *Fixed Retarding Ratio* (FRR) mode. The constant k is given as²⁹

$$k = \frac{K - \phi}{E_p} \quad (3.4)$$

where K is the kinetic energy, ϕ is the work function of the analyzer, and E_p is the analyzer pass energy. During the whole kinetic energy scan, the area of sample analyzed and the emission angle remain constant in the FRR mode. In the second mode, the electrons are decelerated to a constant pass energy. Thus, the electrons entering the analyzer have their energies retarded by changing proportions, depending on their kinetic energies. This mode is called *Fixed analyzer transmission* (FAT) mode. During the whole kinetic energy scan in this mode, the area of the sample and the emission angle do vary with the kinetic energy. Clearly from the above definition of these modes, the FRR mode operates at constant *relative* resolution ($\Delta E/E_o$) whereas the FAT mode operates in a constant *absolute* resolution (ΔE), where ΔE is the full width at half-maximum (FWHM) of the photo peak and E_o is the kinetic energy at the peak position. Furthermore, the *absolute* energy resolution of the analyzer is approximately given by²⁹

$$\Delta E = E_o \left(\frac{d}{2R_o} + \frac{\alpha^2}{4} \right) \quad (3.5)$$

where d is the width of the slit, R_o is the mean radius of the hemispheres, and the α is

the half angle of electrons entering the analyzer at the entrance slit (see Figure 3.6).

Electron multipliers:

An electron multiplier of the channeltron type is employed for detection of the energy-selected electrons as shown in Figure 3.6. The channeltron is a small, curved glass tube, the inside wall of which is coated with high-resistance material²⁹. High-voltage is applied between the ends of the tube. An electron entering the low-potential end of the multiplier collides with the inside wall of the tube and generates secondary electrons. These electrons are further accelerated along the tube until they collide with the wall again and produce more secondary electrons (see insert of Figure 3.6). This cascade process continues to produce large numbers of secondary electrons until all the electrons reach the high voltage (or positive) end of the tube. Thus, the channeltron responds to an input of one electron by producing an output pulse. This pulse may last around 10 nanoseconds and contain up to about 10^8 electrons. These pulses are then further amplified by a pre-amplifier and transmitted to the multichannel analyzer. The MCS mode is used to record the output signal by collecting the total number of counts of the electron pulses in a pre-determined time interval.

Sample Preparation

Orientation of the surface

For our channeling experiments it is necessary to have a single crystal. The Al single crystals used in this thesis work were cut and oriented to within 0.5° of the (110) and (100) surfaces using the



Figure 3.7 The Laue x-ray diffraction pattern from Al(110) single crystal surface

Laue x-ray diffraction method³⁰. The as-received, roughly oriented, Al crystal is mounted onto the polishing sample holder and polished mechanically with 400 grit size coated

abrasive sheets until the desired orientation is achieved. The orientation is checked with the Laue x-ray diffraction patterns in the following manner. When the crystal is properly oriented then the axis of symmetry of the Laue spots taken from the polished crystal will coincide with the reference cross of the camera. If the spots do not coincide with the cross, then the angle of the polishing sample holder is changed slightly and polishing is continued until the spots and the cross coincide. After this, the other side of the crystal is polished and oriented in a similar manner. The Laue spots from the well oriented Al(110) crystal surface and the reference cross from the camera are shown in Figure 3.7.

Fine Polishing

After the crystal surface is oriented in the desired surface plane, the sample surface is further polished to obtain a smooth, shiny surface. For this fine polishing, Buehler alpha micropolish alumina particles of different sizes are used in the following order: 5, 1, 0.3, and 0.05 microns. The crystal is then polished with a syton (syton colloidal suspension of silicon polish) solution to get a mirror like finish. Then, the crystal is thoroughly cleaned with acetone, methanol, and deionized water respectively. The mechanical damage of the crystal due to the abrasive polishing is removed by chemical etching of the crystal in a solution for 15 to 30 seconds. The solution used for this chemical etching is composed of 95 ml of deionized water, 1.5 ml of hydrochloric acid (HCl), 1.5 ml of hydrofluoric acid (HF), and 2.5 ml of nitric acid (HNO₃) respectively.

Cleaning in Vacuum : Sputtering and Annealing

In order to perform surface studies, we should start with a very clean surface of the sample under investigation, in our case an Al single crystal. Since aluminum is very reactive with oxygen, it forms a very thick Al_2O_3 oxide layer on top of the Al crystal surface²⁵. In addition to this oxide layer, other contaminants such as carbon, or sulfur may also be present on the surface due to the polishing and cleaning. Thus, to remove these contaminants, the Al crystal is cleaned *in situ* using Ar^+ ion sputtering. A 5 keV sputter gun (4) with a raster control unit is used for this purpose. High purity argon gas is slowly admitted into the ionization chamber (4) through a leak valve (25), where these Ar gas molecules are ionized by electron impact. Purity of the Ar gas going into the chamber is further checked with the RGA. The extracted Ar ions are then accelerated into a focussing system via deflection plates to the sample surface by a high voltage. During the sputtering, the chamber pressure is maintained around 10^{-6} Torr.

Initially, the Al surface is sputtered with 1000 eV Ar ions for two to three hours at room temperature. The Ar ion beam is rastered across the sample in order to cover the whole surface. A typical beam current during the sputtering is around 1 micro amperes. After that, the sample temperature is raised to 100°C , and the surface is further sputtered for another two to three hours. This step is necessary, since at elevated temperatures, the impurities from the bulk can diffuse into the surface, so that they can be sputtered away by the Ar ions. Furthermore, ion sputtering damages the crystal

surface in the surface region. Thus, it is essential to anneal the crystal in order to recrystallize the surface. For this purpose, the sputtered Al crystal surface is annealed for 15 to 25 minutes at 450°C.

The cleanliness of the surface is checked by XPS and HEIS spectra in the following way: The Al 2p XPS core level region from the as-received Al (110) crystal exhibits two different peaks separated by 2.05 eV as shown in Figure 3.8 a. The peak at a lower binding energy is due to the Al photoelectrons originating from the aluminum metal whereas the higher binding energy peak is due to the Al photoelectrons from the aluminum oxide (Al_2O_3) layer. This is a classic example of the chemical shift that can be observed using XPS. The sputtering cycle, ie. sputtering and annealing, is continued until the chemically shifted Al line is completely removed from the XPS spectrum as shown in Figure 3.8 b. Moreover, we also monitored the oxygen 1s and carbon 1s XPS peaks during the sputtering-annealing cycles. Unfortunately we cannot use these peaks to check the cleanness of the Al crystal, since the HA analyzer is also sampling part of the Mo sample holder. But, we can still use these peaks to monitor the initial evolution of the sputtering-annealing process. In addition, we monitor the Al surface peak from the HEIS experiment in between the sputtering cycles. If the sample is clean the measured surface peak area of Al, ie. number of Al atoms/cm² visible to the incident ion beam, should agree with the calculated surface peak area of Al which is simulated using Monte Carlo simulations of the ion scattering experiment³¹. Details of these simulations and the code (VEGAS) that is used to calculate the surface peak area are discussed in Chapter 4 and Appendix III. For the clean Al(110) crystal, ie. after the aluminum oxide component

is removed from the XPS spectrum by several sputtering cycles, a surface peak area of 12.8 ML is observed which agrees well with the simulated surface peak area of 13.0 ML.

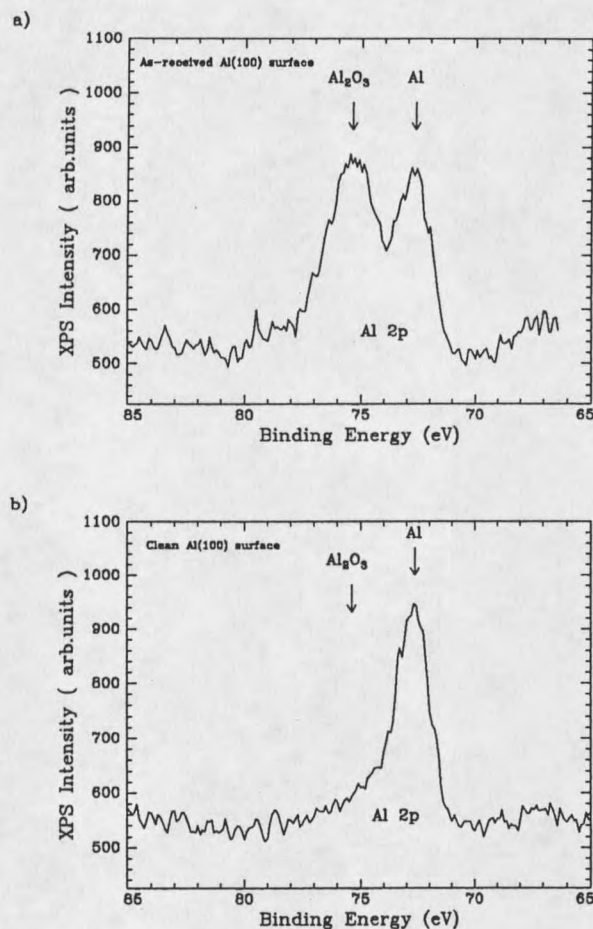


Figure 3.8 : Al 2p XPS spectrum for (a) the as-received (dirty) Al(110) surface and (b) the sputter-cleaned, annealed Al(110) surface. The arrows in the figure indicate the binding energy positions of the Al_2O_3 and the Al photopeaks.

Furthermore, as we discussed in Chapter 2, the quality of the single crystal is related to

the fractional amount of dechanneling, χ_{min} . The calculated value of χ_{min} for Al(110), is 0.025, using equation 2.11 in Chapter 2 together with a Thomas-Fermi screening radius²⁰ of 0.159 Å, Al crystal lattice constant of 4.05 Å, inter-atomic distance of 2.864 Å, and the one-dimensional root-mean-square vibrational amplitude of 0.105 Å, whereas the measured value of χ_{min} is equal to 0.026. This measurement confirms that the quality of our Al crystal is good even after extensive polishing and sputtering.

Thin film deposition

The Ni and Pd films are evaporated onto the Al(110) and Al(100) surfaces using a wire evaporation source. The source consisted of a twisted, double strand of high purity, 0.25 mm diameter, Ni or Pd wire, and a stable DC current supply. These wires are initially outgassed for several hours in UHV. A stable DC current of 4 Amps is passed through the wire to deposit Ni whereas a current of 5 Amps is used to evaporate Pd. The typical deposition rate of these materials at room temperature was around 0.4×10^{15} atoms/cm²/min. The actual coverage of Ni and Pd is determined by using the Ni and Pd surface peak area and equation 2.10. As we discussed in Chapter 2, if Ni or Pd forms ordered overlayers on top of the Al surface, then there should be a Ni-Ni or Pd-Pd shadowing effect present in the film. Because of this shadowing effect we will underestimate the actual coverage of Ni or Pd at normal incidence, where most of our channeling experiments are performed. Therefore, a random orientation (off normal)

HEIS spectrum is taken occasionally to check for this Ni or Pd shadowing effect. The actual coverage of Ni and Pd is always measured in this random orientation. During the evaporation the chamber pressure increased slightly. Analysis of the residual gas showed that this pressure increase is primarily associated with residual hydrogen. The calibrated Pt resistor inside the sample holder registered no significant rise in sample temperature during these evaporations.

Locating the channeling directions

Aligning the incident ion beam along the low index crystallographic direction ($\langle 110 \rangle$, $\langle 100 \rangle$, $\langle 111 \rangle$) of the single crystal is the first and the most important step in our channeling experiments. As we discussed in Chapter 2, when the ion beam is well aligned along the desired crystallographic direction, the backscattered ion yield from the sample will be low compared to the scattering yield for the random direction. In particular, the background yield just behind the surface beak (see Figure 2.2) is at a minimum value when the ion beam is well aligned. We use this behavior to align the ion beam²². From our polishing procedure and the Laue x-ray diffraction pattern, we roughly know the orientation of the crystal. The crystal is then mounted onto the sample holder in a particular orientation. First, we used a laser beam reflected from the crystal through the view ports to get an approximate correlation between the crystal orientation and the rotation (R) and tilt (T) dial settings (see Figure 3.5) of the goniometer, since we know the angles between the view ports. Initially, when the sample is held approximately

normal to the ion beam, a small region of interest (ROI) is defined just behind the surface peak in the backscattering spectrum. While the ion beam current is maintained at a constant value, the sample is rotated back and forth about the normal ($\pm 5^\circ$), and the counts from the ROI in the MCS mode of the multi channel analyzer is monitored during this process. The monitored count rate will go through a minimum during the rotation of the sample. At this minimum value the ion beam is nearly aligned normal to the crystal surface. The sample is held at this minimum value position and tilted back and forth ($\pm 3^\circ$) until the count rate in the ROI passes through another minimum. In principle, the ion beam should be well aligned normal to the surface at these settings of rotation and tilt. However, since a very small coupling between the rotational motion and the tilt motion exists in the goniometer, it is necessary to repeat these procedures several times until the absolute minimum in the count rate in both motions is achieved. At this point axial or normal channeling is established. Most of our experiments are done in this normal channeling direction. Sometimes it is necessary to do channeling experiments in some other direction. To find these other channeling directions the crystal is rotated to bring the desired direction into approximate alignment with the ion beam. The rocking procedure discussed above is then repeated for this new channeling direction.

CHAPTER 4

Monte Carlo Simulations and Embedded Atom Method PotentialsIntroduction

There is considerable interest in understanding the reactions between transition metals and aluminum because of the potential for using the aluminides as metallization layers on semiconductors⁶, and as structural materials⁵. As we discussed in chapter two, high-energy ion scattering (HEIS) is an effective tool for probing the structure of Al-transition-metal interfaces. In chapter 5, we discuss how HEIS and x-ray photoelectron spectroscopy (XPS) were used to investigate the early stages of aluminide formation at the Ni-Al interface. Computer simulations of crystal surfaces and interfaces, employing Monte Carlo (MC) methods, have been used to further understand these experimental results³². Realistic Hamiltonians can be used in these simulations to study surfaces, interfaces, and, especially interfacial reactions. In this chapter we will build the framework for the atomistic simulations used to characterize the Ni-Al interface reaction, *coupled with an experimental check on the accuracy of the simulations*. We used interatomic potentials based on the embedded atom method (EAM)¹⁸ in a Monte Carlo scheme to generate *snapshots* of the atomic coordinates at the interface. Since the EAM has been shown to accurately reproduce portions of the Ni-Al bulk phase diagram³³, various relaxations and reconstruction on metal surfaces³⁴, and composition profiles for

alloys exhibiting surface segregation³⁵, it is reasonable to investigate the reliability of the simulations, i.e., their agreement with the experimental results. The comparisons will at least provide an important test case for the utility of particular EAM potentials, as well as valuable input for further development of the EAM approach to simulate the properties of metal surfaces and interfaces.

In this chapter, ion scattering yields and XPS intensities are calculated using MC snapshots, and compared with measured ion-scattering yields and XPS intensities for the reacted interface. In this approach, correlations of the atomic vibrations, non-Gaussian displacement distributions, disorder in the surface region and intermixing of atoms are taken into account in a natural way, as they are completely determined by the EAM potentials. In the first application of this formalism the effective-medium theory³⁶ was used to describe the interactions between the Al atoms in a study of surface melting³². Medium-energy ion scattering yields (100 keV H⁺) were calculated using snapshots of the disordered surface, and compared with the measured yields. The present study in this thesis work extends this effort in three important ways: (1) use of EAM potentials; (2) application to a bimetallic, reactive interface; and, (3) extension to higher ion energies (1 MeV He⁺). In this chapter we will discuss the simulation procedure to model the reacted interface in detail, and briefly mention how to calculate the high-energy ion scattering yields and XPS intensities from these simulated surfaces. The outcome of these simulations will be discussed together with the experimental results in Chapter 5.

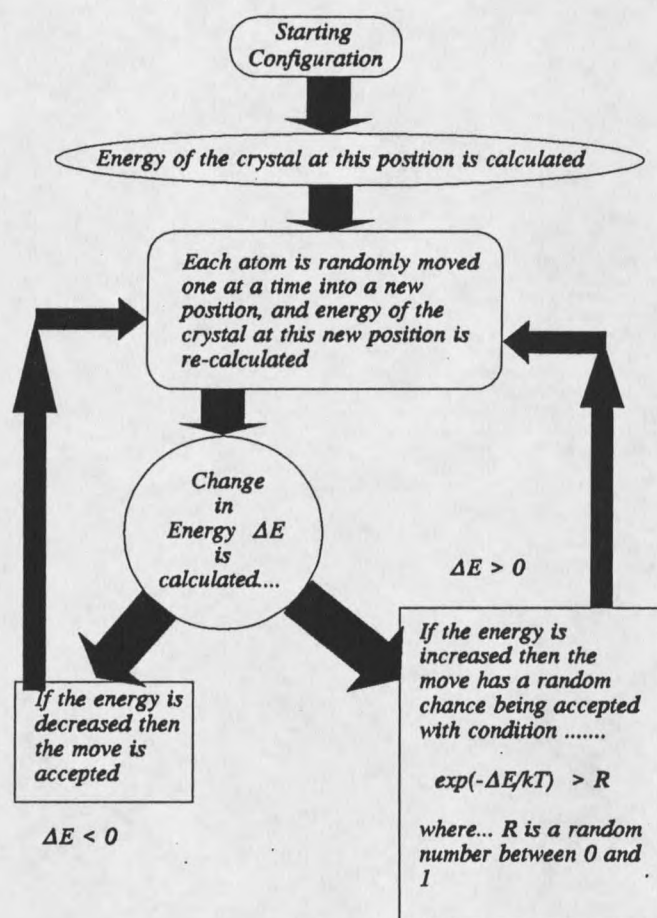


Figure 4.1 Schematic flow diagram of Metropolis scheme in MC simulations.

Ion Scattering simulation

In this section we briefly describe the formalism for the calculation of ion scattering yields from simulated crystal structures. Consider an ion beam incident on a specific configuration X_j of a canonical ensemble, which contains N atoms with the

coordinate of each atom i being given by x_i . The total normalized scattering yield from this particular system is given by the scattering probability per atom $Y_i(e)$ summed over all the atoms in the ensemble. $Y_i(e)$ is defined as the average normalized probability for ions incident along direction e to reflect from atom i and to be detected in a random direction³². Let us further consider, using the Metropolis scheme³⁷ for MC simulation, that M different combinations of the crystal, called "snapshots" have been created. In the simulations, the Metropolis technique leads to a configuration of atoms that results in a minimum energy. The detailed flow diagram of the Metropolis scheme is shown in Figure 4.1. The scattering probability of atom i is then given by

$$Y_i = \frac{1}{M} \sum_{j=1}^M F_i(e, X_j) \quad (4.1)$$

where F_i is the normalized flux of impinging ions at position x_i . Hence, the problem of calculating Y_i is now reduced to calculating the flux $F_i(e, X_j)$ for each snapshot representing a different configuration of the crystal. Calculation of flux F_i can be done by tracking a finite number of ions, L , through the particular snapshot, with each ion impinging at a different position x_0 at the surface³². Interactions between the ions and atoms in the crystal are approximated by a Moliere potential²⁰ of the form

$$V(r) = \frac{Z_1 Z_2 e^2}{r} \left[0.1 \exp\left(\frac{-6r}{a}\right) + 0.35 \exp\left(\frac{-0.3r}{a}\right) \right]$$

$$+ 0.55 \exp\left(\frac{-1.2r}{a}\right)] \quad (4.2)$$

where a is given by

$$a = 0.8853 \frac{a_o}{\left[Z_1^{\frac{1}{2}} + Z_2^{\frac{1}{2}} \right]^{\frac{2}{3}}} \quad (4.3)$$

and a_o is equal to 0.528 Å. Deflection of the ion trajectories by the atoms in the crystal is calculated from this potential. In reality, we cannot assume that the position of atom i is precisely defined by x_i . Instead, atom i may be found within some small volume around x_i . In order to simulate this situation, we consider a small volume around the instantaneous position x_i of atom i , with the normalized Gaussian distribution³²,

$$G(\mathbf{r}, X_j) = \frac{1}{2\pi\delta^2} \exp\left(-\frac{|\mathbf{r}-\mathbf{x}_i|^2}{2\delta^2}\right) \quad (4.4)$$

where δ is smaller than the root-mean-square vibration amplitude of the atoms. The influence of δ in these calculations will be discussed later. The flux F_i is averaged over this distribution function $G(\mathbf{r}, X_j)$. This approach is valid if we choose δ to be very small. Let Φ be the flux of incoming ions in a plane perpendicular to $\mathbf{e}$. Integrating $G(\mathbf{r}, X_j)$ along the k^{th} ion trajectory, we obtain a closed form for the scattering yield of atom i :

$$Y_i = \lim_{\delta \rightarrow 0} \frac{1}{M\Phi} \sum_{j=1}^M \left[\sum_{k=1}^L \frac{1}{2\pi\delta^2} \exp\left(-\frac{\xi_i^2}{2\delta^2}\right) \right] \quad (4.5)$$

where $\xi_i = \xi_i(\mathbf{e}, x_o, X_j)$ is the impact parameter of the k^{th} ion with respect to the position x_i of atom i . Detailed derivations of Equations 4.1-4.5 can be found in the Ref 32. The

complete code for calculating the ion scattering yield is called "Vegas"^{31,32}.

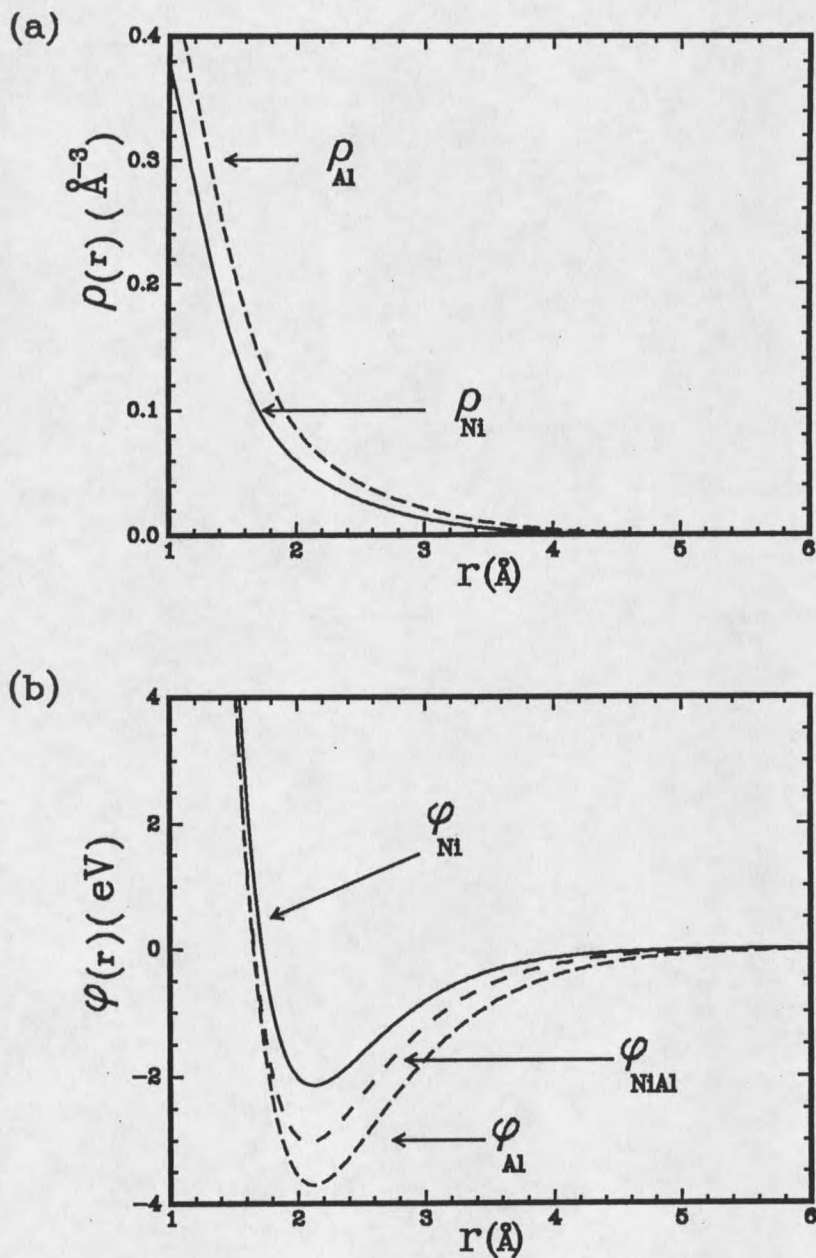


Figure 4.2 The functions comprising the EAM potentials of Ni, Al, and Ni-Al:

(a) function ρ and (b) function ϕ . The solid line represents Ni while the small dashed line and large dash-dash line represent Al and Ni-Al respectively.

Embedded-Atom Method and potentials

From the previous section, using MC simulations and the Metropolis scheme, we created M different configuration of the crystal where each configuration has the probability

$$\frac{\exp \left[-\frac{H(X)}{k_B T} \right]}{\int \exp \left[-\frac{H(X)}{k_B T} \right] d^3 X} \quad (4.6)$$

to be generated. $H(X)$ is the Hamiltonian of the N-atom system. Since the incoming ions move much faster than the atoms in the system, the ions see instantaneous snapshots of the crystal. Thus, the kinetic energy contribution to the total energy can be omitted from $H(X)$, and $H(X)$ just represents the potential energy $E(X)$ of the system. Therefore, in order to generate these snapshots, we need to know the energy $E(X)$ of the crystal at these specific configurations. The energy $E(X)$ of the crystal is calculated by using the embedded atom method (EAM) potentials¹⁸. In this EAM approach, the energy of the crystal (pure element or alloys) is viewed as the energy needed to embed an atom into the local electron density provided by the remaining atoms of the system. In addition, there is an electrostatic interaction (pairwise potential) between the atoms. Hence, the energy of an n-particle homo-nuclear system is given by¹⁸

$$E = \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}}^n \phi(r_{ij}) + \sum_i^n F(\bar{\rho}_i) \quad (4.7)$$

where r_{ij} is the distance between atoms i and j , ϕ is a pairwise interaction potential, F is the embedding function, and $\bar{\rho}_i$ is the density at the location of atom i due to all its neighbors,

$$\bar{\rho}_i = \sum_{j(\neq i)}^n \rho(r_{ij}) \quad (4.8)$$

The density function $\rho(r)$ is given as

$$\rho(r) = r^6 [e^{-\beta r} + 2^9 e^{-2\beta r}] \quad (4.9)$$

where β is an adjustable parameter in the fitting routine.

The pairwise potential is assumed to be a Morse potential¹⁸ of the form

$$\phi(r) = D_M (1 - \exp[-\alpha_M(r - R_M)])^2 - D_M \quad (4.10)$$

The three parameters D_M , R_M , and α_M , define the depth, distance to the minimum, and a measure of the curvature of the potential near its minimum, respectively.

To ensure that the interatomic potential and its first derivatives are continuous, both $\phi(r)$ and $\rho(r)$ are forced to go smoothly to zero at the cutoff distance, r_{cut} . This r_{cut} is also used as a fitting parameter in the fitting routine. Thus, these five parameters D_M , R_M , α_M , β and r_{cut} , which define $\phi(r)$ and $\rho(r)$, are optimized by minimizing the root-mean-square deviation between the calculated and measured properties of the pure material, such as the cohesive energy, lattice constant, elastic constants, bulk modules, and vacancy formation energy¹⁸.

TABLE I. Optimized EAM potential parameters for Ni, Al, and Ni-Al alloy¹⁸

Fitting Parameters		Ni	Al	NiAl
D_M	(eV)	1.5335	3.7760	3.0322
R_M	(Å)	2.2053	2.1176	2.0896
α_M	(Å ⁻¹)	1.7728	1.4859	1.6277
r_{cut}	(Å)	4.7895	5.5500	5.4639
β	(Å ⁻¹)	3.6408	3.3232	
g	(eV Å ³)	6.5145	-0.2205	
S			0.61723	

The energy expression for a binary alloy system (like Ni-Al), in this EAM approach, is given by¹⁸

$$\begin{aligned}
 E = & \sum_{i_{Ni}} F_{Ni}(\bar{\rho}_i) + \sum_{i_{Al}} F_{Al}(\bar{\rho}_i) + \frac{1}{2} \sum_{i_{Al}, j_{Al}} \phi_{AlAl}(r_{ij}) \\
 & + \frac{1}{2} \sum_{i_{Ni}, j_{Ni}} \phi_{NiNi}(r_{ij}) + \frac{1}{2} \sum_{i_{Al}, j_{Ni}} \phi_{AlNi}(r_{ij}) + \frac{1}{2} \sum_{i_{Ni}, j_{Al}} \phi_{NiAl}(r_{ij}) \quad (4.11)
 \end{aligned}$$

with i_{Ni} , i_{Al} indicating summation over Ni and Al atoms respectively. For the Ni-Al alloy, the functions ϕ_{NiNi} , ϕ_{AlAl} , ρ_{Ni} , ρ_{Al} , F_{Ni} , and F_{Al} are all determined from the fits to the

properties of pure element. The cross potential term ϕ_{NiAl} can be obtained by fitting the alloy properties which were derived from the above energy Equation (4.11), to the experimental values. Of course ϕ_{NiAl} is equal to ϕ_{AlNi} . Furthermore, using two different transformations¹⁸,

$$\rho'_A(r) = S_A \rho_A(r) \quad (4.12 \text{ a})$$

$$F'_A(\bar{\rho}) = F_A\left(\frac{\bar{\rho}}{S_A}\right) \quad (4.12 \text{ b})$$

and

$$F'_A(\bar{\rho}) = F_A(\bar{\rho}) + g_A(\bar{\rho}) \quad (4.13 \text{ a})$$

$$\phi'_{AA}(r) = \phi_{AA}(r) - 2g_A\rho_A(r) \quad (4.13 \text{ b})$$

where A can be either Al or Ni, one can show that Equation (4.7) is invariant under these transformations, while Equation (4.11) is not, because these transformations change the alloy energy without affecting the pure elements energy. Moreover, only one parameter (S_{Al}) is required to scale the ρ , since the alloy energy is unaffected if both ρ_{Al} , and ρ_{Ni} are scaled by the same amount. Thus, these seven parameters (D_M , R_M , α_M , r_{cut} , S_{Ni} , g_{Ni} , and g_{Al}) are used in the fitting procedure to improve the quality of the alloy potentials as well as to calculate the cross potentials. Fitting parameters for Ni, Al, and Ni-Al alloys are given in Table I. The functional form of the semi-empirically-fitted EAM potentials are shown in Figure 4.2 (a) and (b).

Bulk simulation

We first performed MC simulations for the Al fcc bulk-crystal at room temperature (300 °K) in order to optimize some simulation parameters for the surface simulation. A crystal consisting of a box of 256 free atoms was used for these simulations. Periodic boundary conditions were applied in all three orthogonal directions. In the starting configuration, the lattice constant of 4.05 Å was used. In this bulk simulation, a scheme slightly different from Figure 4.1 was employed in order to speed things up. That is, once in a while, after attempting to move the atoms one at a time into a new position, the whole crystal was simply enlarged or shrunk by a given factor. The new energy and difference (ΔE) in energy were calculated and the same condition as in Figure 4.1 was used to check whether or not the change in volume was accepted. This volume change was done, so that if the crystal starts out in a configuration that was too small or too large, it will quickly find the proper size.

From this bulk simulation we obtained three valuable results. First, we wanted to make sure that our simulation routine was working fine. In order to check this, we evolved the crystal for 500 cycles and calculated the cohesive energy of the crystal (energy per atom). We define one "cycle" as one attempted move for each atom in the Metropolis scheme. If the simulation code was working fine, then we should get the same value for the cohesive energy of the crystal as the experimental value, since this energy was used to determine the EAM potentials initially. Simulated values of the cohesive energies for Al and Ni crystals agreed very well with the experimental values

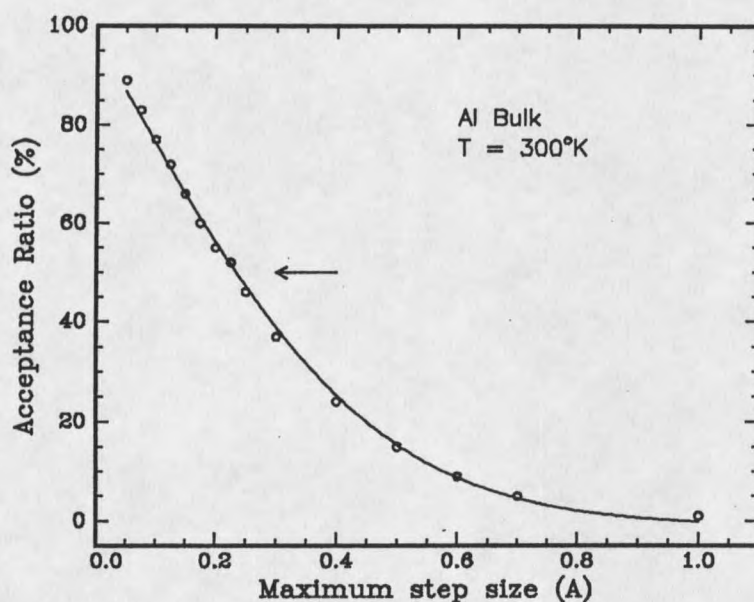


Figure 4.3 Acceptance ratio in the Al bulk simulation as a function of maximum step-size.

(-4.45 eV for Ni and - 3.36 eV for Al)¹⁸. Secondly, the root-mean-square vibration amplitudes are important if the simulations are to reproduce accurately the ion scattering data because vibrations unshadow the atoms along the rows (see Chapter 2). From these room temperature simulations we find that the simulated vibration amplitude of Al atoms (0.10 Å) is in excellent agreement with the experimentally obtained value (0.105 Å)¹⁹. A similar calculation for the Ni crystal also reveals the good agreement between the experimental (0.065 Å)¹⁹ and simulated (0.06 Å) values. Finally, in MC simulations the

acceptance ratio of the attempted moves is very important and it is always maintained around 50% by adjusting the step-size of the atom displacements. The acceptance ratio as a function of maximum step-size for Al atoms in the bulk crystal is shown in Figure 4.3. It can be seen from the figure that the acceptance ratio decreases with increasing step-size. This behavior is expected because at a higher step-size the atoms are moved a larger distance from the previous configuration and the resulting energy change is larger, while for a smaller step-size, the atoms are moved only by a small distance and hence, with a smaller change in energy, there is a good chance that these moves will be accepted. We find that for the maximum step-size of $0.2 \text{ \AA}$, about 50 % of the attempted moves are accepted (see figure 4.3). Hence, in all our surface simulations, we have set the maximum step-size to be equal to $0.2 \text{ \AA}$.

