



A new phase of titanium on aluminum surfaces : epitaxial growth and hydrogen uptake properties
by Adli Ahmad Saleh

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:

In this study, we report the growth of thin epitaxial Ti films with a face-centered cubic structure on the Al(110) and Al(001) surfaces at room temperature. Bulk-like Ti phases exist in nature either in a hexagonal close-packed crystal structure at room temperature or in a body-centered cubic crystal structure at temperatures higher than 877°C. The observed fcc structure is stabilized by the Al substrate, where the Ti-Al interfacial energy exceeds the strain energy associated with structure misfit. A maximum thickness of about 5 ML is measured for a flat fcc Ti film, at which thickness the strain energy and the interfacial energy are comparable. The Ti film is pseudomorphic with the Al cubic structure, and only a slight distortion of 2.4% in the (001) interplanar distance is measured. Beyond this thickness, the film undergoes a transformation that involves the readjustment of the Ti atomic positions in the film to accommodate the Ti bulk-like structure.

Thermal diffusion of Ti overlayers into the Al substrate was also investigated. Thin Ti films deposited at room temperature diffuse into Al when heated at 400 °C. The Ti atoms react with the Al substrate, where they occupy fcc lattice sites, substituting for the Al host atoms. Approximately 93% of the Ti atoms occupy such sites distributed over a depth of 300 Å.

Hydrogen uptake measurements of Ti films with various thicknesses were also carried out: The total uptake of the films, after exposure to H₂ gas, correlates well with their atomic structures. Only a limited uptake is observed for Ti films with an fcc structure, and is attributed to surface adsorption of hydrogen. However, a relaxed film exhibits a relatively large uptake. These observations may be understood in terms of either a decreased solubility because of the reduction in the Ti atomic volume in the new fcc phase, or a surface kinetic barrier that blocks hydrogen from diffusing into the film.

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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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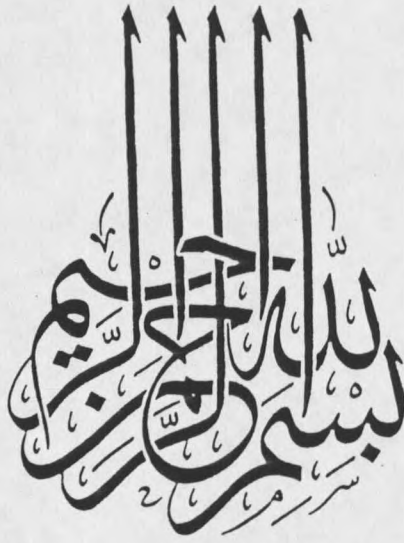
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ابنكم عريض

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ABSTRACT

In this study, we report the growth of thin epitaxial Ti films with a face-centered cubic structure on the Al(110) and Al(001) surfaces at room temperature. Bulk-like Ti phases exist in nature either in a hexagonal close-packed crystal structure at room temperature or in a body-centered cubic crystal structure at temperatures higher than 877°C. The observed *fcc* structure is stabilized by the Al substrate, where the Ti-Al interfacial energy exceeds the strain energy associated with structure misfit. A maximum thickness of about 5 ML is measured for a flat *fcc* Ti film, at which thickness the strain energy and the interfacial energy are comparable. The Ti film is pseudomorphic with the Al cubic structure, and only a slight distortion of 2.4% in the (001) interplanar distance is measured. Beyond this thickness, the film undergoes a transformation that involves the readjustment of the Ti atomic positions in the film to accommodate the Ti bulk-like structure.

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CHAPTER 1

OVERVIEW

Epitaxial growth of ultrathin metallic films on single crystal substrates in an ultrahigh vacuum (*UHV*) environment continues to receive a considerable amount of attention.¹ These systems exhibit interesting physical properties and are important in the search for new materials. The interfacial strain associated with the misfit between the substrate and overlayer lattice structures, as well as the difference in the surface free energy between the overlayer and the substrate materials, circumscribe the formed structures. The modified electronic and atomic structures in the overlayer may result in different physical properties for the deposited film as compared to those of the bulk material. Palladium, for example, shows an enhanced magnetic susceptibility associated with the expansion of the Pd unit cell in the Au-Pd-Au epitaxial structure.² Also, thin Pd films on Mo(100) exhibit a reduced hydrogen uptake relative to that for bulk Pd.³ An interesting subgroup of these bilayer systems is one in which metastable overlayer phases form due to the adatom-substrate interaction. In these systems, new phases, or phases that exist only at elevated temperatures are stabilized on the substrate surface at room temperature. For example, face-centered cubic (*fcc*) Co films grow epitaxially on Cu(001) substrates, and body-centered cubic (*bcc*) Co films can be grown on Fe(001) thin films, whereas bulk Co exhibits a hexagonal close-packed (*hcp*) structure at room-temperature.^{4,5} An *fcc* Co film of up to 30 monolayers (ML) in thickness was observed to grow epitaxially on a Ni(001) surface.⁶

Besides the study of epitaxial growth in bimetallic films, exploring metallic alloying in thin films at the atomic level provides for understanding the macroscopic properties of the alloy, and for exploring possible means of materials modifications. In this respect, transition metal aluminides have attracted a great deal of interest for their technological applications and have generated a considerable amount of research concerning the various structural aspects responsible for their properties.^{7,8,9} In particular, several Ti-Al alloys exhibit high specific strength, strength retention at high temperatures, oxidation resistance and high melting temperatures. Because of these properties, these alloys are receiving a great deal of attention for their potential applications as aerospace structural materials to be used in the National Aerospace Plane (NASP).¹⁰ The addition of small amounts of metal dopants like Nb are used to overcome problems such as lack of room-temperature ductility, as well as high-temperature embrittlement. Thin Ti-Al films are also of interest for their applications in the microelectronics industry as diffusion barriers between silicon and Al metallization layers in semiconductor devices, improving thermal stability as well as hillock growth resistance.^{11,12}

Although an enormous wealth of data is available on intermetallic films, more work needs to be performed to help understand the underlying phenomena responsible for their properties. This thesis is an integral part of an ongoing program to understand the fundamentals of the surface physics involved in the growth of ultrathin intermetallic layers in the early stages of formation, and their hydrogen uptake

properties. We believe that such studies are important not only from a fundamental point of view, but also from an applied perspective because the nature of the surface plays a vital role in determining properties like oxidation and hydrogen uptake.

In this study, we examined the growth of thin Ti films on Al(110) and Al(100) surfaces. During the growth process, the atomic structures of the overlayer and the substrate were monitored *in-situ*. Ti films up to 12 ML thick, were deposited on both surfaces. The growth was done in increments of about 0.5 ML, and the structure was characterized after each coverage increment. We found that the films grow epitaxially up to a critical thickness, after which the growth mode changes in character. The main focus of this thesis is the characterization of the epitaxial growth from an atomic point of view. Although the structure of the thicker films, beyond the critical thickness, was also of interest, our findings were not as conclusive. Hydrogen uptake of these films was also measured. These measurements were done as a function of exposure to H₂ gas, and the experiments were terminated after saturation. We found that epitaxial *fcc* films exhibit a minimal hydrogen uptake when compared with the uptake of the films with thicknesses exceeding the critical thickness. The Ti/Al diffusion as a function of temperature was also studied. In this respect, no appreciable diffusion was observed up to a temperature of 350°C. For films annealed at higher temperatures, it was observed that Ti diffuses into the Al substrate, and primarily occupies *fcc* lattice sites, substituting for Al atoms.

A combination of complementary surface techniques was used to verify the initial

state of the clean and ordered Al surfaces. These techniques were also used to monitor the growth of the deposited Ti layer at various stages of the experiment. The primary technique is high energy ion scattering (*HEIS*), where a collimated beam of about 1 MeV He^+ ions is incident along a major crystallographic direction of the Al single crystal, and backscattered ions with various energies are counted. *HEIS* provides a precise measurement of the overlayer coverage when the ion beam is incident in a random direction. The major reduction in the backscattering yield in the aligned geometry (ion channeling), compared to random alignment, provides a capability to probe solid state atomic structures. The shadowing of the underlying atoms by the surface atoms is also central to the utilization of the technique as a surface probe. Unlike most electron spectroscopies, *HEIS* is not restricted to probing the surface. Instead, it provides a non-destructive depth profiling capability.

The technique of X-ray photoemission spectroscopy (*XPS*) was used to monitor surface contamination levels during the cleaning process and to examine the nature of the overlayer growth during the Ti deposition process by measuring changes in the substrate photoelectron intensity. Measurements of the binding energies provide additional information to determine the chemical state of the film/substrate system. Also, the angular dependence of the emitted photoelectron intensity was used to complement our channeling measurements. This technique is referred to as x-ray photoelectron diffraction (*XPD*). The wave-like nature of the photoelectrons emitted from a source atom leads to an interference pattern at the detector location as a result

of scattering from surrounding atoms. In the high electron kinetic energy regime, the central maximum of the interference pattern becomes very intense, while the secondary maxima subside significantly. This effect is referred to as forward focusing, and is utilized to study surface structures. To our knowledge, this is the first time *HEIS* and *XPD* have been integrated on the same system as complementary techniques.

Hydrogen uptake measurements were done using elastic recoil detection analysis (*ERDA*). In this technique, a collimated beam of about 2 MeV He^+ ions is incident at a grazing angle on the sample surface. The protons recoiled in the forward direction as a result of He-H collisions are energy analyzed and counted.

The following is a list of acronyms frequently used in this thesis:

<i>AES</i>	Auger electron spectroscopy.
<i>ERDA</i>	Elastic recoil detection analysis.
<i>HEIS</i>	High energy ion scattering.
<i>HA</i>	Hemispherical analyzer.
<i>LEED</i>	Low energy electron diffraction.
<i>ML</i>	Monolayer.
<i>MCA</i>	Multichannel analyzer.
<i>RBS</i>	Rutherford backscattering spectrometry.
<i>RGA</i>	Residual gas analyzer.
<i>SP</i>	Surface peak.
<i>UHV</i>	Ultrahigh vacuum.
<i>UPS</i>	Ultraviolet photoelectron spectroscopy.
<i>XPS</i>	X-ray photoelectron Spectroscopy.
<i>XPD</i>	X-ray photoelectron diffraction.

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CHAPTER 2

EXPERIMENTAL TECHNIQUES

Because of the susceptibility of surfaces to contamination in an atmospheric environment, it is critical to conduct certain experiments involving surface phenomena in a vacuum chamber where surfaces are kept clean long enough to carry out the necessary measurements. For a typical surface, a calculation of the areal atomic density yields a value of 10^{15} atoms/cm². A computation for the rate at which contamination takes place leads to the result that the whole surface would be completely contaminated after exposing the sample to a pressure of 10^{-6} Torr for one second, i.e. 1.0 Langmuir (L). However, it should be mentioned that this calculation is based on a worst-case scenario: a sticking coefficient of unity is assumed. In reality, the contamination rate depends a great deal on the chemical nature of the surface, as well as the degree of reactivity of the residual gases in the chamber. Thus it is necessary to maintain a very low pressure in the vicinity of the surface. This environment is referred to as an ultrahigh vacuum (UHV) environment when a pressure of about 10^{-10} Torr, or lower, is maintained in the chamber for the duration of experiments. This pressure gives the experimenter a time period of about 10^4 seconds to carry out the measurements before the surface is seriously contaminated, thus corrupting the measurements. In addition, all ion- and electron-based surface analytical techniques require high vacuum

environments because the mean-free-path associated with ions and electrons is very short in air. Because of the low breakdown-voltage of gases at intermediate pressures, this environment is also necessary when high voltages need to be maintained, as is the case with X-ray sources, lens elements and electron multipliers in electrostatic analyzers, as well as in electron and ion sources. Hot elements like wire filaments are also severely affected by low vacua, leading to very short lifetimes.

In this study, a combination of surface analytical techniques was employed in the initial characterization of the sample surface, as well as in the study of the formation and the properties of the new structures. While high energy ion scattering (*HEIS*) was used as the main analytical technique, X-ray photoemission spectroscopy (*XPS*), and low energy electron diffraction (*LEED*) were combined to complement our studies. Elastic recoil detection analysis (*ERDA*) was also used to study the hydrogen uptake properties of systems under study.

In this chapter, a description of the experimental setup which was used is presented, and the basic physical principles of the various surface analytical techniques, except for *ERDA* which will be discussed in the next chapter, are introduced.

2.1 Experimental Setup

2.1.1 Ion Scattering Chamber and Vacuum System

The majority of the experiments presented in this thesis were carried out in the ion scattering *UHV* chamber. This chamber is made out of stainless steel and its inside is covered with mu metal to provide a magnetic field-free-region. This is especially important during *XPS* measurements in the low kinetic energy regime as well as during *LEED* measurements. The chamber is connected to a 2-MV Van de Graaff accelerator through a differentially pumped beam line. Schematic diagrams of the chamber are shown in Figures 2.1(a) and 2.1(b). The chamber is usually baked at a temperature of 150°C for 36 hours to eliminate water, oil vapors and other adsorbed gases. After baking the chamber, a pressure of 1.0×10^{-10} Torr was typically obtained which is essential for carrying out surface studies. In addition to the chamber, the vacuum system consisted of a Balzers TPU110 (110 l/s) turbomolecular pump, a Leybold-Heraeus DA8 (190 l/min.) backing rotary-vane pump, a Varian (120 l/s) sputter-ion pump, and a titanium sublimation getter pump. The getter pump is efficient for pumping reactive molecules like hydrogen, oxygen and carbon dioxide. An optically dense foreline trap full of an absorber material is used to prevent backing pump oil vapor from backstreaming into the vacuum chamber. Two sorption pumps are used to evacuate the gas introduction line and reservoir prior to exposure experiments in which

gases are introduced through a leak valve. Argon gas is also introduced to the sputter gun using the same mechanism. A Varian nude ionization gauge is used to monitor the pressure in the chamber during the various stages of the experiment. A 5.0 kV sputter gun is also available for cleaning the samples.

The chamber is equipped with a Dycor Electronics quadropole residual gas analyzer (RGA) to monitor the different gas components during various phases of experiments and for leak detection. Because of the low ion yield at high vacuum, the ion current is often amplified by means of an electron multiplier. A mass spectrum of the residual gas at an operating pressure of 1.4×10^{-10} Torr is shown in Figure 2.2.

2.1.2 Sample Holder and Goniometer

The sample holder consisted of a Mo block fastened to a three-axis goniometer which also allows for two independent translations. The angular rotations of the sample are controlled using three accurate feed-through shafts with an angular precision of about 0.1° . This goniometer was essential to carry out the channeling measurements as well as the photoelectron diffraction measurements. The sample holder includes a thin W filament for sample heating and a Pt resistor to monitor the sample temperature. The Mo block is electrically insulated using quartz rods to allow charge integration during ion scattering experiments. The sample is mounted in the block such that the rotation and tilt axes are approximately in the same plane.

2.1.3 X-ray Photoemission Facility

An XPS facility was used consisting of an X-ray source, electrostatic analyzer, and counting electronics. The X-ray source consists of a water-cooled VSW TA10 twin-anode providing characteristic x-rays of Al $K\alpha$ ($h\nu=1486.6$ eV) with a line width of 0.85 eV, and Mg $K\alpha$ ($h\nu=1253.6$ eV) with a linewidth of 0.70 eV. A thin Al window, 5.0 μm in thickness, is mounted in front of the source to prevent stray electrons from reaching the sample and to minimize contamination of the sample due to filament degassing and evaporation. The X-ray source is mounted on a bellows to allow the introduction and the retraction of the source near the sample and to avoid damage to the thin Al window when maneuvering the sample. X-ray radiation intensity is stabilized by controlling the filament emission current. This stability is critical when studying the changes in photopeak intensities, e.g. to model the growth morphology of a thin film. It is also essential to maintain a stable X-ray intensity during photoelectron diffraction experiments. A filament current of 3.0 A, an electron emission of 20 mA, and an anode voltage of 10 kV are typically used in our studies. A 100 mm VSW hemispherical analyzer (HA100) is used to analyze the kinetic energy of photoelectrons emitted from the sample. Potentials for lenses, hemispheres, and the electron multiplier are all set using the VSW HAC5000 control unit. The sample is set to ground potential during the measurements. The control unit allows the collection of data in the fixed analyzer transmission (FAT) mode, and consequently maintains a fixed electron energy resolution. In this mode, the kinetic energy of electrons is retarded by a variable factor

so that electrons enter the hemisphere with a fixed pass energy. The HAC5000 also allows a fixed retardation ratio (FRR) throughout the spectrum to maintain a fixed sampled area. The FRR mode is useful when scanning a wide energy range of the spectrum, and therefore allows the comparison of peak intensities to determine surface composition. On the other hand, the FAT mode is useful when scanning the intensity of photoelectrons emitted by specific atomic elements. Pass energies of: 10, 25, 50 and 125 eV, and retarded ratios of 5, 10, 50 and 100 are allowed. The pass energy of 50 eV is typically used, giving reasonable energy resolution of 1.0 eV and maintaining an acceptable signal intensity. A number of scanning rates are also allowed during the measurements. A scan rate of 0.1 eV/sec is used to scan individual peaks, while larger rates are used to scan wider kinetic energy ranges.

During energy scanning, emitted photoelectrons with a certain kinetic energy are deflected 180° after entering the hemisphere, and are then incident on a single channel electron multiplier (channeltron). The electron multiplier is made out of a curved tube, with a length-to-diameter ratio of about 100:1. The tube is coated with high resistance material, where the surface becomes a continuous dynode. Electrons are incident on the low potential end of the multiplier, causing secondary electrons to be emitted from the tube walls. These electrons are accelerated along the tube causing more secondaries to be emitted. Due to this avalanching process, a large number of electrons is produced at the high potential end of the multiplier. A gain of about 10^8 is obtained. This process is analogous to using a combination of discrete dynodes in the conventional

photomultiplier. A charge sensitive preamplifier is used to shape the electron pulses, which are then filtered, amplified and finally counted using a PC based multichannel card and software. To obtain yield *versus* energy scans, the *XPS* control unit is triggered to start, and the PC based acquisition system is set to acquire data simultaneously. The time-to-energy conversion is obtained from the width of the energy window and the scan rate, both of which are set by the *XPS* analyzer control unit. The experimental setup used to perform the *XPS* measurements is shown in Figure 2.3.

2.1.4 Helium/Hydrogen High Energy Particle Detection and Energy Analysis

Energy analyses of backscattered particles for *HEIS* and *ERDA* measurements were performed using two bakable, passivated, implanted, planar silicon (PIPS) detectors. The *HEIS* detector is mounted on a rotatable arm, and is located 3" away from the sample. The detector position is set at a scattering angle of 105° for channeling measurements. A circular aperture, 0.125" in diameter, is placed in front of the detector subtending a solid angle ($\Delta\Omega$) of 3 milliradian.

The *ERDA* detector is positioned at a fixed scattering angle of 25° , and is mounted on a vacuum feed-through shaft permitting a variable solid angle for particle collection. Typically, the detector is positioned 4.2" away from the sample, subtending a solid angle of about 0.8 milliradians. An Al foil, 8.0 μm thick, is placed in front of the detector to filter out the forward scattered He particles due to the primary beam.

This thickness was chosen based on the average projected range of He^+ ions in Al. The stopping cross-section of He is considerably larger than that for protons in Al, hence permitting the passage of protons through the stopper foil with some definite energy loss.

Hydrogen and helium ions create electron-hole pairs in the depleted region of the reverse-biased *p-i-n* junction of an area diode. The number of created pairs is directly proportional to the energy of the incident particles, provided we use a thick enough depletion layer, and provided also that the bias field is strong enough to prevent electron-hole recombination.¹ The detectors that were used in this study have an active thickness of 100 μm , which far exceeds the H and He ranges in Si for the ion energy ranges of interest. The electrical contacts to the Si wafer are ion-implanted which makes them withstand baking up to 200 °C. Current pulses due to incident energetic particles vary in height linearly with the energy of each incident particle. These pulses are shaped, amplified and finally sorted according to their heights using a set of electronic units and a PC-based acquisition card and software. Energy resolution of about 20 keV is obtained in the range of interest. A schematic diagram for the charged-particle detection system is shown in Figure 2.4.

2.1.5 Van de Graaff Accelerator

The ion scattering chamber is connected to the 2 MV Van de Graaff accelerator via a differentially pumped beam-line. The accelerator is used as a variable flux source

of-well focused and collimated H^+ and He^+ beams. Primarily, the accelerator consists of an ion source and an evacuated column with a strong potential gradient of about 10^6 V/m. It is connected to a field free evacuated beam pipe that leads to a strong analyzing magnet and then to the chamber. He or H_2 gas is leaked into the ion source, where an *rf* field is used to ionize the gas. Ionization is enhanced by means of a quadrupole magnet located around the ionization vessel. A potential gradient is established and maintained along the column by means of the continuous charging of the positive terminal (a shiny dome-shaped steel overlay). This is accomplished using a highly insulated belt that transfers positive charges from a (0-30) kV spray charge power supply to the high-potential end of the column. The column includes a large number of equipotential electrodes, connected in series with a string of resistors between the high potential terminal and ground.

During the operation of the accelerator, a delicate balance between charge deposited on the terminal and charge leakage to ground through different channels is maintained. An important channel is the one in which charge is transferred to a collection of sharp pointed needles positioned directly above the terminal. These are referred to as the corona points, while the charge transfer is referred to as the corona current. The corona points are brought closer to the terminal to lower the terminal potential, and are retracted away from the terminal to increase the potential. This control mechanism allows the fine adjustment of the potential gradient, while the coarse adjustment is obtained using the variable spray charge power supply. The corona points

are also essential in the voltage stabilization circuit. The stabilization is accomplished via the outgoing ion beam and analysis magnet. A small perturbation in the potential gradient is translated into a deviation in the kinetic energy of ions accelerated down the column. The switching magnetic field deflects the ions with the desired energy into the scattering chamber. An ion beam with higher kinetic energy will have a smaller deflection, while ions with lower kinetic energy will have a larger deflection. Two collector slits, horizontally positioned inside the beam line, a few millimeters apart, are used to measure a portion of the current associated with the ion beam. These slits are part of a feed-back circuit where an appropriate voltage, proportional to the measured difference in the slit current, is applied to the corona points to reduce or increase the corona current, affecting the charge balance on the accelerator terminal and thus stabilizing the ion energy.

2.1.6 Leybold Vacuum Chamber

LEED and *XPS* measurements for the Ti/Al(110) experiments were done in a Leybold vacuum chamber. The general characteristics of the *XPS* capability in this chamber are similar to those discussed earlier in section 2.1.3. An additional feature is a variable-size slit, located at the entrance of the electrostatic hemispherical analyzer. This slit is utilized to avoid contributions to the photoelectric signal associated with the sample holder and other surroundings. The chamber also features a 5.0 keV Ar^+ ion gun for surface sputter-cleaning. Sample heating is accomplished by passing a current

through a thin W coil immediately below the sample. A thermocouple wire is used to monitor the sample temperature. A quartz crystal oscillator (*QCO*) was used to monitor the film thickness during deposition. The chamber also features a Varian *LEED* optics and controller. The sample was transferred back and forth, under vacuum, between the *XPS* chamber and the *LEED* chamber. Ti depositions were done in the *XPS* chamber. A schematic diagram of the system is shown in Figure 2.5.

2.2 Analysis Techniques

2.2.1 High Energy Ion Scattering

This study is primarily based on results obtained from ion scattering experiments. The significance of the technique stems from its effectiveness in characterizing bulk and surface structures in terms of their absolute atomic compositions and crystallographic orientations. Ion scattering can be applied in a variety of modes depending on the objective of the study and the complexity of the experimental setup. This technique will be discussed briefly in the following two sections for the purpose of organizing the discussion. First, we discuss the standard and more widely used application of ion scattering used in elemental analysis and absolute coverage measurements. Second, we present the technique as a structural probe, emphasizing its use as a surface tool.

2.2.1.1 High Energy Ion Scattering/Standard Applications

In high energy ion scattering, also referred to as Rutherford backscattering spectrometry (*RBS*), a well-collimated ion beam of He^+ or H^+ is incident on the target, with a kinetic energy of 1-3 MeV, and with an ion current of about 10 nA.² Normally, the ion beam is incident on a sample area of a few mm^2 . These particles are energetic enough to penetrate the atomic electronic cloud, and to interact with the positively charged nuclei of the target via the Coulomb potential. Energy and number analyses of backscattered particles are used to explore the composition of solid targets. To a good approximation, the angular distribution of the elastically scattered particles can be described using the classical Rutherford cross-section. Considering a binary event, since multiple scattering events can be neglected in this case, the differential cross-section in the laboratory frame is given by:

$$\frac{d\sigma}{d\Omega} = \left[\frac{Z_1 Z_2 e^2}{2E_o \sin^2 \theta} \right]^2 \frac{[\cos \theta + (1 - (M_1/M_2)^2 \sin^2 \theta)^{1/2}]^2}{\sqrt{1 - (M_1/M_2)^2 \sin^2 \theta}} \quad (2.1),$$

where E_o is the energy of the incident particle, M_1 and M_2 are masses of the incident and target particles respectively, Z_1 and Z_2 are atomic numbers of the incident and target particles respectively, and θ is the scattering angle. For target atoms with the ratio M_1/M_2 less than unity, the cross-section has a non-zero value for all values of θ .

The energy of the particles scattered from the surface atoms is simply related to the

energy of the incident particles; namely, it is directly proportional to the energy of the incident particles. This is expressed by the following relationship:

$$E = K(\theta, \frac{M_1}{M_2}) \cdot E_o \quad (2.2).$$

The constant K is called the kinematic factor and can be obtained by requiring energy and momentum conservation during the collision. The kinematic factor is given by:

$$K = \left[\frac{\sqrt{M_2^2 - M_1^2 \sin^2 \theta} + M_1 \cos \theta}{M_2 + M_1} \right]^2 \quad (2.3).$$

Because of the nature of the two previous equations, the energies of the outcoming particles are related to the masses of the target atoms, since the geometry is known for a certain experimental configuration. In principle, the energy measurements of the scattered particles lead to the elemental analysis of the sample since each element has a unique atomic mass. However, because of the finite energy resolution of the spectrometer, the mass resolution is limited. The measurement of the ion scattering yield provides a means for counting the target atoms in an absolute sense. The Rutherford cross-section, the number of incident ions, and the solid angle of the detector are used to normalize the yield.

In a realistic situation, this description is still too simplistic, and other aspects need to be taken into account. For example, for a semi-infinite target geometry, the ions that do not backscatter from the target surface continue to traverse the sample at finite energy loss rates, due to a variety of electronic excitations and low scattering angle nuclear encounters. In effect, this process leads to the variation of E_o in the above equations. The energy loss per unit length experienced by the ions is a well-studied problem, and loss rate values are tabulated for a wide variety of elements and compounds over a wide range of particle energies. However, this makes the mathematical problem of concentration profiling transcendental, and thus it must be solved approximately. This is because the energy loss of the ions is a function of the sample composition, the very quantity we want to measure. Hence, the solution to the problem must be approximated numerically. A typical approach to resolve this difficulty is to divide the solid into a finite number of thin layers of uniform compositions, where the energy loss is assumed constant throughout each layer. The computer program, *RUMP*, is often used to extract concentration profiles from backscattering spectra. *RUMP* is also used to simulate backscattering spectra expected for an almost arbitrary set of target, beam, and detector parameters.³

Since composition profiling using *RBS* is not the focus of this thesis, we shall not present the formal treatment here. This formalism is presented in many books and research papers.² Instead we will emphasize those aspects which were used in the course of this study, namely the ion yield and energy distribution due to scattering

from thin solid films. The energy spectrum can be expressed in terms of a narrow peak located at KE_o on the energy axis. This is because of the small energy spread of the backscattered particles. The area of the peak is given by:

$$A = (Nt) \cdot \sigma(E_o, \theta, M_1/M_2) \cdot \Delta\Omega \cdot Q \quad (2.4),$$

where Q is the time integrated current of incident ions, $\sigma(E_o, \theta, M_1/M_2)$ is the scattering cross-section, $\Delta\Omega$ is the solid angle subtended by the detector, and Nt is the number of target atoms per unit area of the film. Several approximations are made when using equation (2.4). Firstly, the film is assumed to be thin enough so that there is no appreciable energy loss as the beam traverses the film. Secondly, the detection solid angle is assumed to be small enough so that the scattering cross-section can be approximated by the differential cross-section. A third, less obvious, approximation is the assumption that the underlying atoms within the film are not shadowed by overlying atoms. As will be discussed in the next section, this phenomenon can be utilized in the study of crystal and overlayer structures.

While the ion energy distribution associated with the scattering from a thin solid film is a narrow peak, the energy distribution of particles due to a semi-infinite target is broad, and thus can be approximated by a step function. One can obtain the height of the spectrum due to a thick substrate by considering the yield, H_o , in a small energy width δE corresponding to a thin slab, δx in thickness. Equation (2.4) can be rewritten as follows:

$$H_o = (N\delta x) \cdot \sigma \cdot \Delta\Omega \cdot Q \quad (2.5).$$

In addition, δx can be represented in terms of δE , in the first approximation, through a generalized stopping cross-section factor $[S_o]$, such that:

$$\delta x = \frac{\delta E}{[S_o]} \quad (2.6),$$

where $[S_o]$ is given by:

$$[S_o] = \frac{1}{\sin\alpha} \frac{dE}{dx} \Big|_{E=E_o} + \frac{K}{\sin(\theta-\alpha)} \frac{dE}{dx} \Big|_{E=KE_o} \quad (2.7),$$

where α is the grazing exit angle and where the surface energy approximation is used. Combining equations (2.5) and (2.6), we obtain an expression for the height of the step due to a semi-infinite substrate:

$$H_o = N \cdot \frac{\delta E}{[S_o]} \cdot \sigma \cdot \Delta\Omega \cdot Q \quad (2.8).$$

The situation where a thin film of an unknown thickness is deposited on a semi-infinite substrate is frequently encountered. In this case, equations (2.4) and (2.8) are combined, and the following expression is used to calculate the areal density of the film:

$$(Nt)_o = N_s \frac{A_o}{H_s} \frac{\delta E}{[S_o]} \frac{\sigma_o}{\sigma_s} \quad (2.9),$$

where the subscripts s and o are used to denote the substrate and the thin overlayer, respectively. Equation (2.9) is an alternative to equation (2.4) when the substrate material is known. The need to measure Q and $\Delta\Omega$ is eliminated. Figure 2.6 depicts a calculated spectrum for a Ti film, 50 Å in thickness, on an Al substrate; typical experimental parameters are used in the simulations. The *RUMP* program was used to generate the spectra.

2.2.1.2 High Energy Ion Scattering/Structure Probe

In the previous section, the atomic structure of the target was assumed to be completely random. Hence, such treatment applies more to amorphous solids where all target atoms within the probing depth contribute the same yield regardless of where they are over a depth range in which energy loss of ions may be neglected. This assumption is implicit when using equations (2.4) and (2.8). When dealing with single crystals and ordered overlayers, this assumption is obviously no longer valid.

For an ion beam incident along a certain crystallographic direction, i.e. along a row of atoms, the Coulomb interaction with the target nuclei perturbs the ion trajectories in a peculiar way. Namely, the ions are steered away from the atomic rows into the open channels of ordered structures. As a result the backscattering yield is

greatly reduced compared to the case for a random incident ion direction. This phenomenon is known as channeling, and constitutes a rather powerful surface technique.⁴ The channeling effect is illustrated in Figure 2.7, where the top atom shields the underlying atoms down the atomic rows due to the shadow cones. Assuming a pure Coulomb interaction, the radius of the shadow cone, R_c , is defined in terms of the trajectory of ions that most closely approach the second atom in the row. The expression, in CGS units, is given by:⁴

$$R_c = \sqrt{\frac{Z_1 Z_2 e^2 d}{E}} \quad (2.10),$$

where d is the interatomic distance along the rows. For a 1.0 MeV He^+ ion incident on aluminum along the [100] direction, the value of $R_c = 0.081 \text{ \AA}$ at $d = 4.05 \text{ \AA}$, the lattice constant of aluminum. This value of R_c is much larger than the nuclear dimensions, and thus causes the complete shielding of the underlying row of atoms in a static lattice. According to this picture, only surface atoms contribute to the ion backscattering yield, because only then is a nuclear close-encounter possible. The energy distribution of the scattered ions can be represented by a narrow surface peak at energy KE_o . Figure 2.8 illustrates the major reduction in the backscattering yield from aluminum when ions are channeled, compared to the case for random incidence, and also illustrates the concept of a surface peak.

In reality, the shadowing effect is more complicated because of the thermal vibrations of target atoms about their equilibrium positions. For example, the one-dimensional, *rms* vibrational amplitude, u_1 , of aluminum atoms at room temperature is about 0.095 Å, exceeding the shadow cone radius.⁵ This indicates that the static model, described earlier, is an oversimplification of the problem. In this picture, each of the underlying atoms has a finite close-encounter probability which can be calculated by the convolution of the ion flux distribution with the atom position distribution governed by thermal motion. Generally, this calculation leads to diminishing close-encounter probabilities for deeper atoms as compared to those for atoms near the surface. For example, the close-encounter probability of the second atom in the row is given by:⁴

$$P_2 = \left[1 + \frac{R_c^2}{4u_1^2} \right] e^{\frac{-R_c^2}{4u_1^2}} \quad (2.11)$$

The area under the curve of the energy distribution of the backscattered ions is directly related to the sum of the close-encounter probabilities of the atoms in the row, P_{ce} . For a surface with Σ rows per unit area, and according to equation 2.4, the yield in the surface peak area is given by:

$$A = \Sigma \cdot P_{ce} \cdot \sigma \cdot \Delta\Omega \cdot Q \quad (2.12)$$

Using this equation P_{ce} can be evaluated experimentally. It should be noted that the premise of the technique lies in this equation. The structure of surfaces can be studied by comparing P_{ce} as measured by experiment with P_{ce} as calculated from models and computer simulations of the scattering process. Obviously, the validity of these studies is constrained by the accuracy of the models used. One rather important modification to the earlier discussion is in the ion-atom interaction potential. The Coulomb potential is not sufficiently accurate to calculate the ion flux distribution for impact parameters larger than 0.1 Å. Instead a Thomas-Fermi model for the atomic interaction potential is used. A modified shadow cone radius, R_M , is generally utilized. R_M is substantially smaller than R_c for high- Z elements and at low incident ion energies.

A universal curve for the summed P_{ce} has been calculated in terms of the ratio ρ/R_M , where ρ is the two-dimensional *rms* vibrational amplitude.⁶ This curve is a result of computer simulations and is shown in Figure 2.9. The predictions obtained from this curve are in good agreement with the experimental results for a large number of perfect crystals with incidence along the various directions. In reality, however, perfect crystals are rarely encountered, and surface phenomena like reconstruction, relaxation, and adatom adsorption effects need to be treated.

Extensive computer simulation codes of ion scattering are often used for the calculation of the individual close-encounter probabilities, P_i . In the course of this study, we used the *VEGAS* computer code to simulate our scattering experiments.⁷ *VEGAS* allows the creation of three-dimensional lattices. Atom types, coordinates, and

vibrational amplitudes can be set by the user. This flexibility allows the simulation of reconstructed, and relaxed surfaces. It also allows the simulation of overlayers with arbitrary structures. Beam and detector parameters are also set as a part of an input file. The output of the simulations consists of the individual close encounter probabilities for all the atoms in the lattice. The results of channeling simulations from an ideal Al(100) surface are shown in Figure 2.10. These results are in good agreement with experiments.

Ion channeling is well suited to study overlayer/substrate interactions. Figure 2.11 illustrates how this technique can be utilized in these studies. An epitaxial growth of overlayers results in a decrease in the surface peak areas due to the substrate and the film (Figure 2.11 b). Overlayer relaxation is associated with an increase in the substrate peak area and a decrease in the overlayer peak area when the ion beam is aligned with an overlayer off-normal direction (Figure 2.11 c) and vice versa. On the other hand, an increase in the substrate peak area as a function of overlayer thickness, where the ion beam is aligned with the substrate, is indicative of a reaction in which the substrate atoms are displaced from their equilibrium positions as shown in Figure 2.11 c. The applications of ion channeling to study the epitaxial growth of titanium on an aluminum surface is explained in detail in Chapters 4 and 5.

Ion channeling can be used to study the impurity lattice sites in a host crystal. This is done by measuring the ion scattering yields as a function of the angle of ion incidence, for the impurity and for the substrate. The resulting plots are referred to as

rocking curves, and they reflect the spatial symmetries of both species. These curves can also be used to determine the atomic structures of ordered overlayers relative to these of single crystal substrates. Both of these methods are utilized in the study of the Ti/Al systems, and these uses are further illustrated in Chapters 4 and 5.

2.2.2 X-ray Photoelectron Spectroscopy

When photons interact with materials, bound electrons may be excited provided the photon energy, $h\nu$, exceeds the binding energy of the electrons. Some electrons may escape the material. This phenomenon is known as the photoelectric effect and electrons emitted through this channel of excitation are referred to as photoelectrons.⁸

In X-ray photoemission, a flux of photons with a well-defined energy is generated by the bombardment of a Mg or an Al anode with a beam of high kinetic energy electrons, typically 10 keV, from a hot wire filament. This leads to the ionization of atomic inner-shells, where holes are created. Subsequently, the ionized core levels are filled through electronic transitions, and photons are emitted with the characteristic energies of the transitions, e.g. $p \rightarrow s$, which are referred to as K_α transitions. When using Al and Mg anodes, the transitions $K_{\alpha 1,2}$, corresponding to the doublet decays of $2p_{1/2} \rightarrow s$ and $2p_{3/2} \rightarrow s$, are isolated and dominant transitions with line widths of 0.85 eV for Al and 0.70 for Mg. Other transitions are also allowed and generally contribute to the complexity of the photoelectron energy distribution curves (EDCs). For example, the $K_{\alpha 3,4}$ transition gives rise to photopeaks with relative

intensities of 8% at kinetic energies about 10 eV higher than those of the main photopeaks.

The kinetic energy of an emitted electron is given by the energy difference between the photo-excited state and the final ionized state of the system. According to Koopman's theorem, the energies of all electrons in the system remain constant during ionization and thus the kinetic energy of the photoelectron is given by:

$$E_k = h\nu - E'_b \quad (2.13)$$

where E'_b is the binding energy of the electron measured with respect to the vacuum level. For a metal, a more conventional reference for the binding energy, E_b , is the Fermi level, in which case the electron kinetic energy is expressed as:

$$E_k = h\nu - E_b - \phi_s \quad (2.14)$$

where ϕ_s is the work function of the surface, and is the binding energy of the least bound electron in the metal.

Generally XPS is surface sensitive. Its depth sensitivity is related to the inelastic mean-free-path of the photoelectrons, also referred to as the escape depth, which is only dependent on the kinetic energy of the electron in a first approximation. This energy dependence is represented by an empirical universal curve, where the escape depth has an absolute minimum of about 5Å for an electron kinetic energy of about 50 eV. Consequently, photon energies and/or core levels are chosen to increase or diminish

surface sensitivity, depending on the required measurement. However, as we will show in Chapter 4, considerable deviations from this curve are frequently observed, especially for ordered structures.

Although photoemission is not restricted to the core levels, we shall only consider core-level X-ray photoemission spectroscopy. The analysis is much easier then since only isolated excitations are involved and the band effects are avoided, for the most part. The areas of the photopeaks corresponding to the core-level excitations can be used for chemical composition analysis of the sample. However, it should be emphasized that this is an approximation, and is valid only when the secondary phenomena like plasma loss features and shake-up lines have negligible effects. The variations in the relative intensities of the substrate and overlayer signals are used to study growth morphology. They are also used to determine the overlayer/substrate structures in the photoelectron diffraction mode, which will be discussed in the next section. The core-level photopeaks are also superimposed on a sizable background due to electron inelastic scattering which makes the extraction of the net peak areas somewhat troublesome.

The measured line shape for a photopeak can be represented in terms of a convolution of the actual line shape and the instrument response function.⁹ The line shape is expressed in terms of a Lorentzian function of electron kinetic energy, while the response function of the analyzer and the X-ray source is generally represented by a Gaussian. Thus the measured line shape can be written as:

$$N(E) = \int_{-4\sigma}^{+4\sigma} \exp \left[4 \ln(2) \frac{-(E_k - E)^2}{\Gamma_G^2} \right] \frac{dE_k}{\left[1 + \frac{4(E_k - E_L)^2}{\Gamma_L^2} \right]} \quad (2.15),$$

where Γ_L is the natural line width, and Γ_G , the total resolution of the source-analyzer system, can be written as:

$$\Gamma_G = \sqrt{(\Delta E_k)^2 + (\Delta h\nu)^2} \quad (2.16).$$

Here, $\Delta h\nu$ is the line width of the X-ray decay transition, and ΔE_k is the resolution of the electrostatic analyzer. In principle, one should fit the experimentally measured line with a linear combination of the expression above and some acceptable function for the background. However, when working with a nonmonochromatized photon source and with a relatively poor analyzer resolution, i.e., $\Gamma_L \ll \Gamma_G$, the Lorentzian character of the line shape can be ignored, and the actual line shape can be assumed to be a delta function. Hence the peak can be written as:

$$N(E) = A \cdot \exp \left[4 \ln(2) \frac{-(E_L - E)^2}{\Gamma_G^2} \right] + \text{erf} \left[\frac{-(E_L - E)}{\Gamma_G} \right] \quad (2.17)$$

where we have expressed the background as an error function. This method of background modeling is referred to as the Shirley background-subtraction method.¹⁰ This method assumes the background at any point to be due to inelastically scattered electrons, with higher kinetic energy, and is thus proportional to the integrated photoelectron intensity.

2.2.3 Photoelectron Diffraction

When the angular acceptance of the electrostatic analyzer is limited, variations in the photoelectric intensities as a function of emission angle correlate with surface structure. These variations are attributed primarily to the interference of wave functions associated with photoelectrons emitted from source atoms, and those which are scattered by atoms in the forward direction. Hence, this phenomenon can be used to study ordered surface structures associated with film epitaxy.¹¹ This process is shown schematically in Figure 2.12. It should be noted that this diffraction effect is not restricted to the photoelectric effect, but is also observed in Auger electron spectroscopy, in which case electrons are emitted through a different relaxation channel.

We introduce a simple model to explain the angular dependence of the photoelectric intensities. In this model, we consider two atoms (source and scatterer atoms), with a separation $\mathbf{r}$, where the intensity of the photoelectrons, $I(k, \theta)$, is to be calculated. We associate spherical waves with the electrons emitted from the source atom, and with those electrons scattered by the scatterer atom. The electronic wave

function from the source atom can be written as:

$$\Psi = A \frac{e^{ik \cdot R}}{R} \quad (2.18),$$

where k is the electron wave vector, and R is the position vector of the detector. The scattered wave function is given by:

$$\Phi = A \frac{e^{ikr}}{r} \frac{e^{ik \cdot (R-r)}}{R} f(k, \theta) \quad (2.19),$$

where $f(k, \theta)$ is the scattering amplitude. The intensity $I(\theta, k)$ can be expressed as:

$$I(k, \theta) = |\Psi + \Phi|^2 \quad (2.20).$$

Substituting equations (2.18) and (2.19) into equation 2.20 leads to the following result:

$$I(k, \theta) = \frac{A^2}{R^2} \left[1 + \frac{2f_o(k, \theta)}{r} \cos(kr(1 - \cos\theta) + \eta(k, \theta)) \right] \quad (2.21)$$

where we have expressed the scattering amplitude in terms of the scattering strength $f_o(k, \theta)$, and the scattering phase shift $\eta(k, \theta)$ such that:

$$f(k, \theta) = f_o(k, \theta) e^{i\eta(k, \theta)} \quad (2.22)$$

The calculations of $f_o(k, \theta)$ and $\eta(k, \theta)$ are rather complicated since they involve the numerical solution of the Dirac equation by a partial-waves method.¹² To illustrate the angular dependence of the photoelectron intensity, we consider the emission from a cluster of 5 aluminum atoms. The values for $f_o(k, \theta)$ and $\eta(k, \theta)$ for aluminum are substituted into equation 2.21. The results of this calculation are shown in Figure 2.13.

2.2.4 Low Energy Electron Diffraction (*LEED*)

LEED provides a powerful method to perform surface crystallography. This technique is sensitive to changes in the surface structure associated with substrate/adsorbate interactions and with possible phase transitions. Surface reconstructions and relaxations can also be characterized using *LEED*. In a *LEED* experiment, a primary beam of low energy electrons is incident on an ordered surface, and the elastically backscattered electron intensity is measured.¹³ To probe the atomic structure, the deBroglie wavelength associated with the incident electron should be comparable to the interatomic distances ($\sim 1\text{\AA}$). Because the electron energy required to meet this criterion ($\sim 150\text{ eV}$) corresponds to a short electron mean-free-path, the technique is well suited to study surface structures. The interference pattern of the scattered electron waves consists of bright spots on a phosphorus screen. For a perfect

surface with two-dimensional periodicity; the positions of the spots can be calculated using the Ewald sphere construction. The reciprocal lattice associated with the surface is a collection of infinitely long rods perpendicular to the sample surface, and can be calculated in the usual way. In momentum space, each point at which a rod intersects a sphere of radius $2\pi/\lambda$, where λ is the deBroglie wavelength of the electrons, represents the fulfillment of Bragg's condition for constructive interference from surface atoms. Thus, the diffraction spots assume the symmetry of the reciprocal lattice which is uniquely related to one real space lattice. The symmetry of the real surface lattice can be reconstructed using the diffraction spot pattern. Long-range order (LRO) on the surface is necessary to obtain sharp *LEED* spots. Broadening and intensity attenuation of the *LEED* spots are associated with the loss of LRO, e.g. the formation of islands on the surface during film growth.

2.3 Sample Preparation

2.3.1 Crystal Polishing and Orientation

The Al single crystals were mechanically polished several times using silicon carbide paper with a decreasing grit size. The Laue X-ray diffraction method was used to orient the surface of the crystal with respect to the desired crystallographic direction. During this process, the crystals were mounted on the polisher-goniometer to keep track of the degree of surface alignment. Crystals were then flipped, and the opposite surface

was similarly polished. This procedure guarantees that the two crystal surfaces are parallel, which is convenient for the final installation in the vacuum chamber. We estimate that the crystals were aligned to within 0.5° of the required crystallographic plane. This estimate is based on the width of the Laue diffraction spots, and thus is an upper limit on the misorientation. A final, fine polish followed, where solutions with decreasing particle sizes were used, starting with 100 micron and finishing with 0.8 micron particle size. The samples were then cleaned in deionized water, and chemically etched using a solution consisting of HCl, HF, and HNO₃, with concentrations of 1.5%, 1.5%, and 2.5% respectively, for 15 seconds. The chemical etching removes the top layer that is strained due to the mechanical polishing. The crystals were then rinsed with water followed by alcohol, and then dried before mounting in the *UHV* chamber.

2.3.2 Crystal Sputter Cleaning and Annealing

The samples were cleaned in vacuum by repeated cycles of Ar⁺ ion bombardment for several hours with the sample at room temperature, followed by annealing the sample at 450°C for 15 minutes. The 1-2 keV argon ion beam used in the cleaning cycles was rastered over the entire sample surface. The *XPS* spectrum of the sample before cleaning exhibited an Al 2*p* line, with a second component at higher binding energy associated with the oxide (Al₂O₃). The cleaning procedure was repeated until the photopeak associated with the oxide was completely removed from the spectrum. The O 1*s* photopeak could not be used to monitor the Al surface oxide

because the *XPS* analysis area included a small portion of the Mo sample holder surrounding the Al crystal. Figure 2.14 shows the Al photoemission peaks before and after the sample cleaning process. The cleanliness of the surface is confirmed by measuring a *SP* area in a channelling spectrum that is in agreement with the calculated yield from the computer simulations.

2.4 Titanium Film Deposition

Twisted strands of three high purity Ti wires (99.99%), 0.25 mm in diameter and 10 cm in length, were wound into small filaments and then etched in a 20% HF solution. To deposit Ti on the Al surface, these filaments were resistively heated using a constant current power supply to maintain a constant Ti sublimation rate. This source of Ti atoms was mounted 5" away from the Al sample so that a uniform Ti flux was obtained across the sample surface. A deposition rate of about 0.5 ML/min. was typically obtained by maintaining a current of about 4.5 A through the Ti wire. Backscattering was used to measure the total Ti coverage at the different stages of the experiments.

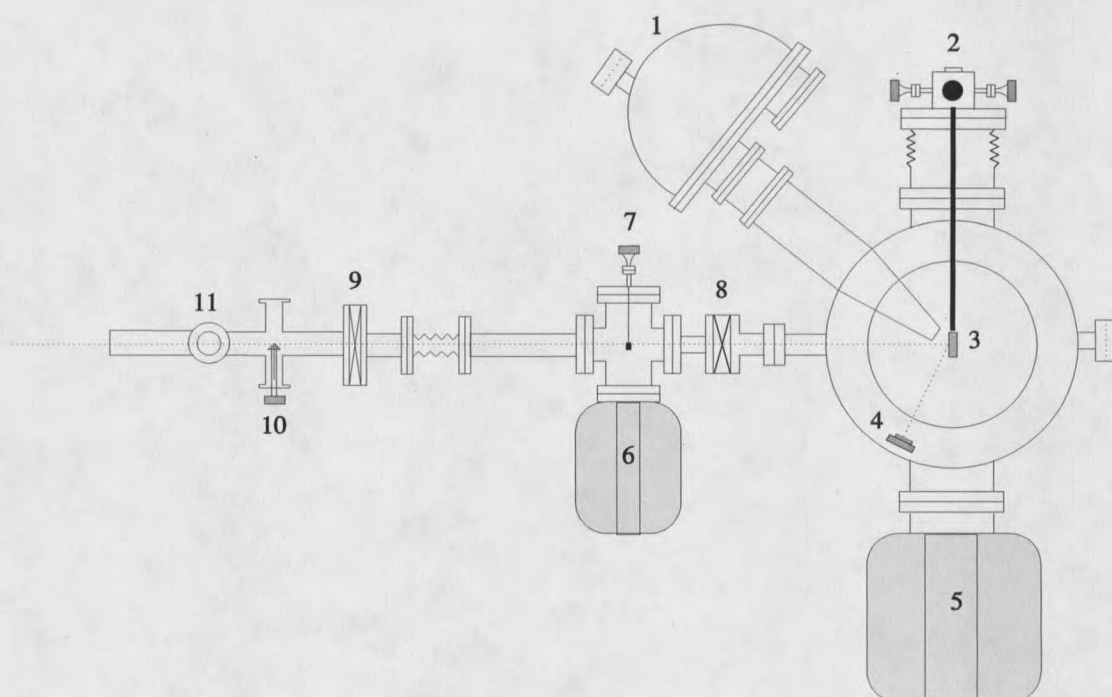


Figure 2.1(a) Side view of the scattering chamber. The following main components are identified: (1) Electrostatic Analyzer; (2) Goniometer; (3) Sample; (4) Particle Detector; (5),(6) Ion Pumps; (7) Blocker; (8),(9) Valve; (10) Beam viewer.

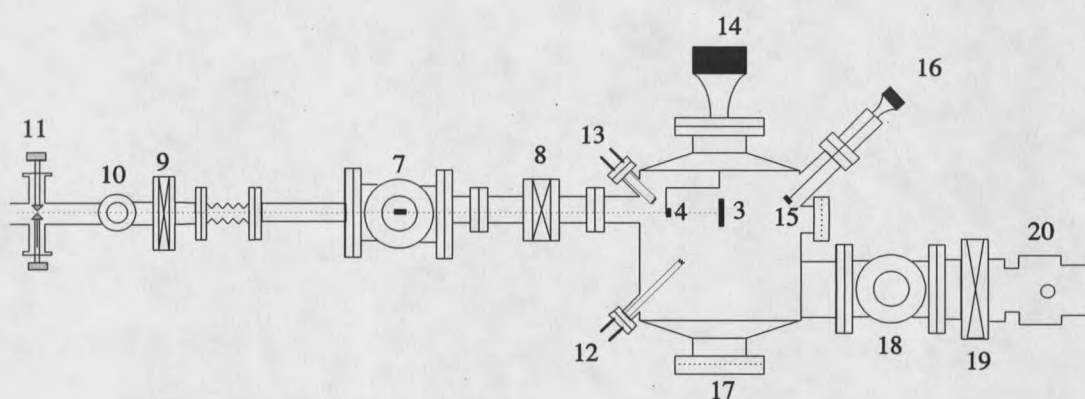


Figure 2.1(b) Top view of the scattering chamber. The following main components are identified: (11) Stabilizer slit; (12) Ti source; (13) Ni source; (14) Detector goniometer; (15) Particle detector; (16) Linear motion feedthru; (17) Viewing window; (18) Ti sublimation pump; (19) Gate valve, (20) Turbo molecular pump (see also Figure 2.1(a)).

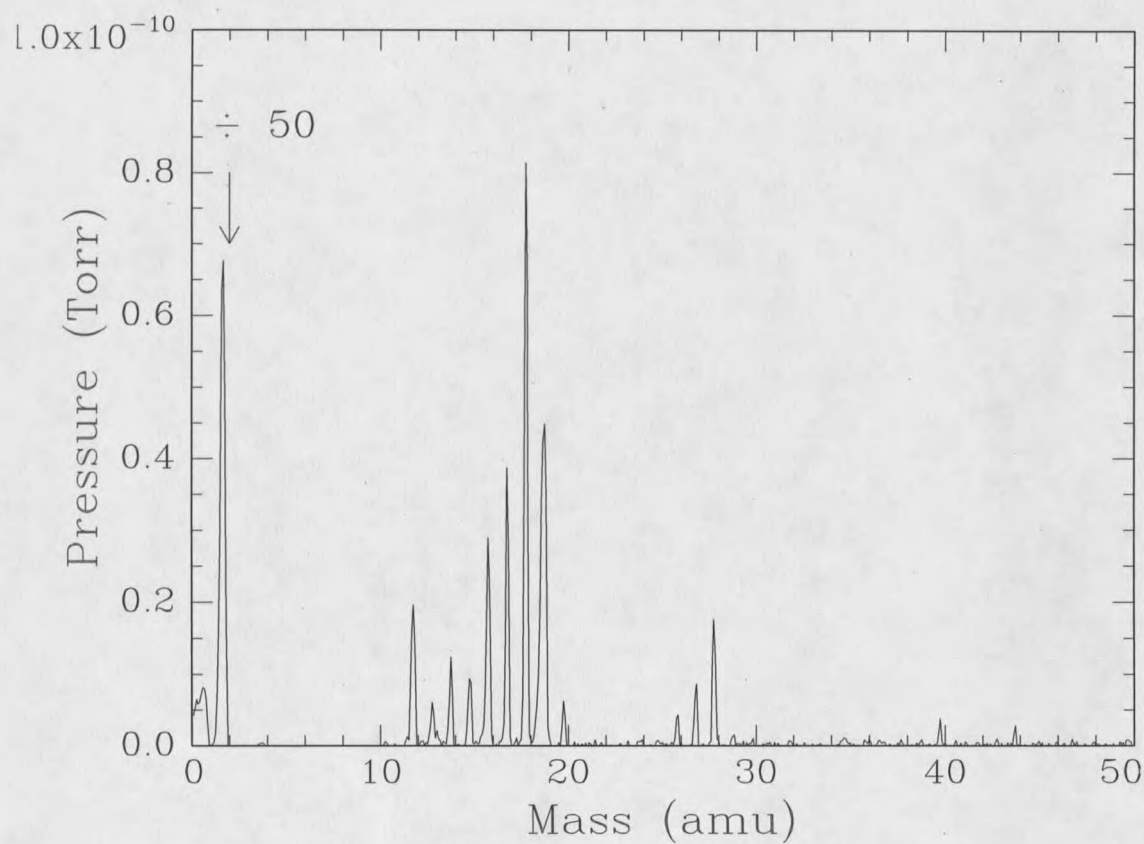


Figure 2.2 Typical mass spectrum of residual gas in the chamber, where hydrogen is the main component, followed by H_2O .

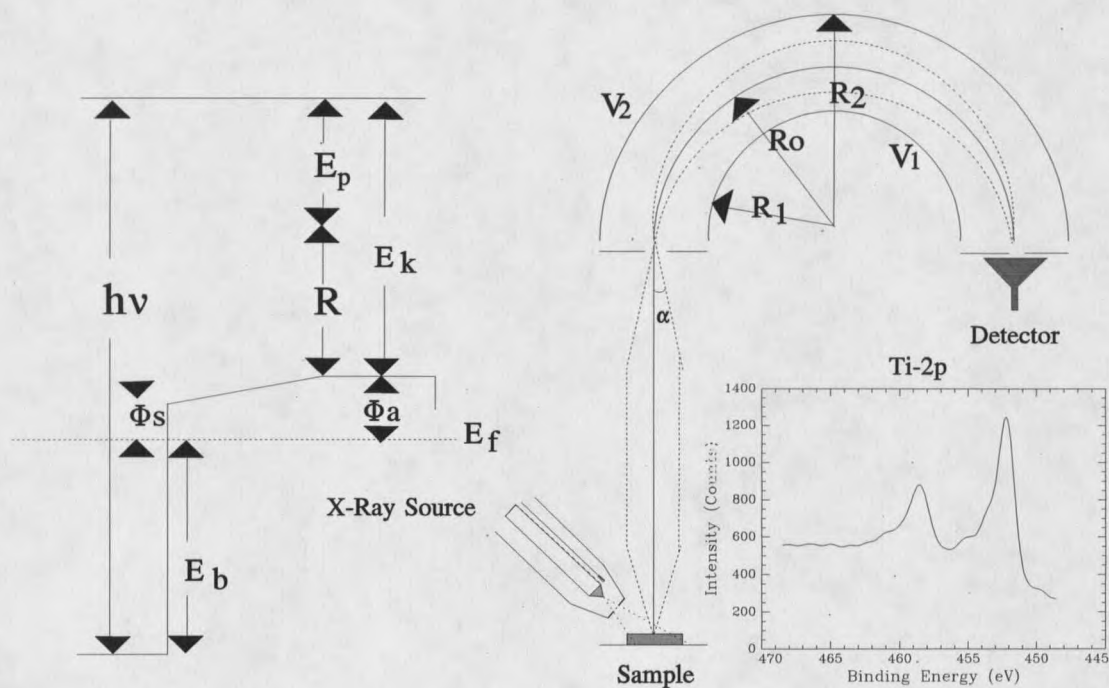


Figure 2.3 Schematic of X-ray photoemission spectroscopy. X-rays excite bound electrons in the sample. The electron kinetic energy is measured using a hemispherical analyzer. The potential difference between the inner sphere and the outer sphere is related to the kinetic energy of detected electrons, E_k , and the radii of the hemispheres such that: $V_1 - V_2 = E_k(R_2/R_1 - R_1/R_2)$.

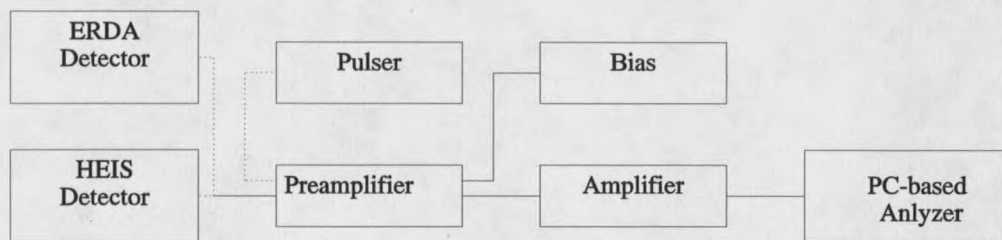


Figure 2.4 Schematic of ion detection in backscattering spectrometry and elastic recoil detection analysis.

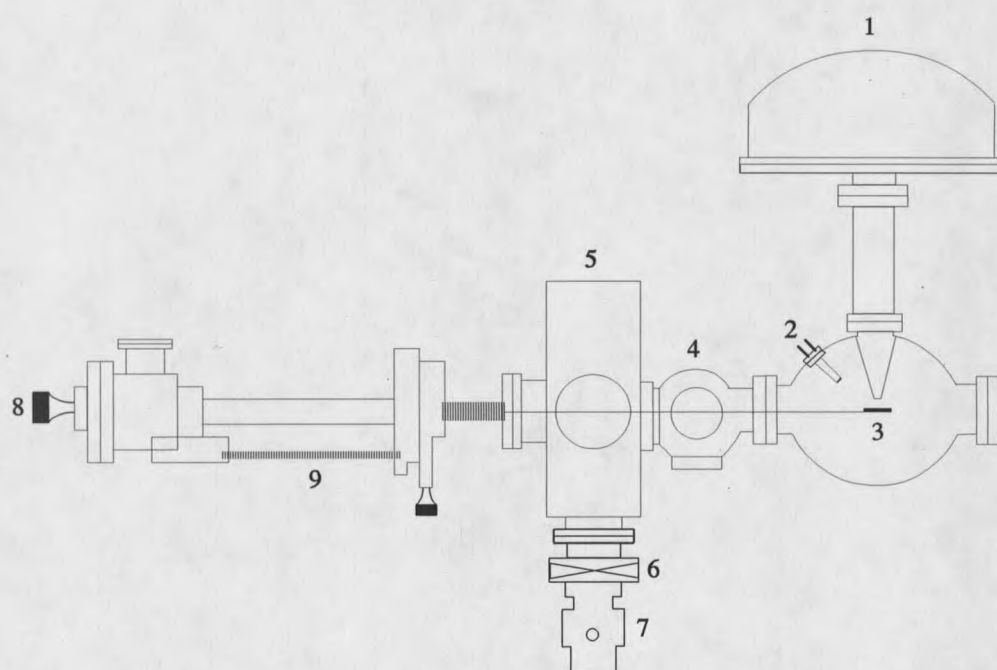


Figure 2.5 Side view of the Leybold chamber. The following components are indicated: (1) Electrostatic Analyzer; (2) Ti Source (3) Sample; (4) *LEED* Chamber; (5) *EELS* Chamber; (6) Gate Valve; (7) Turbo Pump; (8) Goniometer; (9) Sample Introduction System.