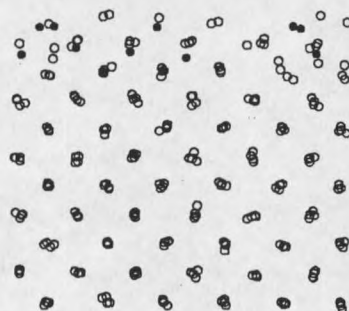
Simulation of Al(110) surfaces

We next performed MC simulations for the clean Al(110) surface at room temperature (300 °K). The crystal contained 48 layers of rectangular Al(110) planes, each with 24 atoms (4 x 6). The bottom six layers were frozen at the bulk Al lattice positions while the upper 42 layers were free to move. Periodic boundary conditions were applied parallel to the surface. There were no constraints imposed in the direction normal to the surface. In the starting configuration all the atoms were positioned at perfect fcc(110) lattice sites with a lattice constant equal to $4.05 \text{ \AA}$. The crystal was initially evolved for 4500 cycles. The ratio of accepted-to-attempted moves was about 54%. Then, while

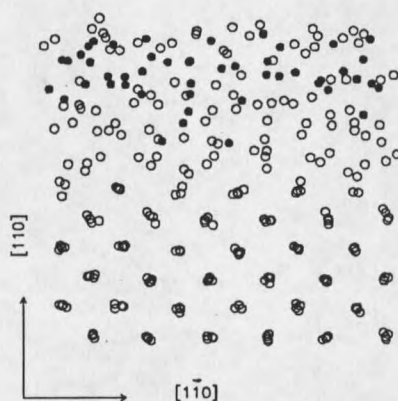
(a) Clean Al(110)



(b) 0.5 ML of Ni+Al(110)



(c) 2.0 ML of Ni+Al(110)



(d) 3.0 ML of Ni+Al(110)

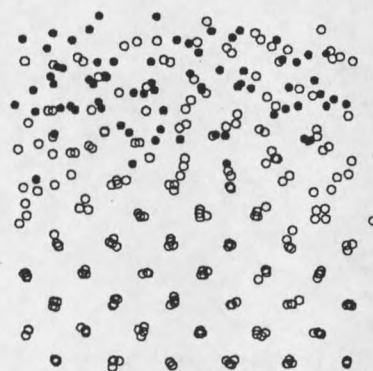


Figure 4.4 Snapshots of simulated Al(110) surfaces for different coverages of Ni: (a) Clean Al(110). (b) 0.5 ML of Ni, (c) 2 ML of Ni, (d) 3.0 ML of Ni. The positions of the atoms are projected onto the (001) plane. Al(Ni) atoms are indicated by open (solid) circles. Only the top ten layers of the crystal are shown.

evolving the crystal for an additional 500 cycles, we periodically stored the atomic configuration of the atoms after every ten cycles, generating 50 snapshots. A typical snapshot of the clean Al(110) surface is shown in Figure 4.4 a, where the positions of the atoms in the crystal are projected onto the (001) plane. Ultimately, 50 snapshots are generated after every 5000 cycles to generate an *average* picture of the evolved crystal.

TABLE II. Comparison of the percentage changes in the interlayer spacing near the Al(110) surface

$d_{n,n+1}$	Simulation EAM	LEED J. N. Andersen ³⁸	LEED J. R. Noonan ³⁹
$d_{1,2}$	-9.2	-8.6 ± 0.8	-8.5 ± 1.0
$d_{2,3}$	+4.3	$+5.0 \pm 1.1$	$+5.5 \pm 1.1$
$d_{3,4}$	-1.2	-1.6 ± 1.2	$+2.2 \pm 1.3$
$d_{4,5}$	+2.9	$+0.1 \pm 1.3$	$+1.6 \pm 1.6$

These simulations correctly reproduced the multilayer relaxation of the Al(110) surfaces^{38,39}. That is, the Al atoms at the surface have fewer neighbors than in the bulk, and consequently move towards the bulk to resaturate their electron density. However, the atoms in the second layer now see more electron density than the bulk value. To correct this, the spacing between layer two and layer three increases. This effect continues, resulting in oscillatory relaxations that persist into the Al(110) surface.

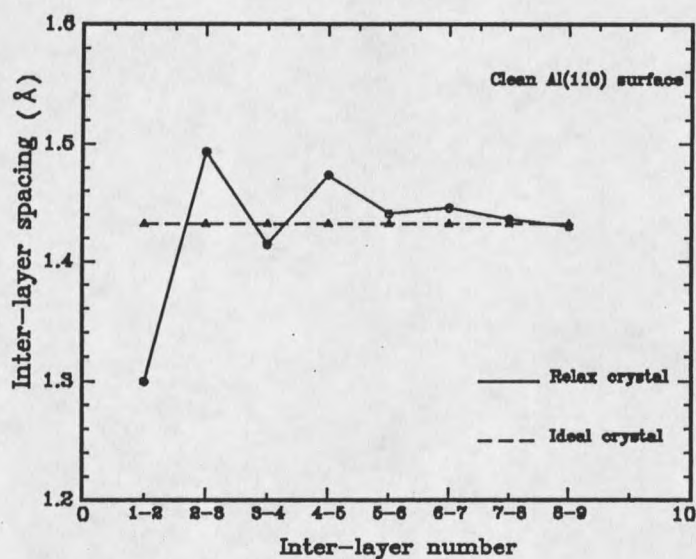


Figure 4.5 Multilayer relaxation: Interlayer spacings in the clean Al(110) surface.

n -($n+1$) represents the inter-layer distance between layer number n and $n+1$.

The oscillatory behavior of the multilayer relaxation of the Al(110) surface is shown in Figure 4.5. Simulated interlayer spacings (percentage change) are also compared with the experimental results in Table II. Clearly the simulated interlayer spacings are in good agreement with the measured spacings. From this we conclude that the EAM describes the Al(110) surface well at room temperature.

Ion scattering simulations were then performed on these snapshots using the method described earlier and in reference³². A total of 200 ions per square Angstrom, with 1 MeV energy, were directed at normal incidence on each snapshot. The influence

of the parameter δ (Equations 4.4 and 4.5) on the ion scattering simulation was investigated on Al(110) snapshots by calculating the ion scattering yield as a function of δ . In Figure 4.6, we plot the number of Al(110) atoms visible to the incident ion beam (scattering yield) for different values of δ . We can immediately see from the figure that there is a minimum yield at a value of δ , around $0.03 \text{ \AA}$. The increase in the ion scattering yield with increasing δ , after passing through the minimum value, was attributed to the fact that with large δ atoms can be found outside the shadow cone which increases the ion yield. This observation suggests the value of δ should be as small as practical, at least smaller than the root-mean-square-vibration amplitude ($0.105 \text{ \AA}$). However, an increase in the ion yield with decreasing δ (region one) was seen due to the influence of δ in the denominator of Equations 4.4 and 4.5. Throughout the simulations we have used δ equal to $0.05 \text{ \AA}$, since we did not want our ion scattering simulations to be influenced by the artificial enhancement at small δ .

To speed up the evolution process and to reduce computing time, we used the following procedure. As mentioned before, the crystal which contained 42 free layers of Al(110) planes was evolved for 5000 cycles. After this initial evolution, the number of free layers in the crystal was reduced to 24 by freezing the bottom 24 layers, since any changes happening at the surface should not be significantly affected by the atoms in these layers, as seen in Figures 4.4 b, c, and d. That is, Al atoms in these layers are still occupying the Al(110) lattice sites. Then this "thin" crystal was evolved for another 4500 cycles. After this, the number of free layers in the crystal was increased to 42 layers and the "thick" crystal was further evolved for another 500 cycles during which time 50

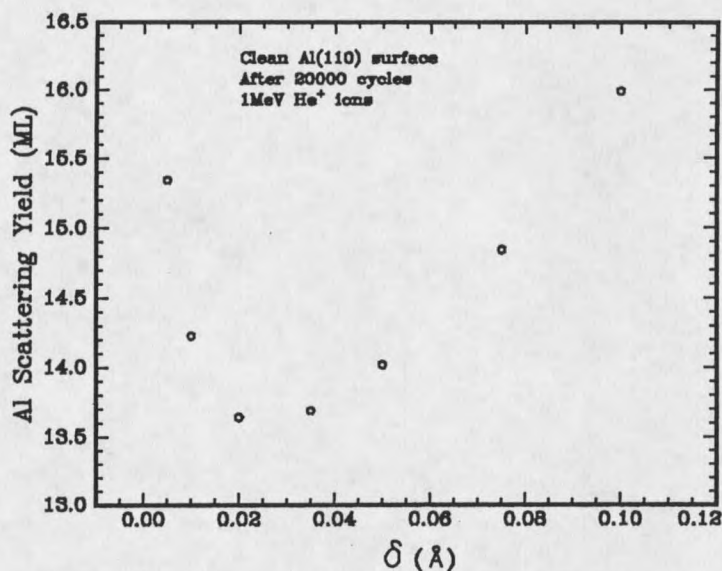


Figure 6

Figure 4.6 Calculated Al ion scattering yield as a function of δ for 1 MeV He⁺ ions at normal incidence.

snapshots were created in a manner described earlier. This increase in the number of free layers in the snapshots was necessary because the high-energy ions channel deep into the crystal and give some contribution to the total ion scattering yield. With this "thin-thick" crystal procedure the cpu time required for equilibration, as discussed later in this chapter, was reduced dramatically. As a check, we also evolved the "thick" crystal from the start for the same number of cycles and performed the ion scattering simulation. We obtained the same ion scattering yield as in the thin-thick crystal approach.

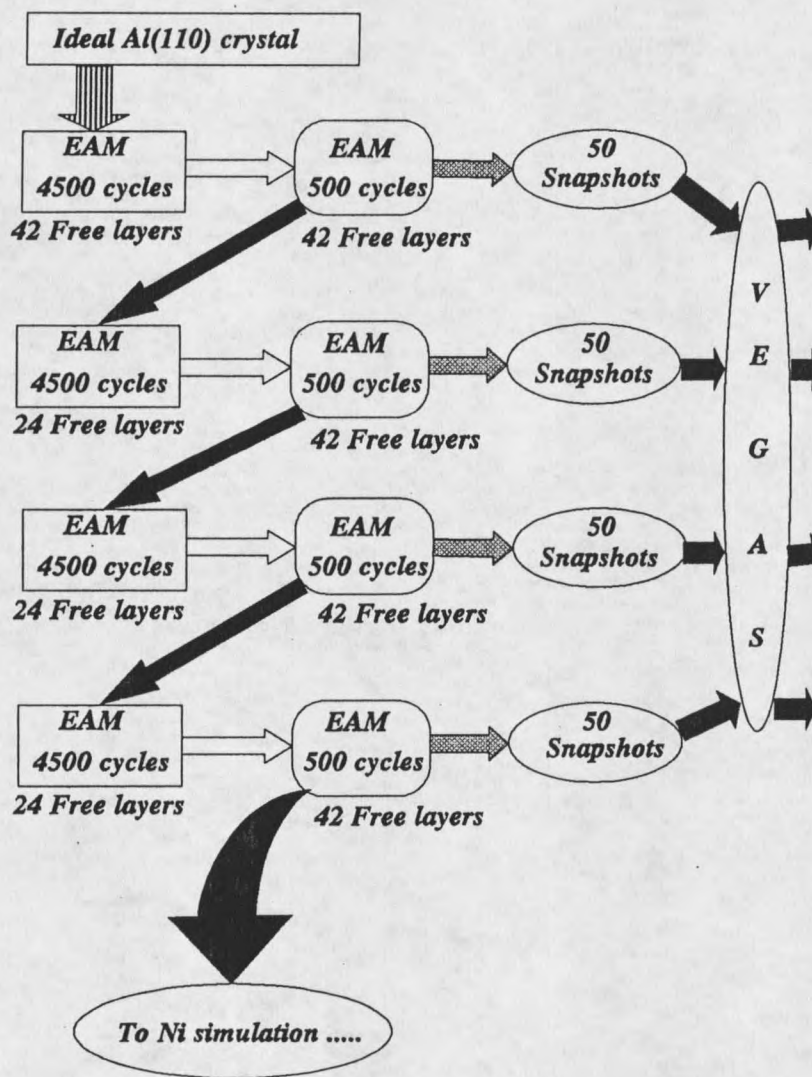


Figure 4.7 Flow diagram showing how the clean Al(110) surface is simulated using the "thin-thick" crystal approach discussed in the text.

The crystal was evolved for 5000 more cycles using the thin-thick procedure, and another independent set of snapshots was generated. A total of 200 snapshots were generated in this manner for ion scattering simulation. A flow diagram

of the simulation procedure for the Al(110) surface is shown in Figure 4.7.

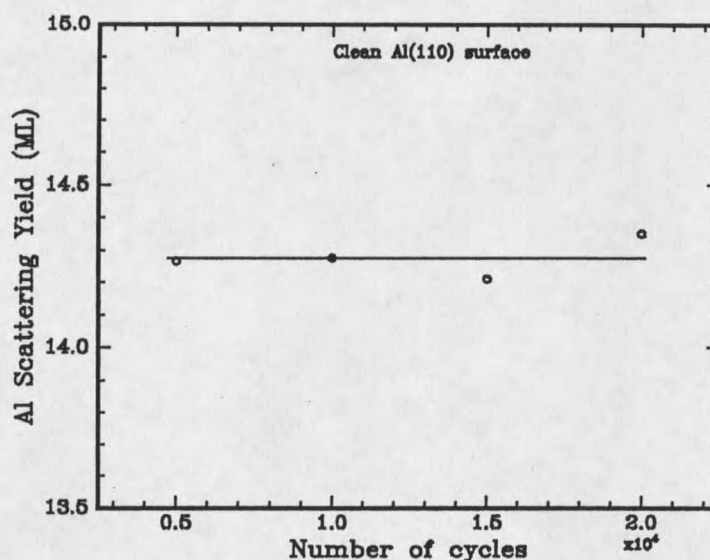


Figure 4.8 Calculated Al ion scattering yield for 1 MeV He^+ ions at normal incidence versus number of MC cycles.

A stationary state in the evolution of the crystal was achieved after 5000 cycles in that neither the total energy nor the calculated ion scattering yield changed significantly with additional cycles as shown in Figure 4.8 where calculated ion scattering yield from the Al atoms is plotted as a function of the number of cycles. We refer to this process as equilibration, although we do not claim that the crystal is in thermodynamic equilibrium.

The calculated ion scattering yield from the snapshots of the Al(110)

crystal, using 1 MeV He^+ ions at normal incidence, was about 15% higher than the experimental yield. Most of this difference can be attributed to an artifact of the MC simulations. The simulated crystal ($4 \times 6 \times 48$) tends to wave back and forth in a direction parallel to the surface. Although the amplitude of this shift is small, it is sufficient to uncover atoms in the deeper layers, making them visible to the high energy ions. This phenomenon is understood and can be reduced by enlarging the simulated crystal in the direction parallel to the surface. Since we calculated the ion scattering yield for each layer, as seen in Figure 4.9, contributions to the yield from deeper layers, associated with the waving motion, can be distinguished from contributions to the yield originating near the surface and associated with reaction and disorder.

In this work we reduced the waving contribution to the yield from the deeper layers by uniformly shifting those layers in the snapshot so as to restore the center of mass for each layer to its starting position. Since this correction is made only *after the snapshots have been generated*, it has no effect on the future evolution of the crystal which continues to wave unrestricted. The shift simply has the effect of restoring the shadowing known to exist in a real crystal along the rows of atoms. The uppermost layers were shifted as a block in the direction required to restore the center of mass in layer 10 since the visibility of these layers to the ion beam is not significantly altered by the waving motion. After these corrections the calculated ion scattering yield for the clean Al(110) surface (14.2 ± 0.6 ML) agreed with the experimental value (12.9 ± 0.7 ML) within the statistical and experimental errors. Nevertheless, we can improve our agreement between the experiment and the simulation by using a smaller value of δ , say

$\delta=0.035 \text{ \AA}$, as seen in Figure 4.6.

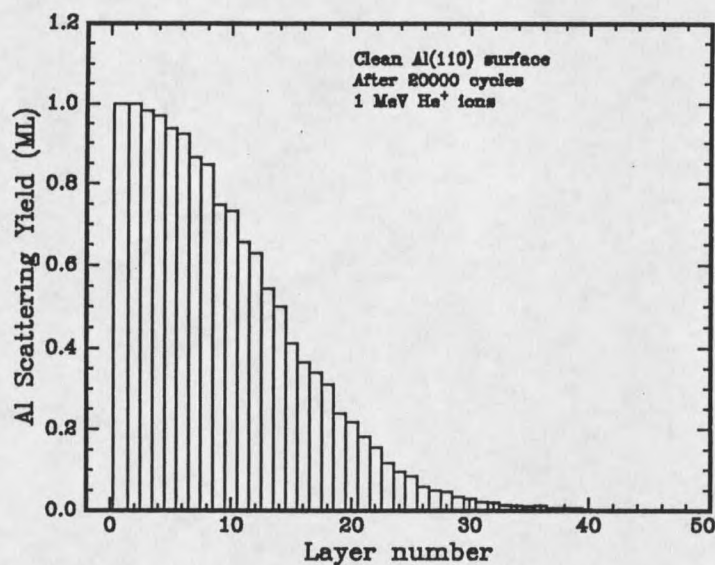


Figure 4.9 Calculated Al ion scattering yield from each layer in the clean, shifted, Al(110) surface.

Simulation of Ni on Al(110) surfaces

In our first overlayer simulation we distributed a monolayer of Ni atoms uniformly on the Al(110) surface, placing them at Al lattice sites above the surface layer Al atoms. After 1500 cycles, we found negligible interdiffusion. Instead, the Ni atoms simply settled down into the rectangular hollow sites, slightly higher than the surface

plane of Al atoms. There was little distortion of the Al lattice as expected since the NiAl(110) plane closely matches with the Al(110) plane (0.6% mismatch)⁴⁰. This simulation leads then to Al shadowing by the Ni atoms and no displaced Al atoms, so the Al yield should decrease rather than increasing with Ni coverage, as we show in the next chapter. This structure seemed stable, at least for 1500 cycles, and we believe it is metastable at room temperature.

We then simulated the overlayer experiment by placing Ni atoms randomly on the already evolved Al(110) surface. The simulation procedure is shown schematically by the flow diagram in Figure 4.10. Initially, 12 Ni atoms (0.5 ML) were placed at random coordinates above the surface. The system was then evolved for 15000 cycles using the "thin-thick" crystal process. That is, the number of frozen layers in the thin crystal was 24, whereas it was 6 in the thick crystal case. After each 5000 cycles, 50 snapshots of the evolved system were created in the manner described earlier, resulting in a total of 150 snapshots. A snapshot for 0.5 ML of Ni on the Al(110) surface is shown in Figure 4.4 b, where the positions of the atoms in the crystal are projected onto the (001) plane. In the figure Al atoms are indicated by open circles while Ni atoms are displayed by solid circles. Surprisingly, a significant number of Al atoms have already been displaced by Ni adsorption at the surface. The figure also shows the onset of disorder in the surface region whereas the layers just below the interface remain well ordered. The ion scattering yield calculated from such snapshots was used first to check for equilibration of the system, and ultimately to compare quantitatively with the measured scattering yields.

The Ni/Al(110) system achieved a steady state after 5000 cycles to the extent that neither the total energy nor the calculated yields changed significantly thereafter. To further check for equilibration we evolved the crystal for another 25000 cycles. The results of these simulations are shown in Figure 4.11 and Figure 4.12.

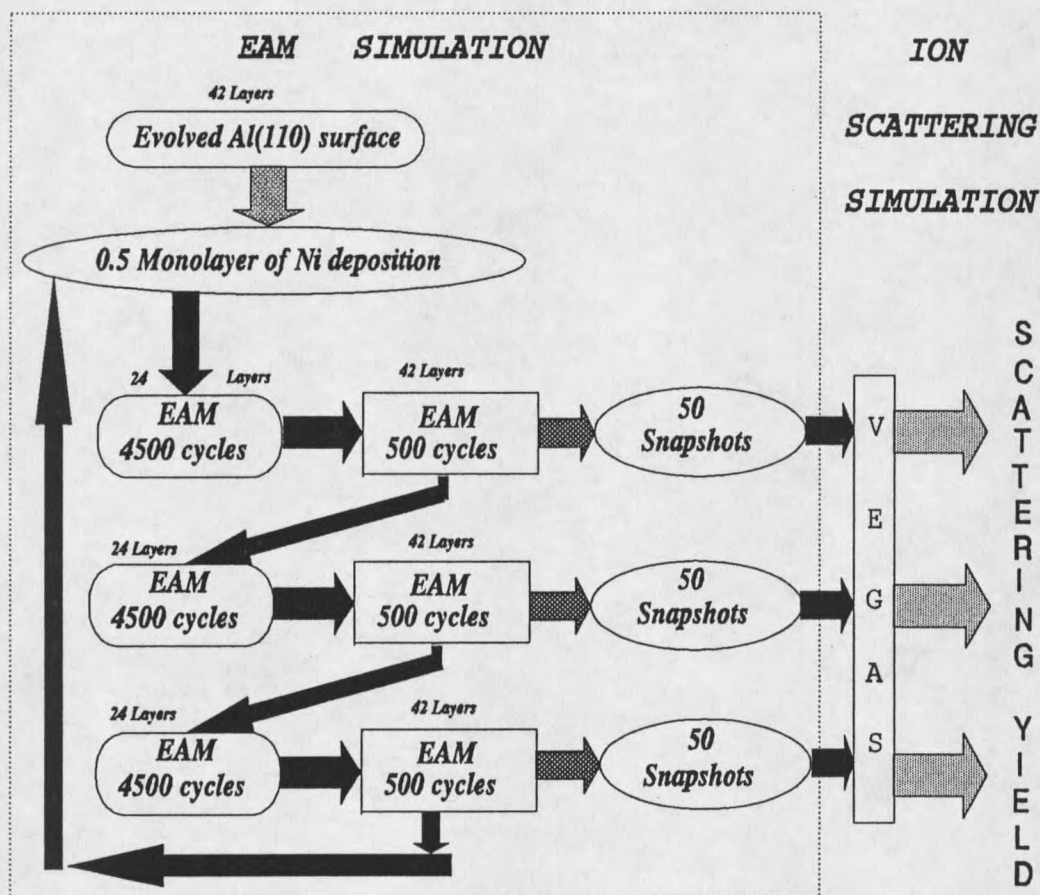


Figure 4.10 Flow diagram showing how the Ni overlayer experiment is simulated using the MC simulations.

The ion scattering yield from the Al atoms and the total energy of the crystal are plotted as a function of cycles in Figure 4.11 (a) and 4.11 (b) respectively. These figures show

that there were no significant changes in the ion scattering yield or the total energy of the crystal between 5000 and 40000 cycles. This observation does not necessarily mean that

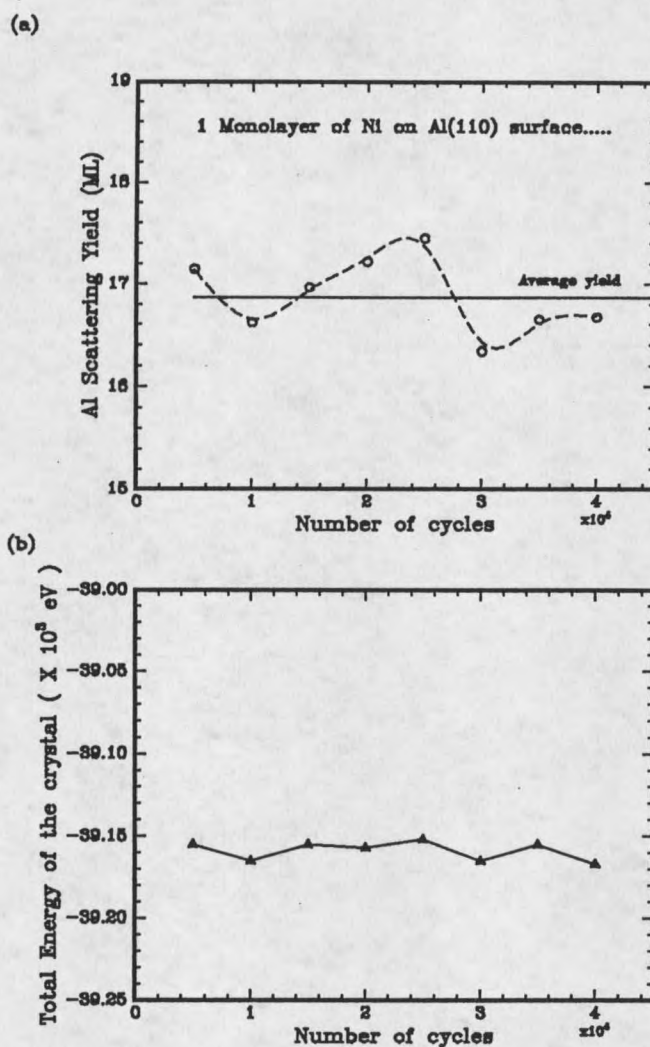
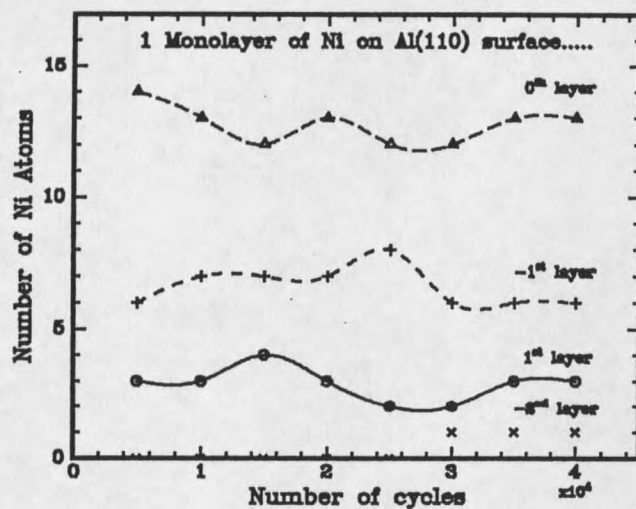


Figure 4.11 (a) Calculated Al ion scattering yield, (b) Total energy of the crystal, as a function of number of MC cycles for 1 ML Ni deposited on Al(110) surface.

all the movements of Ni and Al atoms have stopped. It means only that the number of

atoms visible to the ion beam is no longer increasing, or that no additional Al atoms are moving off of their equilibrium bulk positions. Furthermore, the diffusion process involves atomic exchange and inter-species mixing as may be seen from the number of

(a)



(b)

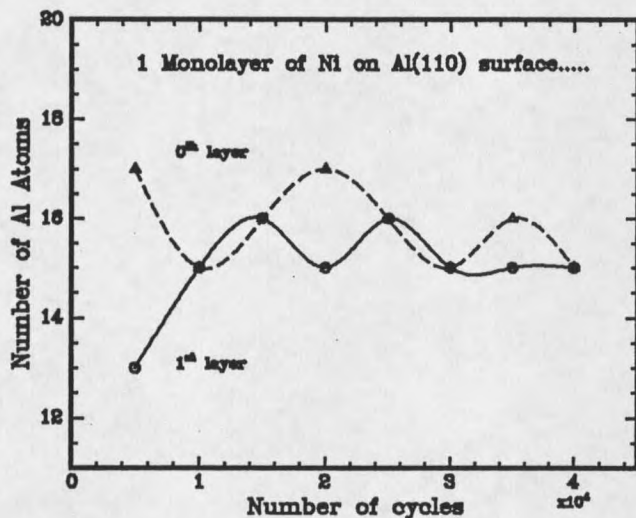


Figure 4.12 Number of atoms in a layer as a function of total number of MC cycles for 1 ML of Ni deposited on Al(110) surface. (a) Ni atoms. (b) Al atoms.

Ni atoms located in some selected layers, shown in Figure 4.12 (a), and the number of Al atoms in these same layers, shown in 4.12 (b) for different cycles. As seen in these figures, there are no significant changes in the number of Ni atoms or Al atoms in each layer between 5000 and 40000 cycles. The definition of layer numbers that we employ in Figure 4.11 and 4.12 is shown in Figure 4.13. We label the surface layer of clean Al(110) as the 0th layer, while the added layers above the surface are denoted as 1st, 2nd and 3rd layers respectively. The layer just below the clean surface (0th) is denoted as the -1st layer.

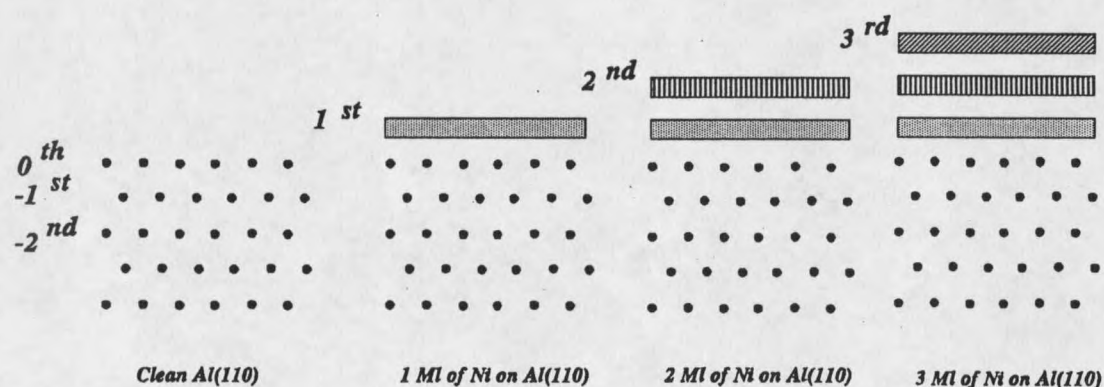


Figure 4.13 Layer definition: The surface layer of clean Al(110) is labeled as 0th layer. Added Ni layers above the surface are labeled as 1st, 2nd, 3rd, etc..

We next deposited another 0.5 ML of Ni atoms randomly on the already evolved Ni/Al(110) system. The same "thin-thick" procedures were used to evolve the crystal and then simulate the ion scattering yields (Figure 4.10). The number of frozen layers was always kept to 24 for equilibration of the system. That is, the number of free layers in the crystal increases with increasing Ni coverage. We continued deposition of Ni atoms, in increments of 0.5 ML, up to 4.5 ML total Ni coverage. The snapshots for 2 ML and 3 ML of Ni on the Al(110) surface are shown in Figure 4.4 c and d, respectively. From these figures we see that with increasing Ni coverage, the Ni-Al(110) interface is becoming more disordered whereas layers below the interface remain ordered. Further analysis of these snapshots is presented in Chapter 5 after we discuss the experimental results.

CHAPTER 5

ULTRATHIN Ni FILMS ON Al(110) SURFACESIntroduction

The interfaces between transition metals and aluminum play an important role in numerous materials applications. In particular, the interface between nickel and aluminum has attracted much attention in recent years because of its potential use in catalysis⁴¹ and the semiconductor industry⁶. The Ni-Al alloys are also of considerable interest for applications as low density, high temperature structural materials⁵. Hence, it is useful to study the detailed geometric and electronic structure of the Ni/Al interface to help in understanding the aforementioned properties. There have been several studies of reaction at Ni-Al interfaces, and the results are not in complete agreement⁸⁻¹³.

To better characterize the evolution of the Ni/Al interface, we have carried out high-energy ion scattering (HEIS) and x-ray photoelectron spectroscopy (XPS) experiments on thin Ni films deposited on Al(110) single-crystal surfaces at room temperature and at 250 °C. We chose this elevated temperature because, for the Ni-Al system, the reaction temperatures are generally reported in the range of 225-325 °C. The results from our experiments are presented in this chapter. Our room temperature results show that Ni atoms react with Al atoms up to 8 monolayers (ML) of Ni coverage, at which point a Ni metal film begins to cover the reacted interface. However, Ni atoms

deposited at 250 °C show little evidence of compound formation at the interface and diffuse hundreds of Angstroms into the Al bulk. Using Monte-Carlo (MC) simulations with EAM potentials, together with ion scattering simulations, we obtained an atomic picture of the interface reaction to compare quantitatively with our room temperature measurements. These simulations reveal a surprising amount of "*near surface dechanneling*" which affects the interpretation of the experimental results. A model calculation of the XPS intensity using the simulated interfaces suggests that the inelastic-mean-free-path for the electrons may be significantly different in these thin disordered overlayers from the value given by standard models for the mean free path.

Experimental setup

The experiments were performed in an ultrahigh vacuum (UHV) chamber which is connected to a 2 MV Van de Graaff accelerator via a differentially pumped beam line as discussed in Chapter 3. The base pressure of the chamber was around 1×10^{-10} Torr. For the high-energy ion scattering experiment, 1.0 MeV He^+ ions were incident on the Al(110) surface along the $[\bar{1}\bar{1}0]$ channeling direction. The Al(110) surface was aligned with the He^+ beam along the $[\bar{1}\bar{1}0]$ direction using the method discussed in Chapter 3. The standard dose of incident He^+ ions for one spectrum was 1.6×10^{15} ions/cm². A solid-state detector was used to collect the backscattered He^+ ions at a scattering angle of 105°.

The XPS spectra were recorded using a 100 mm hemispherical analyzer

(HA) in a fixed-analyzer-transmission (FAT) mode with a pass energy of 50 eV, and a scan rate of 0.1 eV/sec. An Al K_{α} (1486 eV) X-ray source with 200 W power was used to generate X-rays. For XPS measurements, the sample was kept in the channeling alignment, and the photoelectrons entered the HA with a polar emission angle of 30° from the sample normal.

The Al single crystal was cleaned by the method described in Chapter 3. The Ni films were vapor deposited onto the Al(110) surface at room temperature and at 250°C using a wire evaporation source. The arrangement of the apparatus was such that HEIS, XPS, and thin film depositions could be made without moving the sample at all.

In principle, one would like to perform HEIS and XPS experiments after every Ni deposition. But, because of the long data collection time, we divided these experiments into two parts. In the first experiment, channeling spectra were taken after each Ni deposition. In a second experiment, after each Ni deposition, XPS spectra were taken, while channeling spectra were taken only after every four evaporations. Both of these experiments were done at room temperature. Occasionally, a random orientation (off axis) HEIS spectrum was taken to check for any Ni shadowing effects which would affect our coverage measurements. In the elevated temperature experiment, channeling spectra and XPS spectra were taken after each Ni deposition.

By measuring the changes in the surface peak area (SPA) for the Al surface as a function of the Ni coverage, we can usually determine the average stoichiometry of the reacted interface, even if the interface is disordered. The measured Ni SPA is used to calculate the absolute coverage (atoms/cm²) of Ni atoms using equation 2.9 in Chapter

2. In addition, the Ni SPA is used to determine the morphology of the Ni film on the Al(110) surface. The Al SPA and the Ni SPA together are used to study the atomic structure of the reacted interface.

By looking at the satellite structures associated with the Ni 2p core level in XPS, it is possible to identify some of the compounds formed at the interface. In addition, the identification of compound in the reacted regions can be made using the core-level chemical shifts of the Ni atoms. Furthermore, the intensities of the characteristic photoelectron peaks for the Ni and Al atoms can be used to model the morphology of the overlayers.

Results and Discussion

Ni deposition onto Al(110) at room temperature

High-energy ion scattering and channeling

Previous studies of the Ni/Al system have shown that NiAl_3 is the first phase to form at the interface between thick Ni and Al layers. Thermally reacted bilayer experiments¹⁰ and ion mixing experiments¹¹ for Ni-Al indicate that NiAl_3 is the first phase to form at elevated temperatures. Ruckman et al. reported that the NiAl_3 phase formed at room temperature for thin Ni films deposited on Al films⁹. TEM studies of Ni deposited on thick Al films show that NiAl is the first phase to form for a substrate

temperature of 70 °C, while at 250 °C NiAl_3 is formed¹². Thus, the first question we addressed was, whether or not Ni forms NiAl_3 at the Ni/Al(110) interface under the conditions of our experiment. The answer to this question comes mainly from the XPS results. However, the channeling results have to be discussed first, since the Ni coverage and the overlayer growth mode are inferred from them.