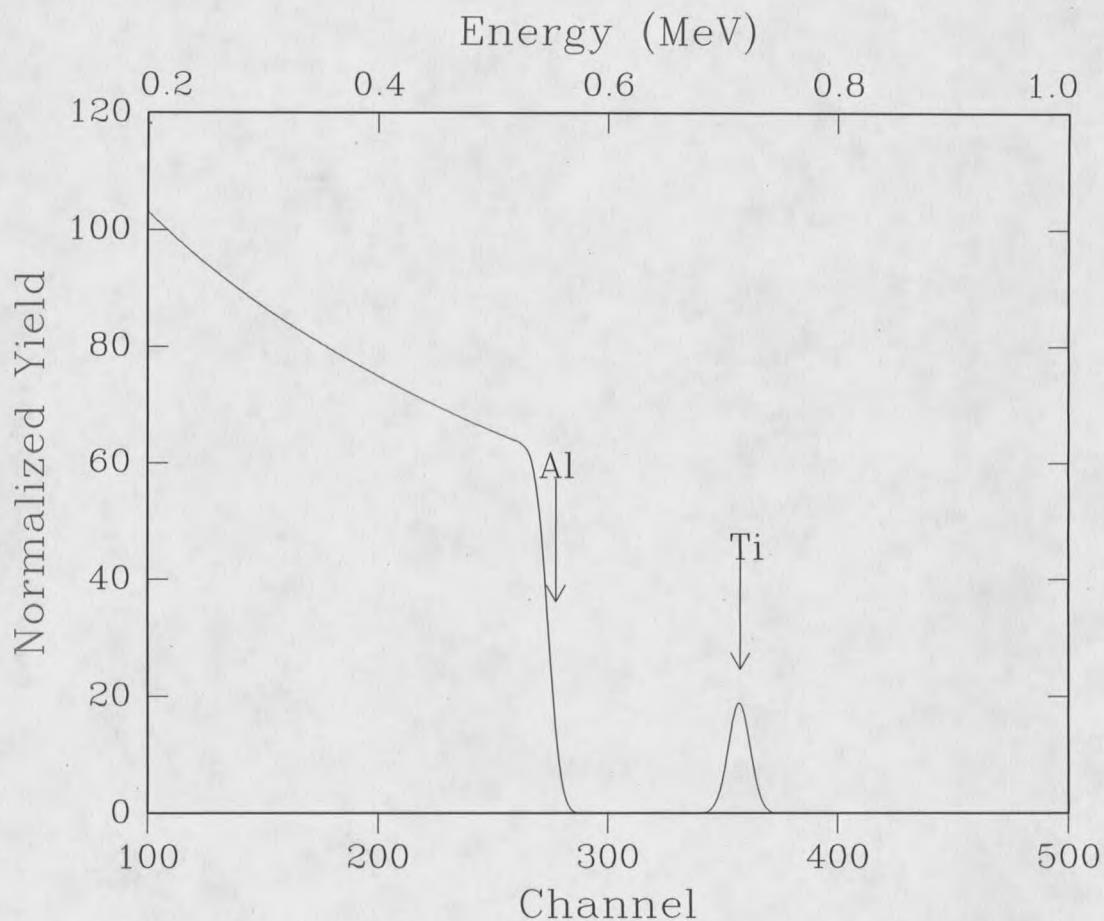


Figure 2.6 A simulated 1 MeV He⁺ ion backscattering spectrum for a 50 Å Ti film on Al substrate using *RUMP*. The backscattering from the Ti film results in a narrow peak, whereas backscattering from the Al substrate results in a nearly step function yield.

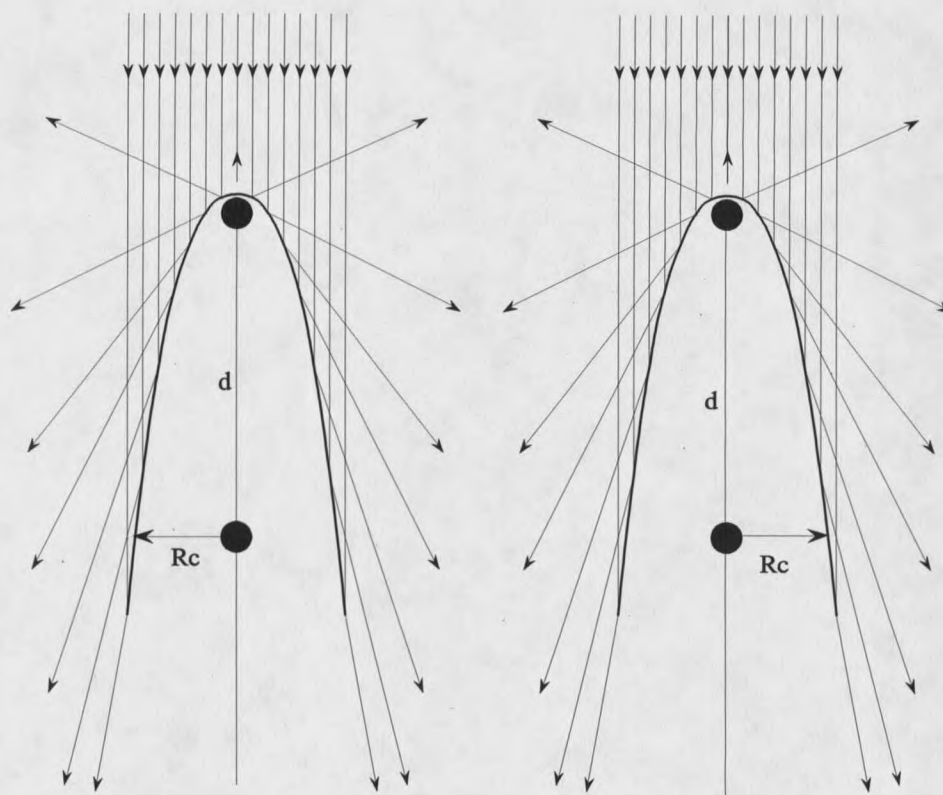


Figure 2.7 A schematic diagram of the shadowing effect. A shadow cone forms with a radius R_c at distance d from the surface. For a static lattice, all underlying atoms are shadowed by the top atom.

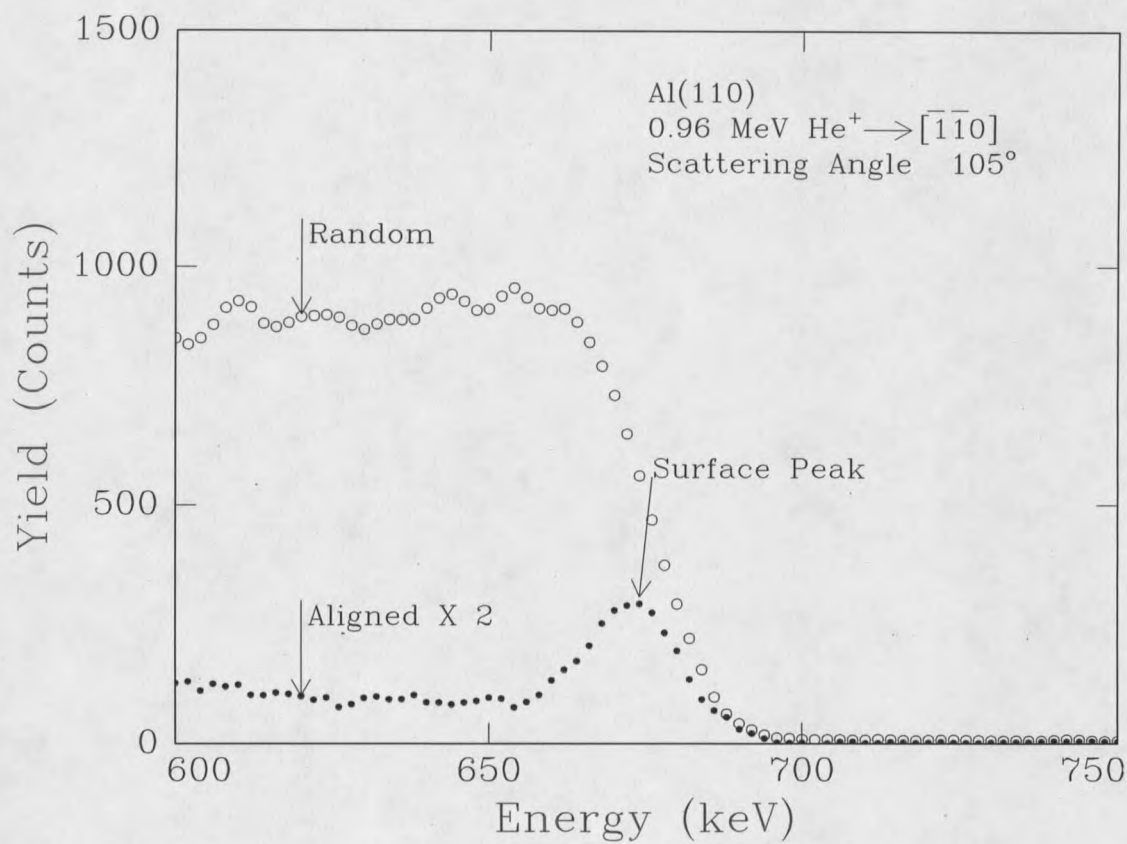


Figure 2.8 Ion scattering spectra, for an Al(110) surface, taken at random incidence (open circles) and with the beam incident along $[\bar{1}\bar{1}0]$ (the solid circles). The yield is reduced dramatically when the ion beam is incident along a major crystallographic direction.

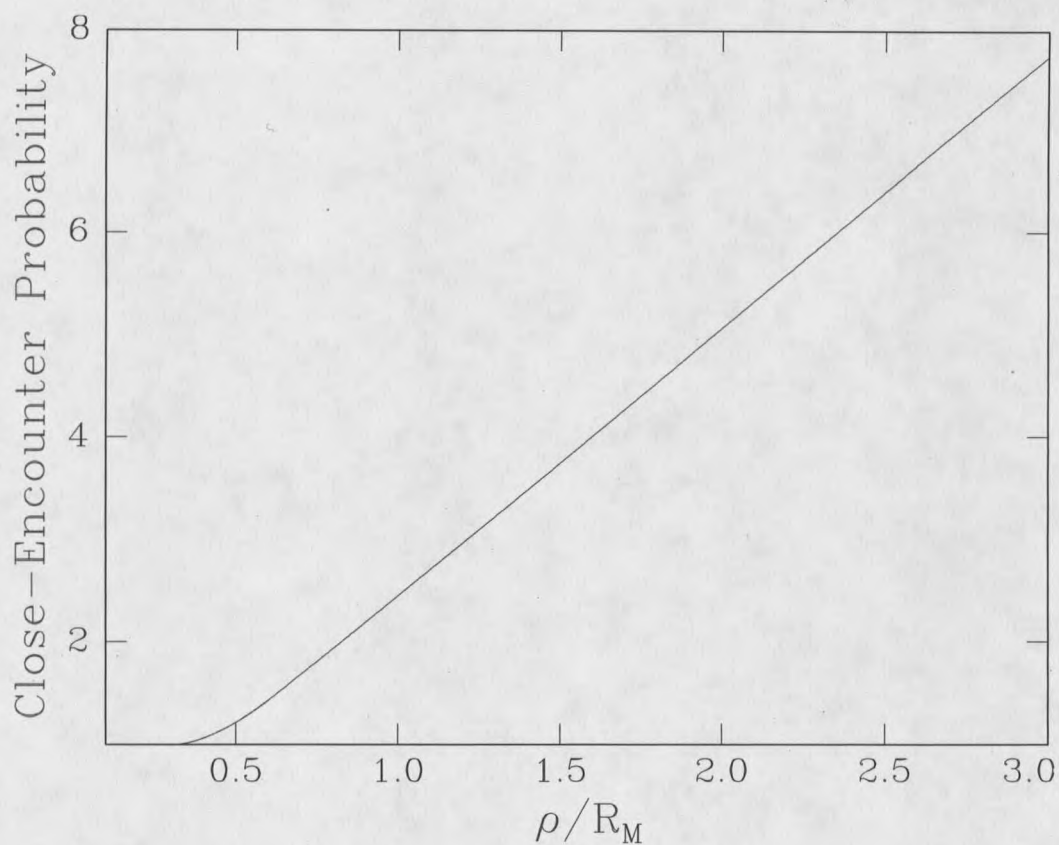


Figure 2.9 The universal curve generated from computer simulations of ion scattering from crystals with bulk-like terminated surfaces. The summed close-encounter probability is calculated as a function of the ratio ρ/R_M .

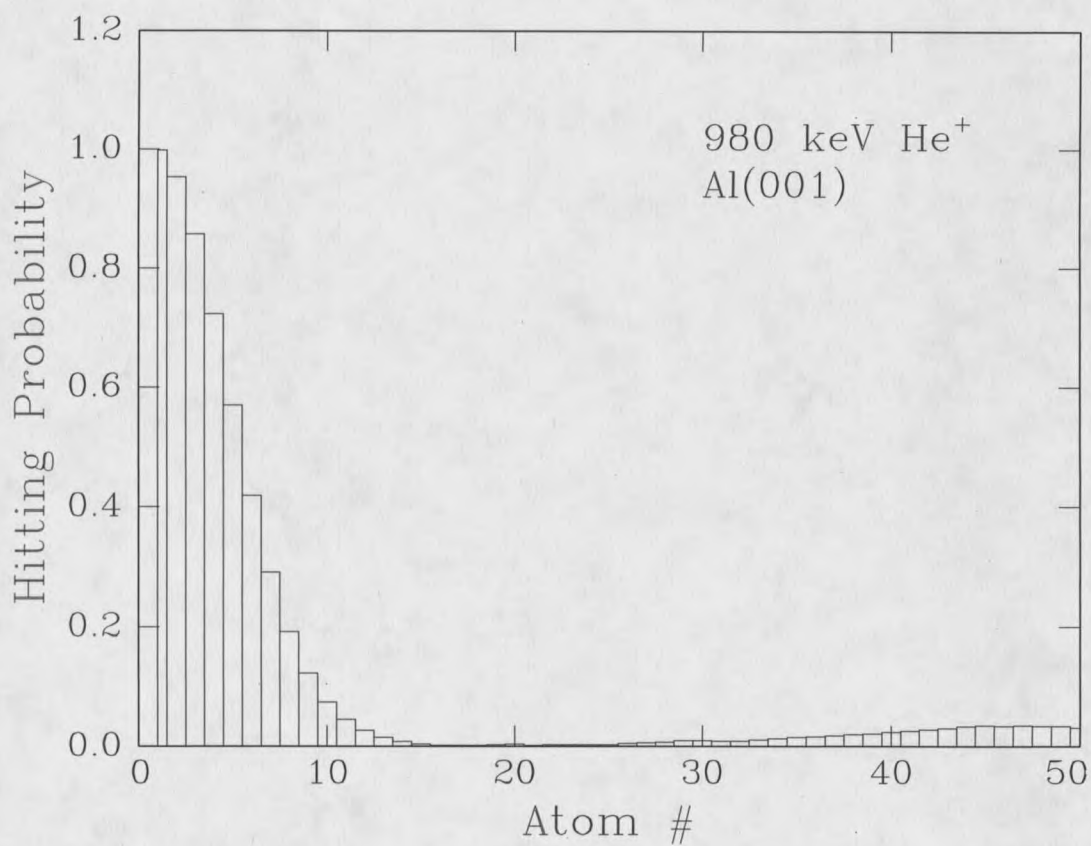


Figure 2.10 The individual close-encounter probabilities, for an Al atomic row in the [001] direction calculated using *VEGAS*.

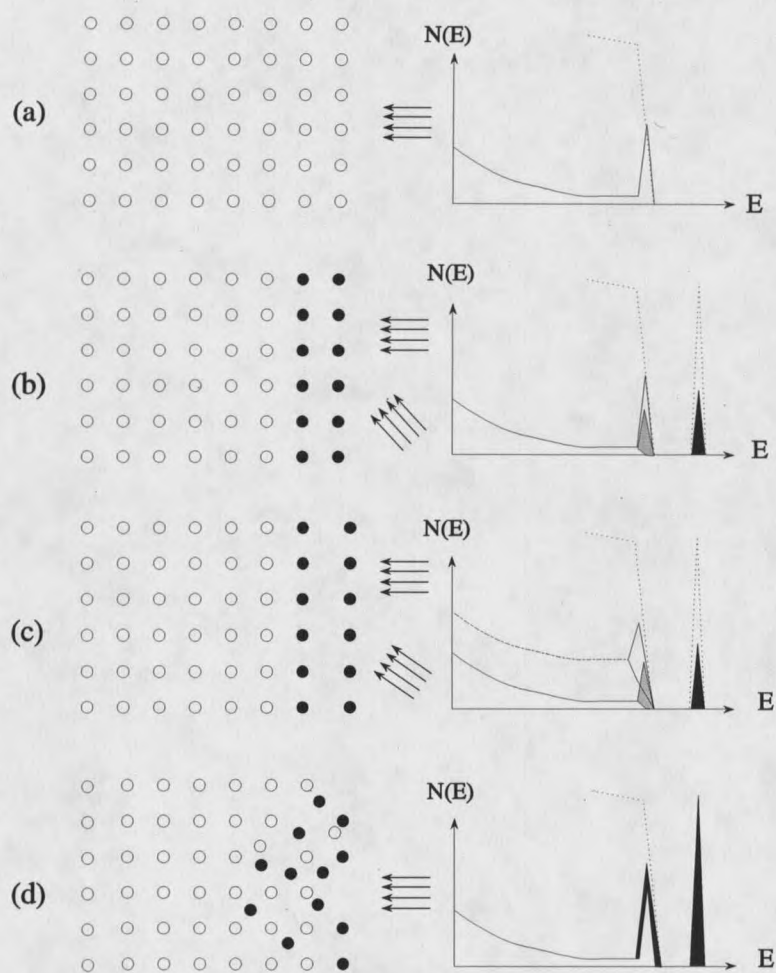


Figure 2.11 Schematics of the application of *HEIS* as a surface probe to study the structure of adsorbate/substrate systems. The variations in the substrate and/or overlayer scattering yield with ion beam direction reflect the microscopic symmetries in the system.

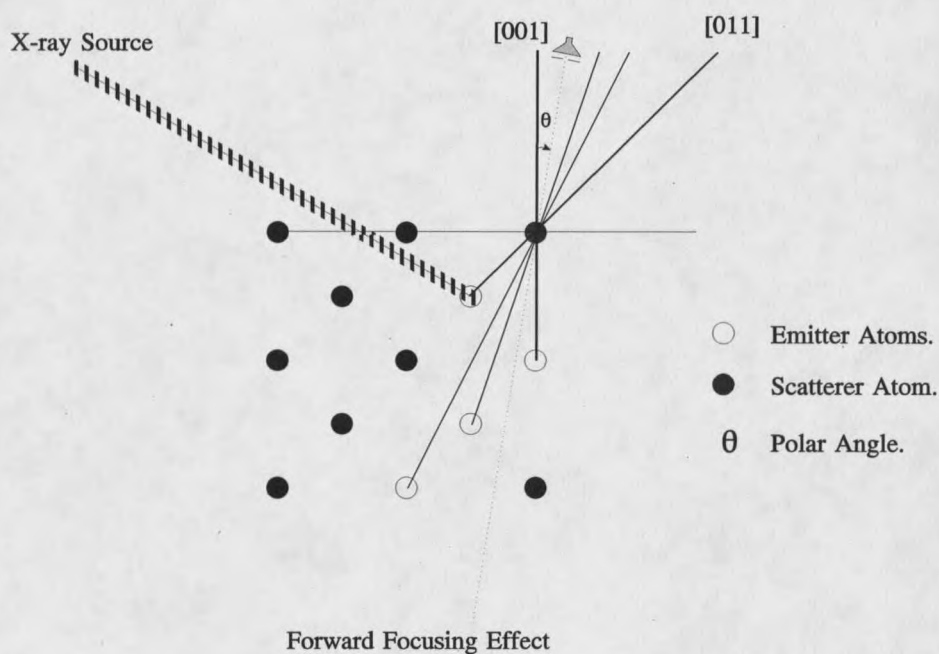


Figure 2.12 Structural diagram for an *fcc* structure in the (010) plane of emission. The directions along which there are forward focusing enhancements in the photoemission peak are indicated. The angular dependence of the photopeak intensity reflects the symmetries of the atomic structure.

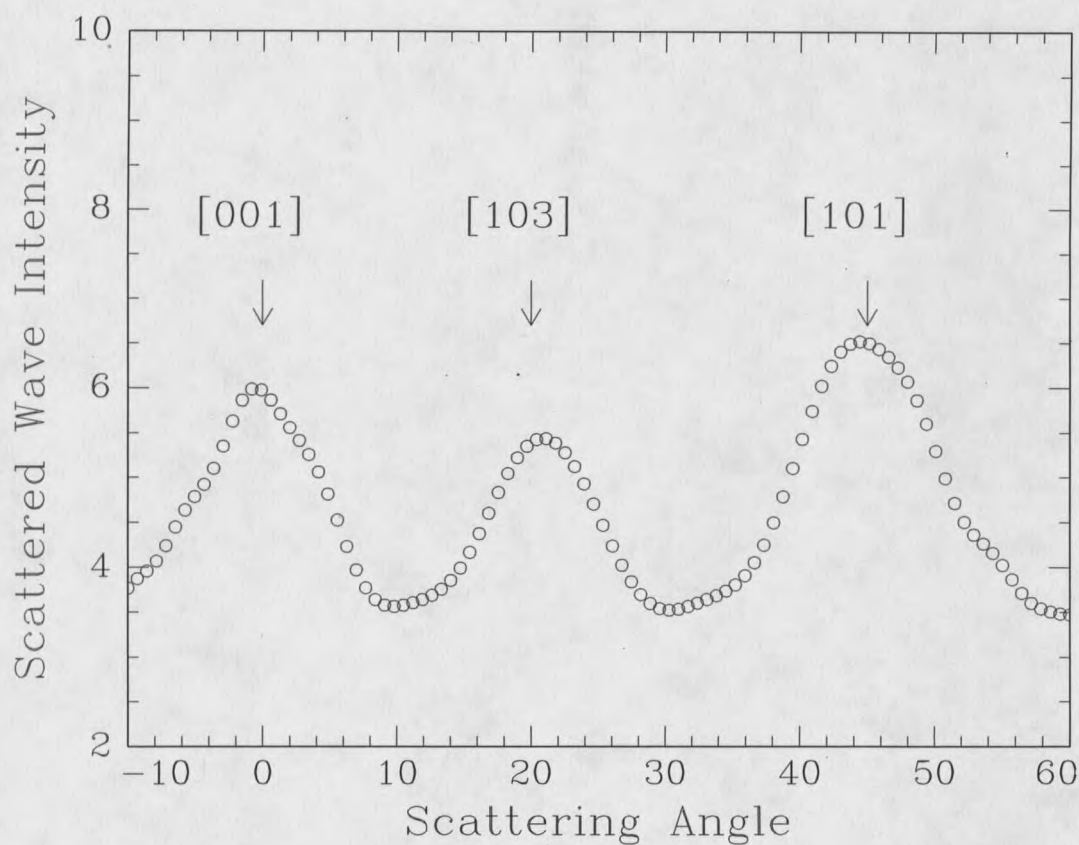


Figure 2.13 Calculated polar angular distributions in the (010) azimuthal plane for Al(001). Equation 2.21 was used to calculate $I(\theta)$ for a structure similar to that shown in Figure 2.12. A kinetic energy of 1000 eV for the photoelectrons was used. The photopeak is enhanced along the major crystal directions. The peak at 20° is due to a combination of enhancements, but mainly to the focussing along [103].

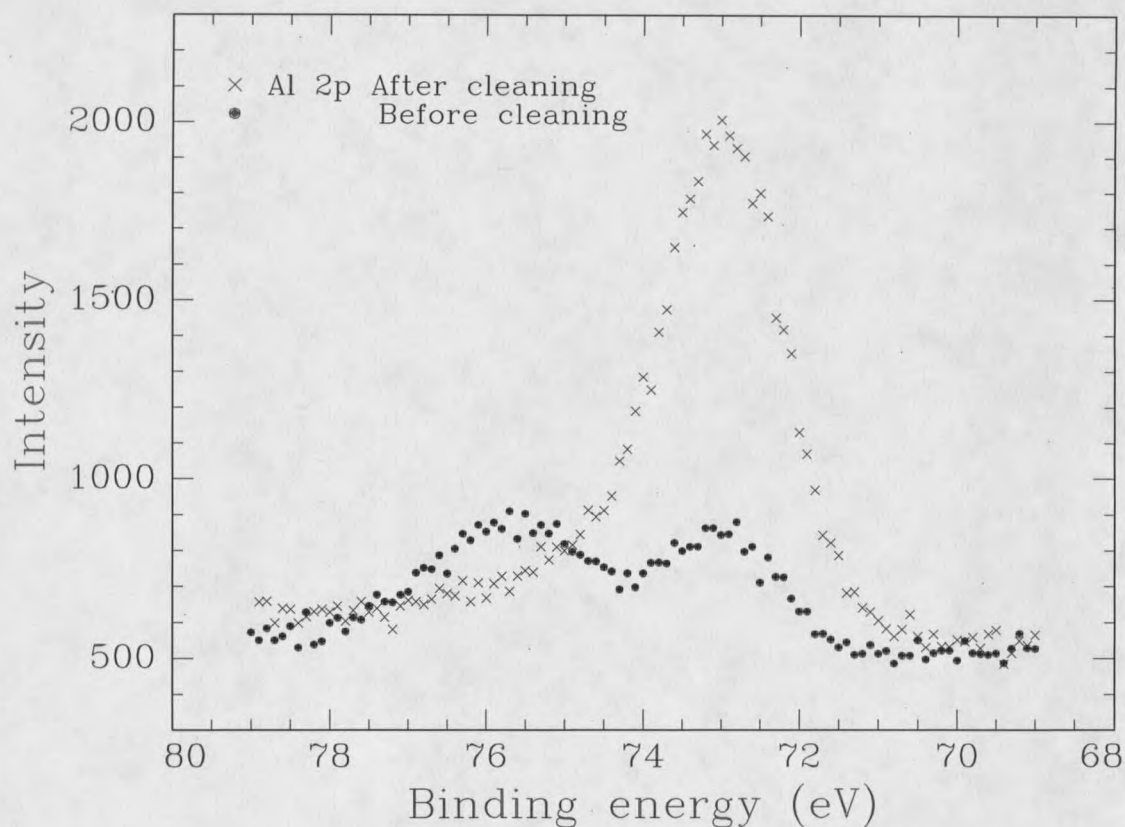


Figure 2.14 Al 2p photopeak before and after cleaning and annealing. Initially, a layer of Al_2O_3 covers the surface. This layer is removed using Ar^+ ion sputtering. The sample is then annealed to remove the surface damage.

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ELASTIC RECOIL DETECTION ANALYSIS

Although hydrogen content of materials impacts their physical and chemical properties significantly, most modern analytical techniques fail to detect its presence.^{1,2} For example, helium backscattering from hydrogen, is forbidden by momentum conservation. And because of hydrogen's electronic configuration, the Auger process is not allowed, while x-ray based techniques are practically blind to hydrogen. Ultraviolet photoelectron spectroscopy (*UPS*) is typically used to study surface hydrogen. However *UPS* is only sensitive to the top few layers corresponding, to the mean-free-path of emitted photoelectrons. In addition, quantitative analysis of the hydrogen content using *UPS* involves standard samples. Nuclear reactions are also used to carry out such studies, where nuclear resonances are employed to measure the hydrogen content as a function of depth. However, these experiments require a source of high-energy ion beams. For example, the nuclear reaction $^1\text{H}(^{19}\text{F}, \alpha\gamma)^{16}\text{O}$ may be utilized, where an incident fluorine ion beam with a particle kinetic energy of 17 MeV corresponds to the reaction resonance energy at the surface.³ Higher particle energies are required to probe deeper in the sample due to the energy loss associated with traversing the sample material. Such experiments are costly, and highly energetic ion beams are not easily accessible. Ions with energy in this range lead to considerable

sample damage. On the other hand, recoil experiments require relatively low particle energies, and a quantitative characterization of the hydrogen depth profile is relatively easy to obtain.⁴ Where backscattering spectrometry is available, only a slight modification to the existing setup is needed to conduct recoil measurements. To carry out recoil analysis measurements, the particle detector is positioned at forward angles and is capped with a thin absorber foil. Nonetheless, to do an accurate analysis, reliable values for the recoil cross-sections are required. In the following section, the basic principles of elastic recoil detection analysis (*ERDA*) will be presented. Then, the experimental considerations to optimize the technique will be discussed. Finally, calculations of the recoil cross-section of hydrogen, caused by an incident helium atom will be presented.

3.1 Basic Principles

Consider a hydrogen atom recoil event due to an energetic helium ion incident at a grazing angle α and at depth x from the surface. When the energy of the incident ion is high enough, a consequent recoil of the hydrogen atom takes place, in which it emerges out of the surface in the forward direction. This process is depicted in Figure 3.1. The energy of the recoiled hydrogen atom can be computed by requiring that energy and momentum be conserved during the He-H binary collision. The energy of a hydrogen atom, E_2 , immediately after the recoil, is related to the energy of the incident helium ion, E_1 , right before the collision, through a constant k such that:

$$E_2 = k(\theta, \frac{M_1}{M_2}) E_1 \quad (3.1),$$

where M_1 and M_2 are the hydrogen and helium atomic masses respectively, and θ is the recoil angle as measured with respect to the incident ion beam. The constant k is referred to as the kinematic factor and is given by:

$$k = \frac{4 M_1 M_2}{(M_1 + M_2)^2} \cos^2 \theta \quad (3.2).$$

Since this event takes place at depth x from the surface, the stopping of the incident ions due to traversing the sample medium should be taken into account. Thus the energy of helium ions, at this depth, is given by:

$$E_1(x) = E_o - S_1 \frac{x}{\sin \alpha} \quad (3.3),$$

where S_1 is the average rate of energy loss per unit length for helium traveling in the sample, and E_o is the energy of the incident helium ions. On the other hand, the recoiled protons lose energy as they traverse the sample on their exit path. Thus using equations (3.1) and (3.3), the energy of recoiled hydrogen atoms, from depth x , is written as:

$$E'_f = kE_o - [S] x \quad (3.4),$$

where $[S]$ is the generalized stopping cross-section given by:

$$[S] = \frac{kS_1}{\sin\alpha} + \frac{S_2}{\sin(\theta-\alpha)} \quad (3.5),$$

and where S_2 is the average rate of energy loss per unit length for protons traveling in the sample. S_1 and S_2 can be evaluated using the tabulated values of energy loss rates, and can be approximated as follows:

$$S_1 = \frac{dE}{dx} \left(E_o - \frac{\Delta E}{2} \right) |_{He, in} \quad (3.6),$$

and

$$S_2 = \frac{dE}{dx} \left(kE_o - \frac{\Delta E}{2} \right) |_{H, out} \quad (3.7).$$

The stopping rates as a function of energy for both helium and hydrogen in aluminum are shown in Figure 3.2. These plots are generated using the *TRIM* computer code.

To filter out the dominant flux of elastically scattered helium ions, a stopper foil is placed in front of the detector. The foil thickness is chosen so that it exceeds the range of incident helium ions in the stopper material for the energy range of interest, and is mounted at the detector entrance. Because of their lower stopping power, the

recoiled hydrogen atoms pass through the foil. Thus, the energy of the recoiled atoms when detected can be expressed as:

$$E_f(x) = kE_o - [S]x - \Delta E_s \quad (3.8),$$

where ΔE_s is the energy loss in the stopper foil, and is given by the difference between E_f and the energy of the hydrogen atoms just before the penetration of the stopper foil, E'_f .

The energy spectrum of the recoiled hydrogen is related to the hydrogen concentration profile such that:⁵

$$N(E_f)\delta E_f = \rho(x)\delta x \cdot \sigma(E_o) \cdot (\Delta\Omega) \cdot Q \quad (3.9),$$

where $\rho(x)\delta x$ is the number of hydrogen atoms in a thin slab of material with thickness δx , σ is the recoil cross-section, $\Delta\Omega$ is the solid angle subtended by the detector, and Q is the total number of incident helium ions. The energy width of one channel, δE_f , can be related to the slab width, δx , by studying the energy loss rate dependence on E'_f and on the stopper foil thickness. Taking small variations of the quantities on both sides of equation 3.4, we obtain:

$$\delta E'_f = -[S]\delta x \quad (3.10).$$

We will demonstrate that in the energy range of interest, and for a particular foil thickness, the recoil energy before the foil penetration, E'_f , is linearly related to the

final energy such that:

$$E'_f = \beta E_f + \gamma \quad (3.11),$$

where β and γ are constants to be determined. It should be noted that this approximation is valid over the range of energies of interest in this treatment. To express E'_f in terms of E_f , a table of energy loss rates of hydrogen in aluminum is needed. These values are well known over the range of interest which are plotted in Figure 3.2. Because the energy loss rate is a function of energy, one needs to evaluate this loss throughout the path in the stopper foil. In this study, we divided the path into a hundred layers of equal width, Δx , 0.08 μm in thickness, through each of which the energy loss was assumed to be constant. For a certain value of E'_f , the energies of the hydrogen atoms are calculated as they penetrate the stopper such that:

$$E(i) = E(i-1) - \Delta x \cdot \left. \frac{dE}{dx} \right|_{E=E(i-1)} \quad (3.12),$$

where $E(i)$ is the energy of the hydrogen atoms after passing the i^{th} layer. In the previous equation, the initial value for the energy $E(0) = E'_f$ and the final value $E(100) = E_f$. This process was repeated over the range of energies 700-1100 keV for E'_f with 10 keV increments. Figure 3.3 shows the results of these calculations. The solid line in the figure represents a linear fit of E_f versus E'_f with values of 0.63 for β , and 642 keV for γ in equation (3.11) above. Substituting this result in equation (3.10) leads to

an expression for the slab width:

$$\delta x = 0.63 \frac{\delta E_f}{[S]} \quad (3.13).$$

This result is substituted in equation (3.9) leading to the following expression for hydrogen volume density:

$$\rho(x) = \frac{N(E_f) [S]}{0.63 \sigma (\Delta\Omega) Q} \quad (3.14).$$

Also, x and E_f are related through equations (3.4) and (3.11), from which we obtain the following expression for x :

$$x = \frac{kE_o - \beta E_f - \gamma}{[S]} \quad (3.15).$$

Equations (3.14) and (3.15) are used to convert the recoil energy spectrum into a hydrogen density depth profile, where each recoil energy E_f is associated with a certain depth x , using equation (3.15), and the yield at this particular energy, $N(E_f)$ is also associated with a particular value for the hydrogen volume density, $\rho(x)$.

3.2 Experimental Considerations

3.2.1 Sensitivity and Probing Depth

In our experiments, a helium ion beam of 1.8 MeV energy, and a stopper foil of 8 μm were used. Figure 3.4 shows the energy of recoiled hydrogen atoms as a function of the recoil angle. Both the energy before and after penetration of the stopper foil are indicated. The energy dependence of the classical Rutherford recoil cross-section is also shown. Although a more realistic calculation of the cross-section deviates considerably from this curve, as discussed in section 3.3, it still can be used for the purpose of this discussion. For recoil angles larger than 40° , the recoil energy drops below 50 keV, which is below the range of energy that we can measure using a solid-state detector. Higher recoil angles are associated with higher cross-sections, yet the loss in energy puts an upper limit on the recoil angles that can be used. Also for practical purposes, only recoil angles larger than 10° can be used in the experiment. These two limiting factors define a relatively narrow angular window within which we can work. To optimize the sensitivity to hydrogen, a recoil angle of 30° should be used. However, the construction of the scattering chamber made 25° a reasonable choice for the recoil angle.

The maximum probing depth is another factor that needs to be investigated. It depends on the choice of geometry and on the nature of the sample material. We define the stopping depth as the depth from which hydrogen recoils with a final energy

of 50 keV or less, after the emergence from the sample and the passage through the stopper foil. Substituting this value for E'_β in equation (3.15), we obtain the following expression for the probing depth $x_{\max}$:

$$x_{\max} = 273 \text{ keV} \left[\frac{1}{\sin \alpha} S_1 + \frac{1}{\sin(\theta - \alpha)} S_2 \right]^{-1} \quad (3.16).$$

Since we selected a recoil angle of 25° to optimize the sensitivity, the maximum depth can still be adjusted depending on the tilt angle α . Figure 3.5 shows the maximum depth as a function of tilt angle. From this figure we observe that an angle of 15° maximizes the probing depth.

3.2.2 Depth Resolution

The depth resolution, Δx , is directly related to the total energy resolution of the spectrometer, ΔE , and is similar to that expressed in equation (3.13):

$$\Delta x = 0.63 \frac{\Delta E}{[S]} \quad (3.17).$$

Contributions to ΔE come primarily from the energy resolution of the detector, ΔE_d , and the energy straggling in the stopper foil, ΔE_s . The expression for ΔE is given by:

$$\Delta E = \sqrt{(\Delta E_d)^2 + (\Delta E_s)^2} \quad (3.18).$$

As mentioned earlier, the energy resolution of the detector is about 20 keV. Also, the energy straggling due to the stopper foil can be estimated using the Bohr formula:⁶

$$\Delta E_s = \sqrt{32 \ln 2 \pi e^4 Z_1 Z_2 N t} \quad (3.19),$$

where t is the stopper foil thickness, N is the foil atomic density, and Z_1 and Z_2 are the atomic numbers of the incident and target atoms respectively. Using the previous equation, we obtain a value of 32 keV for ΔE_s and a value of about 500 Å for the overall depth resolution. Furthermore, it should be noted that other less significant factors contribute to the energy resolution such as multiple scattering, geometrical broadening, and energy straggling within the sample.

3.3 $^1\text{H}(^4\text{He}, ^1\text{H})^4\text{He}$ Recoil Cross-Sections

The measurement of hydrogen content in materials using *ERDA* requires a knowledge of the hydrogen recoil cross-section as suggested by equation (3.14). As a first approximation, one can use the classical Rutherford cross-section:⁶

$$\sigma(E, \theta) = \left[\frac{Z_1 Z_2 e^2 (M_1 + M_2)}{2 M_2 E} \right]^2 \frac{1}{\cos^3 \theta} \quad (3.20).$$

However, as we will see later, this expression for the cross-section deviates

considerably from the measured values at the relevant energy ranges. To overcome this problem, standards with a known hydrogen concentration are used in some cases. Measured proton yields from a sample with an unknown hydrogen content are converted to hydrogen concentration by comparison with the yields from a standard. Obviously, using this method may introduce unnecessary complications in the experimental setup, especially in a UHV system where the chamber is baked prior to carrying out the experiment.

Ideally we would like to obtain an expression for $\sigma(E, \theta)$ similar to that given by equation (3.20), which would represent the problem more realistically. Quantum mechanical scattering theory must be used to better describe this problem. Within this framework, the scattering amplitude is usually expressed in terms of an infinite sum involving the phase-shifts of the partial waves associated with the incident beam. The phase-shifts are induced by the nuclear interaction, which is often imprecisely known. In the presence of spin-orbit coupling, and when the phase-shifts in the partial waves with high orbital angular momentum can be neglected, the scattering cross-section can be written in terms of the phase-shifts in the S and P waves. In the following treatment, we consider the problem of scattering of protons by helium in the center of mass frame of reference. The final calculations can be easily adjusted for the inverse problem in the laboratory frame. The scattering cross-section can be written as:⁷

$$\begin{aligned}
 k^2 \sigma_{C.M.}(\xi, \eta) = & \left| -\frac{\eta}{2} \csc^2 \frac{\xi}{2} e^{i\eta \ln(\csc^2 \frac{\xi}{2})} + e^{i\delta_0} \sin \delta_0 \right. \\
 & \left. + \cos \xi [2e^{i\delta_1^+} \sin \delta_1^+ + e^{i\delta_1^-} \sin \delta_1^-] \right. \\
 & \left. \times e^{i\phi_1} \right|^2 + \sin^2 \xi \sin^2(\delta_1^- - \delta_1^+)
 \end{aligned} \tag{3.21},$$

where ξ is the scattering angle, and where k , η , and ϕ_1 are related to the reduced mass M , and to the velocity at infinite separation, v , through the following relationships:

$$\begin{aligned}
 k &= \frac{Mv}{\hbar}, \quad \eta = \frac{2e^2}{\hbar v} \\
 e^{i\phi_1} &= \frac{1+i\eta}{1-i\eta}
 \end{aligned} \tag{3.22}.$$

In principle, the scattering cross-sections can be evaluated over all energy and angular ranges using equation (3.21), provided the knowledge of the phase-shifts δ_0 , δ_1^+ and δ_1^- . However, the calculation of the phase-shifts involves the nuclear interaction potential which is basically unknown. Hence, a large number of experiments have been aimed at the evaluation of the phase-shifts based on the measurement of the scattering cross-

sections. The resulting data are compiled and tabulated by Dodder *et al.*⁸ In our study, we use the tables to evaluate the energy dependence of the phase-shifts over the energy range of interest. This is done by fitting the phase-shifts to third order polynomial functions. Substituting the results of fitting into equation (3.21) provides the method of computing the cross-sections for all values of energies and all angles of interest. Figure 3.6 shows the fits for δ_0 , δ_1^+ and δ_1^- respectively. It should be emphasized that these fits are not an attempt to model the dependence on energy. They are merely one way to reproduce the tabulated data, and provide convenience for use. Because there is no angular dependence in the phase shifts, equation (3.21) can be used to evaluate the cross-sections for all angles. Figure 3.7 shows the recoil cross-section, at a recoil angle of $\xi = 25^\circ$ in the laboratory frame as calculated using this method. These results are compared to a least-squares fit of the experimentally measured recoil cross-sections, represented by the dashed-dotted line. The dashed line represents the Rutherford cross-section at the same angle. Because the nuclear forces play a minor role at low kinetic energies, the three curves give the same values for the cross-section in this regime. However, at higher kinetic energies, the deviation becomes more appreciable, and is about 100% for an incident He^+ energy of 2.0 MeV.

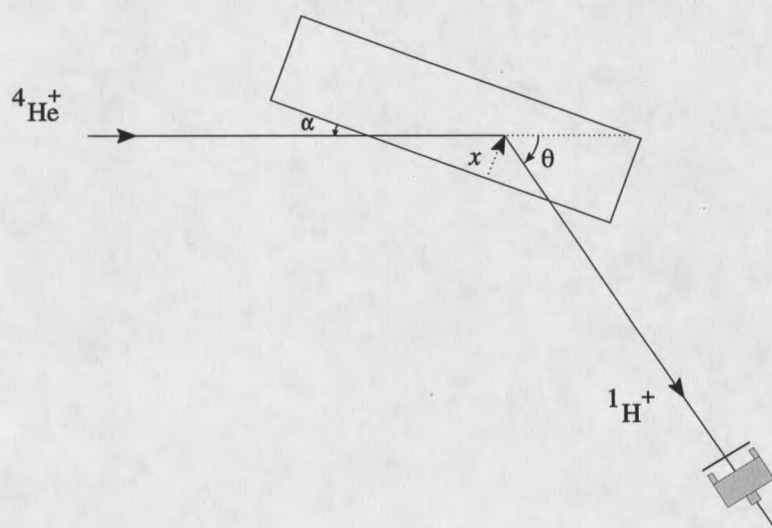


Figure 3.1 A schematic diagram of the *ERDA* setup. An incident He^+ ion causes the hydrogen atoms to recoil; the latter are detected and counted using a solid-state detector. An Al stopper is used to filter the He^+ ions scattered in the forward direction.

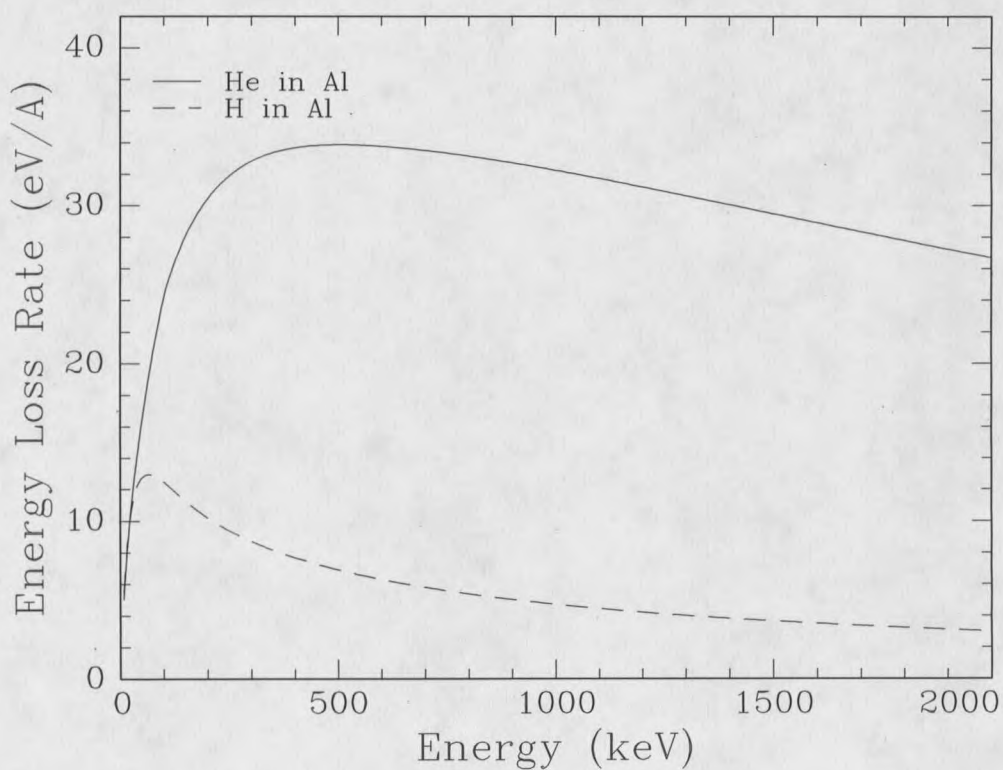


Figure 3.2 Helium and hydrogen stopping powers in Al as a function of energy. Helium has higher stopping in the energy range of interest. This effect is used to filter out the helium particles before they enter the detector by placing an Al stopper foil at its entrance.

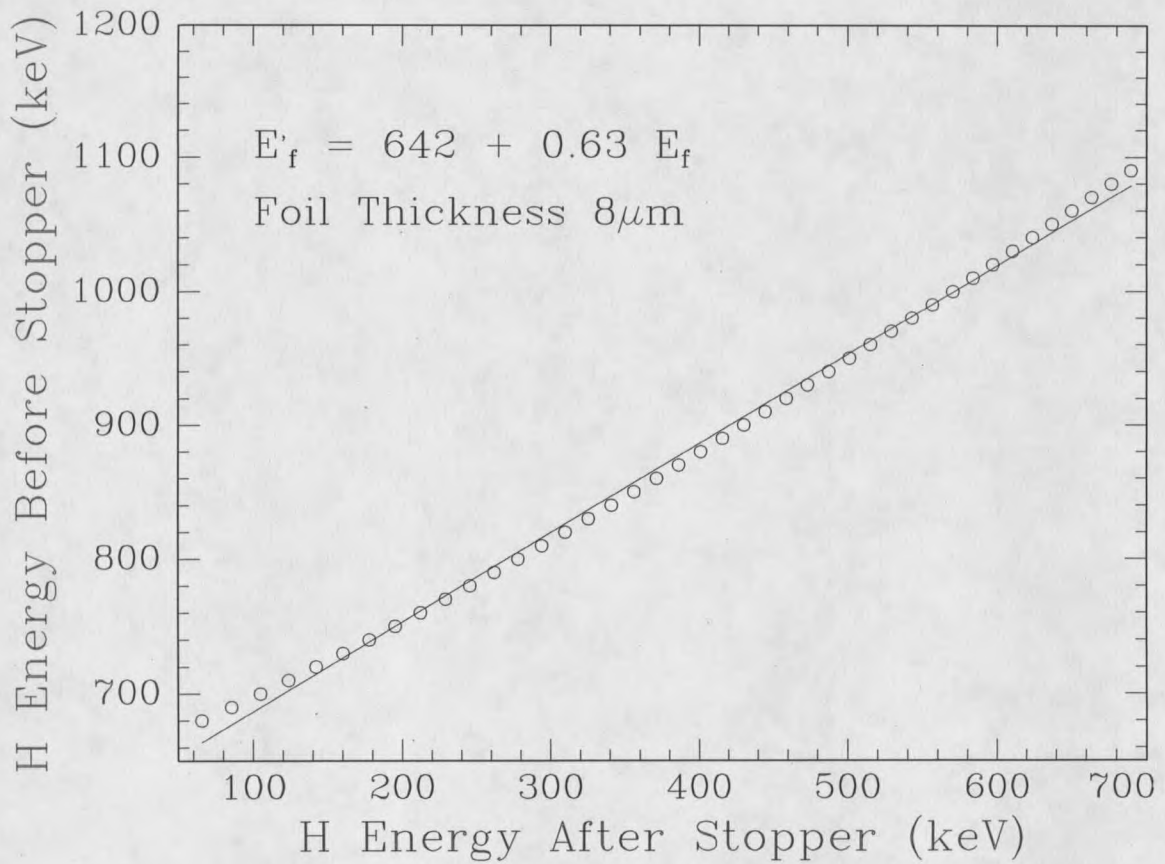


Figure 3.3 A plot relating the proton energies before and after their passage through an $8\mu\text{m}$ Al stopper foil. To a good approximation the relationship is linear (see equation 3.11).

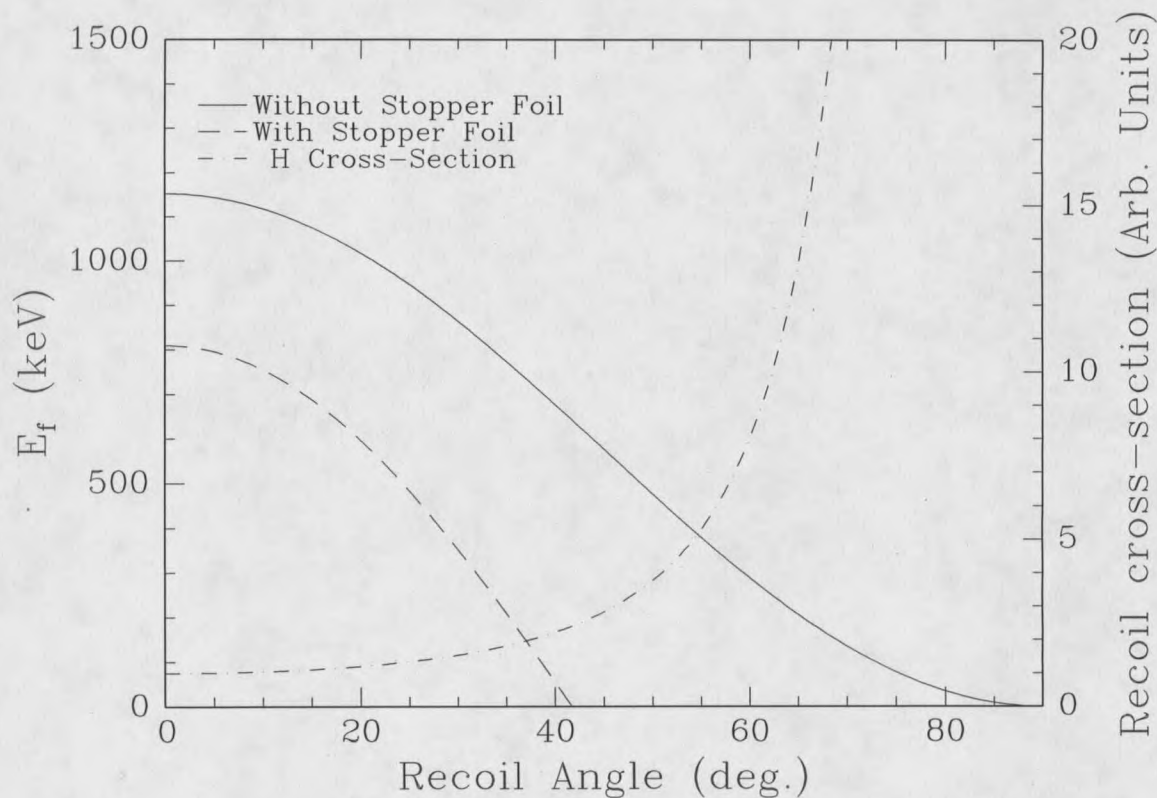


Figure 3.4 The final proton energy as a function of the recoil angle without a stopper foil (the solid line), and with an 8 μm foil (dashed line) placed at the entrance of the detector (left axis). The dashed-dotted line represents the dependence of the classical cross-section on the proton recoil angle (right axis).

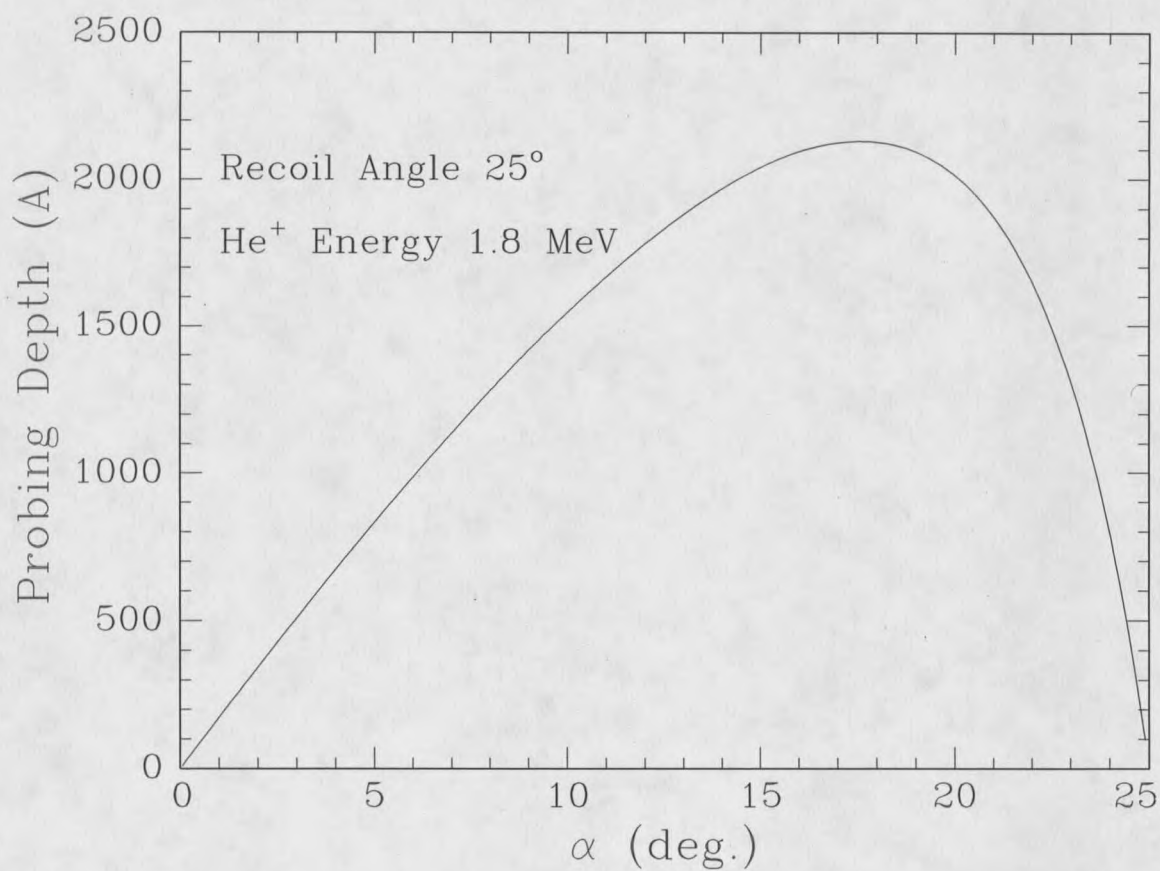
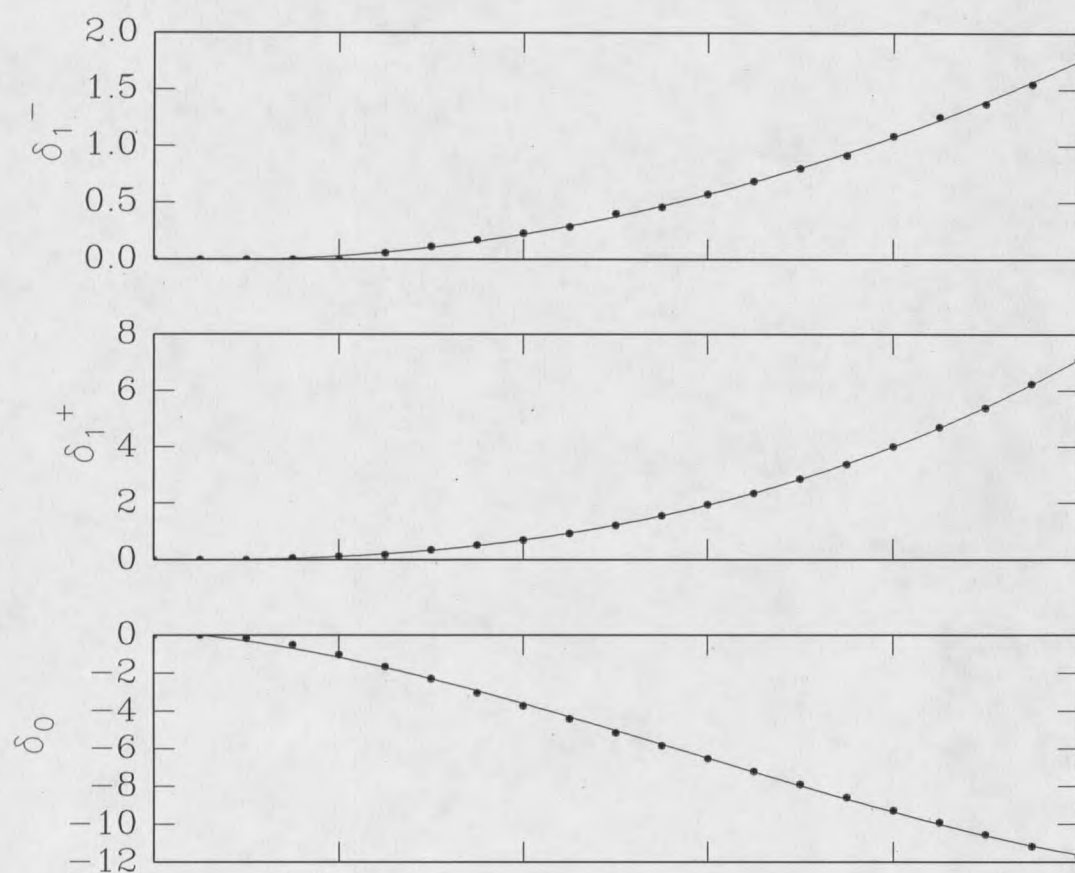


Figure 3.5 The maximum probing depth as a function of grazing angle in aluminum. The curve is calculated for a recoil angle of 25° , and He⁺ ion energy of 1.8 MeV.



Proton Energy (MeV)

Figure 3.6 The phase shifts in the S and P partial waves, in degrees, as a function of proton energy. The values of the phase shifts are obtained from Reference 8. The lines through the data points are polynomial fits obtained using a least-squares method.