In Figure 5.1 we plot the channeling spectra for Ni and Al for several Ni depositions. The arrows and the dotted lines in the figure indicate the energetic positions of the surface Ni and Al atoms. For clarity, the channeling spectra for the clean Al(110) surface (open circles) and after 0.98 ML of Ni deposition on the Al(110) surface (solid circles) are shown in the insert of Figure 5.1. One monolayer (ML) here is equivalent to the atomic density of the Al(110) plane, 0.8622×10^{15} atoms/cm². For each Ni deposition we calculated the number of visible Ni atoms/cm² on the Al(110) surface, using Equation 2.9, the surface peak area of Ni, the Rutherford cross section, and the experimental parameters. This number of Ni atoms on the Al surface was found to increase linearly with the deposition time throughout the experiment, as seen in Figure 5.2. The deposition rate of 0.37×10^{15} atoms/cm²/min (0.43 ML/min) was obtained from Figure 5.2. To check for possible shadowing of surface Ni atoms, the incident ion beam was directed slightly away from the normal channeling direction, ie. a random direction. A plot of the number of Ni atoms visible to the incident ion beam in the channeling direction versus the actual Ni coverage, obtained from the random direction, is shown in Figure 5.3. We did not see any reduction in the number of Ni atoms visible to

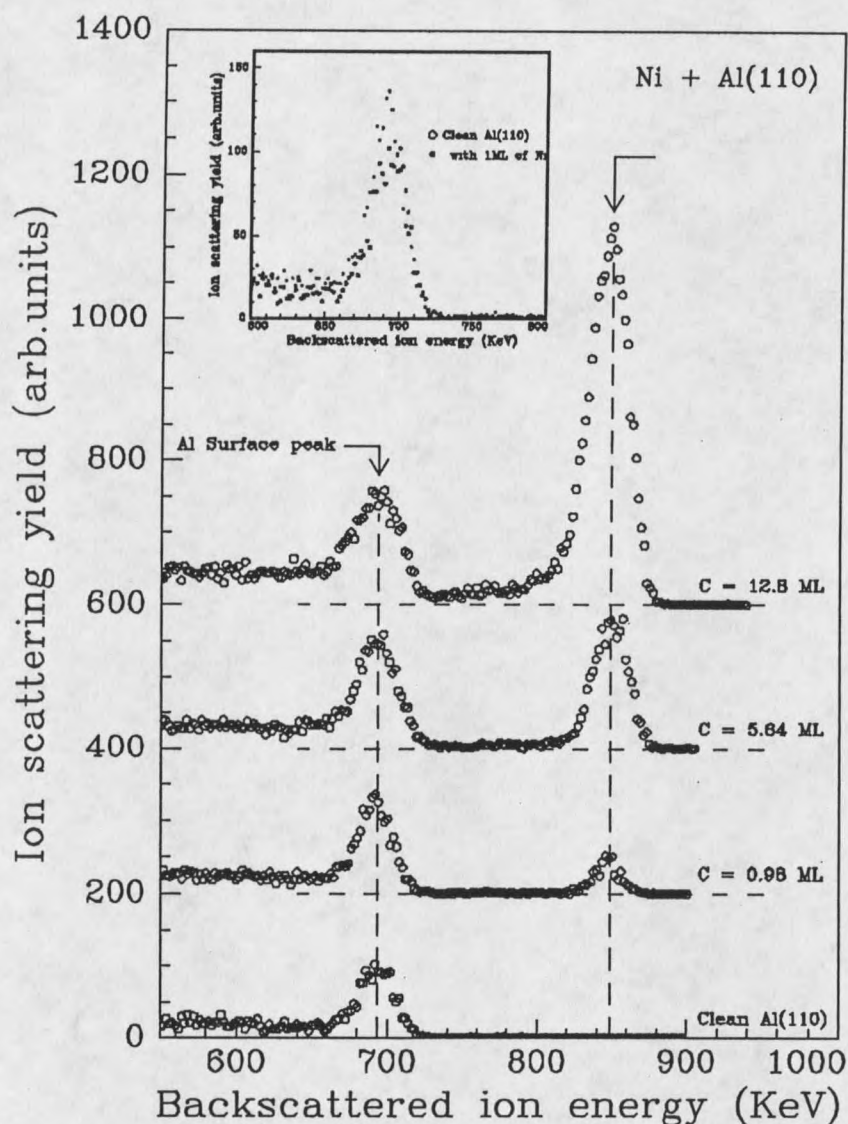


Figure 5.1. Ion scattering/channeling spectra for 1 MeV He^+ ions on Ni + Al(110), for several Ni coverages indicated in the figure. The energies of the Al and Ni surface peaks are indicated by the arrows and the dashed lines. Spectra have been offset as indicated by the dash-dot lines. In the insert backscattering spectra for the clean Al(110) surface (open circles) and for 1.0 ML Ni deposited at room temperature on the Al(110) surface (solid circles) are shown.

the ion beam along the channeling direction, as seen in Figure 5.3. This indicates that there is no shadowing of Ni atoms. Consequently, the Ni coverage was determined precisely by the SPA in the channeling direction for the coverage range studied in these experiments.

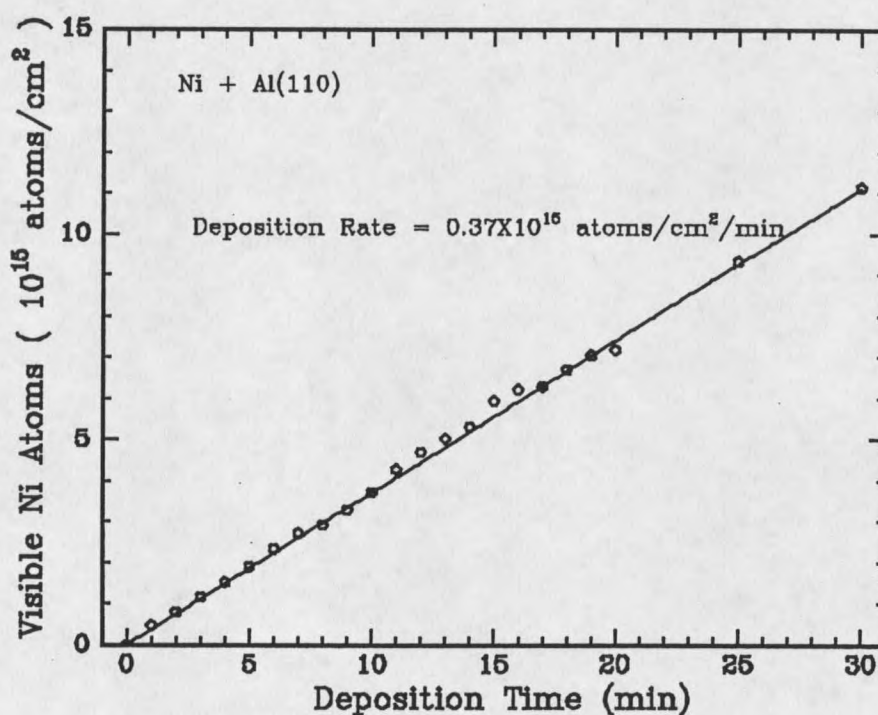


Figure 5.2. Measured ion scattering yield from Ni atoms deposited on the Al(110) surface as a function of Ni deposition time in minutes.

From the insert of Figure 5.1, we can easily see that the Al surface peak area has increased after the Ni deposition of 0.98 ML. This implies that more Al atoms

are visible to the ion beam in the presence of Ni atoms at the surface. That is, surface Al atoms have moved from their initial equilibrium positions and have reduced the shadowing of substrate Al atoms. If the Ni atoms formed an ordered overlayer directly above the Al atoms, we should expect to see a reduction in the SPA of Al, associated with Ni shadowing of Al atoms. Instead, we see an increase in the SPA of Al, which means that Ni and Al

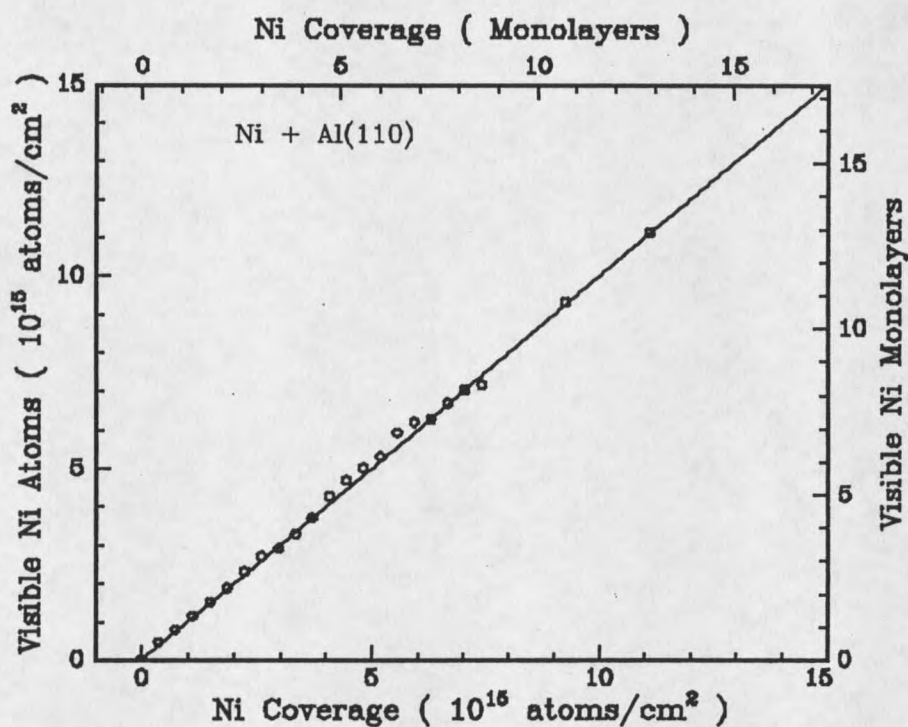


Figure 5.3. Number of Ni atoms visible to the 1 MeV He $^+$ ion beam as a function of average Ni coverage. The solid line shows the yield expected for a random coverage.

atoms are interacting with each other, and the Ni atoms are displacing the Al atoms from their initial positions. This observation rules out the formation of an ordered Ni overlayer at sites directly above Al surface atoms.

Since the surface peak of the Al atoms is superimposed on a background signal, it is necessary to remove the background under the surface peak. A triangular background subtraction method was used for this purpose⁴². In this method we constructed a triangle, as shown in insert of figure 5.1, whose base is equal to the energy difference between the peak position and the minimum yield position behind the surface peak, and whose height is equal to the minimum yield. The area of the triangle is then subtracted from the total peak area of the surface peak. After this background removal, the surface peak area is used to calculate the number of Al atoms visible to the ion beam.

In Figure 5.4 we plot the number of visible Al atoms (Al-SPA) as a function of Ni coverage (Ni-SPA), as determined from channeling spectra similar to those shown in Figure 5.1. Such plots are very useful for developing models for reacted interfaces⁴³. From this figure we can immediately see that more and more Al atoms become visible to the incident ion beam as the Ni coverage increases up to 8.1 ML (7×10^{15} atoms/cm²). There are three main regions to recognize in this figure. In the first region the number of visible Al atoms increases sharply with the Ni coverage up to 2.3 ML. The slope of the curve in this region is equal to 1.97. In the second region the number of visible Al atoms increases with a lesser slope than in the first region, up to 8.1 ML of Ni coverage. In this region the slope is equal to 0.35 Al atom/Ni atom. After 8.1 ML of Ni coverage, the curve seems to saturate towards a line with zero slope.

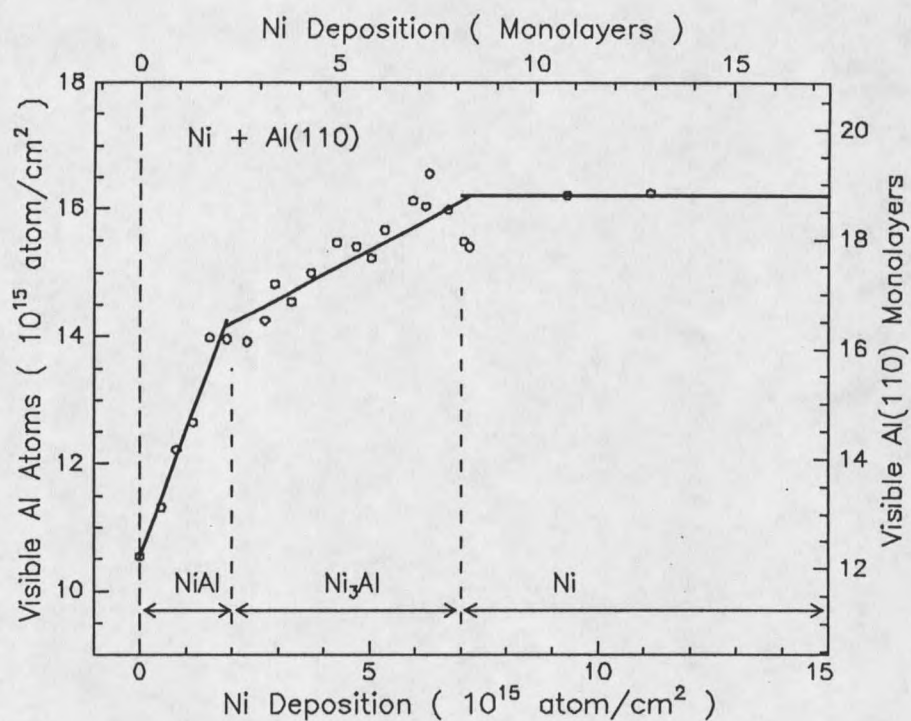


Figure 5.4. Number of Al atoms visible to the ion beam as a function of Ni coverage on the Al(110) surface. The solid lines are the least-squares fit to the data points in three different regions. Three different stages of film growth are indicated.

These observations (Figure 5.1 and Figure 5.4) suggest that Ni atoms are reacting with Al atoms on the Al(110) surface at two different rates, forming a surface

compound at the interface, until a Ni metal film ultimately covers the reacted interface. The reaction continues up to 8.1 ML of Ni coverage at room temperature. For all of the spectra shown in Figure 5.1, there are some Al atoms visible to the incident ion beam at the sample surface. That is, we did not observe any shift in the Al surface peak position even after a Ni coverage of 12.8 ML. This means that there are some Al atoms which are not covered by the Ni film. Furthermore, it is seen in Figure 5.1 that the lower energy tail of the Ni surface peak is broadened at 12.8 ML of Ni coverage compared to that of 0.98 ML and 5.6 ML. This suggests that a very small number of Ni atoms (less than 0.5 ML) have diffused deep into the Al bulk. The presence of these Ni atoms in the Al bulk leads to slight deflections of some He^+ ions, and increases the backscattering yield of the bulk Al atoms, as seen by the increase in the minimum yield behind the Al surface peak in Figure 5.1. On the other hand, since we did not observe any significant broadening of the Ni tail at lower Ni coverages (less than 8 ML), and continuous displacements of the Al atoms are observed for these lower Ni depositions (increase in the Al SPA), we infer that the deposited Ni atoms are staying near to the surface region, resulting in compound formation at the surface.

The large increase in the number of Al atoms visible to the incident He^+ ion beam, measured as a function of Ni coverage and shown in Figure 5.4, indicates that there is a strong Ni-Al reaction at the interface. In a conventional interpretation²⁰ of the results in Figure 5.4, the slopes for ion scattering yields versus Ni coverage are used to determine the average stoichiometry of the reacting interface region. In the present case, a slope of 2:1 in region one would indicate that we are forming an Al_2Ni phase.

However, there is no stable Ni-Al compound with this stoichiometry in the Ni-Al bulk phase diagram¹⁴. Instead, based on the XPS and EAM results discussed below, we conclude that a NiAl compound forms and *near surface* Al atoms are struck by the incident He ions, ie. "*near surface dechanneling*" occurs. The EAM simulations play a vital role in understanding this discrepancy. Furthermore, NiAl has the highest heat of formation and is the most stable phase in the Ni-Al phase diagram¹⁴, so we might expect it to form first.

High-energy ion scattering simulation:

As we discussed in Chapter 4, we have performed MC simulation of our ion scattering/channeling experiment of Ni on the Al(110) surface. In Figure 5.5, we show the experimental and simulated ion scattering yields from the Al atoms as a function of Ni coverage. The experimental results are denoted by open circles while simulation results are designated by solid circles. The solid and dashed lines are intended to guide the eye. The values of the yields at zero coverage have been suppressed. The number of Al atoms visible to the incident ion beam, which was calculated using Monte Carlo simulations, also increases at two different rates, depending on the Ni coverage. It is remarkable that the simulations also show a break around 2 ML of Ni coverage. For the experimental yield, the initial slope is 1.9 Al atoms per Ni atom up to a Ni coverage of 2.2 ML, followed by a slope of 0.39 Al atoms per Ni atom at higher coverages. From the simulation we obtain an initial slope of 2.5 Al atoms per Ni atom up to a Ni coverage

of 2 ML, followed by a slope of 0.38 Al atoms per Ni atom at higher coverages. In comparing these values, we conclude that the simulations are in good quantitative

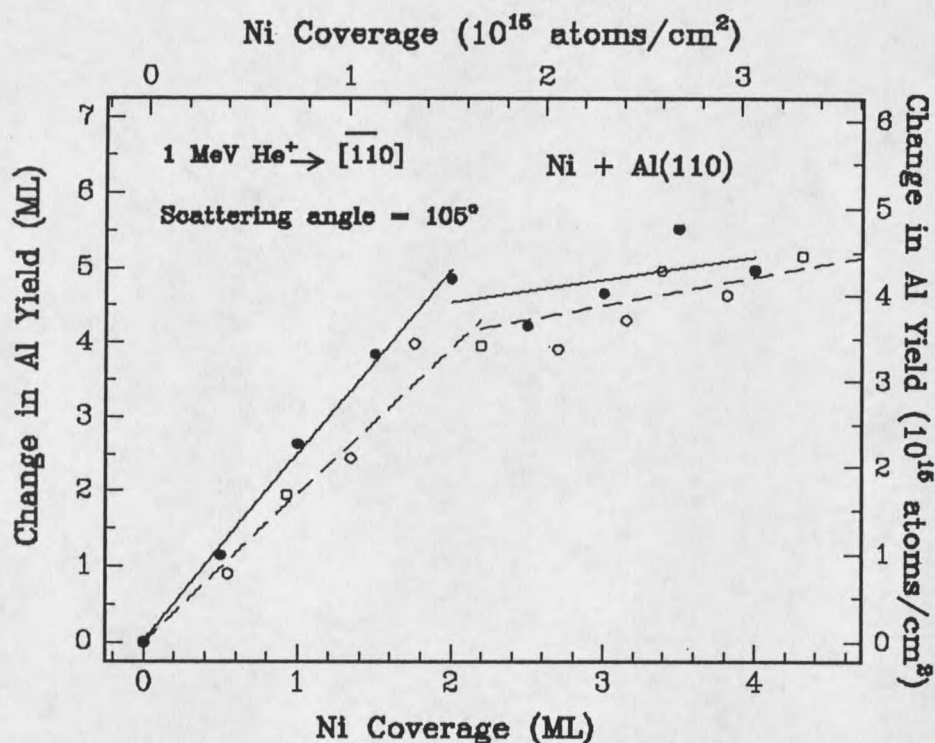


Figure 5.5. Change in ion-scattering yield from Al atoms, relative to the clean surface, plotted as a function of Ni coverage on the Al(110) surface. Experimental values for the yield are shown by open circles. Simulated values of the yields are denoted by closed circles. The dashed and solid lines are the results from least-squares fits to the measured and simulated data, respectively.

agreement with the measured yields. The constant offset between the calculated and

measured yields, which has been suppressed in Figure 5.5, is 1.3 ML, i.e., the difference in the simulated and measured values for clean Al(110). Scattering yields calculated from the Ni atoms as a function of Ni coverage are shown in Figure 5.6 where experimental

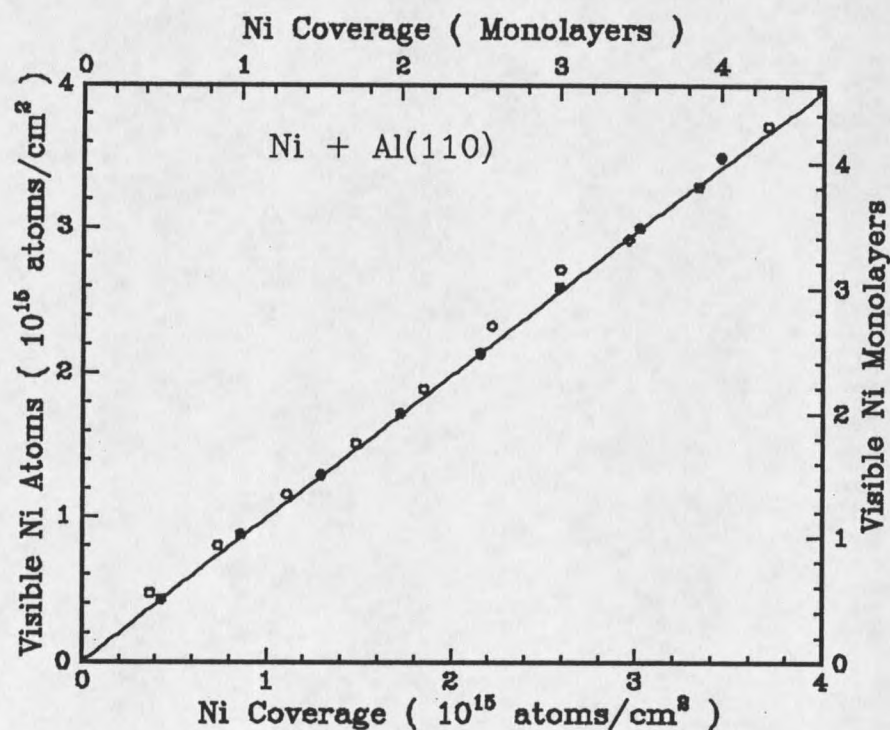


Figure 5.6. Ion-scattering yield from Ni atoms, plotted as a function of Ni coverage on the Al(110) surface. Experimental values for the yield are shown by open circles. Simulated values of the yields are denoted by closed circles. The solid line is the result from least-squares fit to the simulated data.

results are indicated by open circles and simulation results are denoted by solid circles.

Again, the calculated ion scattering yields are in excellent agreement with the experimental results. Both the simulated and the experimental yields increase almost linearly with Ni coverage. From these calculations we conclude that Ni atoms are not forming ordered islands nor sitting on Al lattice sites on top of the Al(110) surface, since almost all of the deposited Ni atoms are still visible to the ion beam. That is, we did not observe any Ni-Ni or Ni-Al shadowing effect.

Since the agreement between simulation and experiment is very good, we can use the simulations to look for an explanation of the discrepancy between the conventional interpretation and our experimental results. This discrepancy can be explained by looking at the layer-by-layer results for the simulated ion yield. In Figure 5.7 the extra scattering yields from the Al atoms in each Al(110) layer, i.e. the difference in scattering yields from Al atoms following the adsorption of Ni atoms, are plotted as a function of Ni coverage. The increase in Al yields from the first 15 layers (top), second 15 layers (middle), and last 10 layers are shown in Figures 5.7 a, 5.7 b and 5.7 c respectively. A number of points can be made based on these figures. First, in Figure 5.7 a and 5.7 b it can be seen that, as the Ni coverage increases up to 2 ML, the extra Al yield from the first 15 layers increases with the rate of 1 Al atom per Ni atom, while the extra Al yield from the middle 15 layers increases with the rate of 1.25 Al atoms per Ni atom. Second, after 2 ML of Ni coverage, the extra Al yield from the first 15 layers increases with a slower rate of 0.35 Al atoms per Ni atom with increasing Ni coverage, whereas the extra Al yield from the middle 15 layers remains constant. The contribution of the last 10 layers to the total ion yield is negligible as seen from Figure 5.7 c, since

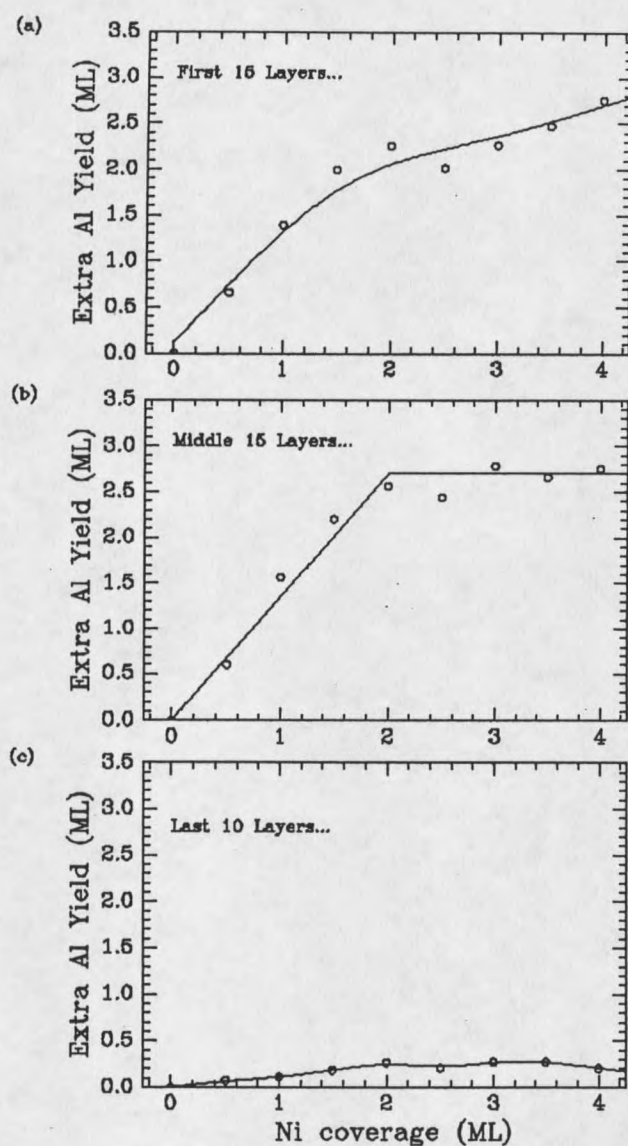


Figure 5.7. Extra simulated ion scattering yield from Al atoms in each layer are plotted as a function of Ni coverage. (a) Extra Al yield from first 15 layers, (b) middle 15 layers, (c) last 10 layers.

atoms in these layers are shadowed by the atoms in the top layers. In the HEIS

experiment the extra ion scattering yield from Al atoms for a particular Ni coverage is equal to the sum of the extra Al yield from figures 5.7 a, 5.7 b and 5.7 c. For the clean Al(110) crystal, the contribution to the total ion scattering yield from the middle 15 layers as well as the last 10 layers should be small, since the atoms in these layers are shadowed by the atoms in the top layers. However, in the Ni-Al(110) system, we observed a significant contribution to the extra Al yields from the middle 15 layers of the crystal. Hence, the presence of disordered Al atoms and relatively heavy Ni atoms near the surface leads to significant deflections of some of the incident ions, and ultimately increased the hitting in the middle 15 layers, which was absent in the clean Al(110) crystal. We refer to this phenomena as a "*near surface dechanneling*" effect. The energy resolution of the solid state detector (20 keV) is insufficient to discriminate between these dechanneled ions and ions backscattered from the top 15 layers where the disordered atoms reside. From the simulations we conclude that *almost half* of the increased Al yield in the initial Ni coverage regime (up to 2 ML) is associated with *near surface dechanneling*. After 2 ML of Ni coverage, the *near surface dechanneling* contribution remained constant. Thus, if we only consider the first 15 layers, then the ion scattering results and the XPS results will be consistent, indicating the formation of a NiAl-like compound up to 2 ML of Ni coverage and Ni₃Al thereafter. The contribution of multiple scattering and dechanneling to the surface peak area has been discussed in the past⁴⁴. However, the typical contribution in that case was much smaller than that seen in our simulations. Thus, our results should raise a caution flag on the future use of the slope to infer compound stoichiometry, at least for high-energy ion scattering experiments

where energy resolution is insufficient to distinguish between the two contributions. In this context, the MC simulations are very important for fully understanding the experimental ion scattering results where epitaxy of the system does not occur.

In region two of Figure 5.4, for Ni coverage from 2.3 ML to 8.1 ML, the slope of 0.35 suggests that the average stoichiometry of the alloy formed here is 1:3, consistent with formation of Ni_3Al . Even at this high Ni coverage, incoming Ni atoms are still actively displacing the Al atoms, but at a slower rate. Since we have a large source of Al atoms in the substrate, we can expect Al atoms to diffuse to the surface. Apparently, the out diffusion of Al atoms from the substrate is inhibited by the existing NiAl reacted layer. We will return to this point later in the discussion.

Above 8.1 ML of Ni coverage, incoming Ni atoms are not effectively displacing the Al atoms as seen from the zero slope of Al yield vs Ni coverage in region three of Figure 5.4. This means, after this coverage the reaction seems to stop and a Ni metal film begins to cover the surface. Up to the maximum coverage of this experiment, we did not see any increase in the SPA of Ni for random incident direction. This absence of an increase in SPA tends to rule out the formation of an ordered Ni overlayer or Ni islands oriented with respect to the substrate channeling direction. We did not have LEED capability in these experiments to check for surface ordering. We conclude that for these highest coverages, a disordered Ni film was formed on the reacted Ni-Al interface.

X-ray photoelectron spectroscopy:

The channeling results by themselves are not enough to justify our suggestion of the formation of different alloy phases at the interface. Fuggle and co-workers⁴⁵ have studied in detail the chemical shifts, satellite shifts, and shapes of the satellite and main 2p photo peak (XPS) of Ni in various Ni-Al alloy systems. They found that the base of the Ni 2p_{3/2} peak becomes more symmetric as the Al concentration in various Ni-Al alloys increases, because the satellite peak changes shape and its separation from the photo peak increases. So, we have used these properties of the XPS peaks to complement the ion scattering results.

Figure 5.8 is a plot of the x-ray photoelectron energy distribution curves for the Ni 2p_{3/2} peak (binding energy 852.65 eV) and the satellite peak for different coverages of Ni on Al(110). Two coverages were selected from each of the three different regions indicated in Figure 5.4. The arrows in Figure 5.8 indicate the satellite peak positions for the Ni, Ni₃Al, and NiAl phases. The spectra have been shifted vertically in order to compare the energy distribution curves. From these figures, one can recognize instantly that the base of the main Ni 2p_{3/2} line becomes less symmetric as the Ni coverage increases. We also see a small chemical shifts in the peak position. Furthermore, the shape of the satellite changes as the Ni coverage increases. The peak position of the satellite moves towards the Ni 2p main line, decreasing the separation of the satellite and the main 2p line. Therefore, we conclude that the shape and separation of these satellites are quite different in these three regions. Comparing these results with

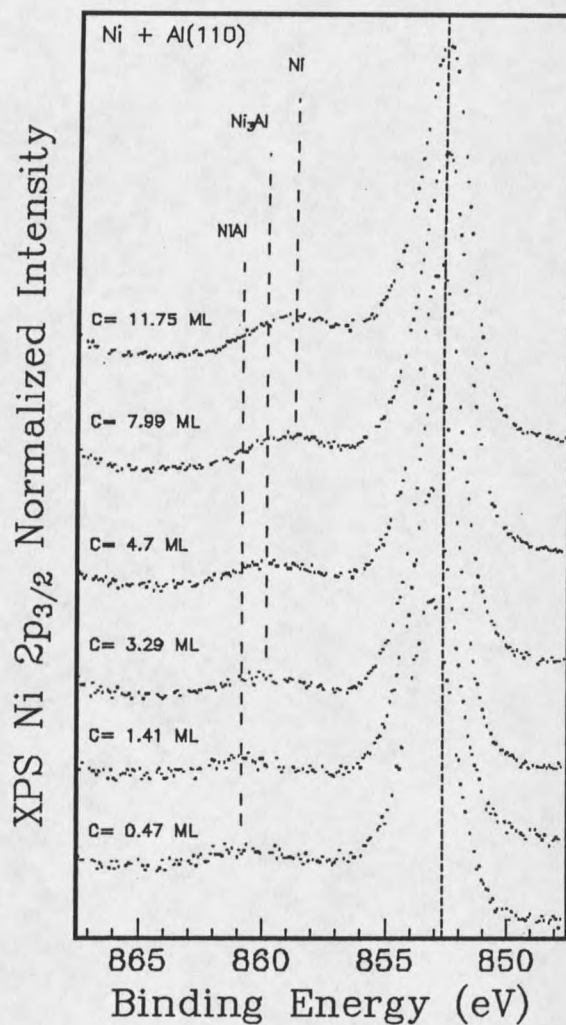


Figure 5.8. Ni 2p_{3/2} XPS spectra from Ni films deposited at room temperature on the Al(110) surface, for selected Ni coverages, normalized to a constant height for the main peak. Satellite peak positions for different Ni-Al phases are indicated by arrows and long-dashed lines. The dashed line indicates the pure Ni 2p_{3/2} peak position (binding energy = 852.65 eV).

Fuggle's XPS spectra for different Ni-Al alloys, we can qualitatively identify the sequence of phases formed, from NiAl to Ni₃Al to Ni metal. For these thin films, we may not actually form the complete crystal structure of the respective phases. Rather, we suggest that the chemical environment of the Ni atoms in our films is similar to that of the Ni atoms in the various Ni-Al phases.

As seen from Figure 5.8, the XPS satellite shapes and its separation from the main peak are different in all three regions of Ni coverages. We summarize the explanation for this behavior as follows. X-ray photoelectron spectra of pure Ni metal show a pronounced "two-hole satellite" at a higher binding energy⁴⁵. Electron energy loss measurements of Ni show that this intense core-level satellite is associated with intrinsic losses⁴⁵. The *d* bands of Ni are partially full⁴⁶, and at the same time, the fermi level of Ni lies in the region where the *d* density of states is high. The Coulomb interaction between the core hole created by the excitation, and the hole in the unoccupied *d* bands leads to a strong satellite feature in the Ni 2p core level lines⁴⁶⁻⁴⁸. In a similar experiment Fuggle⁴⁵ also showed that extrinsic contributions to the satellite of Ni-Al alloys, such as plasmon losses, are negligible compared to the intrinsic losses. Also, the experimental⁴⁹ and theoretical^{46,50} results reveal that the Ni *d* band in NiAl is filled and the *d* density of states at the fermi level is low. Hence, the probability of creating a "two-hole" final state is largely reduced, which will lead to a weaker satellite of Ni in the XPS spectrum for NiAl. Hybridization between Ni *d* bands and Al *p* bands⁴⁶ will also make the satellite weaker. Since the Ni *d* band in NiAl is filled, and the Pauli electronegativity of Ni(1.9) is higher than that of Al(1.5), one would expect that electrons are transferred from Al to

Ni in NiAl. But, both experiments and theory^{45,46} suggest that the net electron transfer occurs from Ni to Al. Using "Wigner-Seitz" charge analysis, S.C. Lui and co-workers⁴⁶ showed that the Ni gains *d* electrons while losing more *sp* electrons to Al, leading to a net electron transfer from Ni to Al. This net electron transfer is the main reason for the binding energy of Ni and its satellite to shift to higher values of binding energy. This behavior is evident in our experiments as seen from Figure 5.8.

The asymmetry in the Ni core level emission is due to the excitations of electron-hole pairs near the Fermi level. Hence, the number of occupied states near the Fermi level will affect the asymmetry of the core line. The symmetry of the core line will be lower, if the number of occupied states is higher near the Fermi level. Since the density of states near the Fermi level in pure Ni is higher than that of Ni in NiAl, the asymmetry in the pure Ni core line would be larger than the Ni core line from NiAl. In fact, this is evident in our experiments, as the asymmetry of the Ni peak increases with the increasing Ni coverage (Figure 5.8).

The same arguments will apply to the Ni₃Al alloy also. The *d* band of Ni is almost filled in Ni₃Al, and the *d* density of states at the Fermi level is low compared to pure Ni but high compared to NiAl⁵¹. This excess amount of unoccupied *d* states (compared to NiAl) in Ni₃Al will increase the probability of creating the "two-hole" final states. Thus, it will give a stronger satellite feature than that of NiAl, but the intensity of this satellite is going to be weaker than in pure Ni. Nautiyal and co-workers⁵¹ showed that a small charge equal to 0.02 electrons is transferred from each Ni atom to the Al atoms in Ni₃Al. This amount of charge transfer is less than that occurring in NiAl (0.06

e compared to 0.15 e). Because of this small amount of charge transfer, the shift in the Ni satellite binding energy will be smaller than that of NiAl. The combined effects of filled *d* band, *p-d* hybridization, and the small amount of charge transfer from Ni to Al, will cause the Ni satellite in Ni₃Al to be quite different from pure Ni and NiAl. Therefore, we can conclude that the electronic properties of the alloys are the main contribution to the change in shape and separation of the Ni satellite in Ni-Al alloys, as well as the shifts in Ni binding energy.

On the basis of the above discussion, we believe that one could easily identify the phases grown at the Ni-Al(110) interface by looking at the shape and the separation of the Ni satellite. Since the shifts and the shapes are purely controlled by the electronic properties and the bonds of Ni and Al in these alloys, the change that we saw in Figure 5.8 with different Ni coverage must be due to none other than the change in the electronic environment of Ni in different reacted regimes. Thus, at least qualitatively, by comparing our line shape with Fuggle's line shapes, we conclude that the sequence of phases formed in our experiment is NiAl to Ni₃Al to Ni metal film.