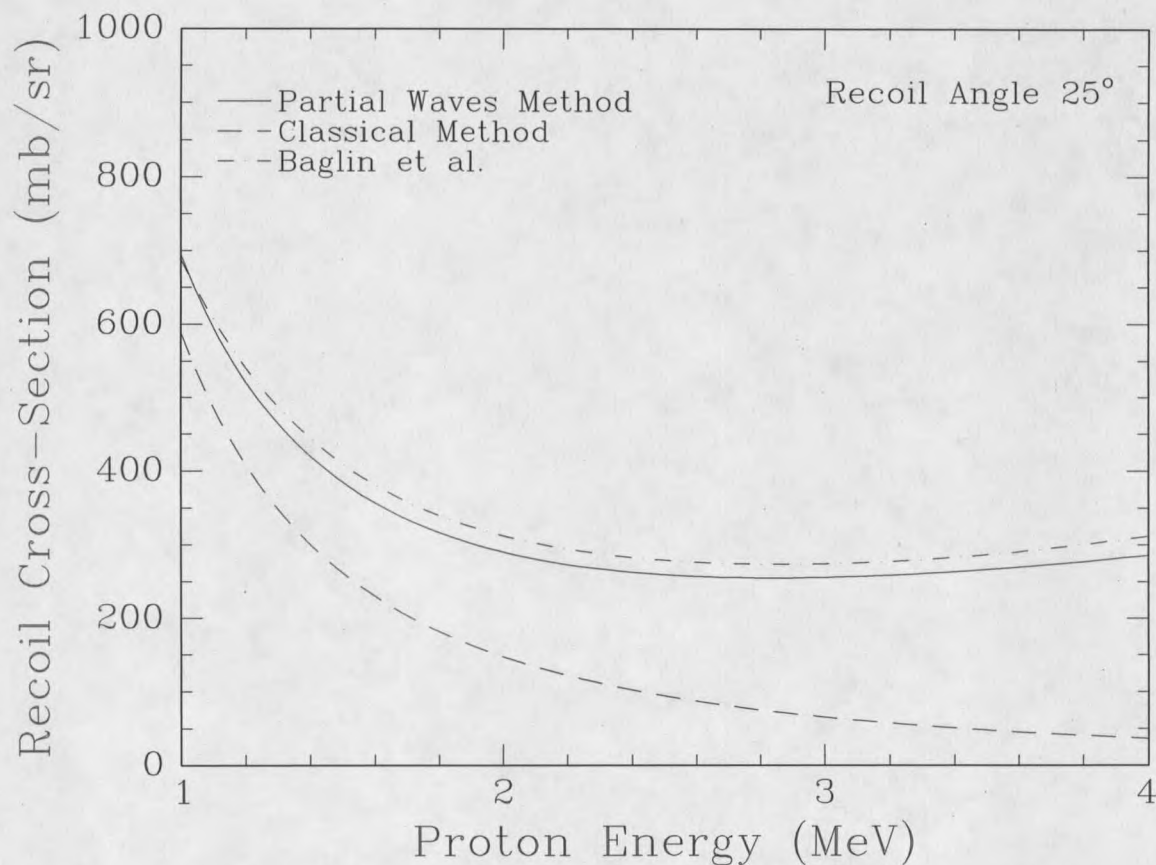


Figure 3.7 The differential recoil cross-section as a function of incident He^+ energy. The solid curve is calculated using equation 3.21. The dashed-dotted line is determined using least-squares fit to experimentally measured cross-sections in Reference 9. The dashed line is the Rutherford recoil cross-section.

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CHAPTER 4

GROWTH OF Ti FILMS ON Al(110) SURFACES

In this chapter, a study of epitaxial growth of Ti films on Al(110) surfaces at room temperature is presented. Ti assumes a hexagonal, close-packed crystal structure in its bulk state at room temperature, with the lattice constants $a = 2.95 \text{ \AA}$ and $c = 4.69 \text{ \AA}$. On the other hand, Al has a face-centered cubic crystal structure with a lattice constant of $4.05 \text{ \AA}$. Using these values for the lattice constants, a mismatch of 4.4% in the nearest-neighbor distances is obtained. The surface free energy of Al is less than half of that for Ti. The Ti-Al phase diagram indicates a negligible solubility of Ti in Al at room temperature. Models based on these physical quantities are often used to explain the growth mode and the structure of the resulting overlayer during the deposition of thin films on single-crystal substrates. In particular, we use a continuum model and the measured value of the critical thickness to calculate the lattice mismatch of the new Ti structure. Our results are based primarily on the comparison of the channeling measurements with results of computer simulations for the He^+ ion scattering process. The *XPS* and *LEED* measurements are used to complement these results.

The study of the integrity of a Ti film deposited on the Al(110) surface after being heated to different temperatures will also be described. The resulting Ti diffusion

is monitored using *RBS/HEIS* methods. In addition, the atomic sites of the diffused Ti within the Al crystal are determined.

4.1 EXPERIMENTAL

Channeling measurements, with the ion beam incident normal to the sample, constituted the primary method in this study. A collimated beam of 0.96 MeV He^+ ions, passing through an aperture of 1.2 mm^2 in area, was used to carry out the measurements. The ion backscattering energy spectrum, at a scattering angle of 105° , was measured to monitor the atomic structures of the Ti film and Al substrate. As was discussed earlier, in Chapter 2, the channeling spectrum exhibits a surface peak (*SP*) with an area that is proportional to the summed close-encounter probability. The sample was aligned with the ion beam incident along the normal direction by minimizing the total yield behind the *SP*. This procedure was repeated iteratively using both the rotation and tilt angles of the sample goniometer. In a preliminary experiment to measure the damage induced by the He^+ ion beam, no appreciable increase in the *SP* area was observed after the exposure to an ion dose of $3.1 \times 10^{16} \text{ ions/cm}^2$. This result established the validity of the ion scattering technique to carry out this study. A dose of $1.56 \times 10^{15} \text{ ions/cm}^2$ was used to collect each spectrum.

The *SP* areas were converted to areal densities of visible target atoms in units of (atoms/cm^2) using equation 2.12. To extract information on the surface structure from the data, the experimentally measured ion yields were compared with the scattering yields calculated using computer simulations of the channeling measurements

for various overlayer-substrate structures, as described below. To measure the Ti coverage, the ion beam is incident in a random direction, i.e. away from any major crystallographic direction. Equation (2.4), and the density of atoms in the surface layer of the substrate were used to convert the Ti yield into coverage in monolayers. *LEED* was used to supplement the short-range structural information, provided by *HEIS*, with information about the degree of long-range-order at the surface of the overlayer. Changes in pattern symmetries and diffraction spot profiles can be attributed to structural modifications in the overlayer during the growth process. In the *XPS* experiments, the attenuation of the Al photopeak intensities as a function of Ti coverage was used to characterize the morphology of the Ti films. In addition, *XPS* was used to determine the amount of contamination on the sample surface during the cleaning process.

To explore the thermal reaction of Ti with the Al surface, the following experiment was performed. A Ti film, 5 ML in thickness, was deposited on a clean Al(110) substrate at room temperature. Since the film thickness is smaller than the measured critical thickness, a flat pseudomorphic film was obtained. The film thickness was monitored during the deposition. The sample was then heated to temperatures of 200 °C, 300 °C and 400 °C. A current of about 2 A, passing through a thin tungsten filament placed behind the sample, was used for heating. The samples were maintained at each of these temperatures for 3 minutes. After heating, the sample was cooled down to room temperature, followed by ion scattering measurements.

The procedures to prepare the Al single-crystal substrate and the Ti vapor source are explained in chapter 2.

4.2 Results

4.2.1 HEIS-Channeling Measurements

Figure 4.1 shows two ion scattering spectra collected after sputter-cleaning and annealing the sample. One spectrum (open circles) was taken with the ion beam incident on the sample in a near-normal, random direction, while the other spectrum (solid circles) was taken with the beam incident along the $[\bar{1}\bar{1}0]$ direction, i.e. normal incidence. For random incidence, the measured spectrum height agrees with the theoretically calculated height¹ using tabulated values for the stopping power of He^+ ions in Al.² The measured value for the normalized, minimum yield, χ_{min} , was 4.0%. The calculated value for χ_{min} is 3.7%, using a one-dimensional thermal vibration amplitude of 0.105 Å and a crystal lattice constant of 4.05 Å.³ This good agreement is important since it serves as a measure of crystal quality. Larger measured values of χ_{min} might indicate, for example, the presence of deeply embedded transition metal atoms remaining from earlier experiments, or defects associated with sputtering and sample preparation, all of which could result in increased ion dechanneling. The measured *SP* area in the aligned spectrum corresponds to 6.8 atoms/row. This value agrees quite well with the theoretical value of 6.9 atoms/row that is obtained by

simulating the scattering of He^+ ions from a clean Al(110) surface. This computer simulation was carried out using the VEGAS code, which uses Monte Carlo calculations and a Moliere screened potential.⁴ A thermal vibration amplitude of 0.105 Å and the known multilayer relaxation of the Al(110) surface were the input parameters in the simulation.⁵ The areas of the surface peaks due to Al were determined using the triangular background subtraction method.⁶ In this method, the area of the shaded triangle, shown in Figure 4.1, and defined by the channel numbers of the *SP* centroid and the minimum yield, is subtracted from the total peak area.

In Figure 4.2, we plot the number of Al atoms/cm² visible to the incident ion beam as a function of Ti coverage. The Al(110) surface density of 0.86×10^{15} atoms/cm² per monolayer was used to convert the Ti coverage into equivalent Al(110) monolayers. The scatter in the Al *SP* areas is associated more with the background subtraction procedure than with the reproducibility of the spectra. The Al *SP* area initially decreases with Ti deposition, indicating a lower Al hitting probability. This decrease is attributed to shadowing of the surface Al atoms by Ti atoms. As more Ti is deposited on the substrate, exceeding the critical thickness of about 5 ML, the initial growth regime is followed by one in which the number of substrate atoms exposed to the incident ion beam increases, as shown by the increase in the Al *SP* areas in Figure 4.2. This increase continues up to a total coverage of 12.5 ML of Ti, at which coverage the experiment was terminated.

A comparison between the *HEIS* spectra collected for aligned and random ion

incidence reveals a slightly smaller Ti *SP* area in the aligned geometry, as shown in Figure 4.3. This small but measurable difference in the Ti hitting probability indicates that the overlayer has some degree of axial alignment with respect to the Al substrate. A plot of the number of Ti atoms visible to the incident ion beam in the aligned geometry versus the Ti coverage, as measured with a random incident direction, is shown in Figure 4.4. Negligible Ti shadowing was observed for Ti coverages less than 4 ML.

4.2.2 *LEED* and *XPS* Measurements

The *LEED* and *XPS* results from our second experiment are shown in Figures 4.5 and 4.6, respectively. After sputter-cleaning and annealing the surface, sharp *LEED* spots in a rectangular pattern were obtained, reflecting the (110) surface symmetry, and also supporting the cleanliness of the Al surface. The low electron beam kinetic energy of 42.0 eV facilitated probing the structure of the topmost surface layers. Pictures of the *LEED* spots are shown in Figures 4.5a-d for the clean surface, and for Ti coverages of 1.4, 2.8 and 5.5 ML, respectively. Ti deposition did not induce noticeable changes in the *LEED* pattern up to a coverage of about 5 ML, at which point the spots broadened and became less intense, as shown in Figure 4.5d. These results are consistent with the initial formation of a pseudomorphic Ti film, followed by some form of non-laminar, or disordered, growth as discussed below.

The variation in the photoemission intensities can be used to further understand

the structure of the overlayer. Peak areas for the Al 2p photopeak were obtained by subtracting a straight baseline background from the original data. A plot of the Al 2p photopeak area as a function of Ti coverage is shown in Figure 4.6. The initial decrease in the photoemission intensity is associated with the formation of a Ti film with uniform thickness. The intensity of the Al 2p photoelectrons decreased to about 40% of the original value after the deposition of 3 ML of Ti. The intensity variation levels off at higher Ti coverages, indicating a change in the character of the overlayer growth mode with additional Ti deposition. This measurement of the critical thickness for the overlayer is smaller than, but in reasonable agreement with, our estimate based on channeling measurements. The variation in the Al 2s XPS peak area as a function of Ti coverage shows the same trends as observed for the Al 2p photopeak.

4.2.3 Thermal Treatment

In the thermal diffusion experiment, channeling measurements were used to examine the film and substrate atomic structures, and random measurements were used to examine the extent of Ti diffusion into the Al substrate. Using equation (2.6), the spatial distribution of Ti atoms can be obtained by measuring the full-width-at-half-maximum (*FWHM*) of the Ti peak in the backscattering spectrum. The results from these experiments are shown in Figures 4.7 and 4.8. No appreciable change in the film atomic structure or thickness was observed until the film was heated to 400 °C, after which point we had two observations. Firstly, the energy spread (*FWHM*) of the ions

scattered from the Ti films increased to 50 keV, compared to the 20 keV peak width for a thin Ti film. This measurement was performed with the ion beam incident in a random direction. Second, we observed an appreciable decrease in the Ti *SP* area of the channeling spectrum. This was accompanied by an increase in the Al *SP* area which is also consistent with a substitutional reaction. Generally, these changes are indicative of substitutional reaction in which Ti atoms are incorporated in the Al crystal displacing some of the Al atoms. Figure 4.8 shows the rocking curves for both Ti and Al after thermal treatment. The Ti curve represents the dependence of *SP* area as a function of the angle between the sample normal and the incident ion beam, relative to the peak area measured with the ion beam incident in a random direction. The Al curve represents the relative angular dependence of bulk ion dechanneling yield. As shown in Figure 4.8, the Ti *SP* area and the ion-dechanneling from Al are minimum at normal incidence.

4.3 Discussion of Results

4.3.1 Observation of *fcc* Ti Films

As shown in Figure 4.2, there appear to be two distinct growth regimes for these ultrathin films of Ti on Al(110), corresponding to Ti coverages of less than, and greater than, 5 ML. The main point of this study is that in the low-coverage regime a flat, pseudomorphic film of *fcc* Ti grows to a critical thickness of approximately 5

monolayers. This is particularly interesting because, while bulk Ti assumes an *hcp* structure at room temperature, and transforms to a *bcc* structure above 877 °C, the *fcc* structure does not occur in the equilibrium phase diagram of Ti at any temperature.⁷ Thus, the thin, *fcc* Ti film is in a metastable condition, confined by the Ti-Al bonding at the interface. A critical thickness is reached, at a Ti coverage of approximately 5 ML, when the strain energy in the film exceeds the interfacial energy, and a modification of the film structure occurs. These conclusions are based on the following considerations.

The observations for low Ti coverages include the following: the Al *SP* peak area is attenuated as a function of Ti coverage (Figure 4.2), the intensity of the Al photopeak is also attenuated with increasing Ti coverage (Figure 4.6), and the *LEED* spots remain sharp and exhibit the rectangular symmetry of the substrate (Figures 4.5a-c). The initial decrease in the *SP* area associated with the Al substrate atoms is attributed to the formation of a pseudomorphic overlayer in which Ti atoms adopt the surface symmetry and lattice constant of the substrate, and thus shadow the underlying Al atoms. This decrease continues for Ti coverages up to about 5 ML, when the Al hitting probability reaches a minimum of 3.9 atoms/row. A linear least-squares fit to this data yields a slope of -0.96 Al atoms per Ti atom, indicating the equivalent shadowing of about one Al atom for every deposited Ti atom. We compared this dependence on Ti coverage to that obtained from computer simulations of the experiment using the VEGAS code.⁴ In these simulations, the Ti atoms were placed

on Al lattice sites above the surface, in a layer-by-layer fashion, with the Al(110) interplanar distance, 1.432 Å. The vibration amplitude for Ti atoms was assumed to be the same as that for Al atoms, namely 0.105 Å. This is a reasonable approximation since the Debye temperature of Ti (380 K) is close to that for Al (394 K).⁸ The results of these simulations at various Ti coverages below the critical thickness are in excellent agreement with the measured yields, as indicated by the filled squares in Figure 4.2. A slope of -1.05 Al atom per Ti atom is obtained from a linear fit applied to the results of the computer simulations.

Our results for Al shadowing as a function of Ti coverage indicate not only that the Ti film is pseudomorphic, but also that it is relatively flat. If any portion of the overlayer were redistributed to form islands, the simulations indicate that there would be less shadowing of the Al atoms than is observed, and measurable shadowing of Ti atoms. For example, the simulations show that Ti-Ti shadowing for a coverage of 4 ML (2 atoms/row) is only 0.05 atoms/row, which is less than our experimental error of about 0.2 atoms/row. However, for a film thickness of 3 atoms/row (6 ML) the calculated Ti-Ti shadowing is 0.23 atoms/row. Thus, for 2 ML of Ti coverage, any redistribution of the Ti atoms to form pseudomorphic islands would lead to a thickness ≥ 3 atoms/row in some regions of the surface, and would result in measurable Ti shadowing. At a Ti coverage of 4 ML, no shadowing of Ti was observed, as shown in Figure 4.4. The measured shadowing of Al atoms corresponds to the maximum value that can be obtained at a given coverage, using the coordinates of the Al lattice.

and our ion energy, and thus supports the model of a flat, pseudomorphic film. The persistence of the *LEED* spots with the substrate symmetry, as shown in Figure 4.5, lends additional support to this model. We also considered the possibility that various orientations of distorted bcc or hcp Ti overlayers were growing on the surface for low Ti coverages, but found that every configuration considered could be eliminated based on the lack of agreement with the ion scattering results for Al shadowing.

The attenuation of the Al photopeak intensity at low Ti coverages, shown in Figure 4.6, further supports a model of flat, pseudomorphic film growth. The solid line in Figure 4.6 shows the variation expected for the Al *2p* photopeak intensity using an ideal, layer-by-layer growth mode. The attenuation of the intensity after the completion of *h* monolayers, plus an additional partial coverage, *x*, of the topmost layer, is described by:⁹

$$I_{Al}(h,x) = w^h (1 - x + xw) \quad (4.1).$$

Here, I_{Al} is the Al photopeak intensity, normalized to the intensity for the clean Al substrate; *w* is an attenuation factor expressed as $\exp(-d/(\lambda \cos\theta))$, where *d* and λ are the interplanar distance in the overlayer, and the inelastic mean-free-path (*IMFP*) for inelastic scattering of electrons, respectively; θ is the photoelectron exit angle relative to the surface normal (0 degrees in this case). An important point in such models of emission intensity is that a flat film gives the greatest possible attenuation of the substrate photopeak intensity. Any combination of layers and islands, i.e. a non-uniform thickness, will lead to a larger intensity than that calculated for laminar

growth.¹⁰ There is some ambiguity, however, in applying this model for emission intensity, since the *IMFP* is not always known. The value for λ obtained from the universal curve can be considerably larger than the value obtained in experiments for very thin epitaxial films.¹¹ Furthermore, when diffraction effects are present, the rate of attenuation is strongly dependent on the emission angle, which can lead to an overestimation of λ .¹² Thus, we took the ion scattering data as strong evidence for the initial growth of a flat film. We then assumed a layer-by-layer growth model for the Al photopeak intensity, and adjusted λ for the best fit to the *XPS* data of Figure 4.6 at Ti coverages below 4 ML. The resulting value for λ was 4.6 Å, considerably smaller than the value of 20 Å, obtained from the universal curve. Larger values of λ would result in less rapid attenuation of the Al emission intensity at low Ti coverages.

While there is little doubt about the structure and morphology of the Ti film at low Ti coverages, the situation at coverages greater than 5 ML is not as clear. The observations are: (1) shadowing of Al atoms gradually decreases, (2) shadowing of Ti atoms is observed, (3) the *LEED* spots broaden and their intensity decreases, and (4) the Al photopeak intensity decreases at a slower rate. Some possible transformations of the film, and the corresponding driving mechanisms, include: the introduction of misfit dislocations, which reduces the accumulated strain in the overlayer; the formation of islands by surface diffusion, which lowers the surface free energy; and, the interdiffusion of Ti and Al atoms at the interface, which lowers

the total energy through the release of the Ti-Al formation energy. We note that the surface free energy for Al, 1.085 J/m^2 , is considerably smaller than that for Ti, 2.570 J/m^2 .¹³ The difference in these values puts a lower limit on the interface energy associated with Ti-Al bonding and film stress. Of the three possibilities just mentioned, the formation of islands would account for all of our observations for Ti coverages above 5 ML. Island formation would result in broad, diffuse *LEED* spots as seen in Figure 4.5d. Island formation would also result in increased Ti-Ti shadowing, and the gradual exposure of previously shadowed Al atoms to the incident ion beam. Finally, the *XPS* intensity rises above the layer-by-layer model calculation, consistent with island formation. Although the islands may still be pseudomorphic with the substrate lattice, the onset of misfit dislocations is quite likely.

Interdiffusion of Ti and Al atoms at the interface is also possible. We note that the formation energy for most observed Ti-Al compounds is negative, ranging from -25 to -38 kJ/mole.¹⁴ These values are only slightly smaller than typical values for the formation energy of Ni-Al, where considerable interface reaction is observed.¹⁵ Furthermore, while the solubility of Ti in Al is negligible at room temperature, there is a limited solubility of Al in Ti.⁷ Thus, out-diffusion of the substrate atoms might begin when some critical thickness is achieved in the overlayer, and defects are introduced into the film. Diffusion of Al atoms into the overlayer could also explain the *XPS* results seen at higher coverages in Figure 4.6,

and, depending on the degree of order, could result in the shadowing of Ti atoms by Al atoms in the overlayer. We do observe considerable interdiffusion when the Ti/Al(110) bilayer is heated above 450 °C. Thus, we conclude that a combination of diffusion and island formation may be occurring for Ti coverages greater than 5 ML.

A final point can be made about the critical thickness at which the pseudomorphic Ti film undergoes a transformation. We make use of an expression derived by Jesser and Kuhlmann-Wilsdorf,¹⁶ based on the earlier work of van der Merwe,¹⁷ which predicts the critical thickness at which the energy in the strained, pseudomorphic overlayer just equals the interface energy associated with a particular lattice mismatch. Using the elastic constants of Ti and Al,¹⁸ we obtain a lattice mismatch of 4.4% for a critical thickness of 5 ML. This mismatch corresponds to an interatomic distance of 2.99 Å, as compared to the nearest-neighbor distance of 2.86 Å in Al. The value of 2.99 Å is very close to the nearest neighbor distance for Ti in the hexagonal structure (2.95 Å). We do not know the interatomic distance for *fcc* Ti since it does not exist in nature, but the behavior of Co may serve as a guide. Cobalt assumes the hexagonal structure at room temperature, with a nearest-neighbor distance of 2.507 Å, and transforms to the *fcc* structure, with an interatomic distance of 2.506 Å, at elevated temperatures.¹⁹ This is reasonable since the main difference between these two structures is the stacking sequence for the close-packed planes. Thus, it is reasonable to assume that *fcc* Ti has approximately the same interatomic distance as the room-temperature hexagonal phase, resulting in the measured critical

thickness of about 5 ML, and in excellent agreement with the predictions of the continuum theory. An interatomic distance of 2.95 Å corresponds to a critical thickness of 5.5 ML.

We also considered other Ti structures as candidates for the pseudomorphic overlayer. The lattice mismatch for bcc Ti is too large, about 16% along [100]. The hcp Ti structure has the appropriate interatomic distance but does not lead to the observed shadowing of Al atoms. γ -TiAl has a face-centered tetragonal structure that closely matches the Al lattice, with a 2% lattice mismatch,⁷ but again cannot account for the Al shadowing results up to 5 ML of Ti coverage. The formation of titanium hydrides on Al(110) was also considered as a possibility in the initial growth stage because Ti has a strong affinity for H. The γ -hydride phase, with a H/Ti atomic ratio of 1.5 or greater, has a face-centered cubic fluorite structure, and a lattice misfit of about 10% with respect to the Al substrate.²⁰ However, we believe that the hydrogen concentration in our Ti films was less than one monolayer, based on experiments on the Al(100) surface. For Al(100) we also observe pseudomorphic growth of Ti up to 5 ML, with shadowing behavior very similar to that shown for Al(110) in Figure 4.2. Forward scattering, elastic recoil measurements (ERDA)²¹ were made to determine the total concentration of hydrogen in the Ti films. The measured concentration of hydrogen in a 5 ML Ti film was negligible. Even our thicker films on Al(100) showed little more than a monolayer of chemisorbed hydrogen at the end of the experiments. Thus, we believe that hydride formation is

not occurring for these Ti films on Al(110).

4.3.2 Thermal Diffusion of Ti Films

As indicated earlier, the *FWHM* associated with the Ti peak in the ion scattering spectrum is an indirect measure of the spatial distribution of Ti atoms within the Al substrate. The Ti peak width remained unchanged until the sample was heated to a temperature of 400 °C. However a 20% decrease in the Ti *SP* area was observed when the sample was heated to 300 °C, as compared to the peak area obtained in the random geometry. This decrease may be attributed to a limited diffusion of the Ti atoms in the near-surface region of the substrate. This is because the difference between the Ti yield in the channeling and random geometries cannot be accounted for on the basis of Ti-Ti shadowing only. Using the results from computer simulations of ion scattering from a flat pseudomorphic Ti overlayer, a decrease of 6% is obtained for Ti-Ti shadowing in a 5 ML thick film. However, because the measured difference is small, we conclude that the film remained localized near the surface. It should be noted that the ability to determine the broadening in the film thickness from the peak width is limited by the energy resolution of the spectrometer. As shown in Figure 4.7, extensive Ti diffusion into the Al substrate results when the substrate is heated to 400 °C. A calculation of the depth over which the Ti atoms were distributed, using equation 2.6, gives a value of 300 Å. This width is considerably larger than the initial film thickness of about 15

Å, resulting in a Ti-dilute Al-Ti compound. At the same time, we observe an appreciable decrease of about 85% in the Ti *SP* area. This decrease is attributed to the Ti diffusion. The shadowing of Ti atoms, presumably by the Al atoms, suggests that Ti atoms occupy atomic sites along the Al crystal rows in the [110] direction. The accompanying increase in the Al *SP* area suggests that the Ti atoms displace the Al atoms and occupy *fcc* lattice sites.

To determine the degree to which Ti atoms substitute for Al atoms in the crystal, the fractional impurity concentration, f_s , is introduced. It is a measure of the fraction of impurities lying along a given lattice row. This fraction is defined in terms of the minimum normalized scattering yields for the host, in this case for the Al crystal, χ_{Al} , and for the Ti impurity, χ_{Ti} , and is written as:

$$f_s = \frac{1 - \chi_{Ti}}{1 - \chi_{Al}} \quad (4.2).$$

χ_{Al} and χ_{Ti} are calculated using the rocking curves in Figure 4.7, and are 5% and 12% respectively. Substituting these values in equation 4.2, gives a fractional Ti concentration of 93%.

4.4 Summary

In summary, we conclude that a flat, pseudomorphic Ti film forms initially for Ti deposition on the Al(110) substrate. Up to a critical thickness of 5 ML, the

Ti/Al interface is abrupt, and no evidence for displacement of Al atoms is observed. For coverages greater than 5 ML, an undetermined combination of island formation and Ti-Al interdiffusion occurs, leading to increased visibility of the Al atoms in ion scattering measurements. The critical thickness of 5 ML is found to be in excellent agreement with the interatomic distance expected for *fcc* Ti, using a continuum model for epitaxial film growth. We also conclude that the flat pseudomorphic Ti films stay intact, apart from some limited diffusion, at temperatures up to 300 °C. When the films are heated to about 400 °C, Ti atoms diffuse into the Al substrate, displacing and substituting for Al atoms in the *fcc* lattice.

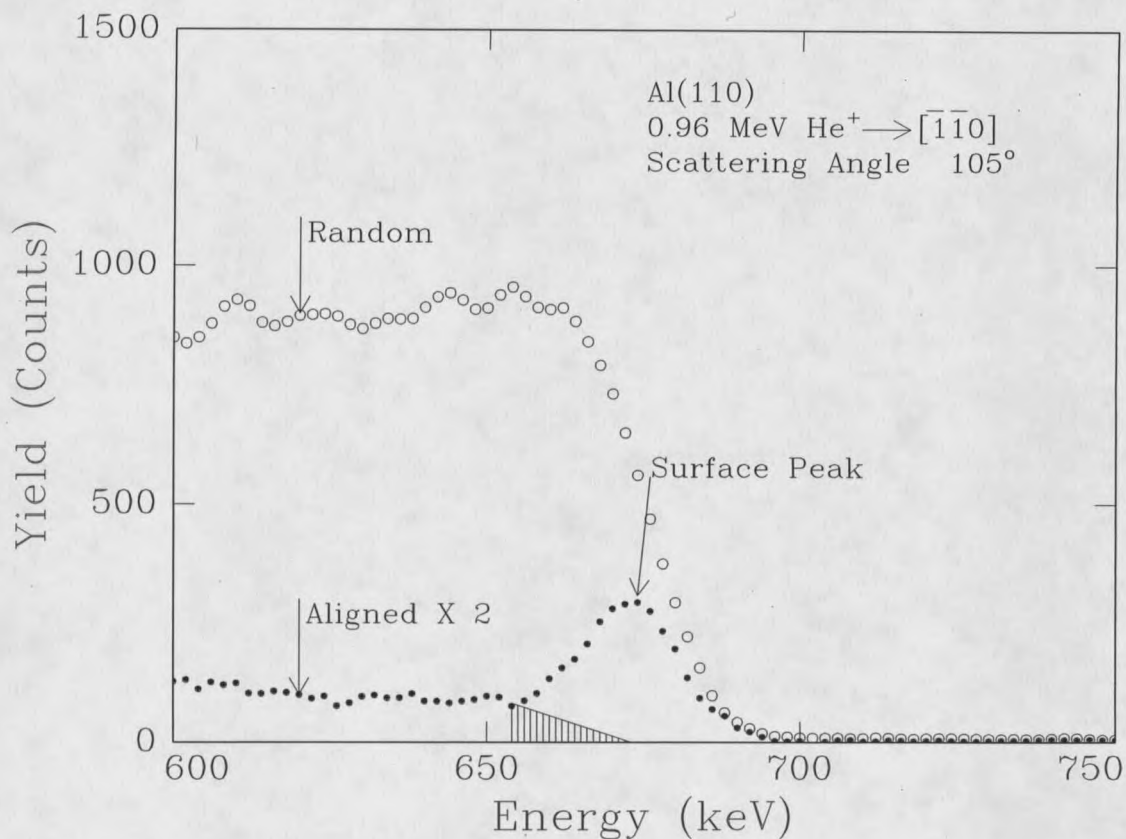


Figure 4.1 He^+ ion scattering spectra at 0.96 MeV incident ion energy for a clean Al(110) surface. The open circles represent the spectrum taken at random incidence, while the closed circles represent that for incidence along the $[\bar{1}\bar{1}0]$ direction. The shaded triangle represents the subtracted background when peak areas are converted to hitting probabilities.

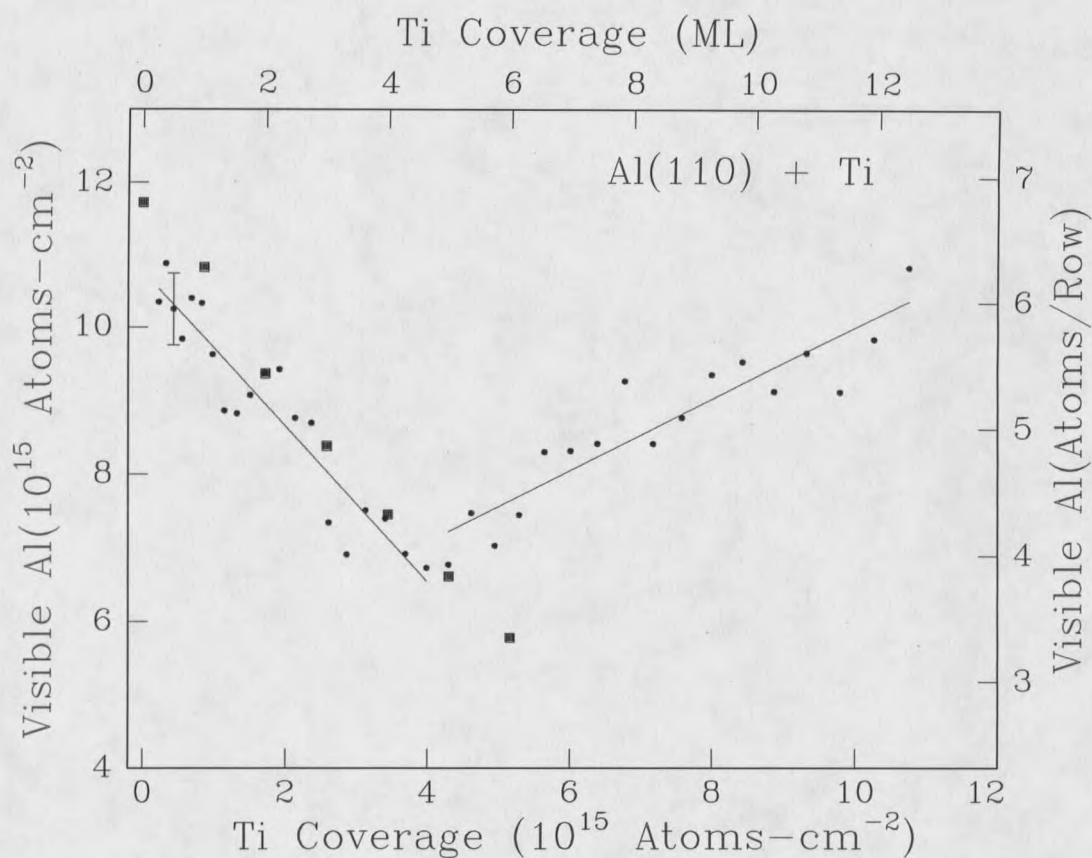


Figure 4.2 Visible Al atoms, at 0.96 MeV incident ion energy, as a function of Ti coverage deposited at room temperature on Al(110). The error bar represents an uncertainty of $\pm 5\%$ in the measurement of *SP* areas. Two regions are indicated. The solid lines are linear fits to the data, intended to guide the eye. The filled squares indicate the expected yield for a flat, pseudomorphic Ti film as calculated using the VEGAS simulation code.

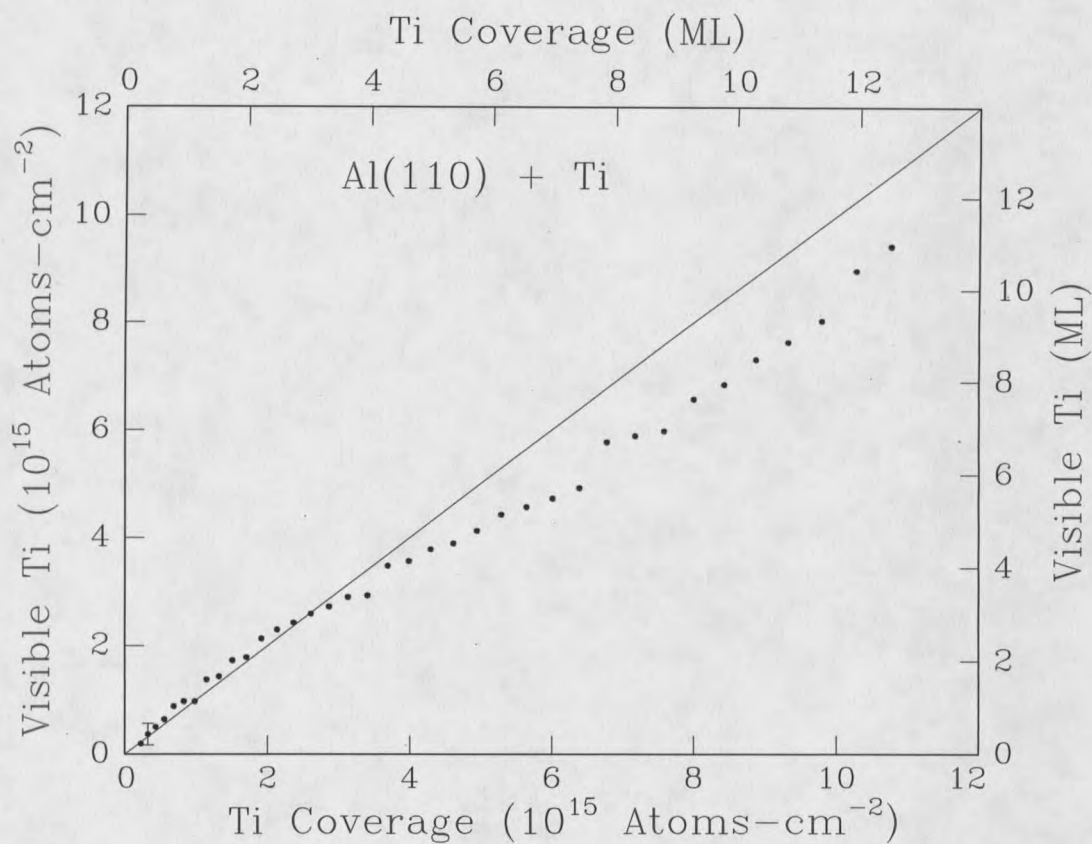


Figure 4.3 He^+ ion scattering spectra at 0.96 MeV incident ion energy after the deposition of 12.0 ML of Ti. The open circles represent the spectrum taken at random incidence while the closed circles represent that for incidence along the $[1\bar{1}0]$ direction. That portion of the spectrum which shows the Ti peaks has been enlarged by a factor of 2.

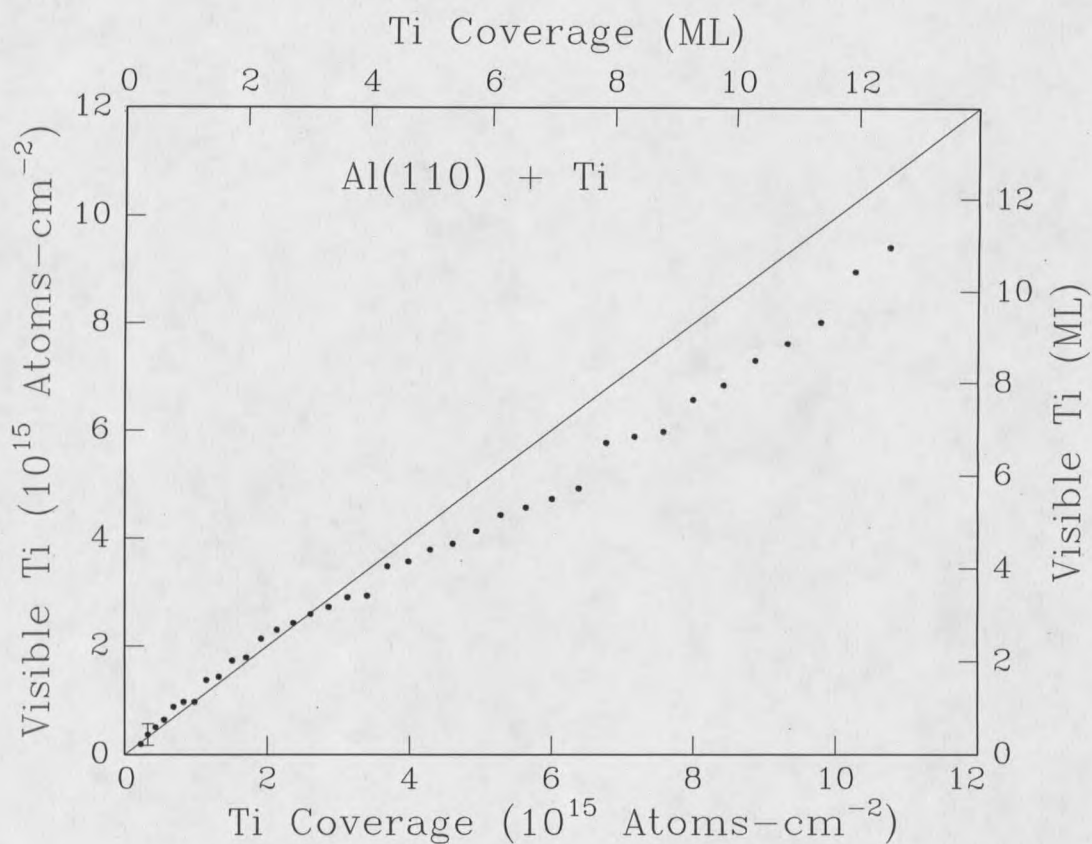


Figure 4.4 Visible Ti atoms, at 0.96 MeV incident ion energy, as a function of Ti overlayer coverage. Evidence for Ti shadowing is observed for coverages greater than 4 ML. The solid line shows the yield measured for a random overlayer.

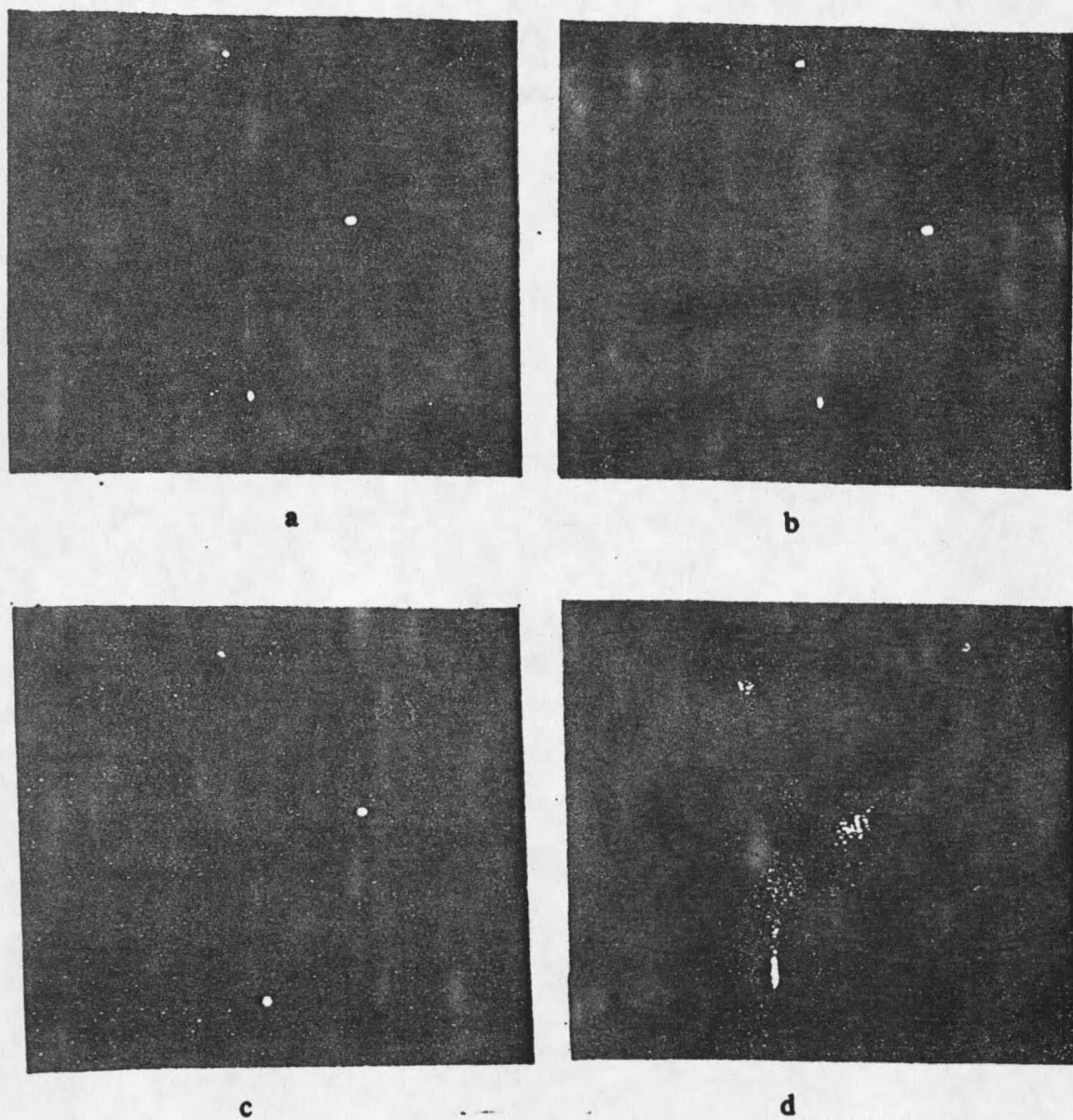


Figure 4.5 *LEED* patterns for Al(110)+Ti at 42.0 eV. The $[1\bar{1}0]$ direction is up in the figure. The spots are the (01), (10), and $(0\bar{1})$ clockwise from the top of the figures. The patterns are for (a) Clean Al, and for Ti coverages of (b) 1.4 ML, (c) 2.8 ML and (d) 5.5 ML.

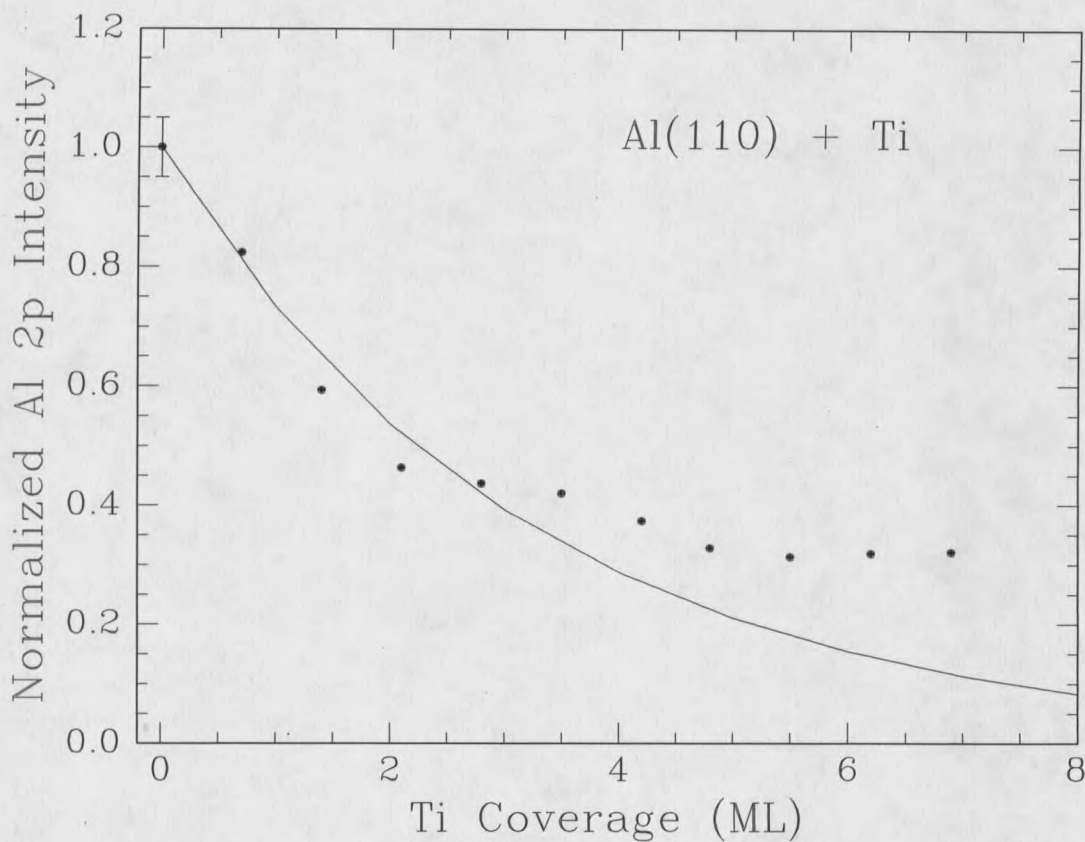


Figure 4.6 Normalized Al 2p photoelectron intensities plotted as a function of Ti coverage on the Al(110) surface. The solid line is the theoretical calculation for a layer-by-layer growth mode, using an attenuation length of 4.6 Å, as discussed in the text. The error bar represents the uncertainty in peak area associated with our background subtraction procedure.

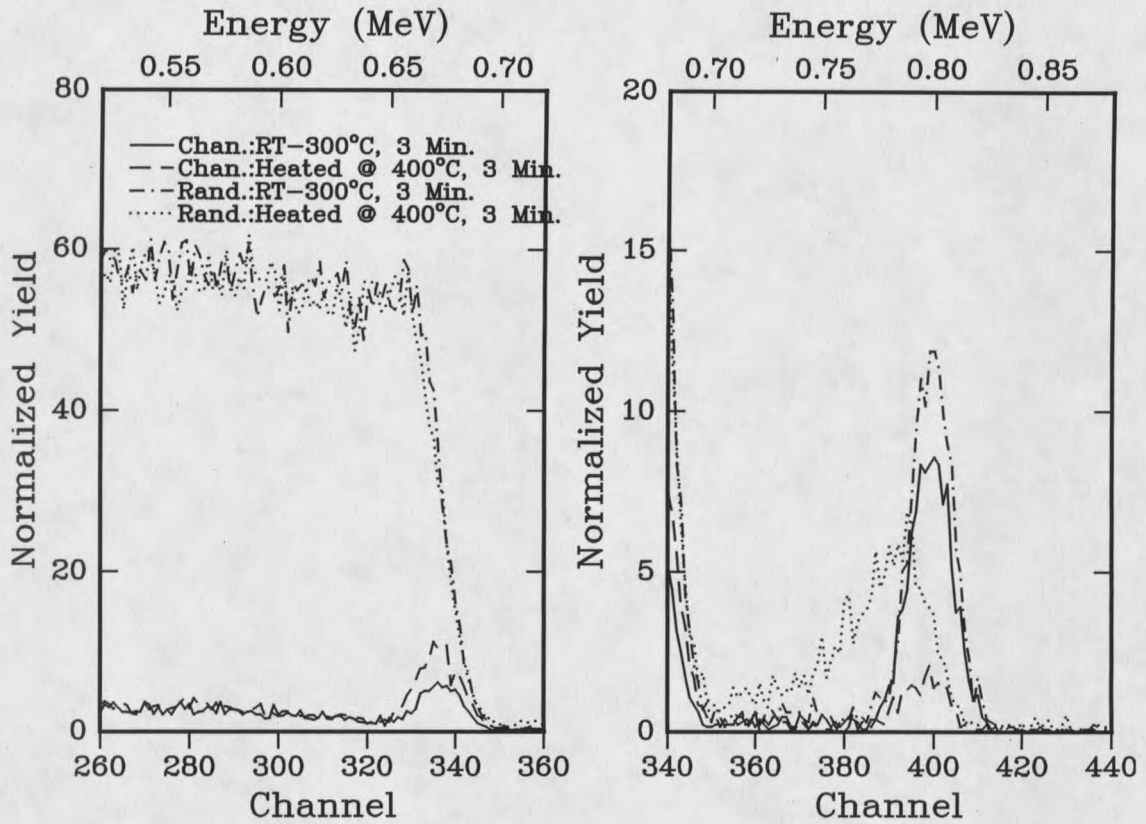


Figure 4.7 He^+ random and normal-incidence channeling ion scattering spectra from Ti/Al(110) after heating to 300 °C and 400 °C. The spectra were collected at room temperature in both cases.

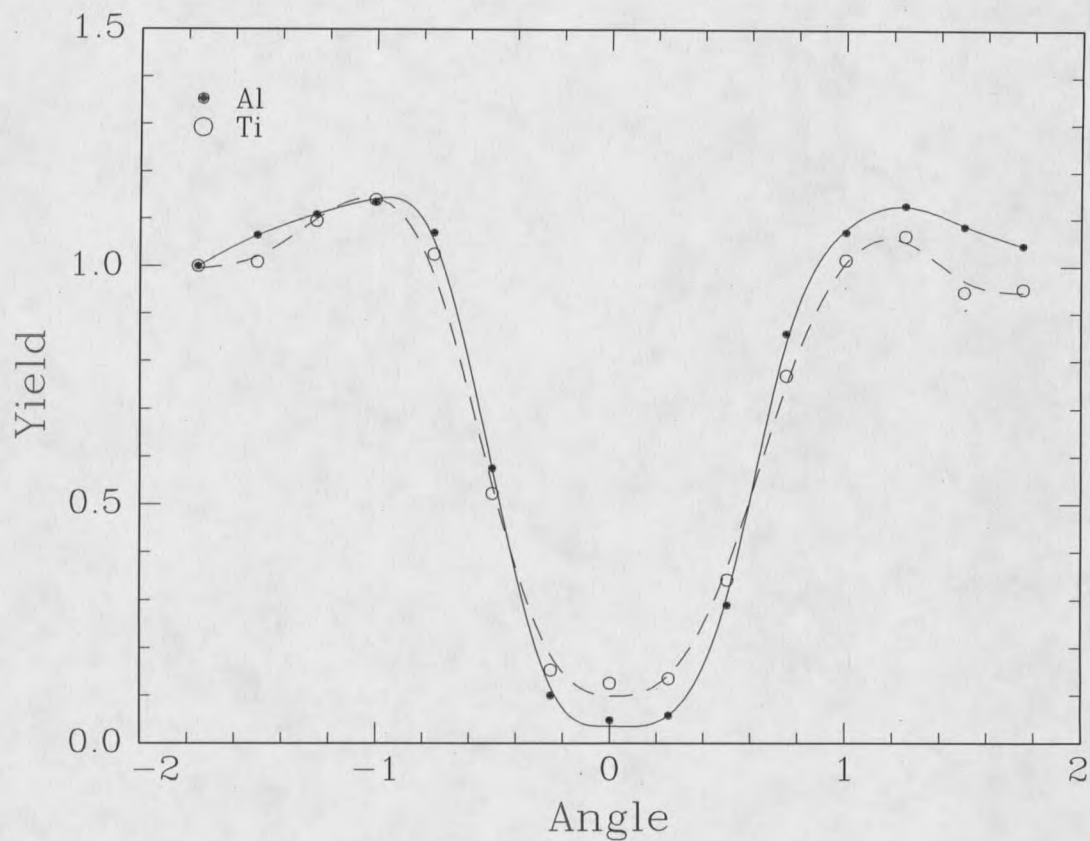


Figure 4.8 The rocking curves about normal incidence for Ti, open circles, and for Al, solid circles. The Al rocking curve represents the normalized bulk dechanneling yield. The Ti curve represents the normalized *SP* area. The yields in both cases are normalized with respect to the yield from random incidence.

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CHAPTER 5

GROWTH OF Ti FILMS ON Al(001) SURFACES

In the last chapter, we presented the study of the epitaxial growth of Ti films on Al(110) surfaces at room temperature. Similar studies on the growth of two other transition metals, Pd and Ni, show that the nature of the growth is dependent on the Al substrate surface orientation. On one hand, Pd films react with both Al(001) and Al(110) surfaces to form the PdAl phase.^{1,2} On the other hand, thin Ni films react with the Al(110) surface to form the NiAl phase, but are not as reactive with the Al(001) surface.^{3,4} As we shall see in this chapter, Ti grows epitaxially on the Al(001) surface, similar to the behavior observed on the Al(110) surface.

HEIS-channeling and photoelectron diffraction measurements were used as the primary tools in this study. An ion scattering experiment was first devised to understand the general features of the Ti growth as a function of coverage. From this experiment we learned that the growth characteristics on Al(001) surfaces resemble those observed in our earlier experiments on Al(110) surfaces. This resemblance is manifested in the behavior of the *SP* area as a function of Ti coverage. The decrease in the Al *SP* area continued up to a film thickness of 5 ML, after which the *SP* area increased with the Ti coverage which is indicative of a transition point in the growth

mode. This experiment was done in the normal channeling geometry. *XPS* measurements were also performed during the Ti film deposition. The attenuation of the Al photopeak area conformed with the ion scattering results. We then designed a set of experiments to further understand the film atomic structure, especially the epitaxial growth regime, which is the central theme of our study. These consisted of carrying out measurements at three different stages: before the transition point, where a 3 ML thick film was grown, close to the transition point and in the epitaxial regime, and beyond the transition point where a film thickness of 9 ML was grown.

To better characterize the structure of the epitaxial film, off-normal channeling measurements were performed to determine the Ti(001) interplanar distance in the overlayer. Photoelectron diffraction measurements, although less accurate in this respect, agree with the findings from the ion scattering measurements. To our knowledge, this study was the first attempt to compare the results from both techniques on the same system.

The hydrogen uptake of the various Ti films was also measured as a function of exposure to the hydrogen gas. We defer the presentation and the discussion of the results of these measurements until the next chapter.

5.1 Experimental

The use of *HEIS*-channeling measurements to probe the surface structure during overlayer growth is presented in Chapter 4. The basic principles of the technique are

introduced in Section 2.2.1.2. Also the preparation of the clean surface substrate and the Ti deposition source is discussed in Section 2.3.2. Similar procedures were followed to prepare the Al(001) single crystals and to deposit the Ti films.

A chamber base pressure of 1.5×10^{-10} Torr was obtained after baking the system. After every experiment, and before the Ti deposition, the sample was sputter-cleaned, annealed, and realigned with the ion beam. During Ti film deposition, channeling measurements, with the ion beam incident along the $[00\bar{1}]$ direction, and photoemission measurements were performed *in situ*. In the channeling experiments, a collimated beam of 0.97 MeV He^+ ions was used. The particle detector was positioned at a scattering angle of 105° to collect the scattered ions. The Ti coverage was determined by rotating the sample out of alignment, but near normal incidence, and then measuring the Ti peak area in the backscattering spectrum. This method is explained in section 2.2.1.1.

Ti films of thicknesses 3 ML, 5 ML, and 9 ML were deposited on the Al surface. The Al *SP* areas were monitored during the deposition of these films. In addition, for the 5.5 ML film, channeling measurements near the $[\bar{1}0\bar{1}]$ direction (rocking curves) were done to determine the (001) interplanar distance in the Ti overlayer. Ti and Al *2p* core level photopeaks were also monitored during the film growth. A beam of X-rays from the Al- K_α transition was used as the excitation source in the photoemission experiments. A fixed pass energy of 50 eV, and a scanning rate of 0.1 eV/s were used. The angle between the sample normal and the electrostatic

analyzer was fixed at $\theta = 30^\circ$. Film deposition, channeling measurements, and XPS measurements were all performed without moving the sample. Occasionally the sample was rotated slightly to measure random spectra. This arrangement helped in maintaining the sample alignment with the ion beam.

The angular dependence of the photopeak intensities associated with Ti and Al core levels was used to complement the channeling measurements. The dependence of the intensities on the polar angle, θ , in the (010) azimuthal plane over an angular range of 0° to 55° was measured for the clean Al substrate and for each of the Ti films. Azimuthal scans of the photopeak intensities at $\theta = 45^\circ$ were also recorded. The scanning was accomplished by rotating the sample in a fixed-analyzer arrangement with angular increments of 1° . For each point in the angular scan, the binding energy ranges that include the peaks of interest were scanned. An angular scan curve represents the variation in the net photopeak area as the sample is rotated.

5.2 Results

5.2.1 HEIS-Channeling Measurements

After sputter cleaning and annealing the Al crystal, it was oriented such that the ion beam was normal to the surface, i.e., the beam was incident in the $[00\bar{1}]$ direction. The crystal was aligned by minimizing the integrated backscattering yield behind the surface peak. Similarly, the sample was aligned with the beam incident in the $[\bar{1}0\bar{1}]$ direction. Channeling spectra with the ion beam

incident along the $[\bar{1}0\bar{1}]$ and $[00\bar{1}]$ directions are shown in Figures 5.1(a) and 5.1(b) respectively. The measured *SP* areas correspond to close-encounter probabilities of 4.9 atoms/row and 6.5 atom/row in the $[00\bar{1}]$ direction and in the $[\bar{1}0\bar{1}]$ direction, respectively.

Figure 5.2 illustrates the basic growth characteristics of the Ti films on the Al(001) surface, as measured using ion channeling. The closed circles in the figure represent the experimental data. For the first 1 ML of Ti coverage, the trend in the *SP* area is not very clear, and may be assumed to be constant to within the experimental uncertainty. However, after this point and up to 5.5 ML of Ti deposited on the substrate, a decrease in the Al *SP* area was observed. An increase in the peak area as a function of Ti coverage is observed after the transition point.

Results of computer simulations of the ion scattering experiment are indicated by the solid squares in Figure 5.2. In these simulations, the Ti atoms were arranged in a flat overlayer and placed on the Al *fcc* lattice sites above the surface. The Al(001) interplanar distance of 2.025 Å was used in simulating the overlayer.

The growth characteristics of the initial stages, described above, were observed when the experiment was repeated and interrupted at Ti film thicknesses of 3 ML, and 5 ML. In these experiments, the Ti and Al rocking curves with the beam incident near the $[\bar{1}0\bar{1}]$ direction were measured. In the 3 ML experiment, the measured variation in Ti *SP* area is insignificant because of the lack of appreciable shadowing for our ion energy. For the 5 ML Ti film the Ti and Al rocking curves are shown in Figure 5.3.

The Ti curve, indicated by the solid circles, represents the variation in the SP area as a function of the angle between the sample normal and incident ion beam. The Al bulk dechanneling yields, indicated by the solid squares in the figure, were used to plot the Al rocking curve. In Figure 5.1(a), the shaded area on the low ion energy side of the spectrum indicates the Al dechanneling yield. The Al and Ti yields were normalized by dividing each measurement by the yield due to scattering with the ion beam incident in a random direction. The solid lines through the points are provided to guide the eye. As we shall see, these curves are instrumental in the determination of the interplanar distance of the epitaxial Ti overlayers.