In Figure 5.9, we plot the average chemical shift of the Ni 2p line (left axis) and the satellite separation between the main Ni 2p_{3/2} line and the satellite peak (right axis) as a function of Ni coverage. Here we calculated the chemical shift as the difference between the binding energy of Ni in the alloy phase and the binding energy for pure Ni metal, averaged over both 2p lines. These plots also show the three distinct regions of behavior, similar to what we saw in the ion scattering results. After the very first Ni deposition we observed a very large chemical shift. This large shift can be

interpreted as due to a very small amount of Ni atoms present in the vicinity of a large

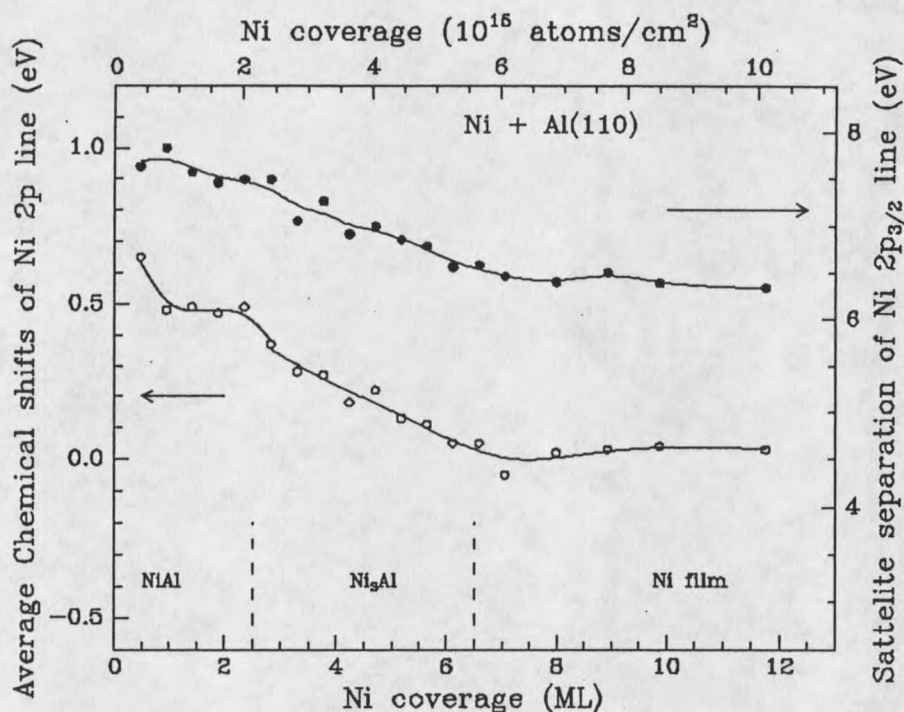


Figure 5.9. The average chemical shifts of Ni 2p line (left axis - open circles) and satellite separation of Ni 2p_{3/2} line (right axis - closed circles), plotted as a function of Ni coverage on Al(110) surface at room temperature. Solid lines are intended to guide the eye.

source of Al atoms. Higher core-level binding energies are also reported for small metal clusters and atoms on inert substrates⁵². The chemical shift then stays constant around

0.5 eV up to 2 ML of Ni coverage. After this, the chemical shift gradually decreases to zero at a coverage corresponding to approximately 6.5 ML, and stays at this value up to the maximum coverage of our experiment. The same trend was observed for the satellite separation with increasing Ni coverage. Up to 2 ML of Ni coverage the separation stays constant with the average value of 7.5 eV, and thereafter it gradually decreases to the bulk value of Ni (6.3 eV) at a Ni coverage of 6.5 ML.

In Table III, we compare our measured chemical shifts for the Ni $2p_{3/2}$ peak, and the separation between the main 2p peak and the satellite peak, with Fuggle's values. The satellite separation was taken as the difference between the binding energy of the satellite and the Ni $2p_{3/2}$ peak. From the table we see that our measured values for the chemical shifts and the satellite separation are somewhat higher than Fuggle's values, but the trend of our values agrees very nicely with theirs. For example, the difference between the satellite separation in Ni and NiAl in Fuggle's case is equal to 1.4 eV, while in our case, it is equal to 1.2 eV. Similarly all the relative shifts agree very well in both cases. However it is important to note a significant difference between the two experiments. In Fuggle's experiments the XPS spectra for pure bulk Ni-Al alloys were measured while we collected XPS spectra for very thin films of the Ni-Al alloys. For the Ni film, which forms after 8.1 ML of Ni deposition (region three), we record a satellite separation of 6.3 eV while for bulk Ni Fuggle reports a value of 5.8 eV. The difference in these values can be interpreted as being due to emission of photoelectrons from very thin reacted Ni-Al films. In very thin films, the charge transfer from Ni to Al may be higher compared to that occurring in the bulk. This excess charge transfer may shift

the satellite peak further to higher binding energies. Higher core level binding energies are also reported for several other systems like Cu/TiO₂(110), Cu/Al₂O₃, and small metal Cu clusters on inert substrates^{52,53}. Furthermore, we did not observe any chemical shifts in the Ni 3p line, however we did see small chemical shifts in the Al 2p line comparable to our experimental resolution. Chemical shifts of the Al 2p line in Ni-Al

TABLE III. Comparison of chemical shifts and satellite separation for the Ni 2p_{3/2} peak in different Ni-Al alloys. The chemical shifts are averaged over both 2p lines for the purpose of comparing with reference 45.

Compound	Chemical Shifts (eV)		Satellite Separation (eV)	
	Our Experiment	Fuggle's Experiment	Our Experiment	Fuggle's Experiment
Ni	0.0 ± 0.2	0.0 ± 0.2	6.3 ± 0.4	5.8 ± 0.4
Ni ₃ Al	0.2 ± 0.2	0.0 ± 0.2	6.9 ± 0.4	6.5 ± 0.2
NiAl	0.5 ± 0.2	0.2 ± 0.2	7.5 ± 0.4	7.2 ± 0.4
Ni ₂ Al ₃	-	0.75 ± 0.2	-	8.0 ± 0.6
NiAl ₃	-	1.05 ± 0.2	-	-

alloys are not available, to our knowledge. If we assume that we are forming NiAl₃ as the first phase, as seen by others, then from Table III, we should see a large chemical shift of about 1.05 eV. These chemical shifts can be measured very easily in our experiment. Since we did not see such a large chemical shift and satellite separation, we

can rule out the formation of NiAl_3 as the first phase to form for thin Ni overlayers on $\text{Al}(110)$ surfaces at room temperature.

Hence, from the line shapes of the Ni 2p core levels and its associated satellite together with the quantitative measurements of their binding energy shifts, we conclude that NiAl is the first phase formed, followed by Ni_3Al at the Ni-Al interface. After 8 ML of coverage, Ni metal starts to cover up the reacted regions. These results are significantly different from the earlier experiments⁸⁻¹³ in which NiAl_3 is the first phase to form at the Ni-Al interface. Of course the format of the experiments themselves are quite different, since in our experiments very thin Ni films were deposited on a single crystal substrate, while in almost all of the other experiments thick Ni films were deposited on a polycrystalline substrate, and subsequently heated. In our experiment we monitored the reaction while we were building up the Ni film on the Al surface at room temperature. Furthermore, the RBS measurements of bilayers at room temperature would not have sufficient depth resolution to detect the thin reacted layer of NiAl which is formed at the interface prior to thermal reaction.

In Figure 5.10 we plot the normalized XPS intensities for the Al 2p peak and the Ni $2p_{3/2}$ peak as a function of Ni coverage. The Al intensity was normalized to the intensity of the clean surface, while the Ni intensity was normalized to its value at the maximum coverage in our experiment (value at 12 ML). The solid lines are intended to guide the eye. The intensity of the Ni 2p peak (Figure 5.10 b) shows distinct breaks at two different Ni coverages. The first break occurs at a Ni coverage of 2 ML, while the second break occurs at around 6 ML of coverage. The Al XPS intensity (figure 5.10 a)

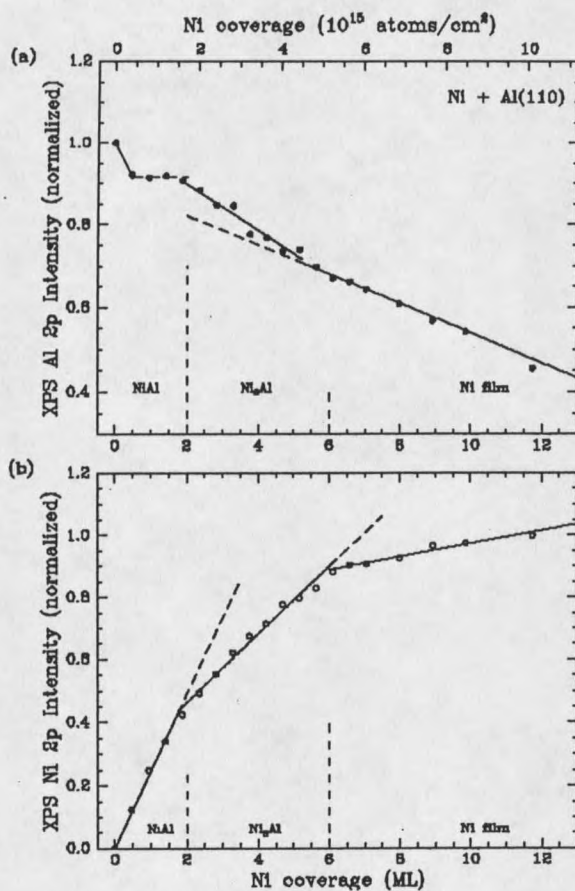


Figure 5.10. Measured XPS intensity of (a) Al 2p and (b) Ni 2p_{3/2} photo emission peaks as a function of Ni coverage. The Ni 2p_{3/2} intensity has been normalized to its value at the maximum coverage of our experiment (12 ML). The Al 2p intensity is normalized to the value for the clean surface. Solid lines are provided to guide the eye. Vertical lines are placed at the break points in the ion scattering yields as determined by Figure 5.4.

also shows three different regions. There is an initial 10% drop followed by a region of

little attenuation in the Al 2p intensity up to 2 ML of Ni coverage. Thereafter, the intensity decreases at somewhat different rates as the Ni coverage increases.

As seen from Figure 5.10 (a), the XPS intensity of Al remains constant up to 2 ML of Ni coverage. This suggests that some of the Al atoms are still present at the surface while the Ni atoms diffuse into the substrate and react with Al atoms. We also observed this effect in our EAM simulation¹⁷. Looking at the snapshots (Fig 4.4 b) very carefully for each coverage and calculating the number of Al and Ni atoms in each layer, we conclude that up to 2 ML of coverage, the incoming Ni atoms move down into the Al substrate, causing Al atoms to move off of their lattice sites. These displaced Al atoms move up into the top layer. This observation is very important, since the high-energy ion scattering experiment performed along normal incidence is insensitive to the movements of the atoms normal to the surface. This also reveals the importance of the XPS intensity calculation for these movements. Thus, in this manner, at least qualitatively the EAM simulation and XPS intensity of Al are in good agreement. We will discuss the quantitative agreement between the simulation and the XPS later. Since we did not see the attenuation of Al signal up to this coverage, we can rule out the formation of a Ni overlayer at the Al interface.

The initial drop of the Al XPS intensity, even after the Al atoms are still present at the surface following the very first Ni deposition, is explained as follows. Elastic scattering of electrons at an ordered single crystal surface will give rise to *forward focussing* along major crystallographic directions⁵⁴. If detection is made along or near a forward focussing direction, which is true in our case, the intensity of the photoelectrons

will be enhanced. If on the other hand the crystal is disordered, then *defocusing* will occur, resulting in an attenuation in the XPS intensity⁵⁴. This is the case in our experiment. Initially, the well-ordered Al single crystal will exhibit an enhancement in the Al 2p XPS intensity. By depositing Ni on the Al surface, this forward focusing will be reduced (or the defocusing will be increased) due to the disorder of the Al surface caused by the Ni atoms. Due to this effect, the Al 2p intensity will be decreased even though some of the Al atoms are still present at the surface.

The Al intensity began attenuating again after 2 ML of Ni coverage, confirming the formation of a Ni-rich compound at the surface. The persistence of the Al signal even after 12 ML of Ni coverage also suggests that the Ni film, which formed after 8 ML of Ni coverage, is inhomogeneous. Thus the Al signal could be due to Ni islands or cluster formation or some holes in the Ni film. An analysis of the Ni 2p_{3/2} peak shows that the intensity increases (Figure 5.10 b) at three different rates, depending on the Ni coverage. This indicates that the Ni signal is attenuating differently in these regions. These changes may be attributed to island formation of Ni or compound formation between Ni and Al. As pointed out by Smith and his co-workers¹, for Pd on Al(111), it is very difficult to distinguish between these two cases with intensity analysis alone. However, comparing the ion scattering results obtained for Ni in a random direction with those for a channeling direction, we know that Ni atoms are not forming islands ordered with respect to the Al substrate, at least up to the maximum coverage of our experiment.

XPS intensity simulation:

So far, the good agreement between the simulated and experimental ion scattering yields suggests that the MC simulations are correctly describing the movements of Al and Ni atoms in the plane normal to the incident ion beam, ie. parallel to the surface, since high-energy ion scattering experiments performed with ions at normal incidence are only sensitive to these movements. Hence, with these calculations we can only characterize the lateral movements of Ni and Al atoms in the surface, even though Ni atoms and Al atoms are moving quite a bit in the normal direction. In order to characterize the normal movements of the atoms the XPS intensities are calculated from the MC simulated snapshots, since the XPS intensities are sensitive to the movements along the normal direction. We use a simple model in which an exponential decay for the intensity of the photoelectrons through the layers (distance) is assumed. Furthermore, attenuation of the intensity is described by the inelastic mean free path of the electrons λ . We define z_0 as the z coordinate of the top most layer of the snapshots, and z_i as the z coordinate of the i^{th} atom in the crystal, as shown in Figure 5.11. Then the photoelectron intensity from this atom is given by^{20,26}

$$I_0 \exp \left[\frac{-(z_i - z_0)}{\lambda \cos \theta} \right]$$

with I_0 is the unattenuated intensity if the atom resides at the surface, and θ is the polar emission angle between the surface normal and analyzer (30° in our case). The

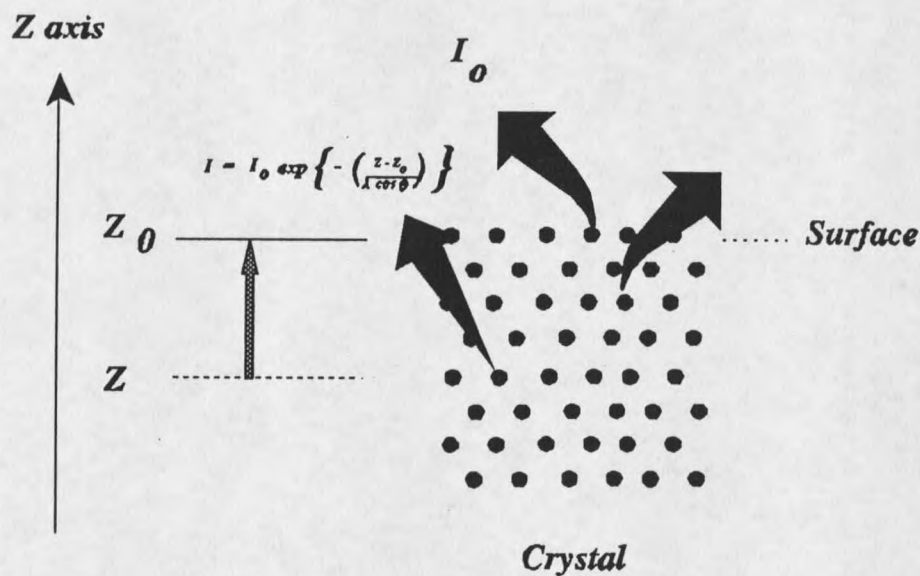


Figure 5.11. Schematic of the coordinate system of the EAM simulated-crystal snapshot that is used for the XPS intensity calculation.

photoelectron cross section for the particular transition is also absorbed into I_0 . Then, the total XPS intensity from the adsorbate (Ni) and substrate (Al) will be given by the following Equations:

$$I_{Ni} = I_{0,Ni} \sum_{i=1}^{N_{Ni}} \exp \left[-\frac{(z_{i,Ni} - z_0)}{\lambda_{Ni} \cos \theta} \right]$$

and,

$$I_{Al} = I_{0,Al} \sum_{i=1}^{N_{Al}} \exp \left[-\frac{(z_{i,Al} - z_0)}{\lambda_{Al} \cos \theta} \right]$$

where N_{Ni} and N_{Al} are the number of Ni and Al atoms in the snapshots, and λ_{Ni} and λ_{Al} correspond to the inelastic electron mean free path for Ni and Al respectively. The $z_{i,Ni}$ and $z_{i,Al}$ are the z components of the i^{th} Ni and Al atoms respectively. Since the z_i 's are determined by the MC simulation, and θ is determined by the experimental geometry, only the λ 's and I_0 's are adjustable parameters in the above equations. But the I_0 's are just scaling factors (constants) in these equations. Therefore, the λ is the only fitting variable in these calculations. The justification for varying λ is discussed below. Of course, the value of λ can be obtained from the universal curve^{55,56}. However, the value of λ for an overlayer can change dramatically in thin films⁵⁷. In addition, if the overlayer film is disordered or the detection is made along the forward focusing direction, then the value of λ for the substrate may also deviate significantly from the universal curve. We applied the above equations to the MC simulated snapshots, and varied λ to give the best fit to the XPS Ni and Al intensities of Figure 5.10.

In Figure 5.12 we plot the simulation result for the XPS intensity of the Ni 2p peak for different values of λ_{Ni} . We have varied the value of λ_{Ni} from 1 Å to 13.51

$\text{\AA}$, where the final value of λ was obtained from the universal curve for the kinetic energy of the Ni 2p line. Results for some selected values of λ are shown here. All these

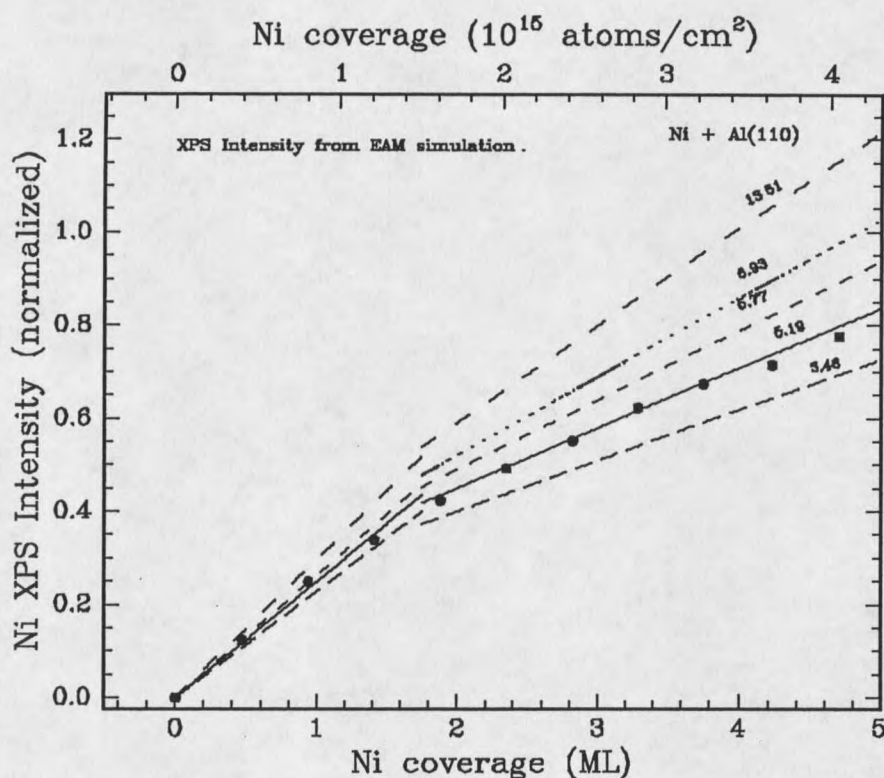


Figure 5.12. Simulated XPS intensity of Ni 2p line for different values of λ , plotted as a function of Ni coverage. Solid circles are the experimental result. The lines are the calculated results for the Ni XPS 2p line as described in the text ($\lambda=3.46 \text{ \AA}$ dashed-dashed line, $\lambda=5.18 \text{ \AA}$ solid line, $\lambda=5.77 \text{ \AA}$ dashed-dot line, $\lambda=6.93 \text{ \AA}$ dot-dot line, $\lambda=13.51 \text{ \AA}$ dashed-dot-dot line).

intensities were normalized by the same I_0 , which was obtained from the best fit to the data. Goodness of the fit was checked by comparing the ratio of slopes before (S_1) and after (S_2) the first break, in both experiment and simulation. Although the fit seems to be very good in figure 5.12, we still have some fluctuations in the simulated XPS intensity data (figure 5.13), due to the statistical nature of the simulation. From these figures we can immediately see that the break in the Ni XPS intensity is prominent for smaller values of λ_{Ni} . Interestingly, the break in the Ni XPS intensity also occurs around 2 ML of Ni coverage. The best fit to the Ni data [$S_1(\text{expt})/S_2(\text{expt}) \approx S_1(\text{simu})/S_2(\text{simu})$] is obtained for $\lambda_{Ni} = 5.19 \text{ \AA}$, which is significantly different from $13.6 \text{ \AA}$. We performed an analysis similar to that described for the Ni intensity for the Al XPS intensity. The best fit to the Al data is obtained for λ_{Al} equal to $15 \text{ \AA}$, which is also different from the value obtained from the universal curve ($20.2 \text{ \AA}$). Comparisons between the experiment and simulation of Al and Ni XPS intensities are shown in Figure 5.13 a and 5.13 b respectively. Experimental results are denoted by open circles while simulation results are designated by solid circles. The solid lines are intended to guide the eye. Clearly, both simulated (Al and Ni) intensities show the same behavior as the experiment. Interestingly, the simulated Al intensity also shows the initial drop in the intensity followed by the plateau up to 2 ML of Ni coverage. Therefore, from these ion scattering and XPS calculations, we conclude that the MC simulations not only provide a good description for the lateral movements of the atoms, but also describe the normal movements as well.

We also modeled the XPS intensities with the standard approach as

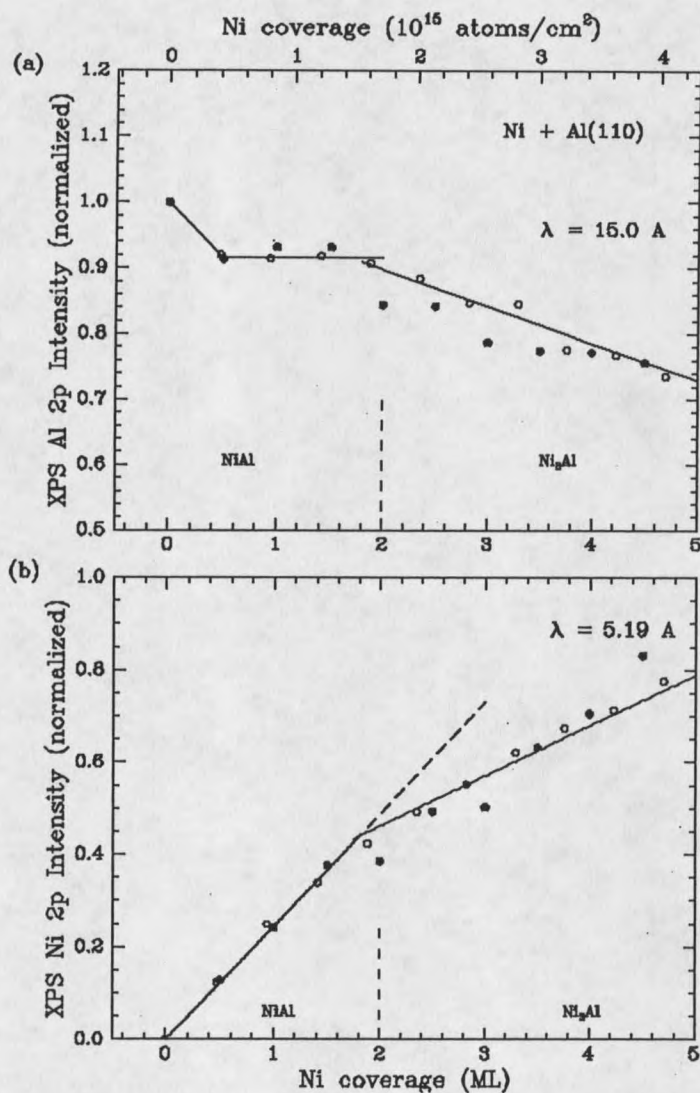


Figure 5.13. Simulated (best fit to the data) and measured XPS intensity of (a) Al 2p and (b) Ni 2p_{3/2} as a function of Ni coverage. Simulated results are denoted by solid circles while experimental results are shown by open circles. The best fit to the data was obtained with $\lambda_{\text{Ni}}=5.18 \text{ \AA}$ for Ni and $\lambda_{\text{Al}}=15.0 \text{ \AA}$ for Al, respectively. Solid lines are intended to guide the eye. Vertical lines are placed at the break points in the ion scattering yields.

described by Ossiciani²⁶ and Smith¹. In this model we assumed that we formed three distinct regions with some particular island thickness and three different compounds in a Volmer Weber mode. We also assumed that within one island we formed alternating layers of Ni and Al. There are several other assumptions involved in this model which ultimately led to reasonably good agreement with the experiment. However, due to the many assumptions involved in these calculations, we trust our MC intensity calculation better than this model, even having only a single fitting parameter. In the future we expect that these types of simulations will be useful for understanding both the ion scattering and the XPS results.

Exploring the snapshots :

Since the simulated ion scattering yields and the XPS intensities are agreeing quantitatively very well with the measured values, we can hope that the MC simulations are correctly describing the Ni-Al(110) reaction at room temperature. Therefore, by investigating the snapshots in several different ways we may be able to get more insight about the reaction and growth process of Ni on Al(110). First, we comment on the utility of the snapshots in understanding the Ni-Al reaction as measured by ion scattering. The normalized layer occupancies, l , i.e. the number of atoms in layer i divided by the number of lattice sites in the Al(110) layer (24 atoms), are plotted in Figure 5.14 as a function of Ni coverage. Al layer occupancies, Ni layer occupancies, and total (Ni+Al) layer occupancies are shown in Figures 5.14 a, 5.14 b and 5.14 c

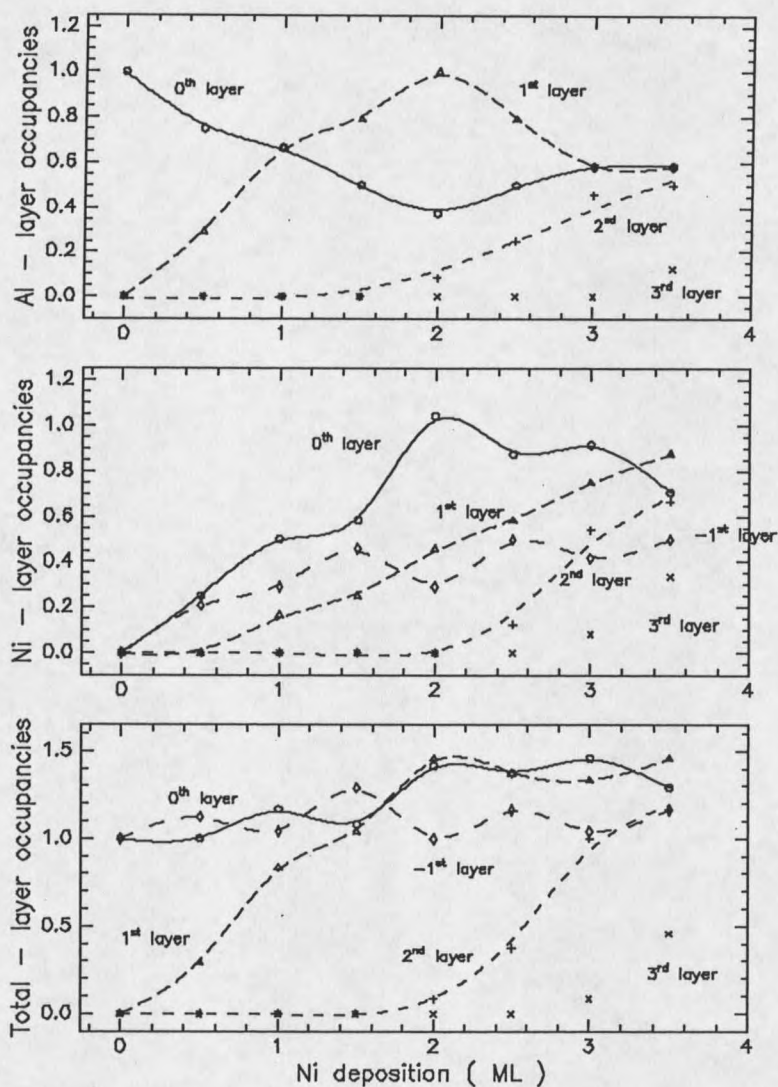


Figure 5.14. Normalized layer occupancies [number of atoms in a layer divided by the number of sites in an Al(110) layer] as a function of Ni coverage, for (a) Al occupancies, (b) Ni occupancies, and (c) total occupancies in each layer. The surface layer of clean Al(110) is labeled as the 0th layer. Added layers above the surface are labeled as 1st, 2nd, etc.

respectively. The lines are provided to guide the eye. The layer numbers used in Figure 5.14 are defined in Chapter 4 and Figure 4.12. Briefly, the surface layer of clean Al(110) is labeled as the 0th layer, while the added layers above the surface are denoted as 1st, 2nd and 3rd layers respectively. The layer just below the surface (0th) layer is denoted as -1st layer. At zero Ni coverage the layer occupancies of the 0th and -1st layers are one, while the occupancies of other layers (1, 2 and 3) are zero, as expected for a clean Al crystal.

A number of points can be made based on these figures. First, in Figure 5.14 b it can be seen that as the Ni coverage increases up to 2 ML the occupancy of Ni atoms in the 0th layer increases immediately, while the Ni occupancy in the 1st layer becomes non-zero only after 0.5 ML of Ni deposition. This indicates that initially the deposited Ni atoms move down into the Al substrate, causing Al atoms to move off of their lattice sites. These displaced Al atoms move up into the 1st layer above the surface, as shown in Figure 5.14 a. That is, the occupancy of Al atoms in the 0th layer decreases up to 2 ML of Ni coverage, while the 1st layer Al occupancy increases. This behavior is also evident from the Al XPS intensity profile (Figure 5.10 a), since the Al XPS intensity remains unchanged up to 2 ML of Ni coverage. In fact, for 1 ML of Ni coverage, about 0.3 ML of Ni occupies the layer below the 0th layer (i.e., at -1st layer) as seen from Figure 5.14 b. Note that some of the Ni atoms moved in to the -1st layer, and a few Al atoms moved out of layer -1, so that the total occupancy in this layer almost stays constant at the clean Al(110) occupancy number. Second, Al atoms do not move into the 2nd layer until a coverage of 2 ML of Ni is achieved. Similarly, deposited Ni atoms do not stay in the 2nd layer until a coverage of 2 ML is attained. Thus, Al atoms,

piling up in the 1st layer, and Ni atoms accumulating in the 0th layer, contribute to an overall increase to 1.5 for layer occupancies in layers 0 and 1, as seen in Figure 5.14 c. Saturation of the total layer occupancies for layers 0 and 1 seems to occur after 2 ML of Ni deposition. This increased density at the Ni-Al interface, compared to the clean Al(110) layer density, appears to be associated with the reduced reaction rate, and corresponding decreased slope for Al ion yield, seen in Figure 5.4 after 2 ML of Ni coverage. That is, after 2 ML of Ni deposition, the Al atoms from layers -1 and below will have more difficulty penetrating the dense phase layers, since most of the diffusion paths which were available earlier in the clean Al(110) layers are now blocked by extra atoms in these layers. Furthermore, looking again at Figures 5.14 a and 5.14 b, we see that after 2 ML of Ni coverage the occupancy of Al atoms in layer 1 starts decreasing. At the same time the Ni occupancy in layer 1 is still increasing. Thus after 2 ML of Ni deposition we see the evolution of the interface toward a more Ni-rich composition, such as Ni₃Al, as suggested by the reduced slope for ion yield in Figure 5.4 and the Ni 2p line shape in XPS in Figure 5.8.

The evolution of the Ni-Al(110) system is further illustrated in Figure 5.15, where a top view of the first two Al surface layers is shown for two different Ni coverages. This is the view that He ions see as they impinge on the surface. Hence, looking at the snapshots in this view will give more insight into the ion scattering results. The clean Al(110) surface is shown in Figure 5.15 a, while 0.5 ML of Ni on the Al(110) surface is shown in Figure 5.15 b. The positions of the Al atoms in these figures are projected onto the (110) plane. First layer Al atoms in a clean Al(110) crystal are

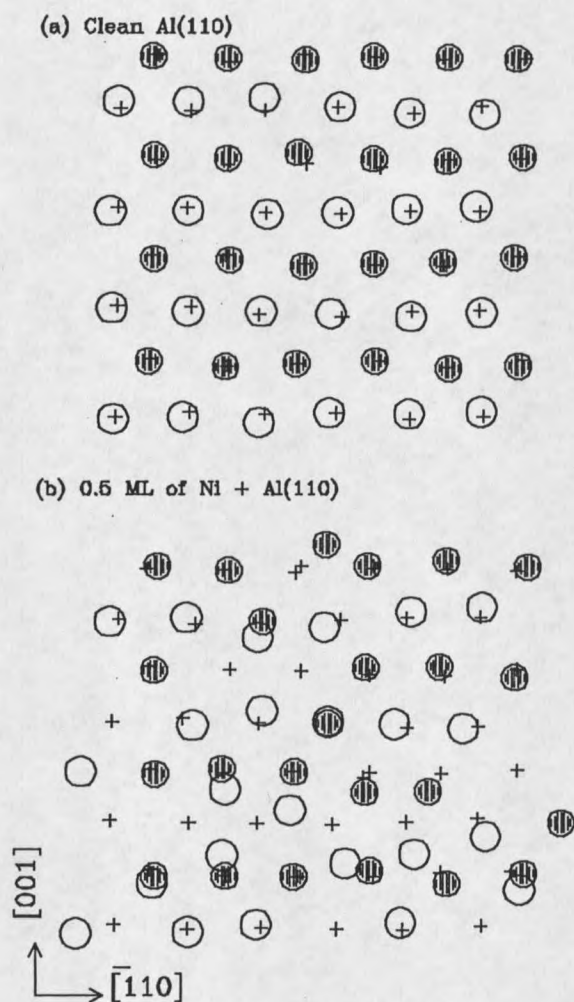


Figure 5.15. Top view of the snapshot of the simulated Al(110) surface for two different coverages of Ni: (a) Clean Al(110), and (b) 0.5 ML of Ni on Al(110). The positions of the atoms are projected onto the (110) plane. First layer Al atoms in the clean surface are indicated by open circles while the second layer Al atoms are indicated by shaded circles. The +’s are displaying the third and fourth layer Al atoms. Only the first four Al layers of simulated crystal are shown.

denoted by open circles while the second layer atoms are displayed by shaded circles. The +’s denote the third and fourth layer Al atoms. A number of points can be made based on these figures. First, in Figure 5.15 a, it can be seen that the first two layers of the clean Al(110) layers are very well ordered, and Al atoms in these layers are shadowing the atoms in the third and fourth layers. Consequently, the deeper atoms in these strings are also shadowed mainly by the atoms in the top two layers. Nevertheless, due to the thermal vibration, atoms in these strings are partially visible to the ion beam and will contribute to the total ion scattering yield. However, deposition of Ni atoms on the Al(110) substrate results in a disordered Al surface starting from the initial stages of the growth process as may be seen from Figure 5.15 b. Clearly we can see that most of the top layer Al atoms are displaced from their original fcc lattice positions. Actually, some of these displaced Al atoms are moved into the very top layer as seen in Figure 4.4 b. Furthermore some of the second layer Al atoms are also displaced from their initial position by the incoming Ni atoms. Hence, these displaced Al atoms not only completely uncover some of the third and fourth layer Al atoms but also partially uncovered others, as seen in Figure 5.15 b, where more +’s are visible now. Thus, unshadowing of the Al atoms in the lower layers will increase the ion scattering yield of Al from its clean value as seen from Figure 5.4, because more Al atoms are now visible to the incident ion beam. Finally, we can see from Figure 5.15 b, that two atoms in the third and fourth layers are moved quite a bit from their ideal lattice position. This is because some of the deposited Ni atoms moved into these layers and caused the Al atoms to move away from their equilibrium positions. Basically, we observed almost the same behavior of Al and Ni

atoms in the crystal for Ni coverages up to 2 ML.