5.2.2 X-ray Photoemission Measurements

Figures 5.4(a) and (b) show Al and Ti photopeaks respectively. These two *XPS* spectra were taken after the deposition of 5 ML of Ti on the Al substrate. These figures illustrate the *XPS* peak fitting and the Shirley background subtraction method used to extract the net areas in both cases. This nonlinear least-squares fitting of the yield is based on the expression in equation 2.15. The Al photopeak was fit using one Gaussian component plus an error function background. Similarly, the Ti $2p_{1/2}$ and $2p_{3/2}$ peaks were each fit to a Gaussian component and an error function background. The separation between the two Ti peaks was fixed using the known spin-orbit splitting.⁵ The centroids and the amplitudes of the peaks were allowed to vary during the nonlinear least-squares fitting procedures. The amplitudes of the error functions

representing the background were also allowed to vary, while their positions were set to be identical with the Gaussian peak centroids.

Figure 5.5 shows the net Al photopeak area as a function of Ti coverage. The attenuation in the Al photopeak did not begin until the Ti coverage exceeded a thickness of about 1 ML. After this thickness, the photopeak decreased in area throughout the experiment. The decay in the Al peak area, the solid circles in the figure, is compared with an exponential decay represented by the solid curve. The data deviates from this decay at high Ti coverages. The Ti peak area increases, and then tends to saturate beyond a thickness of about 6 ML.

5.2.3 Photoelectron Diffraction Measurements

The dependence of the photopeak intensities on the Al crystal orientation was first measured before the Ti deposition experiments. Photopeak polar and azimuthal scans were measured for the clean Al surface. Figure 5.6 shows the Al $2p$ photopeak polar scan in the (010) polar plane. To extract the net photopeak areas, the fitting procedure explained in the previous section was used. The peak intensity is enhanced in the major directions of the crystal. The enhancements at $\theta = 0^\circ$ and at $\theta = 45^\circ$ are associated with the central diffraction peaks in the [001] and [101] directions respectively. These two peaks are also often referred to as forward focussing peaks. The peak at an angle of about 22° is due to a combination of first-order diffraction associated with forward focussing along [001] and [101], and with forward focussing

in the [103] direction. The Al 2*p* photopeak azimuthal scan, at a polar angle $\theta = 45^\circ$, is shown in Figure 5.7. The two major peaks in the azimuthal distributions are associated with the forward focusing along [101] at $\phi = 0^\circ$ and along [011] at $\phi = 90^\circ$.

The angular distributions of the photopeaks were measured again after the deposition of thin Ti films. Figure 5.8 shows the Ti 2*p* photopeak polar scan for the 3 ML Ti film as compared to that of the clean Al 2*p* photopeak. The Ti photopeak distribution clearly exhibits enhancements in the [001] and [101] directions coinciding with those for the Al 2*p* level. The Ti 2*p* azimuthal scans were also measured, and results similar to those in Figure 5.7 were obtained. This is illustrated in Figure 5.9 which shows a comparison between the azimuthal scans for the 3 ML Ti film and the clean Al surface. A polar distribution curve was also measured for the 5 ML Ti film. The results from these measurements are shown in Figure 5.10, where the angular position of the enhancement near [101] is slightly shifted to the left. As we shall see in the next section, this observation correlates with the results from ion scattering experiments. In particular, these results generally agree with the observation that the angular location of the minima in the Ti and Al rocking curves do not coincide.

The results from the ion scattering experiments suggest that perfect pseudomorphy is interrupted beyond a Ti film thickness of about 5.5 ML. Photoelectron diffraction measurements support this model for a 9 ML Ti film. The photoelectron polar distribution curve for this film is shown in Figure 5.11. Although the enhancement along [001] was still present, the enhancement along [101] was absent.

5.3 Discussion of Results

In Chapter 4, we concluded that flat *fcc* Ti thin films grow epitaxially on the Al(110) surfaces in the low coverage regime. The experimental results, presented above, indicate that the growth of Ti on the Al(001) surface exhibits similar characteristics in this regime. Hence, the arguments made in discussing the Ti/Al(110) system generally apply to the present discussion. In this section, we will discuss how the above results can be used in characterizing the atomic structure of the Ti films.

There are two major growth regimes for Ti films on the Al(001) surface. In the low coverage regime, an epitaxial nearly *fcc* film structure is observed. After the critical thickness of 5.5 ML is reached, the strain energy exceeds the Ti-Al interfacial energy resulting in the interruption of epitaxy. The first 1 ML of Ti atoms occupy off-row sites and thus do not result in Ti-Al shadowing preceding the formation of the flat *fcc* Ti overlayer. Beyond the critical thickness, the film structure cannot be completely characterized on the basis of our results. These conclusions are established upon considering the results from the *HEIS*, *XPS* and *XPD* experiments.

As can be seen from Figures 5.2 and 5.5, the Al *SP* area and the Al *2p* photopeak intensity remain constant during the deposition of the first monolayer of Ti. Both of these observations are consistent with a model in which Ti atoms occupy subsurface sites in the Al substrate at this initial stage. These two figures also show that the Al *SP* and photopeak areas both attenuate as more Ti is deposited. To model

the Ti growth, the rate at which the number of visible Al atoms decreases is compared with the decrease in the summed close-encounter probability (*SCEP*) for Al atoms, obtained from the computer simulations of He^+ ion scattering. Also, the measured attenuation in the Al photopeak area is compared with that associated with the laminar growth of a flat Ti overlayer. The solid squares in Figure 5.2 represent the Al *SCEP*, as a function of Ti film thickness, obtained from the computer simulations. We note that the *SCEP* obtained from the simulations agrees with the measured number of visible Al atoms for the clean surface. The bulk Al lattice constant and vibration amplitude were used to simulate the Ti film. It appears that results from the simulations deviate from the experimental results in the submonolayer regime. However, the subsequent attenuation rate for the visible Al atoms obtained from the simulations agrees with that obtained from the experiment. This agreement is evidence for Ti epitaxial growth. Attenuation rates of 1.1 ML of Al per deposited Ti ML are calculated for the number of visible Al atoms as obtained from the experiment, and for the *SCEP* as obtained from the simulations. Hence, we conclude the formation of pseudomorphic Ti film on the Al surface. Changes in these interplanar distances would result in a decrease in the measured shadowing. The error involved in converting the Al *SP* area into visible Al atoms is primarily due to the background subtraction method, which is illustrated in Figure 5.1. The method involves the subtraction of the area of the shaded triangle from the total peak area. The determination of the location of the ion yield minimum behind the *SP* becomes more difficult as the *SP* area decreases.

This results in a progressive error which should be kept in mind when comparing the measured values of the number of visible Al atoms with the *SCEP* obtained from the simulations. Consequently, we do not attach a significance to the local fluctuations in the measured results. Instead, we only consider the average decrease in the measured values. However, we make one exception when considering the submonolayer growth stage, since the *HEIS* and *XPS* results correlate well, as indicated earlier. A more detailed discussion of the comparison with the computer simulation is developed in Chapter 4.

The change in the Al $2p$ photopeak areas as a function of Ti coverage can be modeled using equation 4.1, which represents the attenuation in the substrate XPS signal due to a laminar overlayer growth. The solid curve in Figure 5.5 is a least-squares fit to the data in the region between 1 ML and 5.5 ML of Ti coverage. The inelastic mean-free-path (*IMFP*) was allowed to vary during the fitting procedure. The attenuation in the Al photopeak intensity supports a model of flat film growth. In comparison, all other models lead to less attenuation in the substrate intensity. The resulting value of λ in equation 4.1 is 13 Å. As was discussed in Chapter 4, we do not consider this observation as strong evidence of a flat Ti film because of the ambiguity in the value of λ . The *HEIS* results remain the crucial confirmation for Ti epitaxy on Al surfaces.

The results obtained from off-normal rocking curves can be used to more accurately characterize the Ti film epitaxial structure. In particular, these curves are

used to measure the interplanar distance in the Ti overlayer. In the discussion above, and also in Chapter 4, our conclusions were based on the Ti-Al measured shadowing in the normal incidence channeling geometry. Although the shadowing depends on the Ti-Ti interatomic distance in the overlayer, this dependence is relatively weak, and thus cannot be used to evaluate the lattice constant, $a_{\perp}$, in the Ti film. However, in an off-normal arrangement, the difference between the angular locations of the minimum yield due to Al-Al shadowing and to Ti-Ti shadowing is a measure of the deviation of the film structure from that of the substrate. That is, the angular position of the minimum of the rocking curve near [101] for an epitaxial Ti film, with a lattice constant identical to that of Al, coincides with the minimum of the Al rocking curve at an angle of 45° from the surface normal. On the other hand, stretched or contracted overlayer lattice constants lead to shifts in the angular locations of the minimum scattering yield from the overlayer as compared to that of the substrate. Figure 2.11(c) is a schematic illustration of this effect. As shown in Figure 5.3, the minimum yield for Ti (maximum shadowing) occurs at 44.33° , as compared to 45° , which is the location of the Al minimum yield due to channeling along the [101] direction. Using this difference and the Al lattice constant, we obtain a value of $2.08 \text{ \AA}$, for $a_{\perp}$, the average (001) interplanar distance in the Ti film, as compared to $2.025 \text{ \AA}$ for Al. This measurement was done after the deposition of 5 ML of Ti. Thus we conclude that the Ti film structure matches that of the Al substrate to within 2.8% in terms of the distance between the (001) planes. It should be noted that this measurement is an average of the

overlayer lattice constant. In reality, the lattice constant may vary in a strained overlayer, where it adapts to the substrate structure at the interface and gradually relaxes as a function of distance from the substrate surface. In principle, this variation is manifested in changing the shape of the rocking curve as compared to an overlayer with a uniform interplanar distance. However, this change is expected to be too small to be measured for such a thin film. Our choice of using the Al bulk dechanneling yield to plot the Al rocking curve, instead of the Al *SP* area, is significant. As we indicated earlier, the background subtraction method introduces large uncertainties in the measured *SP* areas. This problem becomes worse when the beam is off-axis because of an increased background behind the surface peak. In addition, the Al atoms near the surface may be strained because of the Ti overlayer, and thus the surface structure may not be a good reference for comparison. On the other hand, the variations in the yield due to bulk dechanneling reflect the bulk symmetries and directions, and are thus more useful for comparison.

The results of the angular distribution curve of the Ti *2p* photoemission peak area confirm our findings from *HEIS*. As shown in Figure 5.8, this curve exhibits a peak near the polar emission angle of 45° for the 3 ML Ti film. This peak coincides with the Al *2p* photpeak enhancement along [101]. Similarly, the azimuthal scan at a polar angle of 45° exhibits enhancements that are consistent with the Al cubic structure as shown in Figure 5.9. Such results illustrate the significance of the *XPD* measurements in complementing the ion scattering experiments. The Ti-Ti shadowing

in a 3 ML thick film is small, in the MeV ion energy range, and thus cannot be used to accurately measure the overlayer atomic structure. Such a condition on the overlayer thickness is not a requirement in *XPD*. Also, an *HEIS* study of an adsorbate/substrate system may become complicated in the case where the adsorbate atom is lighter than that of the substrate, due to the difficulty in extracting the net *SP* areas. However, we believe that *HEIS* is superior to *XPD* in terms of the accuracy and precision in the determination of the overlayer lattice constant when the elemental conditions are favorable. This is because an ion scattering rocking curve is about 1° in width, compared to a typical value of 10° for the width of an *XPD* peak.

For the 5 ML Ti film, an angular shift of about 1° is observed in the Ti *XPD* peak along [101] compared to the Al *XPD* peak. This value is calculated based on the location of the maxima of the two peaks. This shift is about 30% larger than those obtained from the ion scattering results along the same direction. However both techniques indicate a larger value of $a_\perp$ in the Ti overlayer. We note that the *XPD* peaks are relatively flat near the maxima, which introduces large uncertainties in the measurements. We estimate an error of about 0.5° in the measured value of the peak locations. A better approximation may be obtained by fitting the distribution to a particular peak shape before extracting the peak centroids. A future project includes the application of this approach to our data. Preliminary results from this project still suggest lattice constant values that are larger than that obtained from *HEIS*.⁶ This difference can be understood when the underlying principles of both techniques are

considered. While *HEIS* probes the whole depth of the film, the photoemission signal is biased to reflect the atomic structure of the topmost layers. Thus the *HEIS* results give an average value for $a_{\perp}$, while *XPD* gives a value that is more representative of the less strained top layers.

So far we have considered the coverage regime in which the Ti film grows epitaxially on the Al(001) substrate. Based on the *HEIS* results, we obtain a value of about 5.5 ML for the critical thickness after which the structure undergoes a transformation to reduce the accumulated strain. This value is only slightly larger than that obtained for the growth of Ti on Al(110), where we obtained 5 ML for the measured critical thickness. In this respect, the arguments introduced in Chapter 4 apply to the present discussion. Namely, the measured critical thickness is consistent with a lattice constant mismatch of 4%, where we have used the expression developed by Jesser *et al.*⁷ This mismatch corresponds to an interatomic distance of 2.97 Å, as compared to 2.86 Å, the nearest-neighbor distance in Al. The value of 2.96 Å is close to the nearest-neighbor distance in the hexagonal close-packed structure of Ti (2.95 Å). Although bulk *fcc* Ti does not exist in nature, it is reasonable to assume that it would have the same interatomic distance as in the *hcp* structure (see Section 4.3.1).

For Ti coverages exceeding the critical thickness, the atomic structure of the films is more difficult to determine. Based on our observations, several scenarios are possible in which the film transforms so that the strain is relieved. These include the introduction of misfit dislocations, formation of Ti islands, and Ti-Al interdiffusion.

Each of these transformations were discussed in Section 4.3.1 and may account for the observation in the Ti/Al(110) and Ti/Al(001) systems. However we can rule out transformations involving pseudomorphic Ti islands or Ti-Al ordered structures. We base this conclusion on the results from the angular distribution of the Ti 2*p* photoemission peak in Figure 2.11. While the peak at 0° is still present, indicating a degree of axial alignment with the Al substrate, the *XPD* peak at 45° disappears from the distribution curve. A more comprehensive angular scan of the Ti photopeak may reveal a more detailed picture of the atomic structure of the transformed films. However, because such measurements are time consuming, they may lead to serious sample contamination.

5.4 Summary

We conclude that thin Ti films grow epitaxially on Al(001) surfaces in a fashion similar to that observed in the growth on Al(110) surfaces. The Ti atomic structure seems to perfectly match the Al fcc lattice in the directions parallel to the surface plane. A slight deviation of 2.8% is observed in the direction perpendicular to the surface plane. A critical thickness of 5.5 ML is obtained, which is consistent with the mismatch between the Al crystal structure and an fcc Ti structure with 2.97 Å for the nearest-neighbor distance, similar to that of the bulk-like hcp Ti structure. Beyond the critical thickness, axial alignment with the substrate is only partially preserved, and off-normal alignment is completely lost according to our *XPD* measurements. The disorder

in the film at coverages larger than the critical thickness may be attributed to a combination of misfit dislocations, Ti island formation, and Ti-Al interdiffusion in the Ti films.

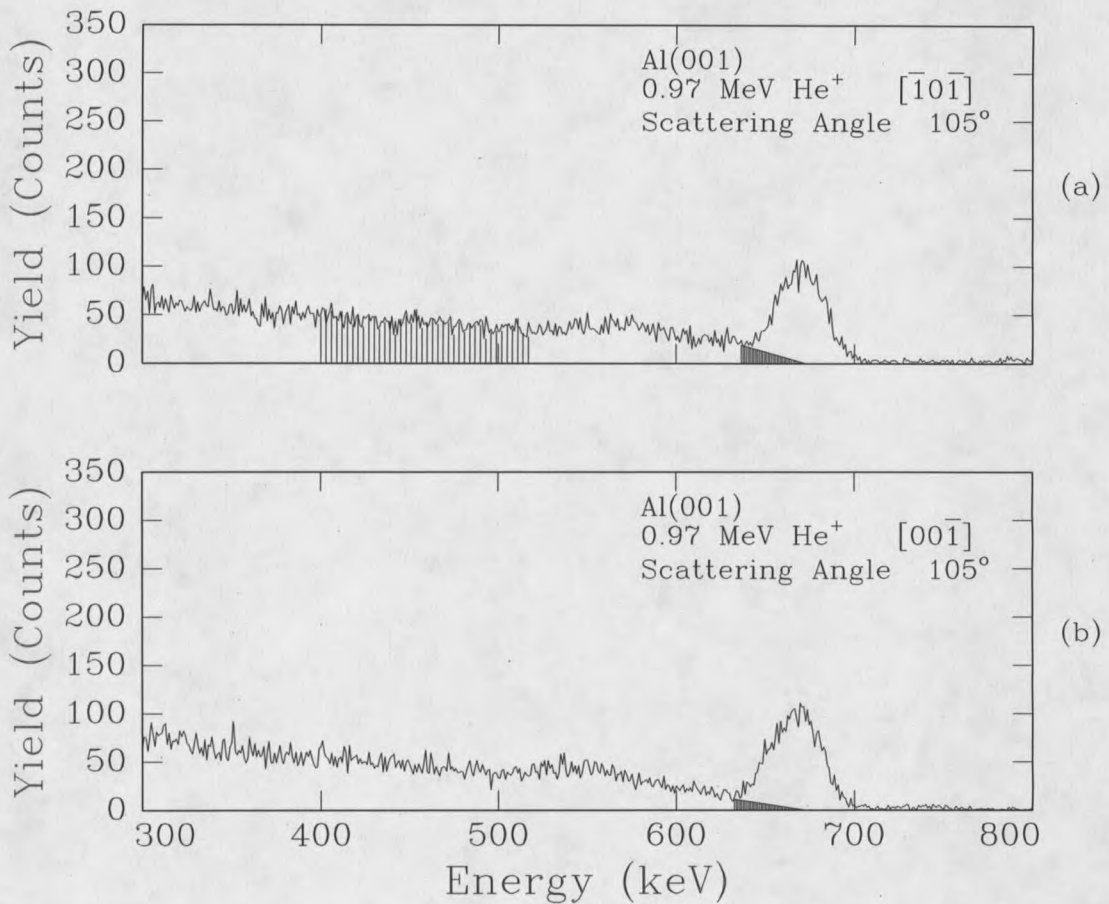


Figure 5.1 He⁺ ion scattering spectra at 0.98 MeV incident ion energy for a clean Al(001) surface. Spectrum (a) is taken with ion beam incident along $[\bar{1}0\bar{1}]$, and spectrum (b) is taken with the beam incident along $[00\bar{1}]$. The shaded triangles represent the subtracted background. The shaded area behind the surface peak in (a) represents the Al bulk dechanneling.

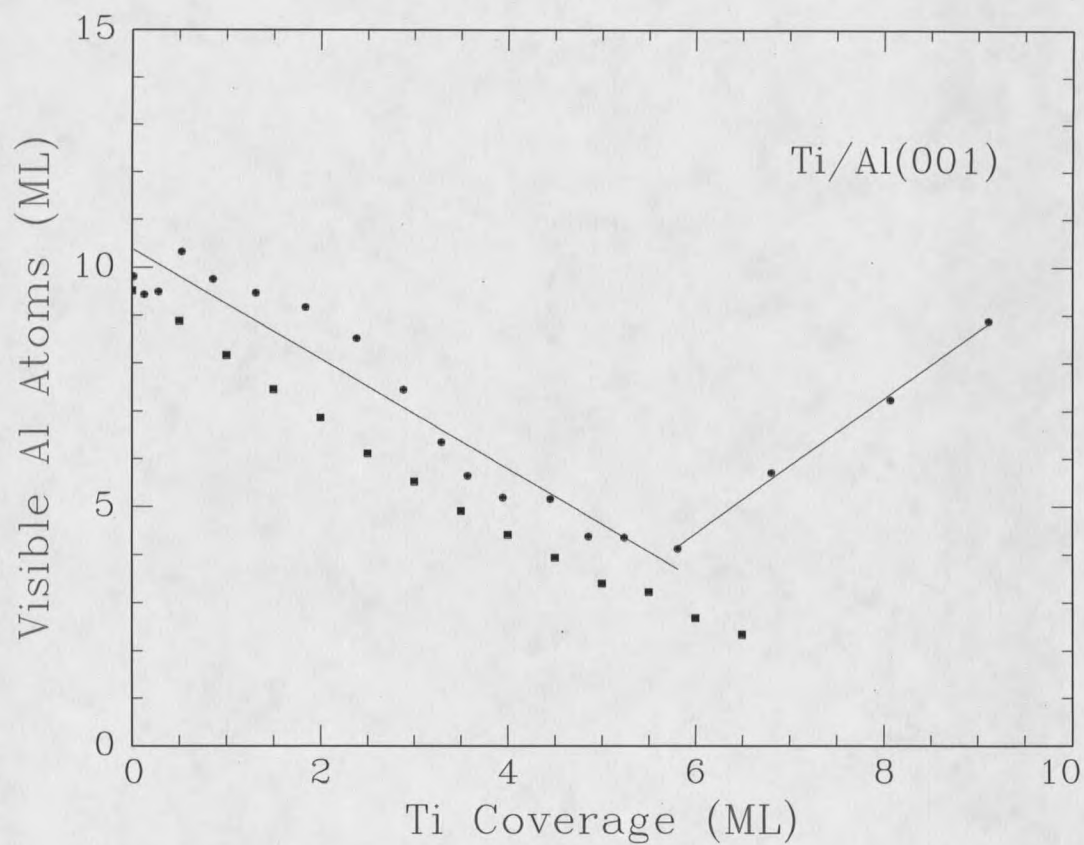


Figure 5.2 Visible Al atoms, at 0.98 MeV incident ion energy, as a function of Ti coverage deposited on Al(001) surface. The solid line is a linear fit to the data and the solid squares indicate the expected yield for a flat pseudomorphic Ti film, calculated using *VEGAS* simulation code.

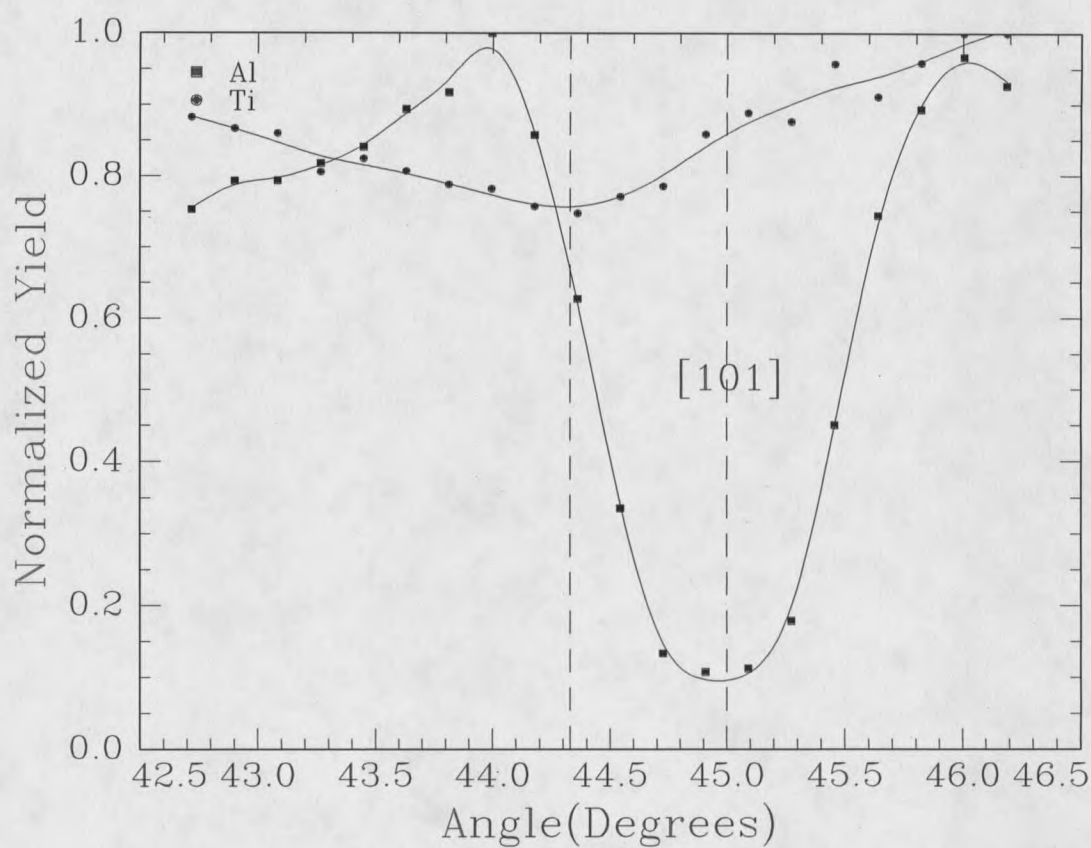


Figure 5.3 The normalized Ti *SP* area and the Al bulk dechanneling yield as a function of the angle of incidence. The separation between the two minima is a measure of the distortion in the interplanar distance in the Ti film compared to the Al substrate.

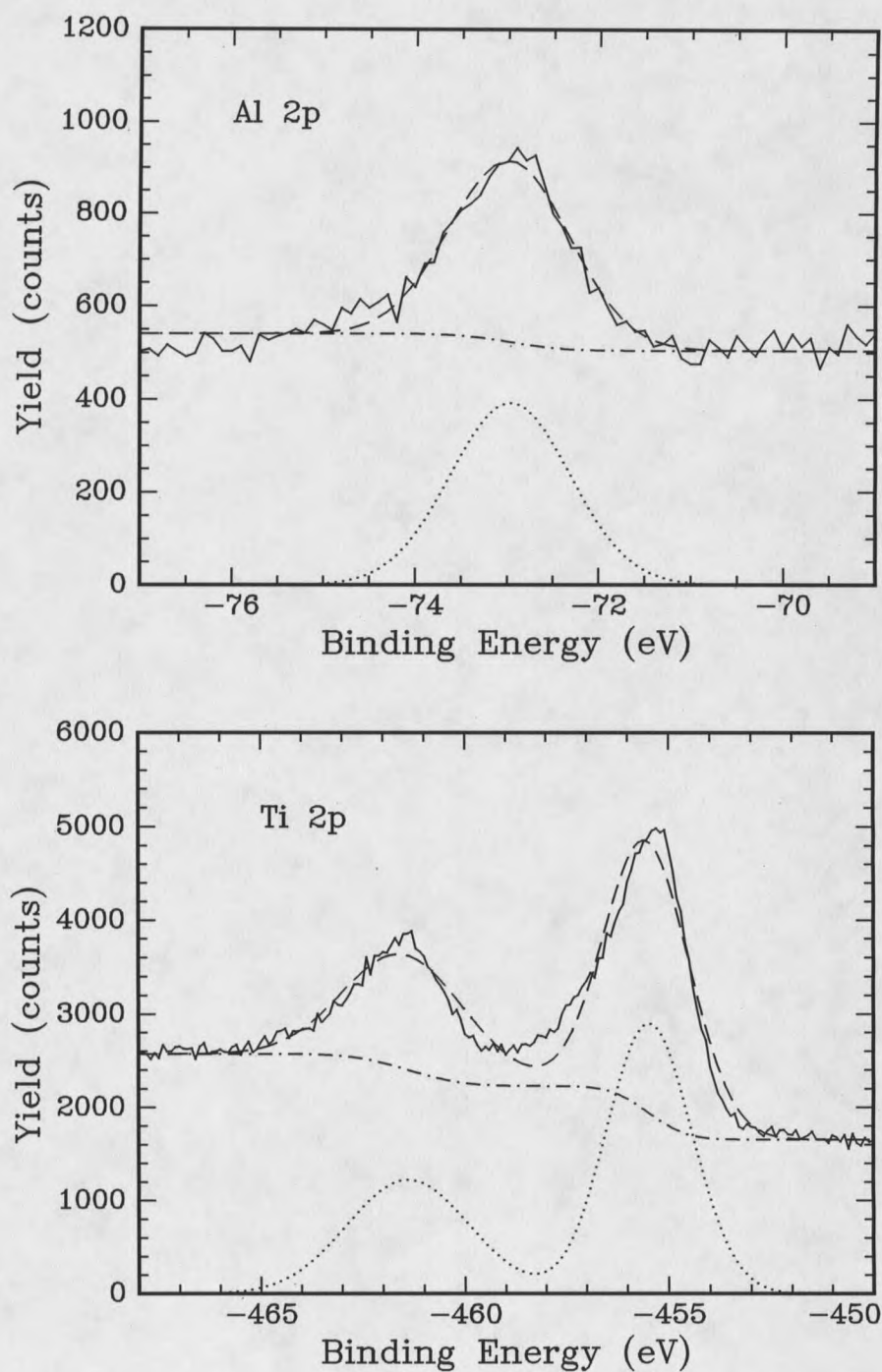


Figure 5.4 Al 2p (a) and Ti 2p (b) X-ray photoemission peaks. The peak in each case is fit to a superposition of a Gaussian component and an error function.

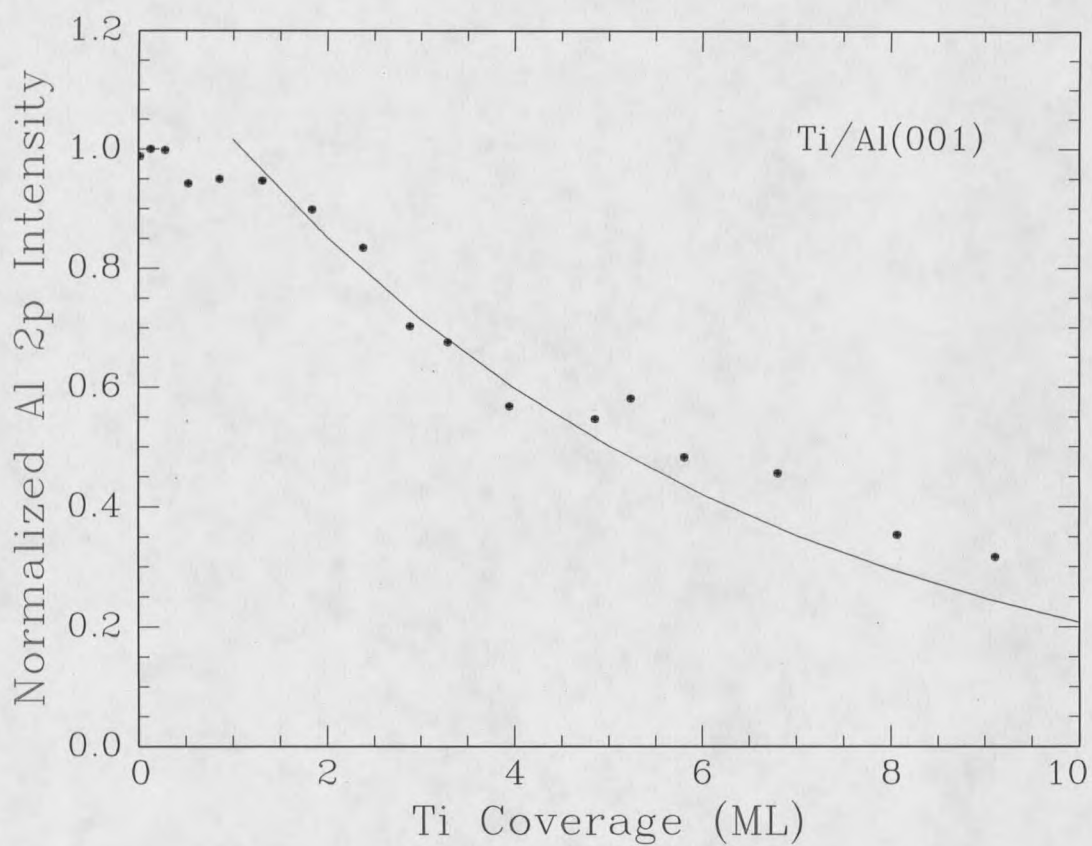


Figure 5.5 Normalized Al 2p photoelectron intensities plotted as a function of Ti coverage on the Al(001) surface. The solid curve represents a model for Ti laminar growth.