The structural evolution of the Ni-Al(110) system was further studied by calculating the average distances between nearest neighbor atoms in each layers. In Table IV, we compare the structure, lattice constant, and nearest neighbor distance for different Ni-Al alloys. From this table we can see that the nearest neighbor distances of NiAl, Ni₃Al, and Ni are very close to each other, but significantly different from Al. Hence, by looking at these distances we may be able to distinguish the different phases formed at the Ni-Al interface during the Ni deposition. In Figure 5.16, the average distances

TABLE IV. Comparison of different structural properties of Al, Ni, NiAl, and Ni₃Al.

Crystal	Structure	Lattice Constant	Nearest Neighbor Distance	Number of Al-Al Neighbor	Number of Ni-Ni Neighbor	Number of Al-Ni Neighbor	Number of Ni-Al Neighbor
Al	F.C.C	4.051 Å	2.863 Å	12			
Ni	F.C.C	3.508 Å	2.481 Å		12		
NiAl	B.C.C	2.887 Å	2.500 Å			8	8
Ni ₃ Al	F.C.C	3.589 Å	2.537 Å		8	12	4

between nearest neighbor atoms in each layer are plotted as a function of Ni coverage.

We considered a spherical shell, with radius R_{shell} , around one atom in a specific layer.

Atoms in side this shell are considered as the nearest neighbors for the atom at the center of the shell. Hence, the average nearest neighbor distance of a particular layer is obtained by calculating the distance between the atoms within the shell and the center-atom, and averaged over the atoms in that particular layer. This procedure is continued for other layers also. Two different values of R_{shell} are chosen for these calculations. In Figure 5.16 a and 5.16 b, we show the calculated nearest neighbor distances for some selected layers using shells with a radius (R_{shell}) of 2.7 Å and 3.2 Å respectively. The value of 2.7 Å for R_{shell} is chosen first because the nearest neighbor distances of Ni, NiAl, and Ni₃Al are closer to this value. It can be seen from Figure 5.16 a that the average nearest neighbor distance between atoms in these simulated surface layers (-2 to 3) is comparable to the NiAl and Ni₃Al nearest neighbor distances, and significantly less than that for Al. This also can be seen in Figure 5.14 and characterized by the increase in the occupancies of the these layers (-2 to 0).

We performed analyses similar to those just described for R_{shell} equal to 3.2 Å, since this value is closer to the Al nearest neighbor distance. From Figure 5.16 b we can clearly see the structural transformation of the interface at around 2 ML of Ni coverage. That is, the average nearest neighbor distances in the Al layers (0, -1 and -2), which are calculated with this R_{shell} , are decreasing with increasing Ni coverage up to 2 ML of Ni coverages. This suggests that the Al atoms in the reacted region are closer to their nearest neighbors than in the clean Al crystal. Furthermore, the nearest neighbor distances saturate upon completion of 2 ML of Ni. All of these values are a little higher than that of NiAl and Ni₃Al since with the higher R_{shell} value we included some of the

atoms in other layers also. It can be further seen in Figure 5.16 *b* that the nearest neighbor distances in layers -3 and -4 are also altered by the Ni atoms. But the values

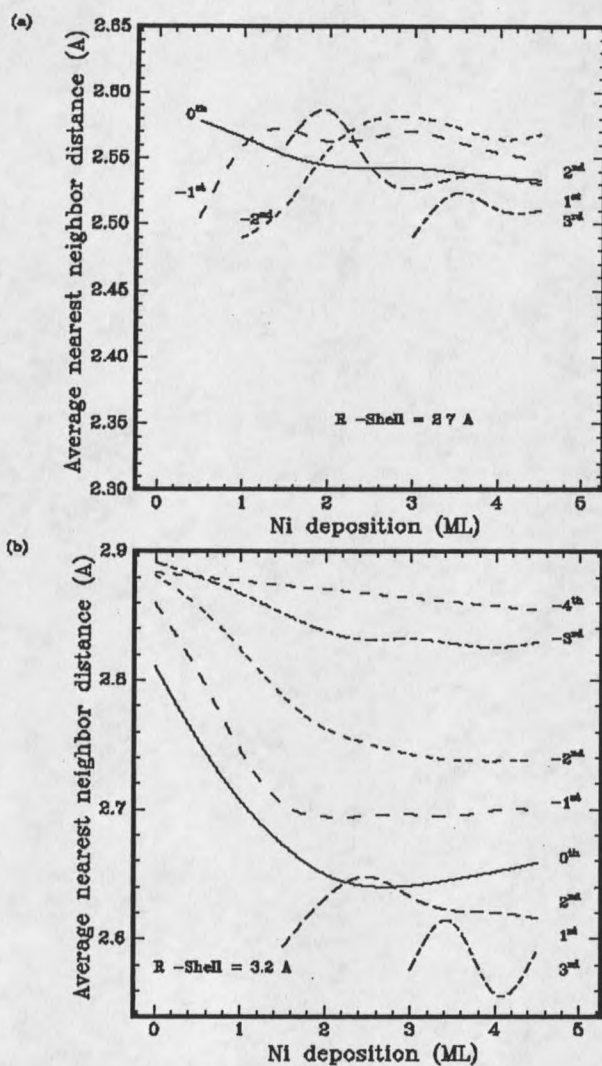


Figure 5.16. Average nearest neighbor distance of atoms in each layer as a function of Ni coverage as shown for two different values of shell radius (a) for $R_{\text{shell}} = 2.7 \text{ Å}$, and (b) for $R_{\text{shell}} = 3.2 \text{ Å}$.

are much closer to the Al nearest neighbor distance than the Ni-Al alloys. This observation confirms that the Al atoms in the layers just below the reacted interface still have some order with respect to the bulk. Unfortunately, from these calculation, we could not pin point the exact phase formed at the interface upon the Ni deposition, since the nearest neighbor distances of NiAl, Ni_3Al and Ni are closer to each other as seen from Table IV.

Slow deposition of Ni

To investigate the influence of deposition rate on the growth mode of Ni on Al(110), we performed an experiment where the deposition rate of the Ni was reduced by a factor of six to 0.064×10^{15} atoms/cm²/min. The ion scattering yields from Al and Ni were collected with the same experimental parameters as those for higher deposition rate experiments. Hereafter, this deposition rate is referred to as a "slow deposition rate" while the deposition rate for Figure 5.4 is called a "fast deposition rate". In Figure 5.17, we plot the measured Al surface peak area, which is converted to the number of Al atoms/cm² (filled circles), as a function of Ni coverage. We have also included the fast deposition results (open circles) to demonstrate the degree of agreement and deviation between these two experiments. For the first half monolayer of deposited Ni atoms, we observed an increase in the number of Al atoms visible to the ion beam, at a rate of 5 Al atoms per deposited Ni atom, which is significantly larger than that obtained for the fast deposition rate. The results after 0.5 ML of Ni deposition are similar to the observation for the fast deposition rate.

With the aid of Figure 5.4 and Figure 5.17, we observe that the growth mode of the first 1/2 ML of Ni on Al(110) is strongly dependent on the Ni deposition rate, and that the reaction of Ni on Al after 1/2 ML of Ni coverage is independent of deposition rate. The explanation for this behavior is not yet clear, but may be explained as follows. The reaction (inter mixing) between Ni and Al is likely because nickel aluminides have an exceptionally large negative heat of formation. Therefore, Al atoms

were moved from their equilibrium position and reacted with Ni atoms at the surface to form a surface compound. Movements of Al atoms are likely given that Al has a lower surface energy than Ni (0.49 eV/atom compared to 0.82 eV/atom)⁵⁸. Since the nearest

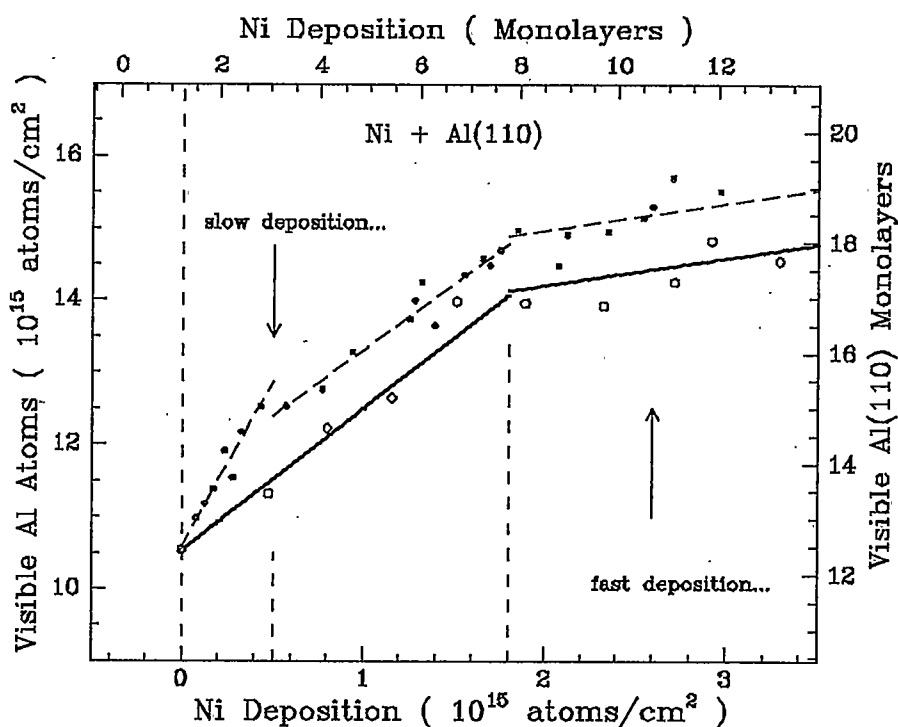


Figure 5.17. Number of Al atoms visible to the ion beam as a function of Ni coverage on the room temperature Al(110) surface, for two different deposition rates of Ni. Results for a fast deposition rate (0.43 ML/min) are shown by open circles, while the results for a slower deposition rate (0.07 ML/min) are shown by solid circles. The dashed and solid lines are the results from least-squares fits to the data

neighbor distance between Al and Ni in NiAl ($2.5 \text{ \AA}$) is $0.3 \text{ \AA}$ smaller than the nearest neighbor distance of Al ($2.86 \text{ \AA}$) in Al crystal, the Al atoms have to move a large distance in order to be a neighbor with the Ni atoms. Such movements of these Al atoms will also disrupt the symmetry of the surface, and thus cause the other Al atoms in the vicinity to move off of their equilibrium positions. These correlated movements will be influenced by the number of Ni atoms present at the surface after each deposition. Since, our deposition rate (slow) is six times smaller than our normal deposition rate (fast), that is, at each deposition, the number of Ni atoms coming to the surface is reduced by a factor of six compared to the normal deposition rate, the number of Ni atoms present at the surface after one deposition is largely reduced. Thus, the Al atoms can move to very large distances from their initial positions and cause the large initial increase in the Al yield as seen in Figure 5.17. This will not happen in the normal deposition rate, because the presence of more Ni atoms at the surface (after one deposition) will reduce the correlated movements of the Al atoms, and thus reduces the Al yield. Furthermore, the large correlated movements of Al atoms might begin to slow down when there are enough Ni atoms present at the surface to prevent the motion of the Al atoms. This may be the case in the slow deposition rate, where after $1/2 \text{ ML}$ of Ni coverage, we already have enough Ni atoms to interfere with the correlated movements of the Al atoms, and thus we observe the change in the Al scattering yield. A second possibility for the larger increase may result from the longer overall experiment time, during which time adsorption of residual gases would result in the faster increase of Al yield. It may well be that the adsorption of residual gas displaces the Al atoms from their initial equilibrium sites. The

probability of this happening is very remote since we checked with the RGA while we deposited Ni and found that only hydrogen was present in the chamber during the evaporation. Finally, one can argue that the initial conditions of the Al surface in our two experiments may be different. But the agreement of the Al yields for the clean surface for these two experiments tends to rule out this possibility. Furthermore, we did not see any change in the line shape of the Al 2p XPS spectra for these two clean surfaces.

Ni deposition onto Al(110) at 250 °C

As mentioned earlier, there is a large amount of work concerning the Ni-Al reaction and its characterization⁸⁻¹³. Most of the work has been done with polycrystalline or bilayer samples and at elevated temperatures. Reaction temperatures observed in these experiments are generally reported to be in the range of 225-325°C. Very few experiments have been reported for room temperature reaction^{9,13}. Thus, in order to explore the temperature dependence of the reaction between Ni and Al, we deposited Ni atoms while the Al(110) surface temperature was maintained at around 250 °C. Ion scattering and XPS measurements were made at a sample temperature of 110 °C. All other experimental parameters were the same as the room temperature experiment. In Figure 5.18, we compare the ion scattering energy distribution curves from these two experiments, deposition at room temperature (open circle) and at 250°C (closed circles) for the same Ni coverage of 1.75 ML. Clearly, the two spectra are significantly different from each other. We can point out several distinctions between these two spectra. First, the well defined surface peak of Ni (50 KeV wide) at room temperature is now spread over a large region (150 keV) at 250°C. This indicates that the Ni atoms are diffusing very deep into the Al substrate. Thus, the number of Ni atoms at the surface region is lower in this case compared to the room temperature deposition. Second, the background behind the Al surface peak is larger in the 250°C experiment than in that of the room temperature experiment. This is due in part to the "bulk" dechanneling effect. That is, the presence of deep lying heavy Ni atoms in the Al bulk leads to significant deflections

of some channeled He^+ ions, and increases the backscattering yield of bulk Al atoms. Channeling is also reduced because of the larger vibration amplitude at elevated temperatures²⁰.

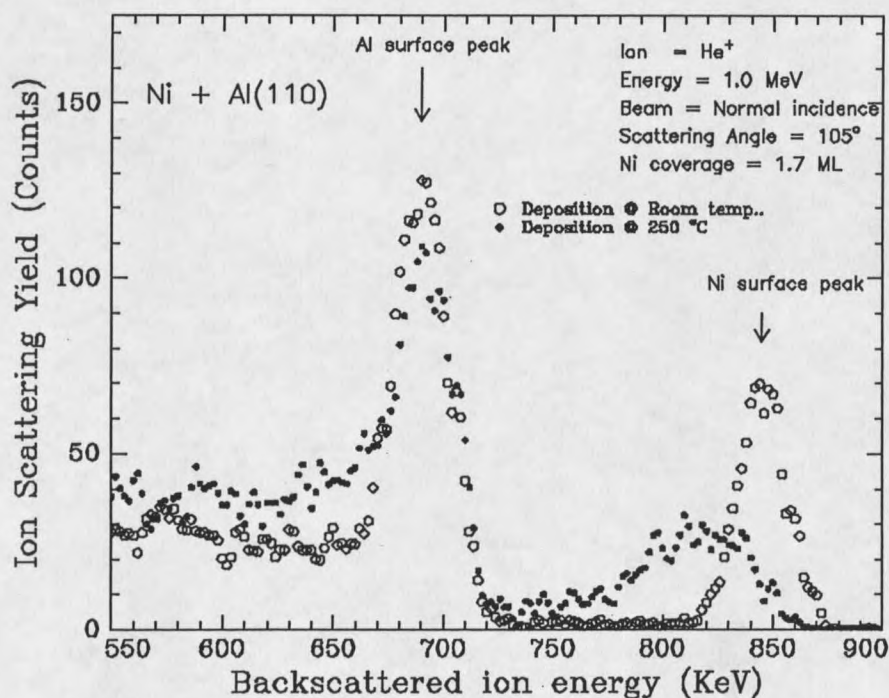


Figure 5.18. Ion scattering/channeling spectra for 1.7 ML of Ni deposited on the Al(110) surface at different temperatures. The room temperature deposition spectrum is shown by open circles, while the elevated temperature (250°C) spectrum is denoted by filled circles. The energies for backscattering from Al and Ni surface atoms are indicated by the arrows.

In Figure 5.19, we plot the energy distribution curve for Ni and Al for several different Ni coverages. The arrows in the figure indicate the surface Ni and Al atoms positions. The spectra have been shifted vertically in order to compare each energy distribution curve more easily. From this figure we immediately conclude that, while some of the Ni atoms are present at the surface with Al atoms (Ni arrow), most of the Ni atoms are diffusing into the Al bulk. The next point to note here is the width of the Ni peak. This peak width is increasing with increasing Ni coverage, indicating that after each Ni deposition, Ni atoms are diffusing deeper into the Al bulk. As mentioned earlier, the presence of these diffusing Ni atoms in the Al bulk causes the "bulk dechanneling" to increase. This increase is very prominent in these figures, as the background behind the Al surface peak is changing with the Ni coverage. After 4.8 ML of Ni coverage the Al surface peak has almost lost its shape on the lower energy side. The Al surface peak height also increased with Ni coverage. The change of the Al SPA with increasing Ni coverage is believed to be associated with the disorder of Al atoms caused by the diffusing Ni atoms. However, it is very unlikely that such an increase in the Al SPA would result from surface compound formation, since, most of the deposited Ni atoms (4.8 ML) are now spread over several hundred Angstroms in the Al crystal. In other words, the concentration of Ni in the Al crystal is very low.

Figure 5.20 shows two ion scattering spectra collected after a Ni coverage of 4.8 ML at 250° C. One spectrum (solid circles) was taken in the [110] channeling direction, while the other spectrum (solid circles) was taken with the ion beam in a random direction. We did not see any reduction in the surface peak area of Ni along the

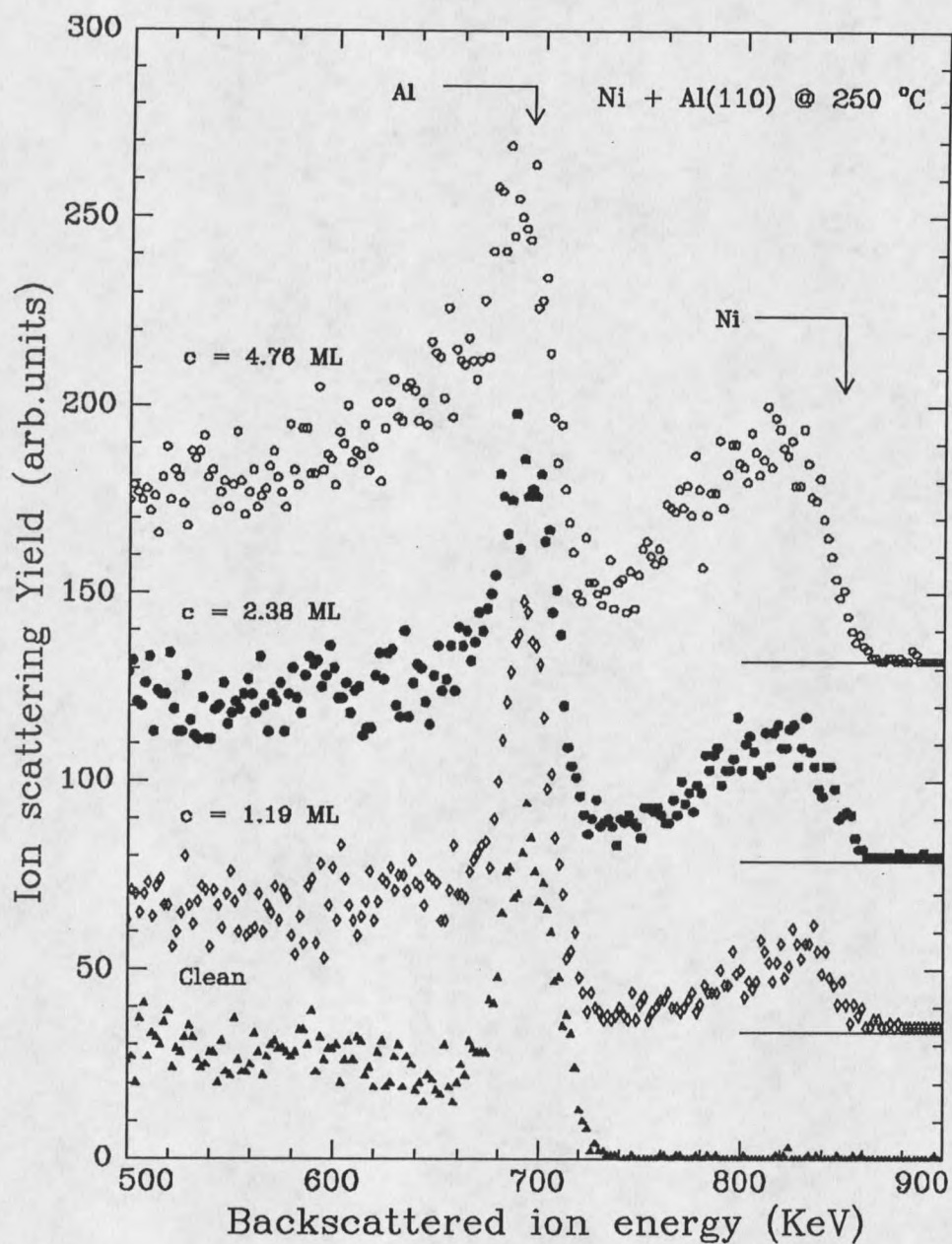


Figure 5.19. Ion scattering/channeling spectra for Ni on the Al(110) surface at 250°C, for different Ni coverages as indicated in the figure. The spectra have been offset vertically as denoted by the horizontal solid lines (right axis). Backscattered energy positions corresponding to Ni and Al surface atoms are denoted by the arrows.

channeling direction. This suggests that no Ni-Ni or Al-Ni shadowing exists in the region. From the backscattering spectrum collected in the

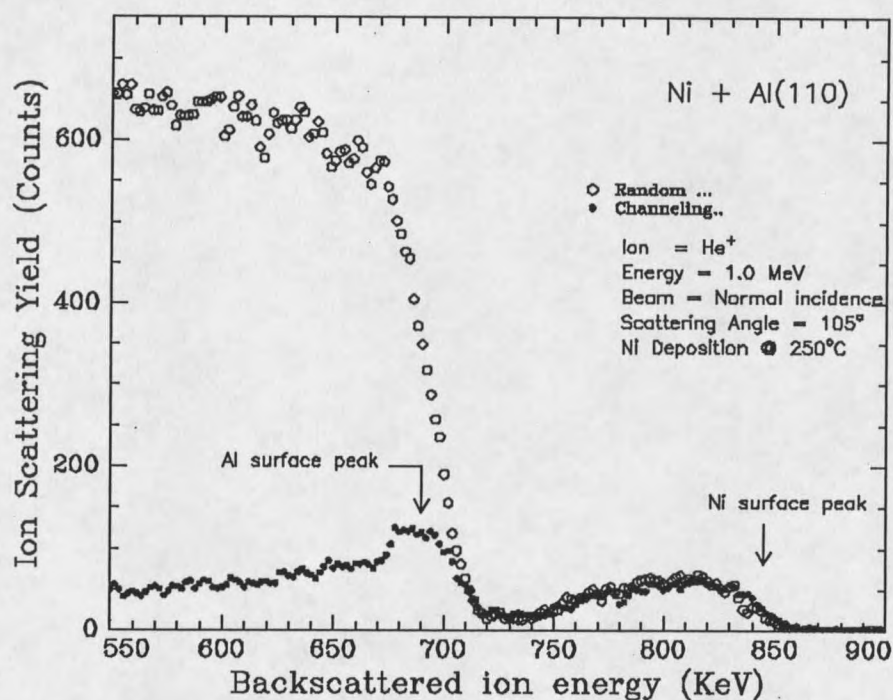


Figure 5.20. Ion scattering spectra (random and channeling) at 1 MeV after the deposition of 4.78 ML of Ni on Al(110) surface at 250°C. The random spectra is denoted by open circles, while the channeling spectrum is displayed by solid circles.

random geometry (Figure 5.20), together with the energy loss of He ions through the Al-Ni interface and some other experimental parameters, we calculated the concentration-

depth profile of Ni atoms in the Al crystal. The *RUMP* computer simulation code⁵⁹ was used for this purpose. The spectrum that we collected in the random direction for the Al

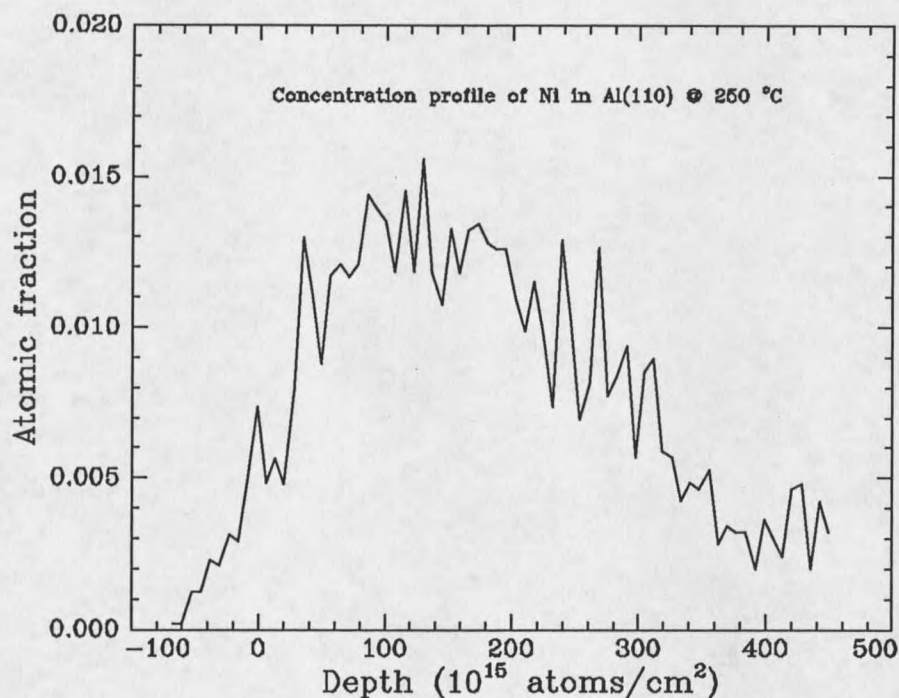


Figure 5.21. Concentration profile of Ni on Al(110) at 250°C for 4.78 ML of Ni.

crystal (Figure 5.20) is not a truly random spectrum because in a single-crystal it is very difficult to find a perfectly random direction once we have aligned the incident beam along the major crystallographic axis. Yet, for the Ni atoms if we move the sample by a little amount, it is sufficient to make the direction random. Thus, we have no problem

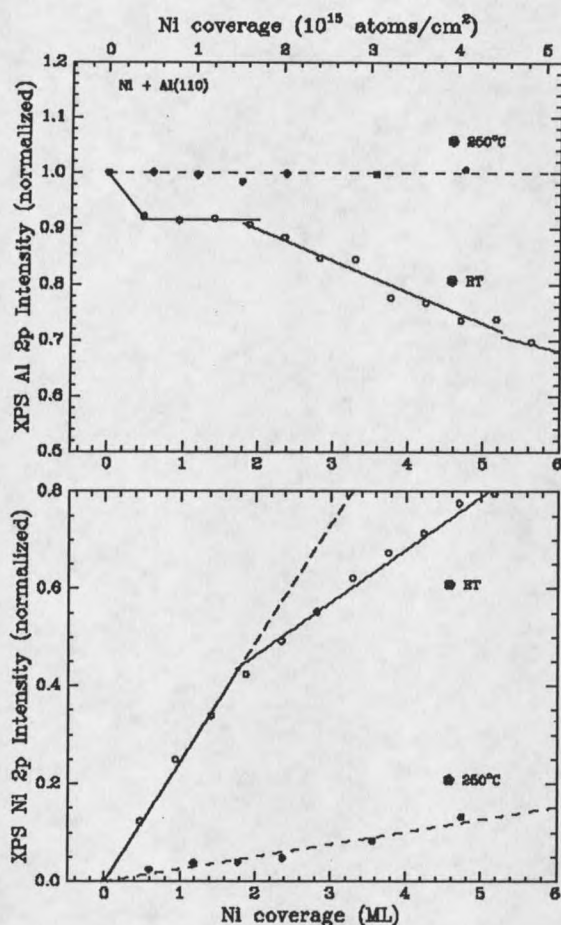


Figure 5.22. Measured XPS intensity of (a) Al 2p and (b) Ni 2p_{3/2} photo peaks (filled circles) as a function of Ni coverage where the Ni atoms are deposited at 250°C. Ni 2p_{3/2} intensity has been normalized to the Ni intensity of the maximum coverage in the room temperature experiment (12 ML). The Al 2p intensity is normalized to the value for the clean surface. For comparison, the room temperature results are also shown by open circles. The solid lines denote the trend of the room temperature results, while the dashed-dot-dashed lines are displaying the elevated temperature results.

finding a Ni random direction, but we have to be careful about the Al random direction. We take account of this problem in our calculations. The calculated concentration profile of Ni, at the very last coverage (4.78 ML), in the Al (110) crystal is shown in Figure 5.21. The atomic fraction of Ni atoms is plotted against the Ni depth in the Al crystal. Here we assumed that the concentration ratio of Ni to Al is 2 to 98 throughout the inter mixed region to get a best fit to the data. From these calculations we conclude that the Ni atoms diffused 400 Å deep into the Al crystal. These calculations also revealed that the Ni concentration is high in the region between 100 to 200 Å deep in the Al crystal.

As discussed before, we can get more information about our system by looking at the XPS results. After each Ni deposition, XPS spectra of the Ni 2p and the Al 2p core levels were collected. Throughout the Ni deposition we observed a very small chemical shift in the Ni 2p_{3/2} peak. In Figure 5.22 we plot (solid circles) the normalized XPS intensities for the Al 2p peak and the Ni 2p peak, as a function of Ni coverage. For comparison purposes, we have included the XPS intensities from the room temperature deposition results (open circles). The Ni XPS intensity at 250°C has been normalized to the value of the intensity at the maximum coverage in our room temperature experiment. As before, the Al XPS intensity has been normalized to the intensity of the clean surface. From these figures it is clear that the behavior of the XPS intensities of both Ni and Al at 250°C are quite different from the room temperature deposition. That is, throughout our elevated temperature experiment, first, the Al intensity stayed almost constant at its clean value. This suggests that even with 4.8 ML of deposited Ni, the Ni atoms do not stay at the surface. Instead they diffuse deep into the substrate. Thus they could not

attenuate the Al signal. Second, the magnitude of the Ni intensities are much weaker than those of the room temperature intensities. Furthermore, the break that we saw in the Ni intensity at 2 ML in the room temperature deposition is absent in the 250°C deposition. These observations also suggest that the number of Ni atoms that are present at the surface region is low. Thus, both the ion scattering and the XPS results are implying the same theme, that is, the Ni atoms deposited at 250°C do not stay at the surface. Instead, they diffused into the Al bulk.

From the above discussions and calculations we can see that the growth mode of Ni deposited at 250°C is completely different from the room temperature deposition. In fact, these results are not surprising, since, even at room temperature Ni atoms want to move down into the Al surface as seen in both experiments and simulations (figure 5.1 and Figure 4.4). Therefore, when we promote the diffusion of the Ni atoms by increasing the temperature of the substrate, they move quickly into the Al bulk.

In summary, we have performed high-energy ion scattering and XPS experiments for thin Ni films deposited on the Al(110) surface at room and elevated temperatures. Deposited Ni atoms at room temperature, continuously displaced the Al atoms for up to 8.1 ML of Ni deposition, indicating a reaction between the Ni and Al atoms. The NiAl phase formed first with the "surface" dechanneling effect present at the interface, followed by the formation of a Ni₃Al phase, until the reaction stopped and a Ni overlayer covered the surface. These results differ from those of previous experiments. Monte Carlo simulations of the Ni-Al interface using EAM potentials also show an

interfacial reaction. Calculated ion scattering yields and XPS intensities from the Al and Ni atoms are in very good agreement with the experimental results. Ni atoms deposited at 250 °C, show no reaction with the Al atoms, but diffuse 400 Å deep into the Al bulk.

ULTRATHIN Ni FILMS ON Al(001) SURFACESIntroduction

The interaction of transition metals with metals has been explored with growing interest, in recent years^{5,6,41}. As mentioned in previous chapters, the nickel-aluminum interfaces are of considerable interest for several applications. In particular, structure and bonding may play a major role in determining stability and adhesion of metal films on a metal substrate. In order to investigate the influence of the structure of various substrate orientations on the overlayer reaction we have performed high-energy ion scattering (HEIS), x-ray photoelectron spectroscopy (XPD), and x-ray photoelectron spectroscopy (XPS) experiments on ultrathin Ni films deposited on both Al(110) and (001) surfaces. In the last chapter we showed that ultrathin Ni films deposited on the Al(110) surface reacted strongly with Al atoms at the interface. For the first two monolayers of deposited Ni on Al(110), a NiAl -like compound was formed with additional *near surface dechanneling* present at the interface. The reaction continued with a different rate, forming a Ni₃Al -like compound for Ni coverages from 2 to 8 ML, at which point a Ni metal film began to grow. So, the question has to be asked as to whether or not Ni films deposited on the Al(001) surface will follow the same trend as Ni on the Al(110) surface. In this chapter we will present and discuss our results for Ni

deposition on Al(001) surfaces and see that the interface evolution is considerably different than that for Al(110) surfaces.

Experimental setup

All experiments were performed in an ultrahigh vacuum (UHV) chamber with a working base pressure of 1×10^{-10} Torr as described in Chapter 3. For the ion scattering measurements a well collimated beam of 1 MeV He ions was incident on the Al surface along the normal [001] direction. The solid state detector was positioned so as to collect scattered ions leaving the crystal with a scattering angle of 105° . Ion scattering spectra were obtained with the He ion dose of 1.6×10^{15} ions/cm². Typical beam currents during HEIS were between 1 and 5 nano amperes.

The XPS was performed with the Al K _{α} line (1486 eV) as the incident radiation. A 100mm hemispherical analyzer in a fixed-analyzer-transmission (FAT) mode was used for these measurements. The XPS measurements used a 50 eV pass energy and each spectrum was obtained with a scan rate of 0.1 eV/sec. All XPS binding energies presented in this thesis are referenced to the Fermi level. The analyzer was positioned to collect emitted photoelectrons with a polar angle of 30° from the sample normal.

The Al single crystal was cleaned using the methods described in Chapter 3. That is initially, the Al crystal was polished mechanically and then it was chemically etched. Following these polishings, the Al crystal was further cleaned in vacuum by successive 1.5 keV argon ion sputtering and annealing cycles.

The HEIS and XPS experiments were performed in the following manner:

At first, after each Ni deposition at room temperature, the channeling experiments were performed to determine the Ni coverage as well as to study the Ni-Al reaction and the surface morphology. Most of the channeling experiments were performed in the normal direction, and the Al SPA and Ni SPA were monitored during this process. However, in order to calculate the actual Ni coverage, the random direction HEIS spectra were also collected once in a while. Following each HEIS measurement, the XPS spectra (Al 2p and Ni 2p) were collected in the same manner as described in Chapter 3 and 4. Nickel was vapor-deposited on the Al (001) surface from a resistively heated Ni wire filament. Typical deposition rates in these experiments were 0.54×10^{15} atoms/cm²/min or 0.44 ML/min. One monolayer (ML) here is equivalent to the atomic density of the Al(001) plane, 1.219×10^{15} atoms/cm².

The photoelectrons emitted from the single crystal surfaces exhibit pronounced enhancement in their intensities at various polar and azimuthal angles⁵⁴. These angles correspond to directions from the emitting atom to overlaying nearest and next-nearest neighbor atoms. Constructive interference between the initial and scattered outgoing waves leads to enhanced forward scattering in these directions. This behavior is called x-ray photoelectron diffraction (XPD). Using this phenomena, we can get additional information about the growth modes, surface alloying, location of the adsorbate, etc. Intensities of the Al 2p (1413 eV kinetic energy) and Ni 3p (1419 eV kinetic energy) photopeaks were monitored at different polar angles in the (010) and (110) azimuthal planes. In principle, one would like to collect the polar scan for a whole range

of angles, but due to the limitations of our detector-goniometer system, we only collected XPD curves over an angular range from 0 to 55°. XPD polar curves were measured by rotating the sample by means of the three axis goniometer with angular intervals of 1°. Three different sets of XPD experiments were performed on the Ni/Al(001) system. First, XPD curves for the Al 2p emission from clean aluminum were collected as a reference. XPD curves from both Al 2p and Ni 3p emission were then collected for three different coverages of Ni, that is, at 1 ML, 5 ML, and 11 ML respectively. The choice of these coverages will be discussed below.

Results

High-energy ion scattering

In Figure 6.1 we show the energy distribution for the scattered ions in the regions of the Al and Ni surface peaks for three different Ni coverages: 0, 0.87, and 2.17 ML. The backscattering spectrum for the clean surface is shown by open circles, while those for 0.87 ML of Ni and 2.17 ML of Ni are denoted by closed circles and triangles, respectively. It can be easily seen from the figure that at a Ni coverage of 0.87 ML the Al yield exhibits an increase. On the other hand, at a Ni coverage of 2.17 ML the Al yield shows a decrease.

By plotting the integrated area of the Al surface peak as a function of Ni coverage we can obtain more detailed information about the growth characteristics. Such

a plot is shown in Figure 6.2, where the number of Al atoms visible to the incident ion beam is plotted as a function of Ni coverage. There are three main regions to note in this figure. Initially, the Al yield exhibits a linear increase up to 1 ML of Ni coverage. After 1 ML of Ni deposition, the Al yield shows a decrease with Ni coverage. This decrease

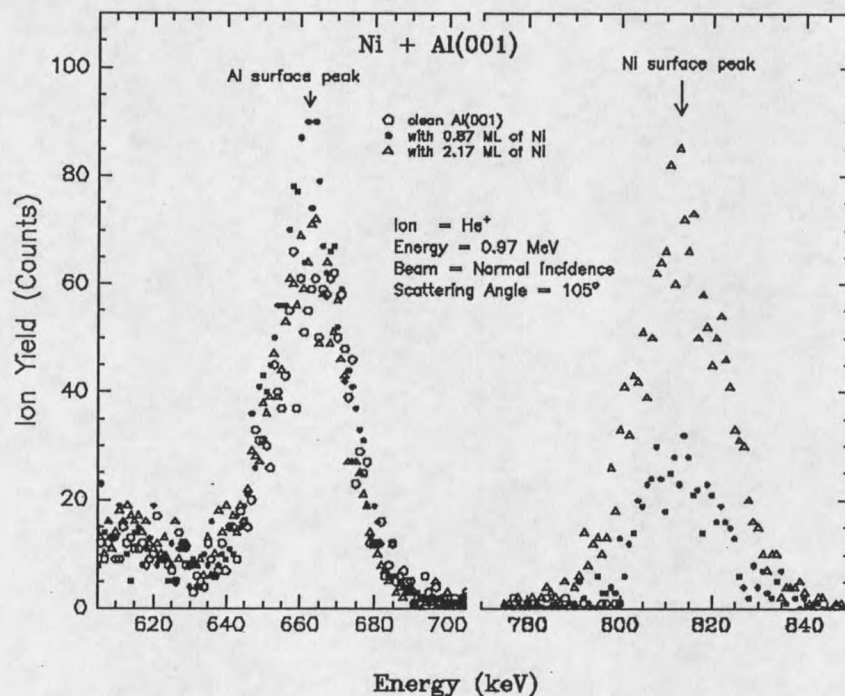


Figure 6.1 Backscattered ion energy spectra for 0.97 MeV He⁺ ions on Ni + Al(001) for three different Ni coverages are indicated in the figure. Open circles denote the clean Al spectrum while solid circles and open triangles represent the spectrum at 0.87 ML and 2.17 ML of Ni respectively.

continues up to 2 ML of coverage. Then, for Ni depositions up to 5 ML, there is an apparent saturation stage during which the Al yield remains almost constant. Finally, for larger coverages, the number of visible Al atoms increases again with a slower rate.

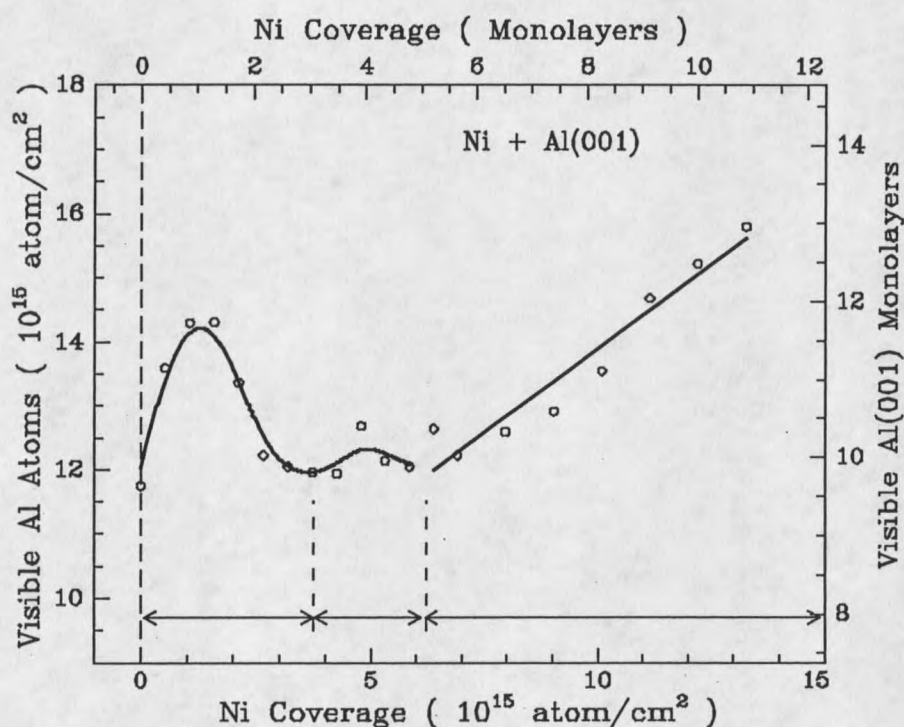


Figure 6.2 Number of Al atoms visible to the ion beam as a function of Ni coverage on the Al(001) surface. The solid lines are intended to guide the eye.

A similar plot of visible Ni atoms as a function of Ni coverage will give some insight about the overlayer formation. In Figure 6.3 we plot the number of Ni

atoms visible to the incident ion beam in the normal channeling direction as a function of Ni coverage, where the Ni coverage is measured in the random direction. The solid line in Figure 6.3 shows the Ni yield measured in the random direction. Evidence of Ni

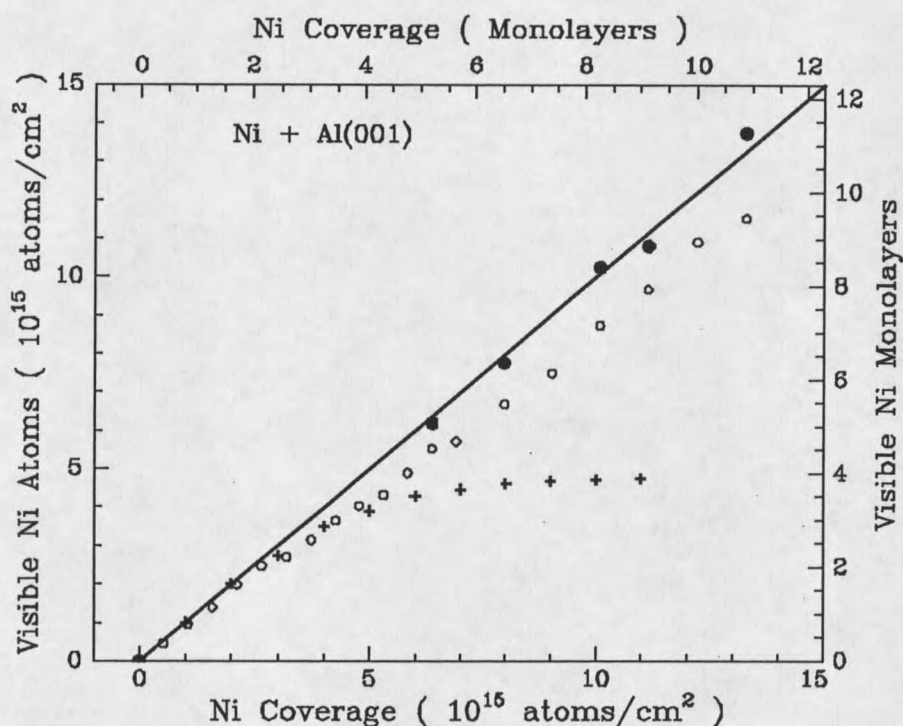


Figure 6.3 Number of Ni atoms visible to the 0.97 MeV He^+ ion beam as a function of Ni coverage. Solid circles are for a random direction while open circles are for the channeling direction. The solid line is the least-squares fit to the random data. The '+'s indicate the yield expected for a layer-by-layer growth of a *bcc* Ni film as calculated using the VEGAS simulation code.

shadowing is observed for coverages greater than 2 ML, where the Ni yield in the aligned direction falls below that measured in a random direction.

In Figure 6.4 we plot the Al surface peak position as a function of Ni coverage. For the first two monolayers of Ni deposition, the Al surface peak position stays almost constant. Upon completion of the second layer of Ni, the surface peak position of Al starts shifting gradually towards lower energies in the spectrum.

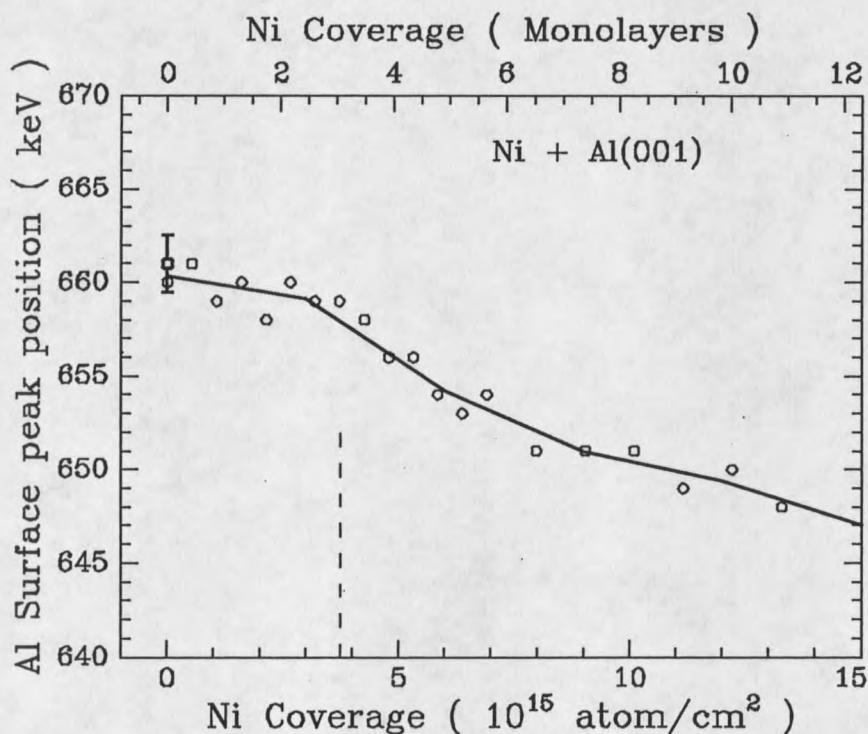


Figure 6.4 Surface peak position of Al as a function of Ni coverage. The error bar represents the uncertainty in the measurements.

X-ray photoelectron spectroscopy

As we discussed in Chapter 5, the chemical shifts, satellite shifts, and shape of the satellite and main 2p photo peak of Ni were used to identify the different Ni-Al phases formed at the interface in our Al(110) experiments. So we have used a similar approach to identify the phases formed at the Ni/Al(001) interface.

Figure 6.5 shows the x-ray photoelectron energy distribution curves for the Ni 2p_{3/2} peak (852.65 eV) and the satellite peak for several Ni depositions on the Al(001) surface. Two coverages were selected from each of the three different regions displayed in Figure 6.2. The dash-dash line shows the photopeak position for metallic Ni. All the peaks shown in figure 6.5 are normalized to give a constant height.

In Figure 6.6, we plot the average chemical shift of the Ni 2p line (left axis) and the satellite separation between the main Ni 2p_{3/2} photopeak and the satellite peak (right axis) for different Ni depositions. Here, the chemical shift is calculated as discussed in Chapter 5. Initially, the chemical shift stays constant around 0.3 eV up to 2 ML of Ni coverage. After this, the chemical shift gradually decreases to zero at a coverage corresponding to approximately 5 ML, and stays at this value up to the maximum coverage of our experiment. The variation in the satellite separation as a function of Ni coverage shows the same trend as observed for the chemical shift.

Figure 6.7 shows the normalized XPS intensities of the Al 2p peak and the Ni 2p_{3/2} peak as a function of Ni coverage. The XPS intensities were extracted from the area under the peaks. The Shirley background subtraction method⁶⁰ was used to

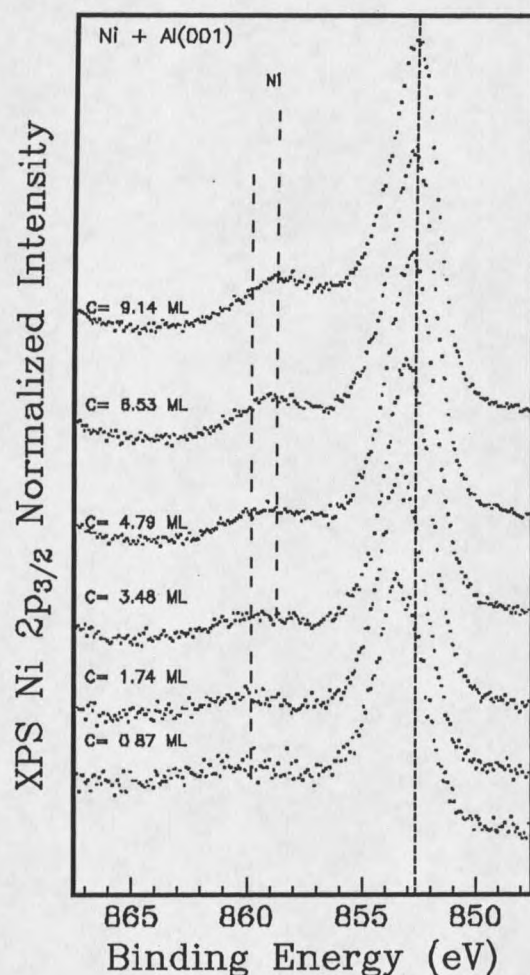


Figure 6.5 $\text{Ni } 2p_{3/2}$ XPS spectra from Ni films deposited at room temperature on the Al(001) surface for selected Ni coverages, normalized to a constant height for the main peak. Satellite peak positions for different Ni-Al phases are indicated by dashed lines.

remove the background under the photopeak. The Al intensity is normalized to the intensity of the clean surface, while the Ni intensity is normalized to its value at the maximum coverage in our experiment. The solid lines are intended to guide the eye.

The intensity (Figure 6.7 a) of the Al 2p photoelectrons decreases to about 20% of the original value after the deposition of 1 ML of Ni. The intensity further attenuates with

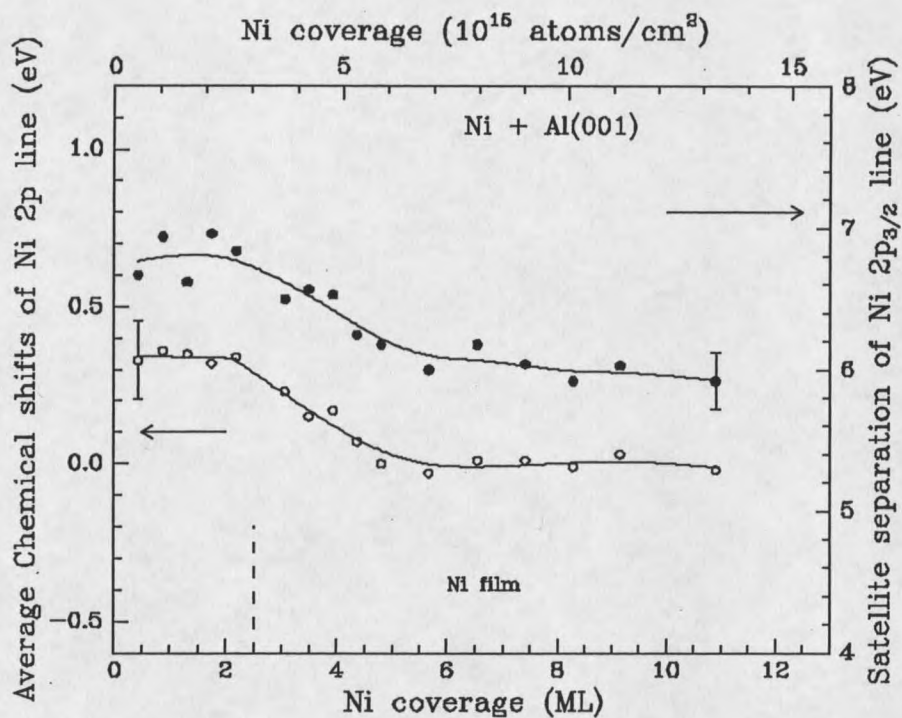


Figure 6.6 The average chemical shift of the Ni 2p line (left axis -open circles) and satellite separation from the Ni 2p_{3/2} line (right axis -closed circles), plotted as a function of Ni coverage on the Al(001) surface at room temperature. Solid lines are intended to guide the eye.

a slower rate at higher Ni coverages, symbolizing a change in the character of the overlayer growth mode with additional Ni deposition. The intensity of the Ni 2p peak

(Figure 6.7 b) shows distinct changes in slope at two different Ni coverages. The first

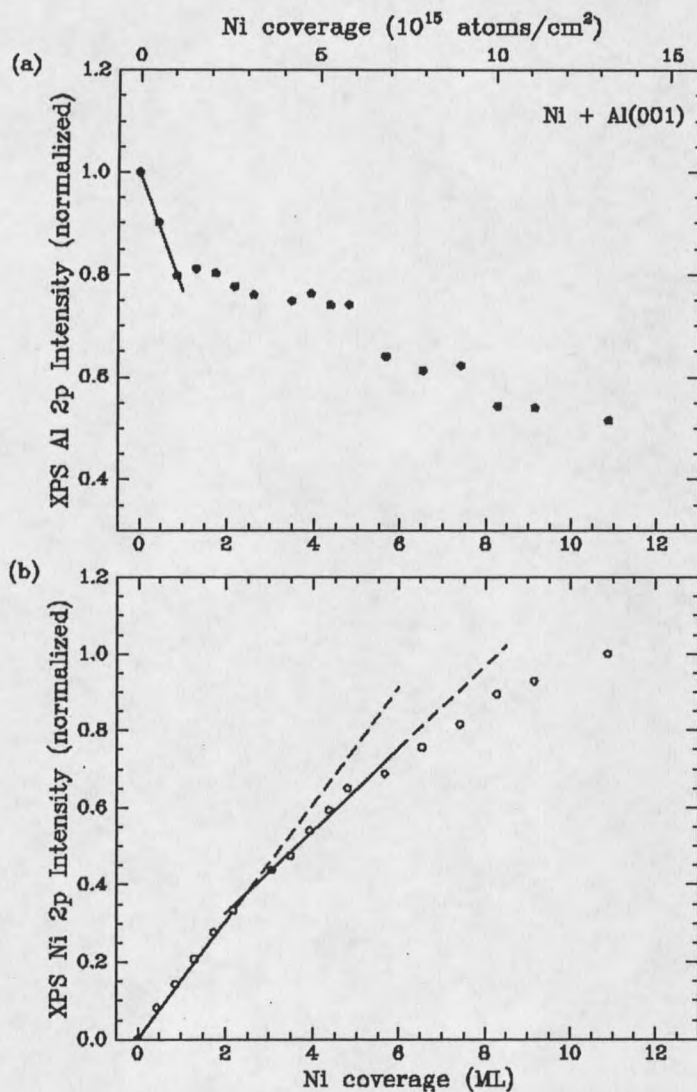


Figure 6.7 Measured XPS intensity of (a) Al 2p and (b) Ni 2p_{3/2} photopeaks as a function of Ni coverage. The Ni2p_{3/2} intensity has been normalized to its value at the maximum coverage of our experiment (11 ML). The Al 2p intensity is normalized to the value for the clean surface. Solid lines are intended to guide the eye.

change occurs at a Ni coverage of 2 ML, while the second break occurs at around 6 ML of coverage.

Photoelectron Diffraction

The structure and the uniformity of the Ni layers can be examined using XPD. Before depositing Ni onto the Al surface, photopeak intensities along a particular azimuthal plane as a function of a polar angle were measured for the clean Al surface. In Figure 6.8 a and b we show the XPD polar scans for the Al 2p signal for two different polar planes, (010) and (110), respectively. Each data point shown in these figures consists of an integrated peak area after a Shirley background subtraction. As we discussed earlier, the peak intensities are enhanced in the major low index directions of the crystal. In Figure 6.8 a the Al 2p polar scan in the (010) azimuth shows a forward-scattering peak at 0° due to next-nearest neighbor Al atoms and a weaker one at 45° due to nearest neighbor Al atoms. In other words, these enhancements in the intensity profile are associated with the central diffraction peaks along the [001] and [101] directions, respectively. In addition to these peaks, broader characteristic peaks near 18.4° are also present in the figure. They are due to a combination of first order diffraction associated with the [001] and [101] directions, and the central diffraction peaks along the [103] direction. Similarly, an intensity scan in the (110) azimuthal plane exhibits a forward-scattering peak at 0° due to next-nearest neighbor Al atoms, along the [001] direction, and a weaker peak at 35.3° due to third-nearest neighbor Al atoms, along the [112]

direction.

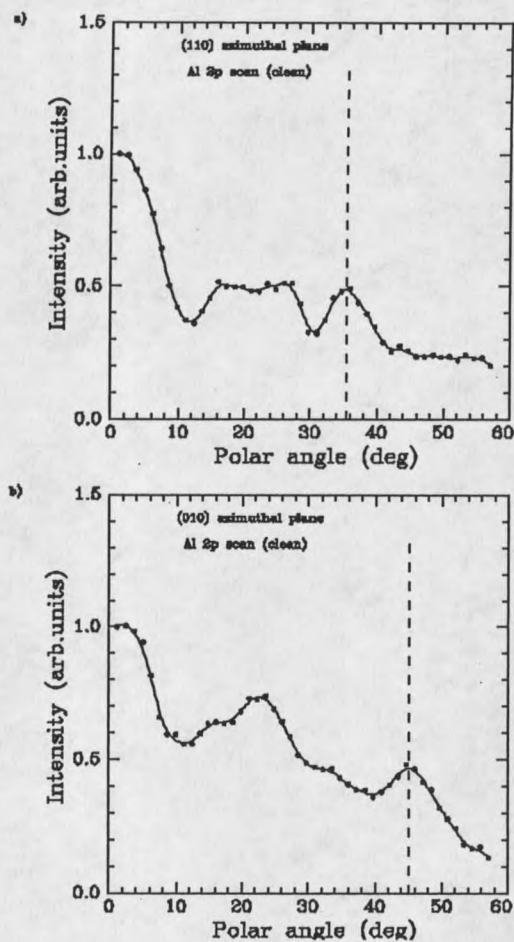


Figure 6.8 Al 2p polar XPD scans for a clean Al crystal in the (a) (110) azimuthal plane, and (b) (010) azimuthal plane. The solid lines are intended to guide the eye.

Photoelectron intensity angular distributions from the Al substrate and Ni films were measured for three different coverages of Ni. These three Ni coverage regimes, 1, 5, and 11 ML of Ni, were selected from the three different regions indicated

in the ion scattering results (Figure 6.2). Figure 6.9 shows the Ni 3p photopeak polar scan for 1 ML, 5 ML, and 11 ML of Ni along the (110) azimuthal plane. For

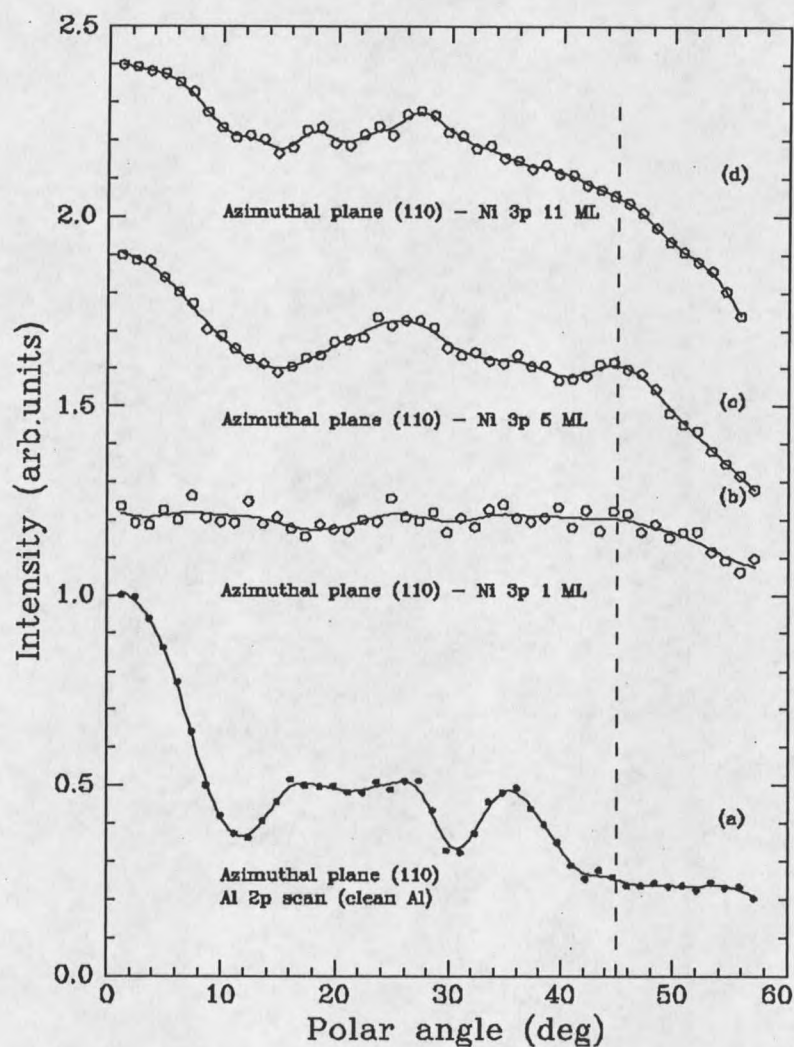


Figure 6.9 Ni 3p polar XPD scans for several coverages of Ni in the (110) azimuthal plane as compared to the clean Al polar scan. (a) clean Al, (b) 1 ML of Ni, (c) 5 ML of Ni, (d) 11 ML of Ni.

comparison, the clean Al 2p photopeak polar scan along the same azimuth is also shown. For 1 ML Ni coverage, the Ni 3p polar scan exhibits approximately isotropic or featureless behavior. In other words the angular intensity distribution resembles the

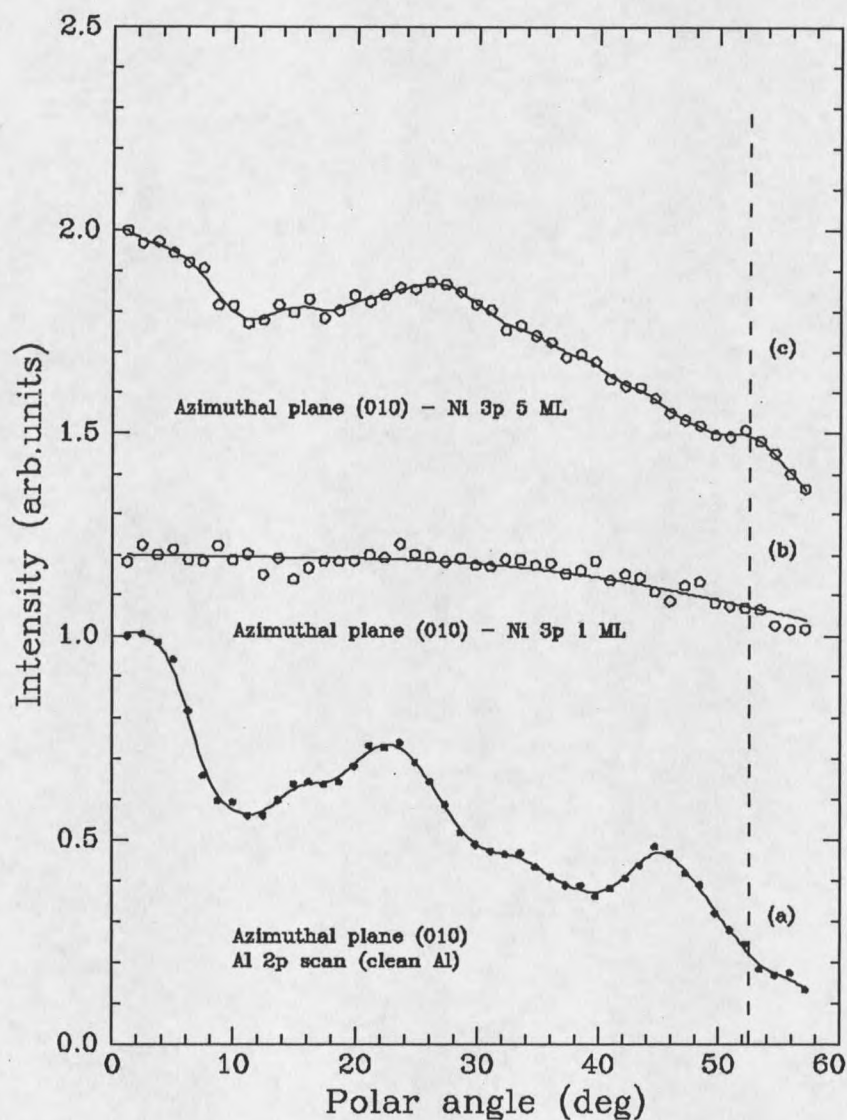


Figure 6.10 Ni 3p polar XPD scans for several coverages of Ni in the (010) azimuthal plane as compared to the clean Al polar scan. (a) clean Al, (b) 1 ML of Ni, (c) 5 ML of Ni.

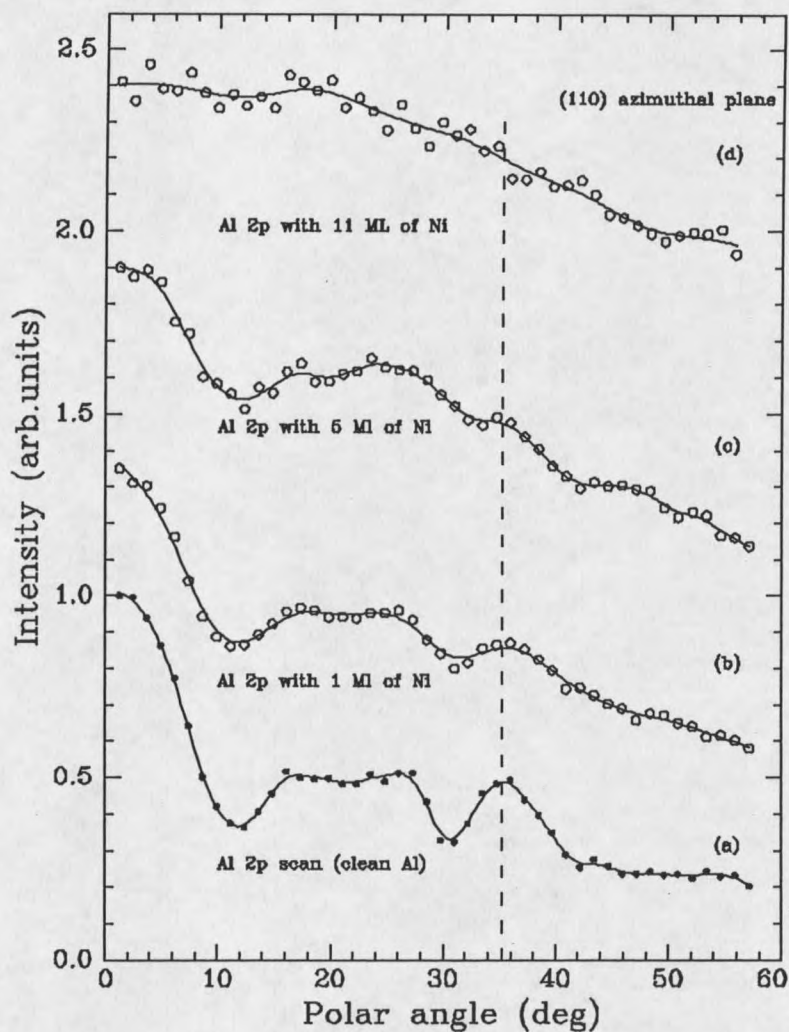


Figure 6.11 Al 2p polar XPD scans for several coverages of Ni in the (110) azimuthal plane compared to the clean Al polar scan. (a) clean Al, (b) 1 ML of Ni, (c) 5 ML of Ni, (d) 11 ML of Ni.

instrument response function. However, the Ni 3p polar scan for 5 ML Ni coverage clearly exhibits enhancements in the 0° and 45° polar angle and has a different profile

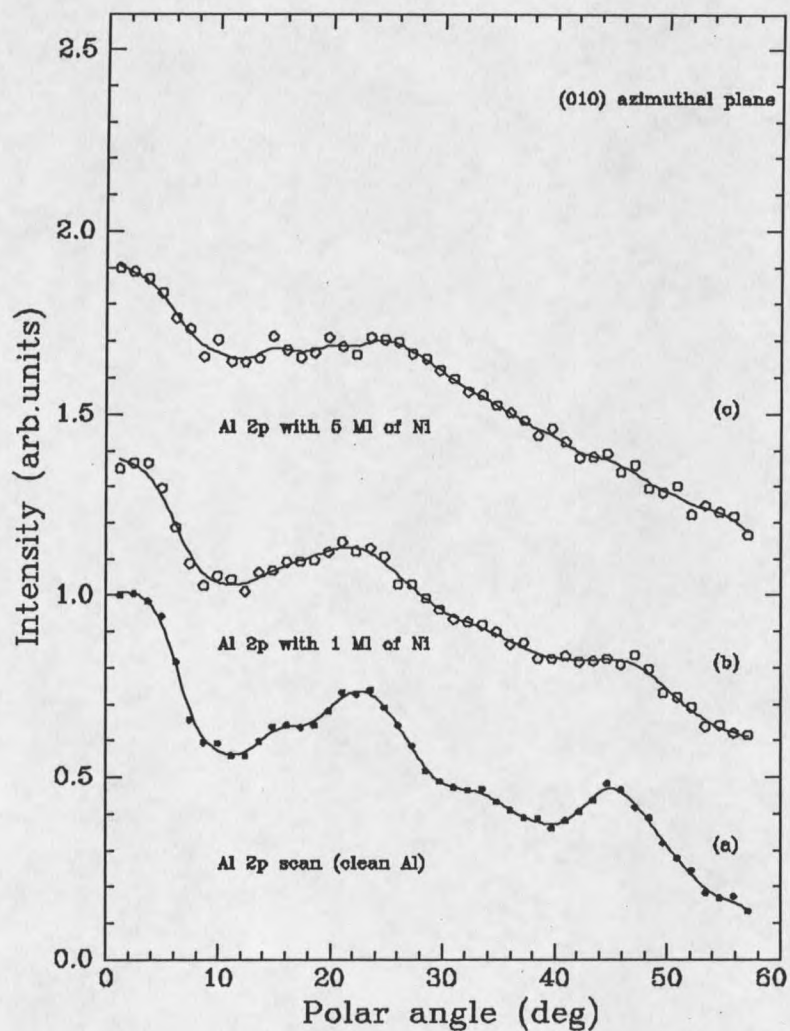


Figure 6.12 Al 2p polar XPD scans for several coverages of Ni in the (010) azimuthal plane compared to the clean Al polar scan. (a) clean Al, (b) 1 ML of Ni, (c) 5 ML of Ni.

than that for the Al 2p scan. The Ni 3p polar scan in the (010) azimuthal plane was also measured for these coverages and is illustrated in Figure 6.10. The clean Al 2p polar

scan in the (010) azimuthal plane is also shown in the figure for comparison purposes. The forward focusing peak at 0° is present in the 5 ML scan. A weak peak is observed at a polar angle of 54° . The different peak positions for Ni in this azimuthal scan indicate that a different atomic structure of Ni is forming on the Al surface. The 1 ML Ni scan in this azimuthal plane shows the same featureless behavior as for the (110) azimuth.

In Figure 6.11, we show the Al 2p polar scan in the (010) azimuthal plane for two different Ni coverages (1 ML and 5 ML). The XPD curve for the clean Al 2p is also shown in the figure as a reference spectrum. A forward-focusing peak at 0° is still present in both curves. For 1 ML Ni coverage the Al forward-focusing peak at 45° exhibits a weaker intensity while at 5 ML coverage this peak is nearly smeared out. Similar behavior is observed in the other azimuthal (110) scan of the Al 2p intensities for different coverages of Ni, and is shown in Figure 6.12.

Discussion

As shown in Figure 6.2, there seem to be three distinct growth regimes for these Ni films on the Al(001) surface, corresponding to three different intervals of Ni coverage. The results of Figures 6.1 and 6.2 suggest that Ni atoms are displacing the Al atoms up to 1 ML of Ni coverage, making them more visible to the incident ion beam. After 1 ML of Ni coverage these figures further suggest that deposited Ni atoms start shadowing the Al atoms. This shadowing of Al atoms by the Ni atoms only continues for Ni coverages up to 2 ML. This behavior of the ion scattering results suggests that

there is some kind of epitaxy or order developing in this system despite substrate disruption. These observations are further supported by the photoelectron diffraction measurements. The Ni XPD curves for 1 ML coverage, shown in Figure 6.9 and 6.10 (second curve from bottom) for the (010) and (110) azimuths, have no structure other than the shape of the instrument response function. It is well understood that the mechanism of electron scattering in the range of energies studied here is dominated by forward-scattering enhancement⁶¹. Hence, the absence of any forward-scattering features is a clear indication that there is no ordered island formation in the first Ni layer, so that the monolayer is relatively flat. The data also rule out significant indiffusion for the first Ni monolayer. The strong initial attenuation of the Al 2p photopeak intensity at 1 ML Ni coverage, shown in Figure 6.7, supports a model of flat Ni film growth.

The flat Ni monolayer can occupy at least two inequivalent sites on the Al substrate. That is, the first layer of Ni atoms can occupy the hollow sites or go instead on top of the Al sites (first substrate layer). Since the Ni diffraction signal is featureless at this coverage, we cannot distinguish between these sites from the overlayer signal alone. However, we used EAM total energy calculations to study the interface registry of the first layer Ni atoms¹⁷. As we discussed from Chapter 4, the total energy of the crystal can be obtained using the EAM potentials. The total energy of the crystal, which contains an Al(001) slab with 1152 atoms and a single Ni atom for the two possible cases of Ni sites (hollow and top), was calculated as a function of the Ni atom height above the Al surface. It should be noted that the total energy calculation was done for an unevolved crystal. The results of these calculations are presented in Figure 6.13,

where the total energy of the crystal is plotted for different heights of the Ni atom. The open circles are the total energy of the crystal with a Ni atom above the hollow site, whereas the solid circles represent the case where the Ni atom is on top sites. The solid and dashed lines are used to guide the eye. Clearly, both curves show a minimum in energy for a particular height of Ni atom. The hollow site calculation shows a minimum at 1.37 Å while the top site calculation shows a minimum around 2.27 Å. Clearly, the hollow site Ni at this minimum height will have a lower energy than the top site Ni atom. That is, the Ni atom occupying the hollow site will be more stable than the top site Ni atom. From this we conclude that the Ni atom prefers to stay in the hollow site rather than in the top site.

We can further justify our overlayer model by using lattice matching arguments for the Al(001) surface and the NiAl alloy crystal structure. That is, because NiAl has the highest heat of formation and is the most stable phase in the Ni-Al bulk phase diagram¹⁴, we might expect it to form first. The ordered NiAl has the CsCl (bcc) structure with Al atoms being in the corner of the cube and the Ni atoms being at the body center of the cube⁴⁰. The cubic lattice constant of NiAl is equal to 2.88 Å. Furthermore, the size of the two-dimensional surface mesh of Al(001) is close to that of bulk bcc NiAl, if the NiAl crystal is rotated by 45° so that the fcc [010] is parallel to the bcc [110] direction. Hence, placing Ni atoms above the hollow sites of the Al surface, with the height equal to 1.432 Å, forms the first two layers of the NiAl ordered crystal structure. However, this structure cannot continue after the first monolayer, since the third layer in ordered NiAl consists only of Al atoms. In order to have this structure Ni

and Al atoms should intermix extensively. This would lead to an increase in the Al ion scattering yield after 1 ML of Ni deposition. But, from Figures 6.1 and 6.2, it is clear that the ion scattering yield of Al atoms decreases after the first monolayer of Ni

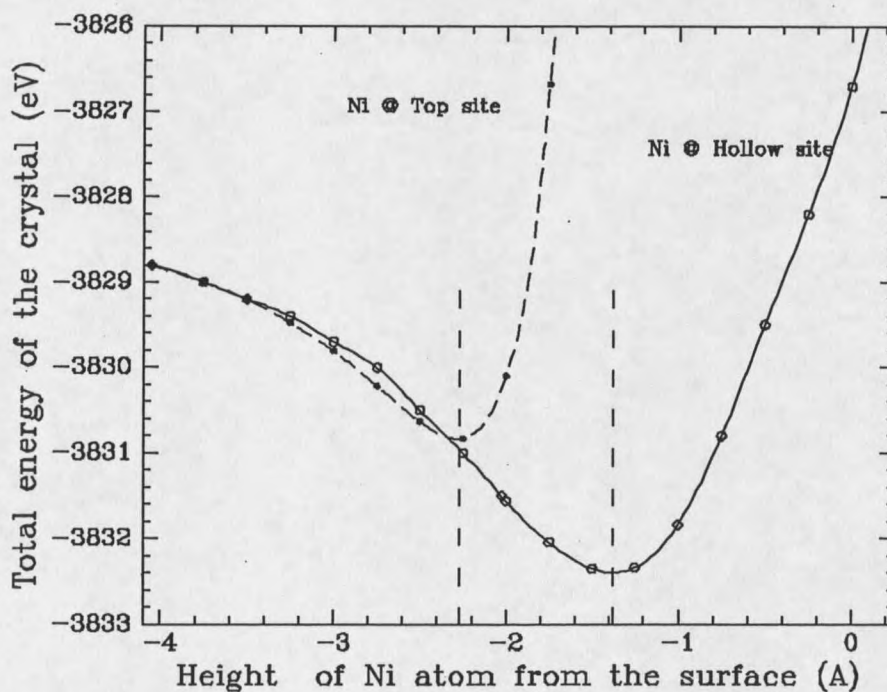


Figure 6.13 Total energy of the Al(001) slab with 1 Ni atom calculated using EAM potentials as a function of the height of the Ni atom from the surface for two different occupation sites of Ni. Open circles are for a Ni atom above the hollow site while solid circles represent a Ni atom at a top site.

deposition. This observation suggests that the Ni atoms in the second layer are shadowing the Al atoms underneath and that this layer is also relatively flat. The growth of the second flat Ni layer can be explained by a formation of the *body-centered cubic (bcc) Ni structure*. We will discuss this later in this section.

If the Ni atoms occupy the hollow atomic sites directly above the Al atoms as we discussed above, then it should be possible to observe a decrease of the Al ion scattering yield when the incident ion beam is in the normal direction. If on the other hand, the positions of the Ni atoms parallel to the surface are off by a fraction of an Angstrom, it would be enough to unshadow the Al atoms⁴⁴, resulting in no change in the Al ion yield. However as shown in Figures 6.1 and 6.2, neither a decrease nor a saturation of the Al ion yield is observed; instead, an *increase* in the ion yield is observed. This increase is partially due to the displacements of the Al atoms at the interface by the Ni atoms. Furthermore, the *near surface dechanneling effect* may also cause the ion scattering yield to increase. That is, the presence of relatively heavy Ni atoms near the surface leads to significant deflection of some of the incident ions, and as a result their probability of collision with the underlying atoms increases. This behavior of *near surface dechanneling* is also observed in the Ni/Al(110) system (Chapter 5).

Even if the structure of the first layer of the Al substrate is somewhat disturbed by the deposition of a ML of Ni, some order still persists. This can be seen from the XPD patterns obtained from the Al substrate for the (010) and (110) azimuthal planes which are illustrated in Figure 6.11 b and 6.12 b. In both figures, Al XPD patterns exhibit the same features as those of the clean scans except for a reduction of the overall

intensity. The peaks at 45° in the (010) azimuth and 35.3° in the (110) azimuth are slightly smeared out, indicating a loss of ordering in the first layer. This kind of growth

Top view of Al(001)

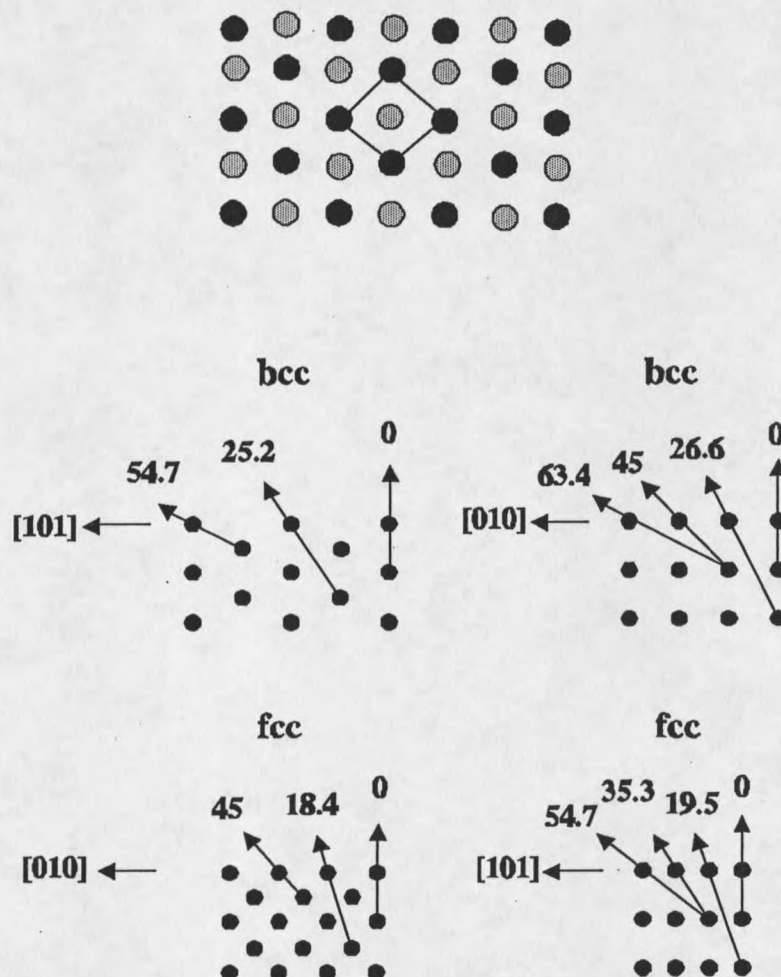


Figure 6.14 Expected forward focusing peaks in the polar scan of *bcc* and *fcc* structures for different azimuthal planes (bottom) and the top view of the Al(001) surface mesh. Solid circles represent the top layer atoms while the shaded circles denotes the second layer atoms.

mode was also observed for thin Al films deposited on the GaAs(001) surface⁶².

As we discussed earlier, the structure of the Ni overlayer after 1 ML of Ni deposition is attributed to the *body-centered cubic* Ni structure based on the Ni XPD scans measured at 5 ML of Ni coverage. The room temperature equilibrium phase of Ni is *fcc*¹⁴. It can be transformed into a *bcc* structure by expanding the axes parallel to the (001) surface, while simultaneously contracting the interlayer spacing along the surface normal direction [001]. To carry out this transformation, we take advantage of the fact that the *bcc* lattice has a smaller interlayer spacing than the *fcc* structure. The transformation of *fcc* Ni into *bcc* Ni can be explained by the hard-sphere model, in which Ni in the *bcc* phase maintains a constant atomic radius, while expanding or contracting its lattice parameters⁶³. From this model we obtain a lattice constant of 2.877 Å for the *bcc* Ni.

There have been several studies of this kind of behavior reported for various metal on metal systems. For example *bcc* Fe(001) thin films were grown on the *fcc* Ag(001) single crystal surface⁶³. There is a good lattice match between the Ag substrate bond length (2.889 Å) and the bulk Fe lattice constant (2.867 Å), if the two crystals are rotated by 45°. Zhang and co-workers⁶⁴ have shown recently that they grow metastable *bcc* Ni(001) and *bcc* Co(001) thin films on *bcc* Fe(001) single crystal surfaces at room temperature. They also pointed out that a small lattice mismatch is sufficient to prevent the growth of metastable phases. The above mentioned hard-sphere calculation of *bcc* Ni reveals that a good lattice match exists between the *bcc* Ni (2.877 Å) and the *bcc* Fe (2.867 Å). Since the Al(001) bond length (2.864 Å) is very close to the bulk

Fe(001) lattice constant ($2.867 \text{ \AA}$), it is reasonable to expect that we can also grow a metastable *bcc* Ni film on the *fcc* Al(001) surface. The only difference between the *bcc* Ni/*bcc* Fe(001) and *bcc* Ni/*fcc* Al(001) lies in the relative orientation of the overlayer and substrate axes parallel to the interface. In the case of *bcc* Ni/ *bcc* Fe, the growth is [001] parallel to the [001] direction in the substrate, while for the *bcc* Ni/ *fcc* Al case it is [110] parallel to the [001] direction in the substrate.

From the results of the polar XPD scans of the Ni 3p core level, for 5 ML of Ni coverage, presented in Figure 6.9 c and 6. 10 c, it is immediately evident that nickel grows in the *bcc* structure with the *bcc* [110] direction parallel to the *fcc* [010] direction. To see this, first consider the forward focusing peaks of Ni in the Al substrate [110] azimuth shown in the Figure 6.9. If Ni atoms form an *fcc* film, according to Figure 6.14 forward focusing peaks should occur at angles of 0° , 19.5° , 35.3° , and 54.7° , as seen in the bottom polar scan curve in Figure 6.9 for clean Al. Instead, the major forward focusing features occur at 0° , 25° , and 45° , which is more consistent with the *bcc* structure. Similarly, the polar scan obtained along the Al(001) [010] azimuth shows forward focusing enhancements at 0° , 25° , and 53° corresponding to the *bcc* directions shown in the Figure 6.14. If on the other hand, Ni forms an *fcc* structure, the forward focusing peaks due to this film will occur at 0° , 18.5° , and 45° , as shown by the clean XPD Al in this azimuth (Figure 6.10 a). Thus, looking at the XPD polar scans in different azimuthal planes, one can easily distinguish between the *bcc* structure and the *fcc* structure. From the identification of the Ni peaks, we conclude that the 5 ML Ni film adopts the *bcc* structure. If on the other hand the Ni deposition results in either a

polycrystalline or a highly disordered film, then the XPD pattern should be isotropic or featureless.

The weak intensities of the 45° and 55° peaks from the Ni film can be attributed to the measurement geometry in our system at grazing emission angles. There are two possible scenarios for these weaker peaks. As discussed in Chapter 1, the number of photoelectrons that can escape from a solid without losing energy decreases with depth x , as $\exp\{-x/(\lambda \cos\theta)\}$, where λ is the inelastic mean free path, and θ is the emission angle. Due to this exponential decay approximately 63% of the photoelectrons contributing to the intensity must originate within a distance of $\lambda \cos\theta$ of the surface. This quantity will serve as a measure of sampling depth. Hence, the sampling depth in XPS is a function of the emission angle, θ , of the photoelectrons, and varies as $\cos\theta$. For example, a spectrum recorded at normal incidence would have three times the sampling depth, hence intensity, of a spectra recorded at 70° to the surface normal. Therefore, from this argument, we can conclude that the photoelectron intensity will fall off as $\cos\theta$ with increasing angle of emission.

In addition to this sampling depth dependence, the XPS intensity will also depend on the size of the incident x-ray spot. Unlike the sampling depth, the spot illuminated by X-rays in our geometry will increase markedly with increasing emission angle, and subsequently reduce the number of photoelectrons reaching the analyzer. This is because, for a constant x-ray flux from the source, and a constant analyzing area, the number of photoexcitations per unit area is reduced for a larger spot size. This dependence of the spot size on the emission angle may cause the intensity to vary as $\cos$

θ . To correct for these factors a background proportional to $\cos\theta$ is divided out from the original XPD spectrum. The results are illustrated in Figure 6.15 where we compare the background corrected XPD curves from the Ni films (top) to the uncorrected XPD curve (bottom) for both azimuthal planes. In the top curves we can now clearly see the 45° and 54° peaks.

Even after the background correction the 54° peak is still weaker than other forward focusing peaks. This low intensity of the peak may be due to a lack of structural perfection in the overlayer, and or island or cluster formation of Ni in the overlayer film. Theoretical calculations carried out by Tong et al.⁶⁵, and experimental studies carried out by Egelhoff et al.⁶⁶ have indicated that due to multiple scattering effects, the enhancement of the XPD peaks is strongest when just a few atoms are in front of the emitter atom. If there are too many atoms present, then the enhancement is strongly reduced⁶⁴. This may very well be the case in our observation of weaker peaks, since ordered islands or clusters will have a larger thickness than the flat film.

In addition to these XPD results, the ion scattering results also suggest that some order exists in the Ni film with respect to the substrate. This can be seen in Figure 6.3, where the number of Ni atoms visible to the incident ion beam is plotted as a function of Ni coverage. As we can see from the figure, up to 2 ML of Ni coverage no Ni-Ni shadowing is observed. This also supports our earlier claim that the first two Ni layers are relatively flat. However, above 2 ML of Ni coverage more adsorption of Ni atoms leads to shadowing of the underlying Ni atoms. This means that some of the Ni atoms in the higher layers adopt the symmetry of the first two Ni layers and thus occupy

the next possible Ni sites.

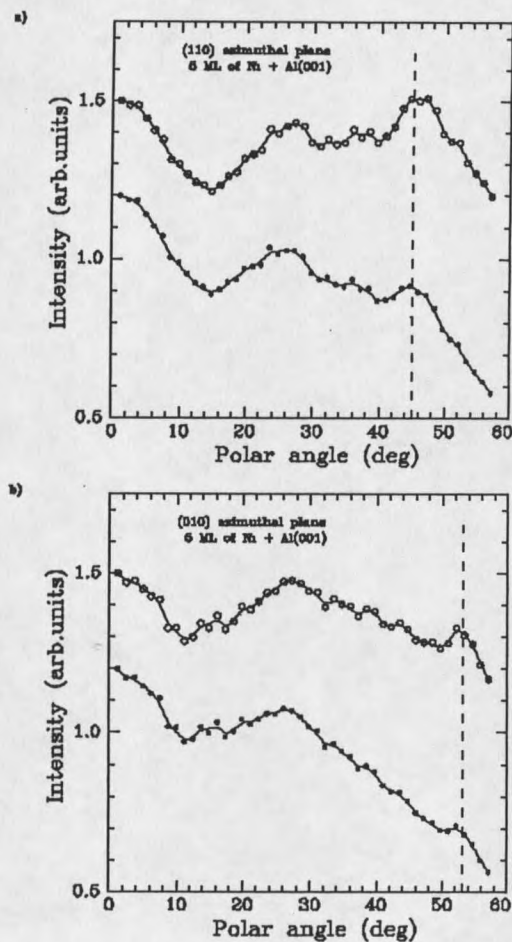


Figure 6.15 Background corrected Ni XPS polar scans in the (a) (110) azimuthal plane, and (b) (010) azimuthal plane. For comparison, uncorrected Ni XPS polar scans in the respective azimuths are also shown.

Formation of ordered Ni islands between 2 and 5 ML of Ni coverage is also supported by the following observations: saturation of the Al ion scattering yield

(Figure 6.2), less rapid attenuation of the Al 2p XPS intensity (Figure 6.7 a), and persistence of the Al 2p XPD forward focusing peaks (Figure 6.11 c and 6.12 c). Saturation of the substrate ion scattering yield, ie. zero slope in Figure 6.2, is the typical behavior corresponding to the island growth mode of an overlayer, as seen for example with Ag on Si⁴³. As we discussed earlier, the first layer Ni atoms are not occupying the atomic sites right above the Al atoms and at the same time Ni *bcc* islands are forming with respect to the first Ni layer. Hence, it is possible for the Al ion scattering yield to remain constant during this coverage regime, as seen in Figure 6.2. Furthermore, a flat overlayer film gives the greatest possible attenuation of the substrate XPS intensity. Any combination of layers and islands will give a lower attenuation than a flat film. Hence, the lower rate of attenuation of the Al 2p photopeak after 1 ML of Ni coverage, as seen in Figure 6.7 a, supports a model of island formation in the overlayer. Finally, the XPD results for the Al 2p polar scans also justify the model with island formation since the Al forward focusing peaks are still prominent in some of the forward focusing directions. However, the 45° peak in the (010) azimuth (Figure 6.11 c) and the 35.3° peak in the (110) azimuth are almost smeared out. Thus, on the basis of the above discussions we believe that up to 5 ML of Ni deposition, Ni grows as a metastable *bcc* structure on the Al(001) surface in a Stranski-Krastanov (SK) like morphology.

As seen from Figure 6.2, a structural change happens after 5 ML of Ni coverage. That is, the Al ion scattering yield gradually starts increasing. To model the Ni overlayer growth, we compared experimentally obtained values for the number of visible Ni atoms to the values obtained from a computer simulation of He⁺ ion scattering,

using the VEGAS code³¹. In these simulations Ni atoms were placed in a *bcc*(100) structure in a layer-by-layer growth fashion with the lattice constant equal to 2.877 Å. The vibration amplitude for Ni atoms was taken to be equal to 0.065 Å¹⁹. The results of this simulations are presented in Figure 6.3, where simulated Ni ion scattering yields are denoted by '+'s. Up to 4 ML of Ni coverage, the simulation and experiment agree reasonably well. But after 4 ML of Ni coverage, the experiment shows only a little shadowing, while the simulated Ni yield shows a substantial amount of shadowing. One growth model which explains these results consists of *bcc* Ni islands approximately 5 layer in height gradually covering the entire surface at a total coverage of 5 ML. Following the coalescence of the *bcc* Ni islands, Ni metal begins to cover the surface, presumably in a disordered structure. The small amount of shadowing still present in the Ni films indicates a degree of axial alignment with the Al substrate. In addition, the shift observed in the Al surface peak position to lower energies side after 5 ML of Ni coverage, as shown in Figure 6.4, also supports the model of coalescence followed by Ni overgrowth. The increase that we saw in the Al ion scattering yield after 5 ML (Figure 6.2) may be due to the *near surface dechanneling effect* associated with the disordered Ni film, or probably some outward diffusion of Al atoms into the Ni overlayer.

Polar XPD scans of Ni and Al in the (110) azimuth obtained at 11 ML of Ni coverage also confirm this coalescing of Ni islands after 5 ML. Figure 6.9 d shows that only the 0° and 25° peaks are present in the XPD scan of Ni while the peak at 45° is completely washed out. These observations indicate a loss of ordering in the film at least along some bond directions while some memory of the *bcc* structure is retained.

The Al polar scan in the same azimuth shows no features, as seen in Figure 6.11 d. This is due to the coalescing of Ni islands covering the surface and attenuating the Al photo-intensity more. As a final point, we show in Figure 6.5 and 6.6 the XPS binding energy, the satellite separation between the main peak and the satellite peak, and the line shape of the main peak and the satellite peak obtained as a function of Ni coverage. These results also support this whole growth scenario, consisting of a thin Ni-Al alloy at the interface, caused by Ni metal.

In summary, we have performed high-energy ion scattering, x-ray photoelectron diffraction, and x-ray photoelectron spectroscopy to characterize the evolution of the Ni/Al(001) interface at room temperature. Initially, up to 5 ML of Ni coverage, a Ni film grows as a metastable *bcc*(100) structure in a Stranski-Krastanov (SK) like growth mode. That is, first a flat overlayer forms, approximately 2 layers thick, and not necessarily commensurate with the substrate lattice. This is followed by island formation. After 5 ML of coverage, the *bcc* islands coalesce to cover the surface. These results are significantly different from the Ni/Al(110) results in which a strong Ni-Al reaction was observed.

CHAPTER 7

ULTRATHIN Pd FILMS ON Al(001) SURFACESIntroduction

The interaction of thin films of transition metals and aluminum has attracted wide attention in recent years, because of their potential use in technological applications^{5,6}. For example, the reaction, morphology, and growth mode of ultrathin Ti and Ni films on single crystal aluminum surfaces have been studied extensively to understand the role of the substrate structure in the evolution of the transition metal-aluminum interface^{3,67}. Saleh and coworkers³ have shown that ultrathin Ti films grow epitaxially on Al(110) and Al(001) surfaces up to 5 ML of Ti coverage. In the last two chapters, we presented our results of the growth of ultrathin Ni films on Al(110) and Al(001) surfaces. These results suggest that Ni films grow differently on these substrates at room temperature. Since Ni and Pd have similar bulk equilibrium phase diagrams with Al¹⁴, and at the same time they belong to the same group in the periodic table, we might expect the behavior of Pd films on Al single crystal surfaces to be similar to that for the Ni-Al system.

Using medium energy ion scattering studies, Smith and coworkers¹ have shown that a strong reaction occurs between Pd and Al when Pd thin films are deposited

on Al(111) surfaces. Their results suggest that an AlPd compound grows on the substrate with sufficient order to allow subsequent epitaxial growth of Pd(111) on the AlPd compound. In this chapter we will present and discuss our results for Pd deposition on the Al(001) surface using high energy ion scattering and x-ray photoelectron spectroscopy.

Experimental setup

The experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of 1×10^{-10} Torr. A detailed description of the equipment can be found in Chapter 3. The He ion energy used in HEIS measurements was around 1 MeV. The channeling measurements were made with the ion beam incident along the $[00\bar{1}]$ direction. As before, a scattering angle of 105° was used to collect the backscattered He ions. The XPS spectra were acquired using an Al K_α X-ray source and a hemispherical analyzer. The analyzer was operated in the fixed-analyzer-transmission (FAT) mode with a pass energy equal to 50 eV. All XPS binding energies presented in this work are referenced to the binding energy of the clean Al 2p core level. Initially, the Al single crystal was cleaned using the methods described in Chapter 3. The typical cleaning procedure in vacuum involved successive cycles of argon ion sputtering with 1.5 keV ions and annealing to 450°C . Surface cleanliness was verified by XPS and HEIS. Palladium was vapor-deposited on the Al(001) surface from a resistively heated Pd wire. No increase of sample temperature was observed during evaporation. As we discussed in Chapter 3, the Pd coverages were determined by HEIS measurements. After each Pd

deposition, HEIS and XPS experiments were performed. In the HEIS experiment the surface peak areas for ions scattered from Al and Pd atoms were monitored. In the XPS measurements, Al 2p and Pd 3d core level spectra were collected in the same manner as described in Chapter 3.

Results

High energy ion scattering

In Figure 7.1 we show the energy distribution of the scattered ions in the regions of the Al and Pd surface peaks for several Pd coverages. Each curve in Figure 7.1 is identified by the Pd coverage. One monolayer here is equivalent to the atomic density of the Al(001) plane, 1.219×10^{15} atoms/cm². The arrows and the dashed lines in the figure indicate the energetic positions of the surface Al and Pd atoms. It can be easily seen from the figure that the surface peak for Al increases with increasing Pd coverage.

In Figure 7.2 we plot the number of Al atoms visible to the incident ion beam as a function of Pd coverage. As we showed in Chapter 5, such plots are very informative to develop models for reacted interfaces. There are two main regions to note here. First, the Al surface peak area exhibits a linear increase with a slope of 1 up to 5 ML of Pd coverage. After this coverage, there is an apparent saturation stage during which the Al surface peak area remains unchanged. A similar plot of number of Pd

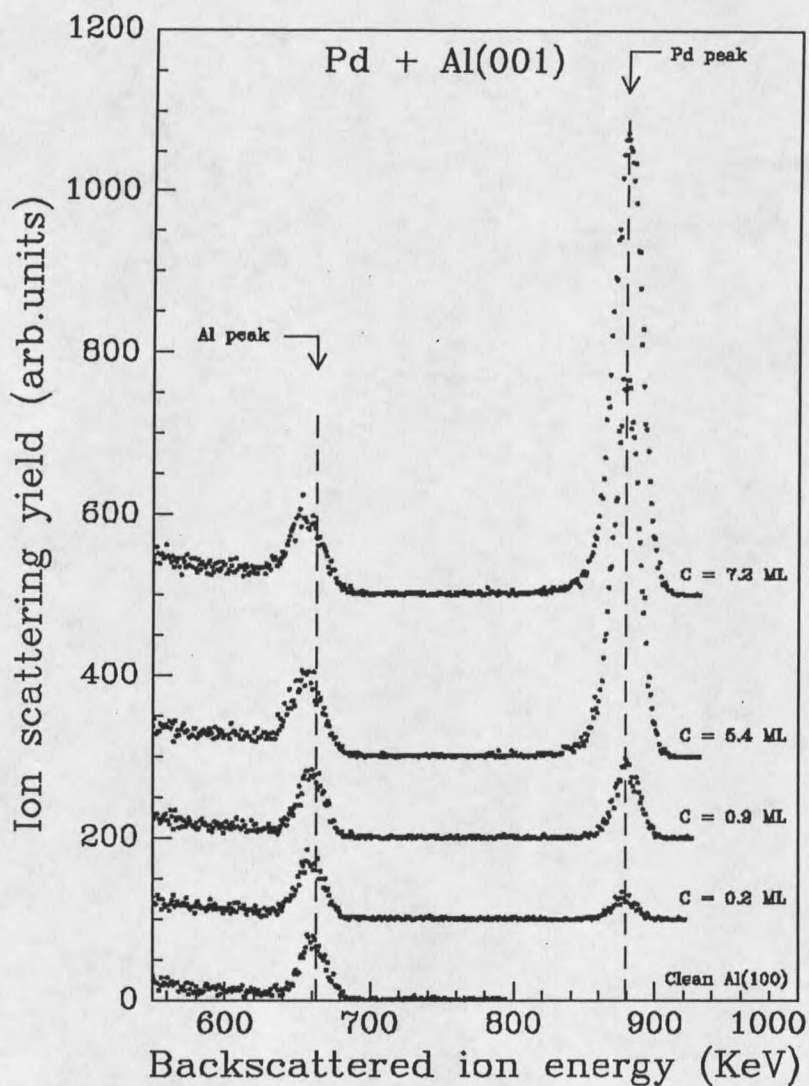


Figure 7.1 Ion scattering/channeling spectra for 1 MeV He^+ ions on Pd+Al(001) for different Pd coverages indicated in the figure. The energetic positions of the Al and Pd surface peaks are indicated by the arrows and the dashed lines.

atoms visible to the incident ion beam in the normal channeling direction as a function

of Pd coverage is shown in Figure 7.3. The actual Pd coverage is measured with the ion beam incident in a random direction. The solid circles in Figure 7.3 show the Pd yields

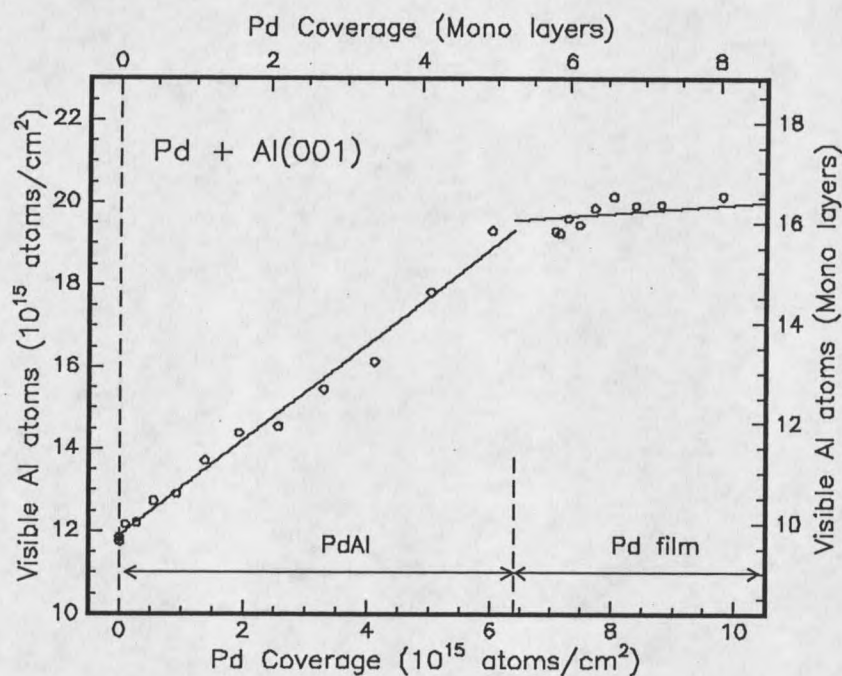


Figure 7.2 Number of Al atoms visible to the ion beam as a function of Pd coverage on the Al(001) surface. The solid lines are the least-squares fit to the data points in two regions. Two different stages of film growth are indicated.

in the random direction. A small, but measurable amount of Pd-Pd shadowing is observed for coverages greater than 2 ML, as seen by the reduction in the Pd yield

obtained in the normal direction compared to that obtained in the random direction.

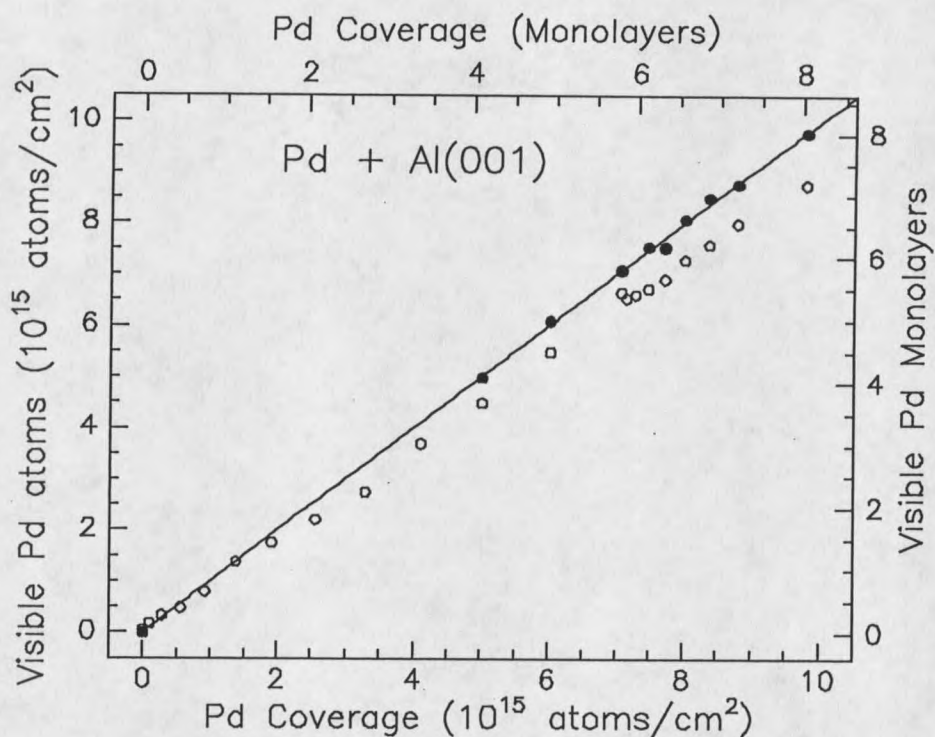


Figure 7.3 Number of Pd atoms visible to the 1 MeV He^+ ion beam as a function of Pd coverage. The solid circles are for a random direction while open circles are for the channeling direction. The solid line is the least-squares fit to the random data.

X-ray photoelectron spectroscopy

Figure 7.4 is a plot of the background-subtracted x-ray photoelectron

energy distribution curves for the Pd $3d_{5/2}$ (binding energy 335.08 eV) and Pd $3d_{3/2}$ peaks for three different coverages of Pd on Al(001). The solid curves through the data are the results from the peak shape analyses discussed later in this section. The arrows in the figure indicate the photopeak positions for the AlPd compound and Pd metal phases. It is seen in Figure 7.4 that the line shape of the Pd peak changes as Pd coverage increases.

Discussion

The results of Figure 7.1 and 7.2 suggest that more and more Al atoms become visible to the incident ion beam as the Pd coverage increases up to 5 ML. This shows that Pd atoms are reacting with Al atoms on the Al(001) surface to form a surface compound. In a conventional interpretation of the results in Figure 7.2, the slopes for ion scattering yields versus Pd coverage are used to determine the average stoichiometry of the reacting interface. In this case, a slope of 1:1 in region one would indicate that we are forming an AlPd compound. But this interpretation is not always true as we illustrated in the Ni on Al(110) case, where *near surface dechanneling* will change the slope. However, based on the XPS results discussed below, we conclude that an AlPd surface compound is formed up to 5 ML of Pd coverage. So, at least in this case, both the HEIS results and the XPS results are agreeing well. In previous studies of Pd on Al(111) Smith and coworkers also reported that the AlPd compound is the initial reaction product on that surface¹.

After 5 ML of Pd coverage, deposited Pd atoms are not effectively

displacing the Al atoms as seen from the zero slope of Al yield vs Pd coverage in region two of Figure 7.2. This means that after this coverage the reaction seems to stop and a Pd metal film begins to cover the surface. The small amount of Pd-Pd shadowing observed in Figure 7.3 suggests that the reacted overlayer as well as the Pd metal film have some degree of axial alignment with respect to the Al substrate.

By performing a detailed peak shape analysis of the Pd 3d XPS photopeaks shown in Figure 7.4, we can identify the compound growing at the Pd-Al interface. As we can see from this figure, the Pd peak shape changes with Pd coverage. At low Pd coverages, the Pd 3d_{5/2} and Pd 3d_{3/2} peaks are centered around 336.75 eV and 342.05 eV, respectively (bottom curve in Figure 7.4). The peaks show a small shoulder toward higher binding energy. However, at larger Pd coverages, the spectra display peaks at 335.08 eV and 340.28 eV respectively (top curve in Figure 7.4). These shifts in the Pd peaks suggest that the photoelectrons originating from the Pd films are experiencing a different chemical environment in these two regimes. The main peak we saw in the lower coverage regime is attributed to the Pd photoelectrons originating from the reacted Pd-Al interfaces. The small shoulder that we saw in this figure is due to the imaging problem of our analyzer. That is, the area imaged by the analyzer lens with the aperture used in our system is slightly larger than the Al crystal so that a small portion of the sample holder is also seen by the analyzer. This means that the XPS Pd spectra consist of a small amount of Pd signal coming from the sample holder in addition to the signal originating from the sample. The Pd metal on the Mo sample holder appears to have little or no chemical shift relative to Pd metal, as seen from Figure 7.4.

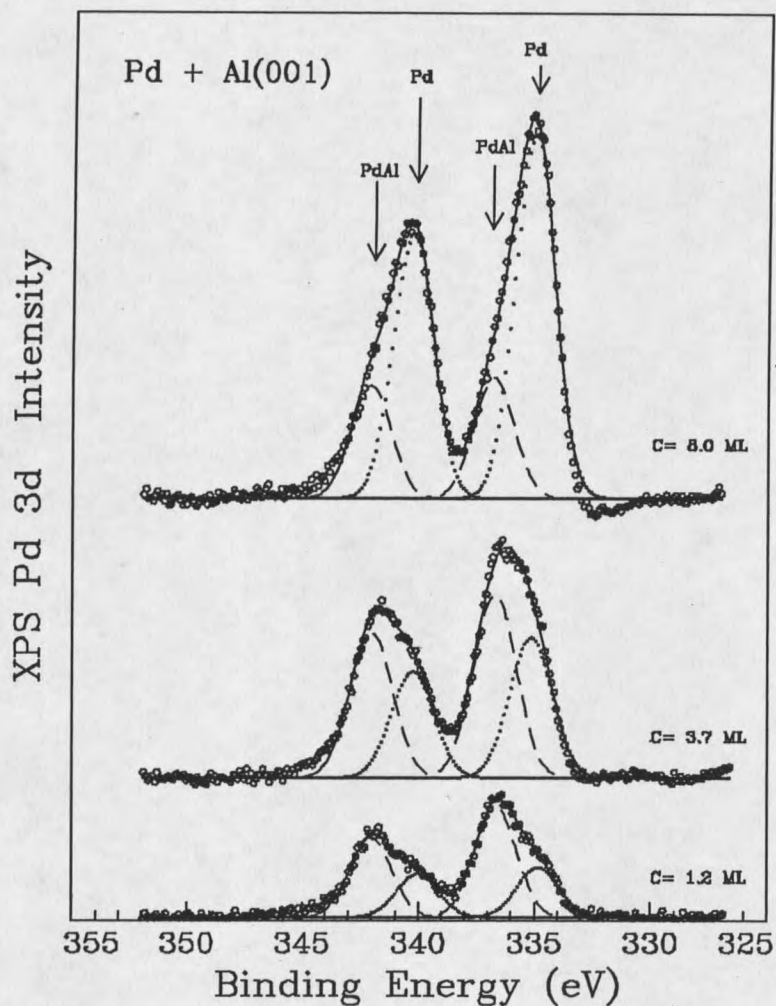


Figure 7.4 Pd 3d XPS spectra from Pd films deposited at room temperature on the Al(001) surface for three different Pd coverages. The solid curves are the results of the XPS peak fittings. The dashed lines represents the Pd photoelectrons originating from the reacted AlPd compound while the dotted lines represents the Pd photoelectrons coming from the Pd metal. Peak positions expected for the AlPd compound and Pd metal are indicated by the arrows.

In order to eliminate this sample holder problem we have carried out a detailed peak-shape analysis of the Pd peaks. Initially, the cubic background method is used to remove the background under the original XPS curves. Then we fit these peaks with four different Gaussian line shapes, each with the same peak width. Two Gaussians were used to represent the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peaks from the Pd metal whereas the other two Gaussians represent the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peaks from the reacted Pd-Al. The amplitudes and the peak positions of the Gaussians were allowed to vary in the fitting routine. The dashed lines and the dotted lines in Figure 7.4 are the outcome of our XPS curve fitting.

The fitted curves shown in Figure 7.4 clearly indicate the Pd peak from the AlPd compound as well as the Pd peak from the Pd metal. Fuggle and coworkers have studied in detail the chemical shifts of the Pd 3d photopeaks in various Al-Pd alloys⁴⁵. They found that the Pd 3d peaks exhibit very large chemical shifts, on the order of 2 eV towards higher binding energies, in the Al-Pd alloys. Their results are summarized in Table V. The results obtained from our XPS curve fittings are also presented in Table V. From the table we see that our measured value of the chemical shift and the separation between the Pd $3d_{5/2}$ and $3d_{3/2}$ peaks are closely matching with Fuggle's values for the AlPd compound, but significantly different than those for Al_3Pd . That is, the chemical shift in the Pd peaks of the AlPd alloy in Fuggle's experiment is equal to 1.9 eV, while in our case it is equal to 1.73 eV. The small difference observed in these values may be associated with the different forms of samples used in these experiments. In Fuggle's experiment, the XPS spectra for pure bulk Pd-Al alloys

were measured while we collected XPS spectra for very thin films of the Pd-Al compound. Hence, the observation of a smaller chemical shift in our experiment is

TABLE V. Comparison of binding energies, chemical shift, and the peaks separation for the Pd $3d_{5/2}$ and $3d_{3/2}$ peaks in different Al-Pd alloys. The chemical shifts are averaged over both 3d lines for the purpose of comparing with Reference 45.

Fuggle's Experiment				
Compound	Binding Energy $3d_{5/2}$ (eV)	Binding Energy $3d_{3/2}$ (eV)	Chemical Shift (eV)	Separation between $3d_{5/2}$ - $3d_{3/2}$ (eV)
Pd metal	335.2	340.45	-	5.25
AlPd	337.05	342.35	1.9	5.30
Al ₃ Pd	337.70	342.90	2.5	5.20
Our Experiment...				
Pd	335.08	340.28	-	5.20
AlPd	336.75	342.05	1.73	5.30

attributed to the emission of photoelectrons from very thin reacted Pd-Al films. Thus, from these observations we conclude that an AlPd surface compound forms at the Pd-Al(001) interface.

In Figure 7.5 we plot the XPS intensities for the two fitted Pd $3d_{5/2}$ peaks as a function of Pd coverage. The emission intensities from the reacted Pd compound are denoted by the open circles while the Pd metal emission intensities are denoted by the

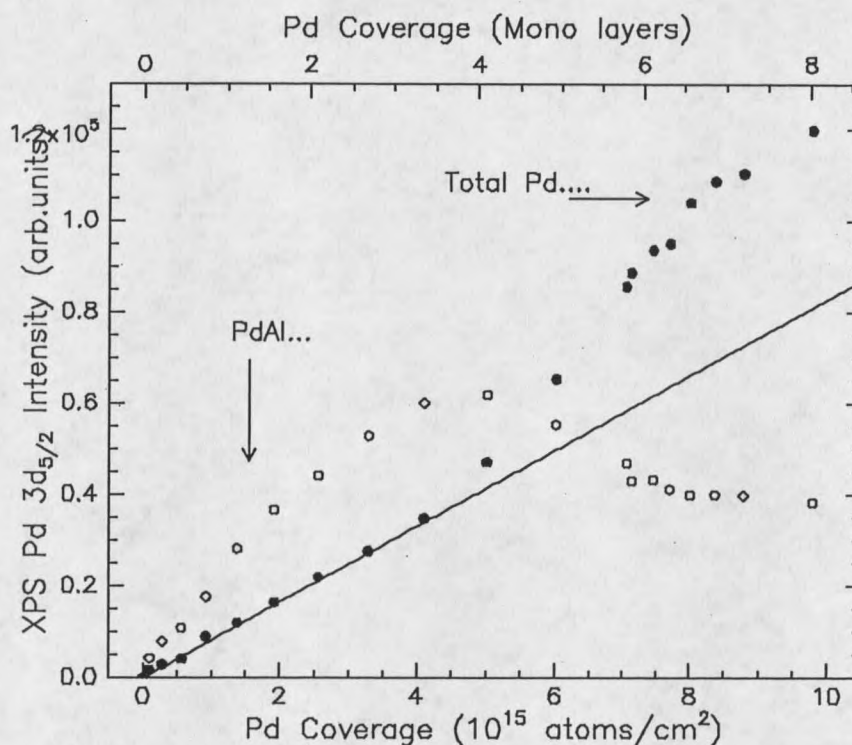


Figure 7.5 Measured XPS intensity from Pd $3d_{5/2}$ peak as a function of Pd coverage.

The open circles are the intensity of the Pd photoelectrons coming from the reacted AlPd compound. The solid circles are the intensity of the Pd metal photoelectrons originating from both the sample and the sample holder.

solid circles. Initially, the intensity from the reacted Pd compound increases smoothly with the Pd coverage up to 4 ML. Upon completion of 4 ML of Pd coverage, the

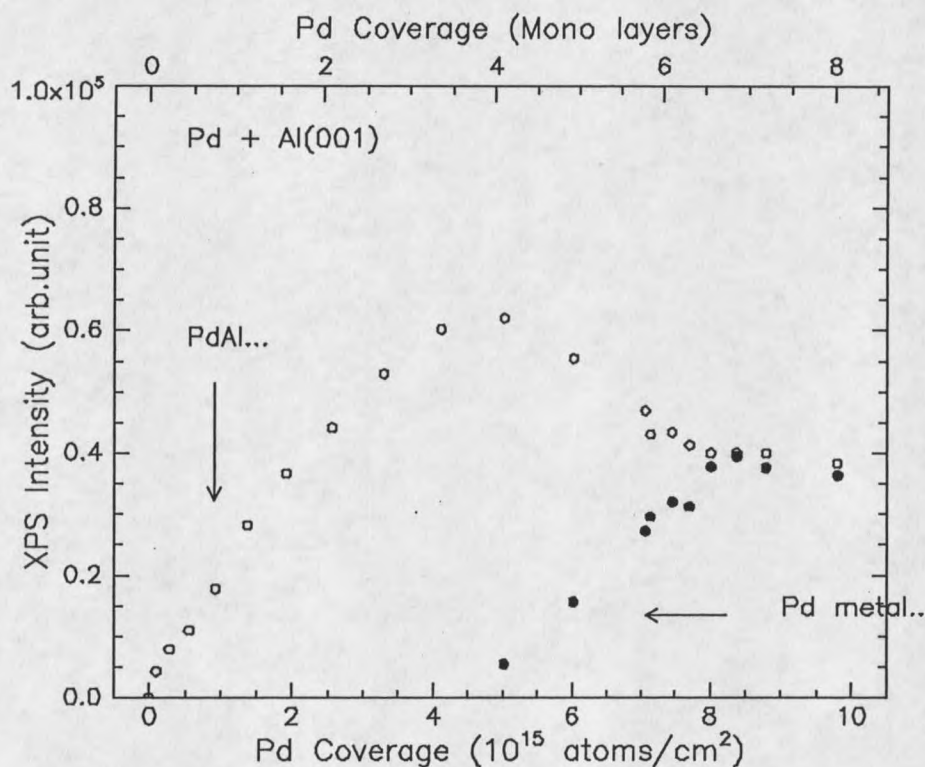


Figure 7.6 Measured XPS intensity from Pd $3d_{5/2}$ peak as a function of Pd coverage.

The open circles are the emission intensity of the Pd photoelectrons coming from the reacted AlPd compound. The solid circles are the emission intensity of the Pd metal photoelectrons originating *only* from the sample.

intensity started to attenuate slowly with increasing Pd coverage. On the other hand, the

intensity of the Pd metal emission increase linearly with Pd coverage up to 4 ML. After 4 ML of Pd coverage a jump in the Pd metal intensity is observed, and it increases at a faster rate with Pd coverage, as seen from Figure 7.5. From these intensity profiles, it is clear that at or around 4 ML of Pd coverage some structural transformation occurs in the Pd films. This can be explained as follows. The initial increase that we see in the Pd metal intensity up to 4 ML of Pd coverage is due to the Pd signal coming from the Pd metal on the sample holder. The increase observed in the reacted Pd compound intensity is coming completely from the sample. However, based on the ion scattering results, after 5 ML of Pd coverage we believe that the reaction between the Pd and Al atoms stops and a Pd metal film begins to grow on the reacted interface. This explains the sudden increase observed in the Pd metal XPS intensity as well as the attenuation observed in the reacted Pd compound XPS intensity. That is, the Pd metal film covering the reacted interface attenuates the Pd reacted compound signal, and at the same time it increases the Pd metal intensity at a faster rate since more Pd atoms are now imaged by the analyzer.

Even after 4 ML of Pd coverage we are still depositing a small amount of Pd metal onto the sample holder, which will also contribute to the total Pd metal intensity. To correct for this, we assumed that the Pd intensity coming from the sample holder is not saturated after 4 ML of Pd coverage, but is instead increasing linearly with the Pd coverage. This assumption seems valid because the Pd metal film is still very thin. Then we subtract this linear increase in the Pd intensity from the total Pd metal intensity. The results presented in Figure 7.6, show more clearly the onset of Pd metal

after 4 ML of Pd deposition. The subtraction process has no effect on the reacted Pd compound since this signal is only coming from the Al-Pd reacted interface. A similar behavior in intensity is observed for the Pd $3d_{3/2}$ peak. Hence, the XPS peak shape analysis supports the model suggested by the ion scattering results.

In summary, we have performed high-energy ion scattering and x-ray photoelectron experiments for thin Pd films deposited on the Al(001) surface at room temperature. Measured Al and Pd surface peak areas for MeV He^+ ions incident normal to the surface show that Pd atoms react with and displace Al substrate atoms. The reaction continues for Pd coverages from 0 to 5 ML, at which point a Pd metal film begins to grow on the surface. The XPS measurements of the Pd 3d photopeaks show a chemical shift that is consistent with the formation of an AlPd compound during the reaction phase and Pd metal thereafter.

CHAPTER 8

CONCLUSION

In this thesis work we have investigated the influence of the substrate orientation on the overlayer growth of ultrathin Ni and Pd films deposited on Al single crystal surfaces. Two different crystal surfaces of Al, the (110) and (001), were used for this purpose. In the studies of ultrathin Ni films on Al(110) surfaces using HEIS and XPS, we observed that the Ni atoms deposited at room temperature continuously displaced the Al atoms up to 8 ML of Ni coverage, indicating a reaction between the Ni and Al atoms. For the first 2 monolayers of deposited Ni, a NiAl -like compound is formed with the *surface dechanneling* effect present at the interface, while for Ni deposition between 2 and 8 ML, a Ni₃Al -like compound is formed. These results differ significantly from the thermally reacted Ni/Al systems where NiAl₃ is the initial reaction product observed. After 8 ML of Ni deposition, a Ni metal film starts to cover the reacted interface.

As discussed in Chapter 4, we developed a new approach to simulate the high energy ion scattering yields and x-ray photoelectron intensities from reacted crystal surfaces, using Monte Carlo numerical simulation methods. In the MC simulations we have used embedded-atom-method (EAM) potentials to calculate the total energy of the system. Simulations of the Ni-Al(110) interface also show an interfacial reaction. Calculated ion scattering yields and XPS intensities associated with the Al and Ni atoms

are in very good agreement with the experimental results. These ion scattering simulations further reveal a surprising amount of "*near surface dechanneling*" occurring just below the interface which affects the conventional interpretation of the experimental results. We also gained more insight into the reaction and growth process of Ni on Al(110) using the snapshots of the crystal which were generated by these simulations.

In the studies of ultrathin Ni films on the Al(001) surface using HEIS, XPS, and XPD, we observed a completely different growth mode of the Ni films. Initially, a Ni film grows as a metastable *body-centered-cubic* structure in a Stranski-Krastanov (SK) mode. This structure is particularly interesting, since bulk Ni exhibits a *face-centered-cubic* structure at room temperature. After 5 ML of Ni coverage, the *bcc* islands coalesce to cover the surface. At this point, a small amount of *surface dechanneling* is observed in the ion scattering results.

The different growth behavior of Ni films which we observed for these two aluminum surfaces may be attributed to the difference in the surface energies of these surfaces. The Al(110) surface has the largest surface energy among the three low-index surfaces of Al, while the Al(111) surface has the lowest⁶⁸. The surface energy of the Al(001) surface is 10% less than that of the Al(110) surface. This difference may be sufficient to alter the growth on the (001) surface. So in this respect, it would be interesting to extend these Ni deposition experiments to the Al(111) surface since Al(111) has the lowest surface free energy. These experiments also merit attention because the (111) surface is the preferred orientation for aluminum and thus we can compare these results to other experiments that were done on Al films⁸⁻¹³.

Ultrathin Pd films deposited on Al(001) surfaces exhibit compound formation between Pd and Al atoms at the interface. Our results suggest that an AlPd-like compound grows on the substrate up to 5 ML of Pd coverage. After 5 ML of coverage a Pd metal film started to cover the reacted surface. Previous experiments for Pd on Al(111) surfaces using medium energy ion scattering also show that AlPd is the first reaction product on that surface¹. Preliminary experiments for Pd on Al(110) using HEIS and XPS also show that a strong reaction occurs at the interface⁶⁹. Thus, based on the above observations we believe that Pd reacts strongly on all three Al surfaces.

As we discussed in Chapter 7, we might expect the behavior of Pd films on Al surfaces to be similar to that for the Ni-Al system. However, from the above discussion it is clear that these two systems behave differently. Even though the surface energies of the Al surfaces are different, still we observed strong reaction in the Pd case. So another factor, the *heat of formation* of these alloys, may play an important role in determining the growth modes. The heat of formation of AlPd is -92 kJ/mole, whereas for AlNi it is -59 kJ/mole⁷⁰. Hence, we believe that the high heat of formation of AlPd causes the Pd atoms to react strongly with Al atoms on all surfaces.

As a final point, it is important to continue the EAM simulation on other surfaces and systems since the results obtained from these simulations can give us more insight into the growth modes observed in these system.

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APPENDICES

APPENDIX I

XPS CURVE FITTING

In XPS, when one element is present in different chemical states or two or more peaks are very close to each other, it is necessary to resolve XPS peaks into different components by means of a non-linear least-squares method. In order to perform these fits, first we should know the exact line shapes of these peaks. The measured line shape of a core-level photopeak is a complex function, and can be represented in terms of a convolution of the natural line shape and the instrument response function⁷¹

The natural line shape is usually expressed as a Lorentzian shape, and it is given by

$$L(E) = \frac{1}{1 + 4 \left(\frac{E - E_L}{W_L} \right)^2}$$

where E is the electron energy, E_L is the centroid, and W_L is the FWHM.

The instrument response function can be represented by a Gaussian shape, and it is given by

$$G(E) = \exp(-4 \ln(2) \left[\frac{E - E_G}{W_G} \right]^2)$$

where E_G is the centroid, and W_G is the FWHM

Thus, the function we must give the computer to represent our core-level line shape is

$$I(E_G) = \int_{-4\sigma}^{+4\sigma} G(E) L(E) dE_G$$

We have to perform this calculation at each data point for each iteration of the minimization routine.

However, in metals, creation of long-lived low energy electron-hole pairs near E_f leads to a skewing of the symmetric line shape towards the low kinetic energy side. Doniach and Sunjic show that the natural line shape of metals can be represented by the following expression⁷²

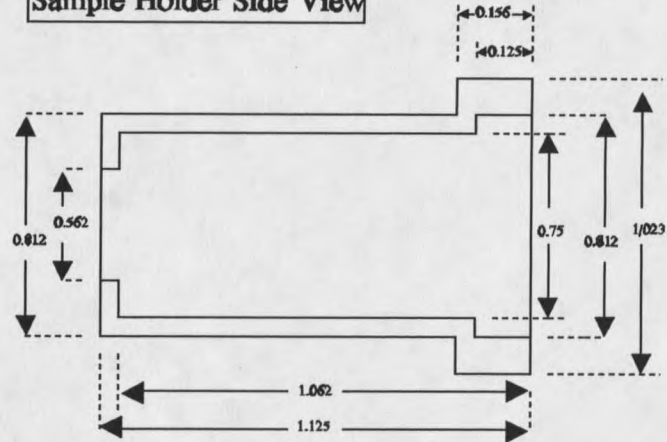
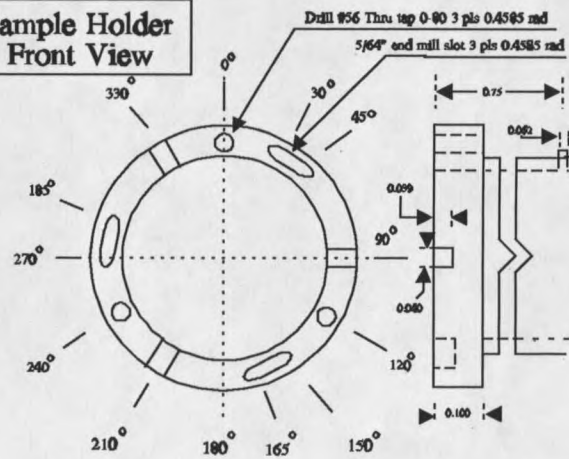
$$L(E) = \frac{\cos\left(\frac{\alpha\pi}{2} + (1-\alpha)\tan^{-1}\left[2\frac{E-E_L}{W_L}\right]\right)}{[(E-E_L)^2 + 4W_L^2]^{\frac{(1-\alpha)}{2}}}$$

where α is the asymmetry parameters.

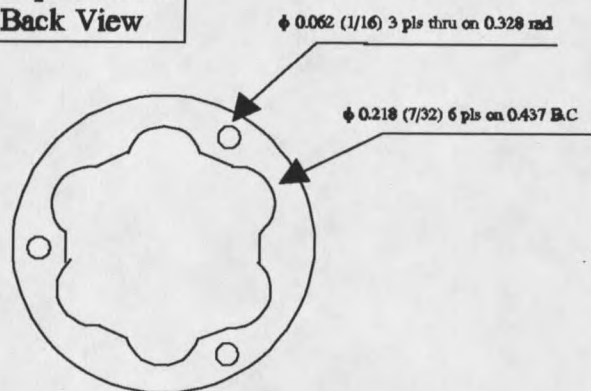
A typical XPS spectrum will have a background which arises from those photoelectrons that have lost energy when traveling through the solid. Thus, some form of background function has to be include in our fitting routine. Shirley⁶⁰ proposed that the increased background be correlated with the peak area. The inelastic scattering energy distribution at kinetic energy E_k is proportional to the number of electrons having energy higher than E_k . We have used this background subtraction method in our fitting routine. In most cases, we have used a Lorentzian line shape and a Shirley background, except in the Pd case where we used a Gaussian line shape.

APPENDIX II

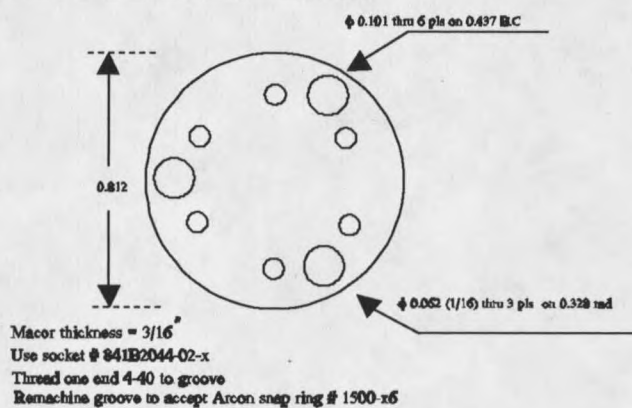
Detailed Drawings of our sample holder

Sample Holder Side View**Sample Holder Front View**

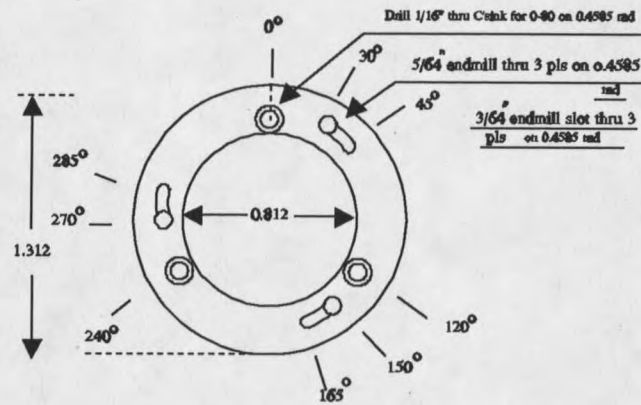
Sample Holder Back View



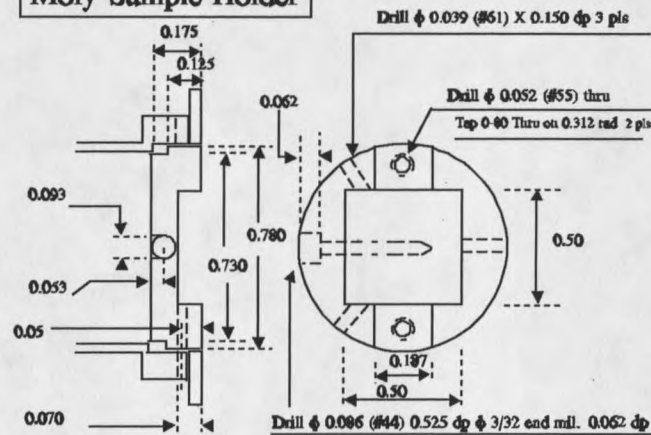
Macor Terminal Pass-thru

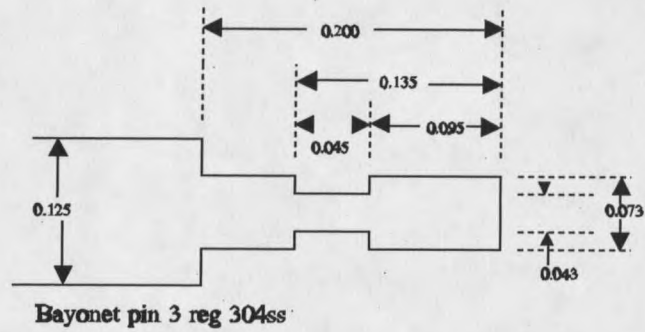
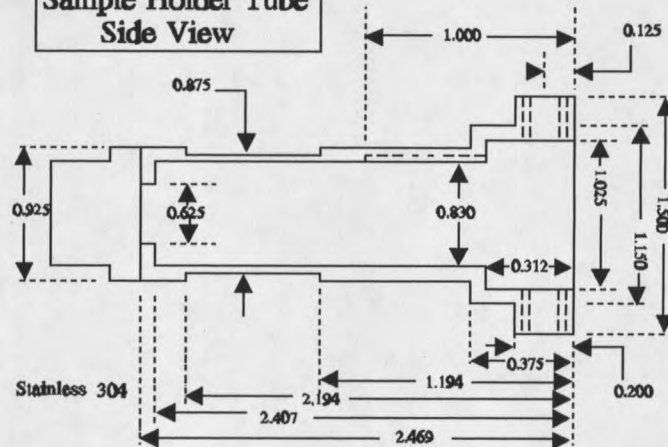


Sample Holder Front Plate

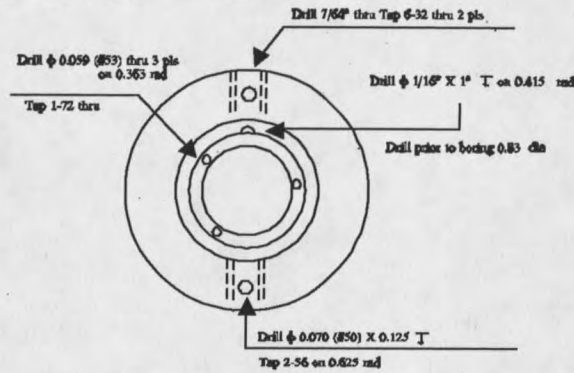


Moly Sample Holder

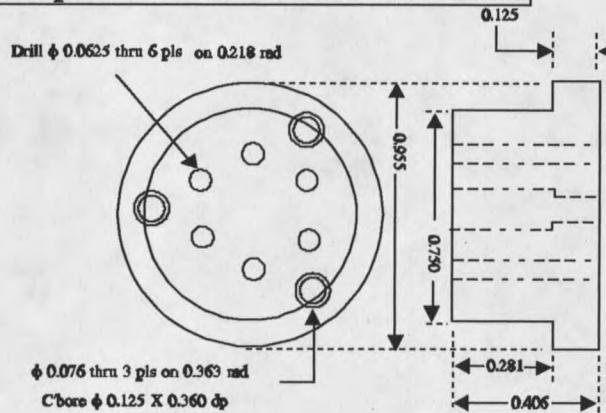


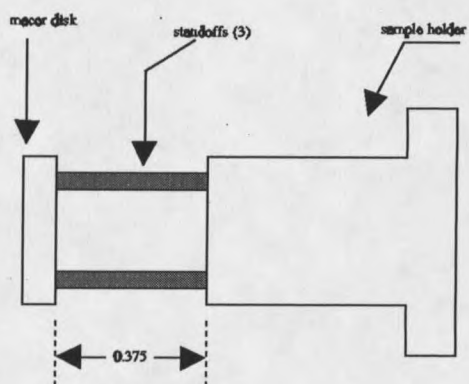
Bayonet Pin Arrangement**Sample Holder Tube
Side View**

Sample Holder Tube Front View



Sample Holder Tube : End Macor Block



Sample Holder Standoffs

APPENDIX III

MONTE CARLO SIMULATION PROGRAM DESCRIPTIONS

PROGRAM: WRITE_CRYSTAL_110.FOR

WRITE_CRYSTAL_100.FOR

WRITE_CRYSTAL_111.FOR

** These programs will build fcc(110), (100), and (111) crystals for the evolution.

PROGRAM: EAMALLOY.FOR

** This program will perform Monte Carlo simulations on a crystal which is generated by the WRITE_CRYSTAL_110.FOR program.

** Two kinds of outputs can be obtained from this program.

(1) General calculations....such as total energy, number of atoms in each layer, vibration amplitudes, etc.

(2) Snapshots of the crystal.

The files containing subroutines and functions in this program are :

READ_CRYSTAL.FOR

* This will read the crystal from a file which is written by the WRITE_CRYSTAL_110.FOR program.

MAKE_TABLES.FOR

- * This will read the potentials from ART VOTER and generate the look up tables for the EAMALLOY program.

SETPARAMETERS_EAM.FOR

- * This will calculate the parameters which are needed for the Monte Carlo process.

START_ENERGY.FOR

- * This will calculate the start energy of each atom.

START_RANDOM.FOR

- * This will start the random number generator.

NEARESTATOMS.FOR

- * This will determine which atoms are within a distance R of each atom.

DISSQUARE.FOR

- * This function will calculate the square of the distance between two atoms.

CPU.FOR

- * This will start the CPU time counter

POTENTIAL.FOR

- * This will calculate the energy of an atom as a function of N and NFCC.

DENSITY.FOR

- * This function replaces the simple lookup method.

PAIR_ENERGY.FOR

- * This function is similar to POTENTIAL.FOR and DENSITY.FOR.

RUN.FOR

- * This program controls the whole Monte Carlo simulation procedure.

DISSNEW.FOR

- * This will calculate the square of the distance between the moved atom and some other atom j.

E_DIFFERENCE.FOR

- * This will calculate the difference in energy for the atomic configuration before and after an atom was moved.

ACCEPT.FOR

- * This will determine whether an attempted move is accepted or not.

MOVEATOM.FOR

- * This will move an atom randomly in x,y,z direction.

WRITE_OUTPUT.FOR

- * This program writes the output to the output files.

OPEN_FILE.FOR

- * This program opens the output file *filename.out* to which all output is written.

AVERAGE.FOR

- * This program calculates the average of the observables after completion of a group.

OBSERVABLES.FOR

- * This will calculate the contribution to observables after each cycle.

FINISH_OUTPUT.FOR

- * This will finish the output to the output file.

REWRITE_CRYSTAL.FOR

- * This will write the crystal as evolved in the main program to a file such

that it can be used again as input file.

WRITE_ENERGY.FOR

- * This will write the energy of the crystal after performing the start up cycles to the output file.

WRITE_MAD.FOR

- * This will write the crystal as evolved in the main program to a file such that it can be used for the ion scattering simulation program. This file only contains the coordinates of all the atoms.

FULL_ENERGY.FOR

- * This will calculate the energy of the crystal completely.

EXACT_ENERGY.FOR

- * This will calculate the total energy of the crystal without using the exponential table.

After the generation of snapshots (*.mad files) from the EAMALLOY program, these snapshots are modified by some other programs.

Program: SHIFT.FOR

****** This will correct the coordinates of the atoms, if the periodic boundary conditions change the atomic coordinates.

Program: CMASS_LAYER_SHIFT.FOR

****** This program will shift the center of mass of each layer, if the center of mass of that layer changed.

After these modifications "ZANDVORT.FOR (VEGAS)" program was used to simulate the ion scattering yields from these corrected mad files.

Outputs (schimmel.out) from the ZANDVORT program, ie. ion scattering yield, for several snapshots (mad files) can be combined using COMBINE_Z.FOR program.

PROGRAM: ADJUST_CRYSTAL.FOR

****** From this program we can adjust the input parameters needed for running the EAMALLOY program.

***** If you run the ADJUST_CRYSTAL program you will get the popup manue which is shown below.

1. Temperature
2. Number of cycles
3. Number of groups
4. Number of start cycles
5. Stepsize
6. Random start seed
7. Mad Vs Normal outputs....
8. Output file name
9. Expand crystal
10. Write comments
11. Add (110) layers only
12. List or change atom type in each layer
14. Add more Ni atoms
20. Write crystal to the file
100. Stop program

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