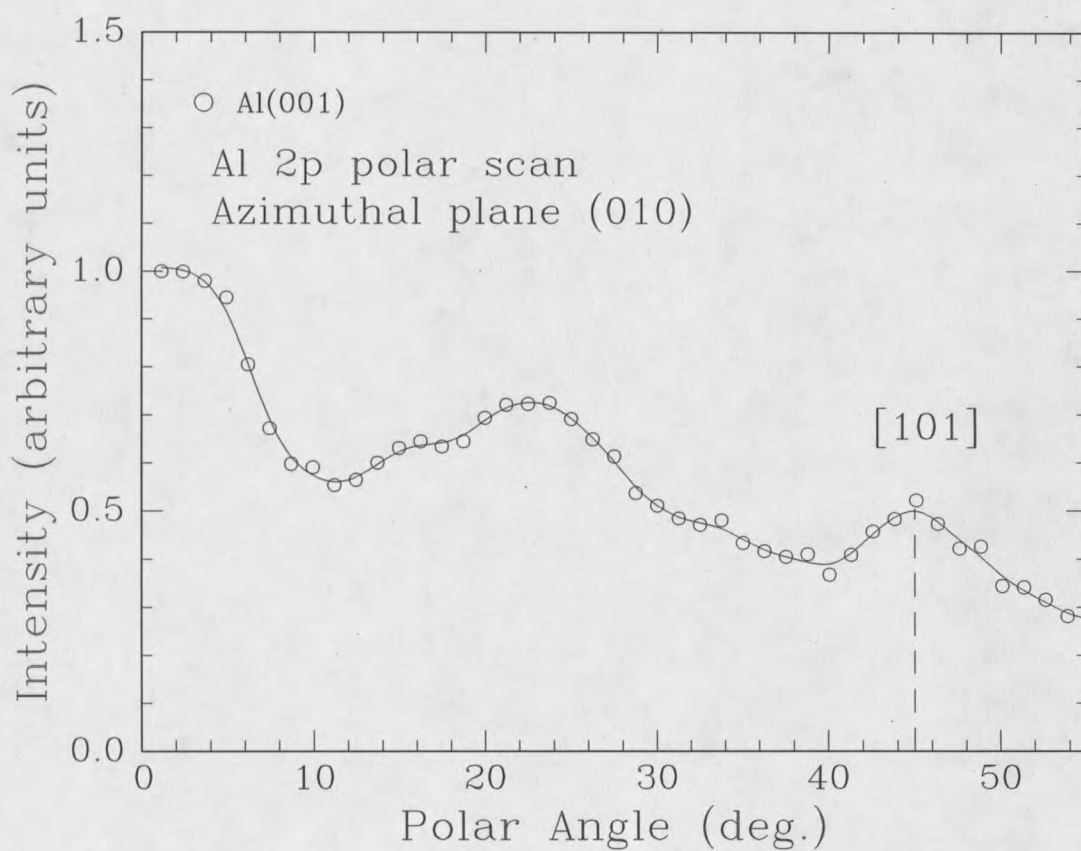


Figure 5.6 Al 2p polar angle distributions in the (010) azimuthal plane for Al(001). The solid line is a spline fit to the data, intended to guide the eye.

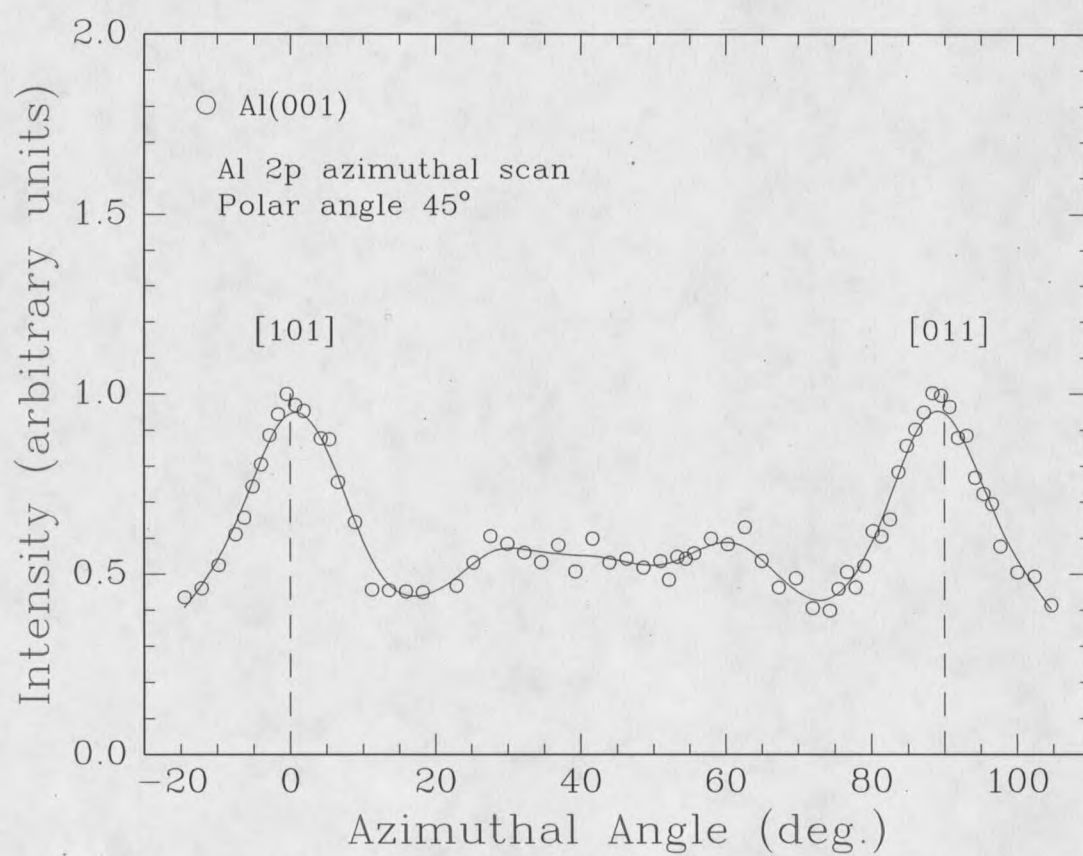


Figure 5.7 Azimuthal angle distribution at $\theta = 45^\circ$ for the Al 2p photopeak.

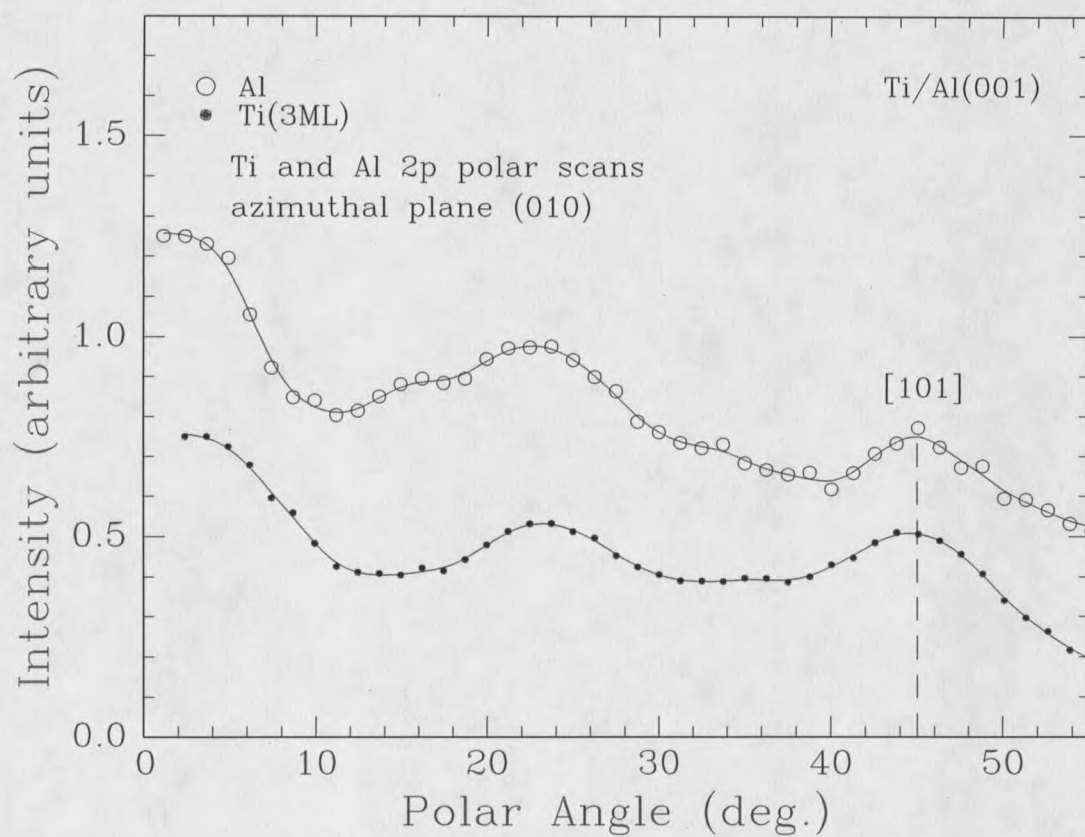


Figure 5.8 Ti 2p polar angle distributions in the (010) azimuthal plane compared to the clean Al distribution, at 3 ML of Ti coverage.

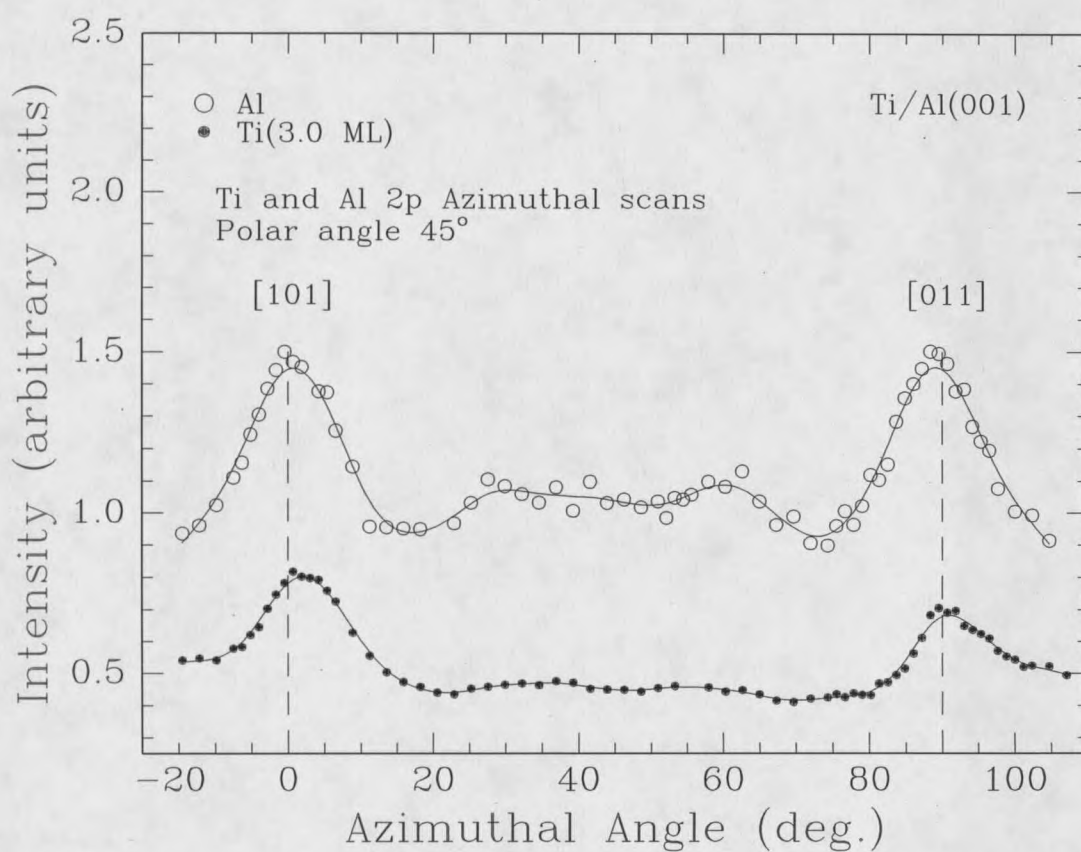


Figure 5.9 Azimuthal angle distribution at $\theta = 45^\circ$ for the Ti 2p photopeak compared to the clean Al distribution, at 3 ML of Ti coverage.

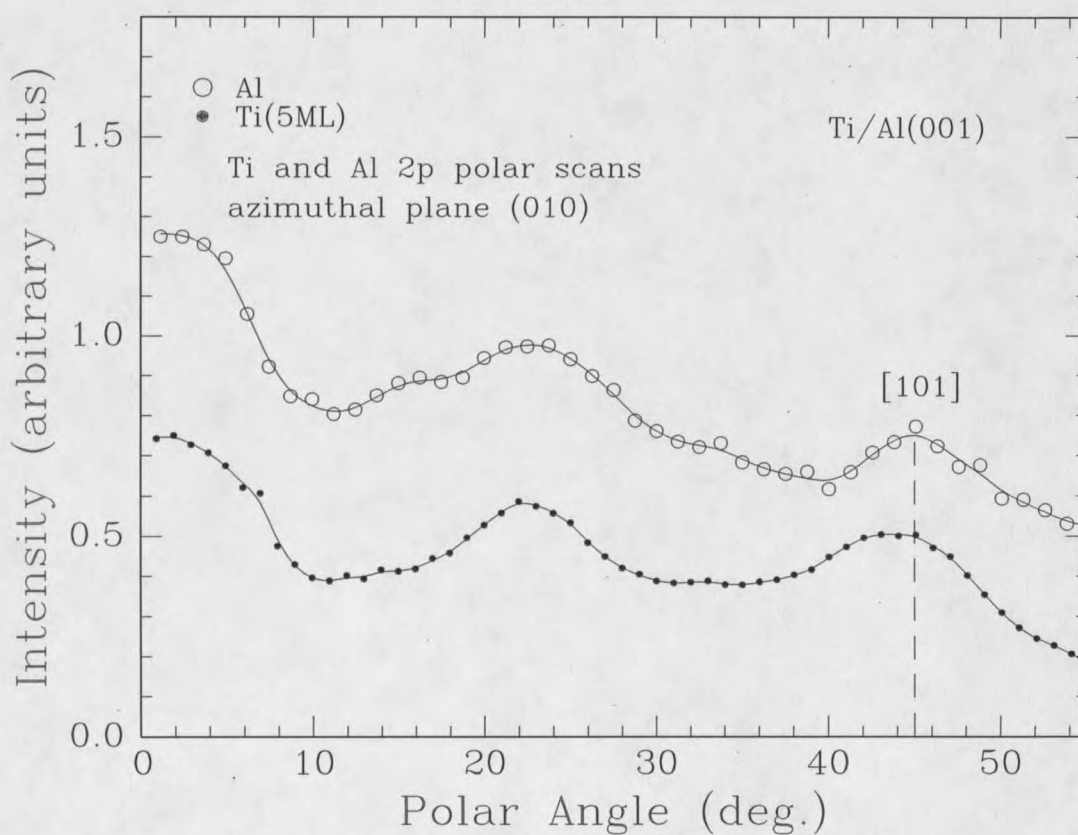


Figure 5.10 Ti 2p polar angle distributions in the (010) azimuthal plane compared to the clean Al distribution, at 5 ML of coverage.

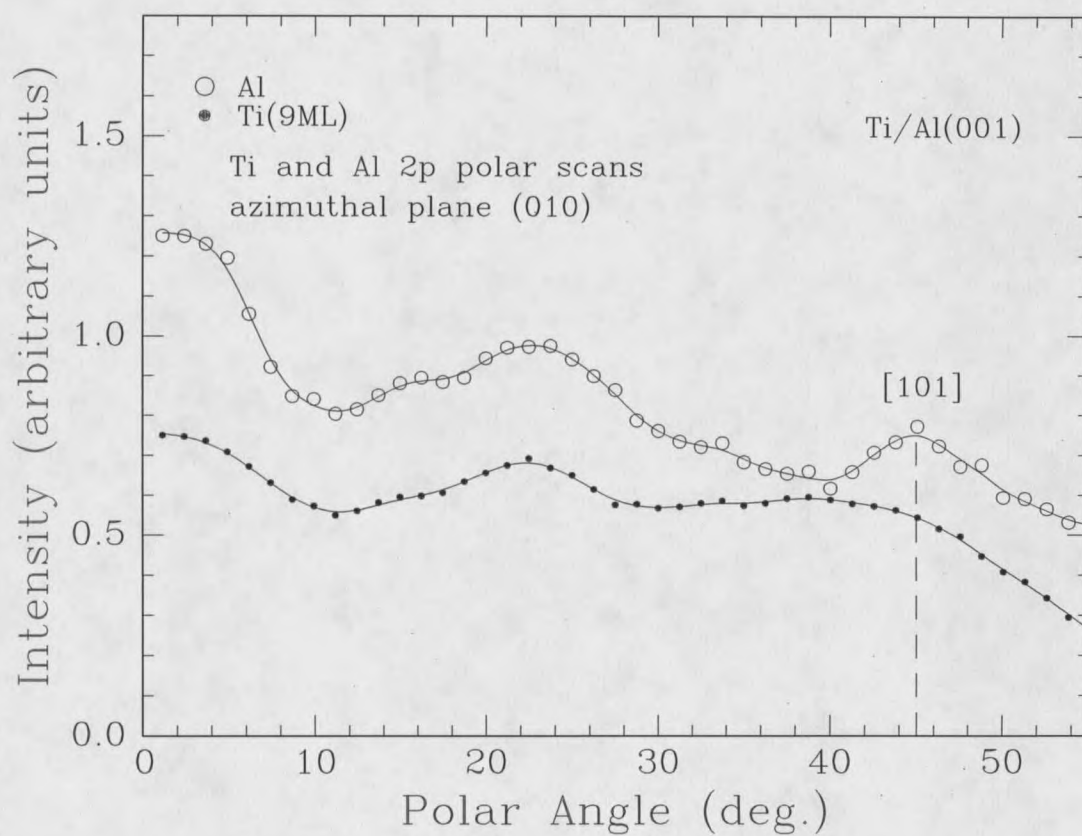


Figure 5.11 Ti 2p polar angle distributions in the (010) azimuthal plane compared to the clean Al distribution, at 9 ML of Ti coverage.

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CHAPTER 6

HYDROGEN UPTAKE BY Ti FILMS ON Al SURFACES

In the last two chapters, we discussed the formation of epitaxial *fcc* Ti films on Al surfaces. We also discussed the departure from this growth mode beyond a certain critical thickness. In this chapter we will present our investigation of the hydrogen uptake of these films at the various stages of their growth. The uptake by the films after the exposure to H₂ gas is measured using elastic recoil detection analysis (*ERDA*). The role which the film structure plays in limiting or facilitating the uptake of hydrogen will be examined.

This study is also a demonstration of the *ERDA* capability to detect and to quantify low levels of hydrogen concentration on the surface, with a sensitivity of about 0.1 ML. A detailed description of the basic principles of *ERDA*, and a description of the experimental setup are given in chapter 3.

6.1 Experimental

A collimated beam of 1.8 MeV He⁺ ions from the 2.0 MV Van de Graaff accelerator, passing through an aperture of 1.2 mm² in area, was used to carry out the *ERDA* measurements. The ion beam was incident on the sample with a grazing angle

$\alpha = 15^\circ$. A bakeable solid-state detector was positioned at a distance of 4.2" from the sample and at a recoil angle of 25° . An Al stopper foil, 8μ in thickness, was placed at the detector entrance to filter out the He^+ ions scattered in the forward direction. The detector was mounted on a linear motion feedthru, thus providing a mechanism to increase the solid angle subtended by the detector. Prior to performing the *ERDA* measurements, backscattering spectrometry was used to measure the incident ion energy and also to verify that the ion beam was incident only on the sample surface. This is particularly important since the sampled area increases to 5 mm in width due to the grazing incidence. The position of the Ti peak on the energy axis, and the backscattering kinematic factor are used to determine the incident beam ion energy.

ERDA measurements were performed in a *UHV* environment, where a chamber base pressure of 1.5×10^{-10} Torr was obtained. The hydrogen contents of the Ti films were measured prior to exposing them to the hydrogen gas. Exposure of the Ti films to high purity H_2 gas was done using a leak valve. The pressure in the chamber was monitored using an ion gauge. The exposure in Langmuirs (L) ($1 \text{ L} = 10^{-6} \text{ Torr s}$) was calculated using the chamber pressure, the exposure time, and the gauge correction factor of 1.8 for H_2 gas. Typically, exposures of up to 100 L were accomplished using a chamber pressure of 10^{-7} Torr, while a pressure of 10^{-6} Torr was used to accomplish higher exposures.

6.2 Results

Figure 6.1 shows a hydrogen recoil energy spectrum for a 9 ML thick Ti film

deposited on the Al(001) substrate. The film was exposed to 4500 L of hydrogen. Using equations 3.2 and 3.4, a value of 0.53 for the recoil kinematic factor, k , and a value of 946 keV for E'_f are obtained. Substituting this value of E'_f in equation 3.11, we obtain a value of 483 keV for E_p , the energy of recoiled surface protons as they enter the detector. This calculation is in agreement with the position of the hydrogen peak shown in Figure 6.1. The width of the peak is primarily due to the energy straggling in the stopper foil, $\Delta E_s = 35$ keV, which is calculated using equation 3.19. The spectrometer (solid-state detector and electronics) contributes to the broadening of the peak because of its finite energy resolution, $\Delta E_d = 30$ keV. The resulting broadening due to these two factors is 46 keV, while the measured *FWHM* is 70 keV. This difference is not surprising since other factors are known to contribute to the energy broadening. For example, a non-uniform stopper foil thickness contributes to the peak width, and thus the depth resolution further deteriorates.

To convert the peak area, A , in a hydrogen recoil spectrum, into total hydrogen concentration, both sides of equation 3.9 are integrated, and the following result is obtained:

$$A = \sigma(\Delta\Omega) Q \Theta \quad (6.1),$$

$$\text{or, } \Theta = \frac{A}{\sigma(\Delta\Omega)Q}$$

where $\Theta = \int \rho(x)dx$ and represents the total hydrogen uptake of the film. In each *ERDA* measurement, the total number of incident particles, Q , was typically set to 1.875×10^{14} .

particles. This number was monitored by integrating the sample current associated with the incident ion beam. During these measurements the sample was biased using a +156 V battery to suppress the emission of secondary electrons. A current supply was also used to compensate for leakage current. The solid angle subtended by the detector, $\Delta\Omega$, was 4.43 milliradians. The recoil cross-section at this energy, $\sigma(E=1.8 \text{ MeV}) = 320 \text{ mb/sr}$, was obtained using the graph in Figure 3.7. Substituting these values of Q , $\Delta\Omega$ and σ in the equation above, the hydrogen uptake in units of atoms/cm^2 can be written as:

$$\Theta = 3.76 \times 10^{12} \times A \text{ atoms/cm}^2 \quad (6.2).$$

It is useful to express the hydrogen coverage in terms of monolayers, where one monolayer is defined as the atomic areal density, Σ , of one layer of substrate surface. Σ for Al(001) is $1.22 \times 10^{15} \text{ atoms/cm}^2$, leading to the following expression for the uptake:

$$\Theta = \frac{A}{308} \text{ (ML)}. \quad (6.3).$$

Thus, a peak area of 308 counts corresponds to a hydrogen uptake of 1 ML. The solid line in Figure 6.1 represents the yield expected from 1 ML of surface hydrogen. The width of the Gaussian was set equal to the energy resolution of the spectrometer.

The hydrogen uptake of Ti films with thicknesses of 3, 5, and 9 ML was measured as a function of exposure to H_2 gas. The results of these measurements are shown in Figure 6.2. The uptake of the 3 ML and 5 ML films saturates at a value of 2.5 ML. On the other hand, the uptake of the 9 ML thick film saturates at a value of 13 ML.

To assess the level of hydrogen uptake by the films due to the exposure to residual gas in the chamber during deposition, the hydrogen content of the 9 ML film was measured immediately after deposition. In this case, *ERDA* measurements showed negligible uptake ($\Theta < 5\%$ ML). *XPS* measurements of the Ti and Al photopeaks after the hydrogen exposure indicate that exposure to hydrogen did not result in surface contamination, e.g. oxidation.

Channeling measurements subsequent to the H_2 gas exposure of the 5 ML film do not indicate any significant changes in the Al or Ti *SP* areas. The hydrogen exposed sample was also heated to 200 °C for 5 min., and then was allowed to cool down back to room temperature. The *ERDA* measurement following the heating process showed a hydrogen content of less than 0.2 ML.

6.3 Discussion of Results

ERDA measurements are based on knocking hydrogen atoms out of the sample. Because of this, one needs to consider if this collision process, upon which the technique is based, interferes with accurately measuring the hydrogen uptake. In other words, the hydrogen content may be depleted during the measurements in such a

situation. For example, this would be the case if the recoil cross-section was too small for the process to be of practical use. The assumption that the recoil measurement does not perturb the hydrogen uptake is implicit when using equation 3.9. In this equation, the yield is assumed to be directly proportional to the number of incident He^+ ions. We tested the validity of this assumption by measuring the hydrogen peak area at intermediate stages of the *ERDA* measurement. In Figure 6.3 we plot the hydrogen peak area as a function of Q , and verify the direct proportionality over the range of ion dose used in our experiments.

The *ERDA* measurements can be used to show how the structure of the Ti films influences their hydrogen uptake properties. The three curves in Figure 6.2 demonstrate this effect in light of our earlier results described in chapters 4 and 5. In chapter 5, we described the epitaxial growth of *fcc* Ti films on the Al(001) surface with film thicknesses up to 5 ML. We also observed the departure from this behavior beyond this thickness. Since the 3 ML and 5 ML films fall in this range of thickness, our results show that the *fcc* Ti films absorb less hydrogen than do bulk-like Ti films at room temperature.¹ The contrast is observed when comparing the uptake of the *fcc* films with the uptake of the 9 ML Ti film, where a relatively large uptake of 13 ML of hydrogen is observed, as shown in Figure 6.3.

We propose that the 2.5 ML of absorbed hydrogen for the *fcc* films are in fact adsorbed on the film surface. This may be due to a diminished hydrogen solubility in the *fcc* films. The γ -titanium hydride phase has a face-centered fluorite structure with

a lattice constant of 4.46 Å, compared to 4.05 Å for the Al substrate lattice constant.² The hydrogen atoms occupy the tetrahedral sites in the lattice. So the formation of Ti hydride would be associated with a reconstruction of the Ti film atomic structure. Our channeling measurements subsequent to the hydrogen exposure rule out this possibility, since such reconstruction would lead to an increase in the Al *SP* area in the ion channeling spectrum. The small uptake in the *fcc* films may also be a result of the formation a stable surface hydride at the initial stages of exposure to H₂. Such a phase may lead to the formation of a kinetic barrier which reduces the rate of diffusion of more hydrogen into the film. Such an effect is observed in experiments involving the hydrogen uptake by Nb.³

The uptake of both the 3 ML and the 5 ML Ti films saturates at the same value of 2.5 ML as shown in Figure 6.2. This observation is significant when considering the underlying reasons behind the blocking of hydrogen. One may argue that the Al substrate may be responsible for the hydrogen obstruction, especially in the case of the ultrathin film of 3 ML. If this was the case, we expect that this effect would be less of a factor for the 5 ML film, and an increased uptake would result.

The 9 ML Ti film exhibits an increased hydrogen uptake of 13 ML, compared to the *fcc* films. The ratio of H to Ti in this film is 1.45:1, compared to 0.50:1, the ratio of H to Ti in the 5 ML *fcc* film. This increase may be attributed to the film structure. Although we do not fully understand the film atomic structure beyond the critical thickness, we know that the structure change at the transition point is associated

with an increase in the Ti interatomic distance to reduce the amount of strain energy in the pseudomorphic films. This is because the atomic volume of Ti in the bulk is 1.77×10^{-23} cm³/atom, compared to 1.66×10^{-23} cm³/atom for Al. Consequently, the increased atomic volume in Ti films exceeding the critical thickness may facilitate the incorporation of hydrogen atoms within the resulting structure. This process can be described as an absorption of the hydrogen, in which hydride formation may occur, in contrast with the surface limited adsorption process in the case of *fcc* Ti films. The hydrogen absorption of the 9 ML film, as a function of exposure to hydrogen, closely resembles that observed for bulk-like Ti thin films. This can be observed when our results are compared with the results from microbalance studies of hydrogen absorption of a 54 Å Ti film, where the absorption saturates at an exposure of about 5000 L. Also, the saturation occurs when the ratio of H to Ti is 2:1. The study concludes that the hydride formation rate is limited by the number of sites available for hydrogen dissociation on the surface.¹

In summary, our results reveal a decreased hydrogen uptake for Ti films less than 5 ML in thickness compared to bulk-like Ti films. This decrease can be explained in terms of their *fcc* structure. The strained films exhibit a smaller atomic volume than both the bulk-like Ti films and the γ -hydride, and thus are likely to absorb less hydrogen. The decreased uptake may also be attributed to the formation of a *surface* hydride that blocks further hydrogen absorption. The 9 ML film exhibits absorption properties similar to those observed in bulk-like Ti films.

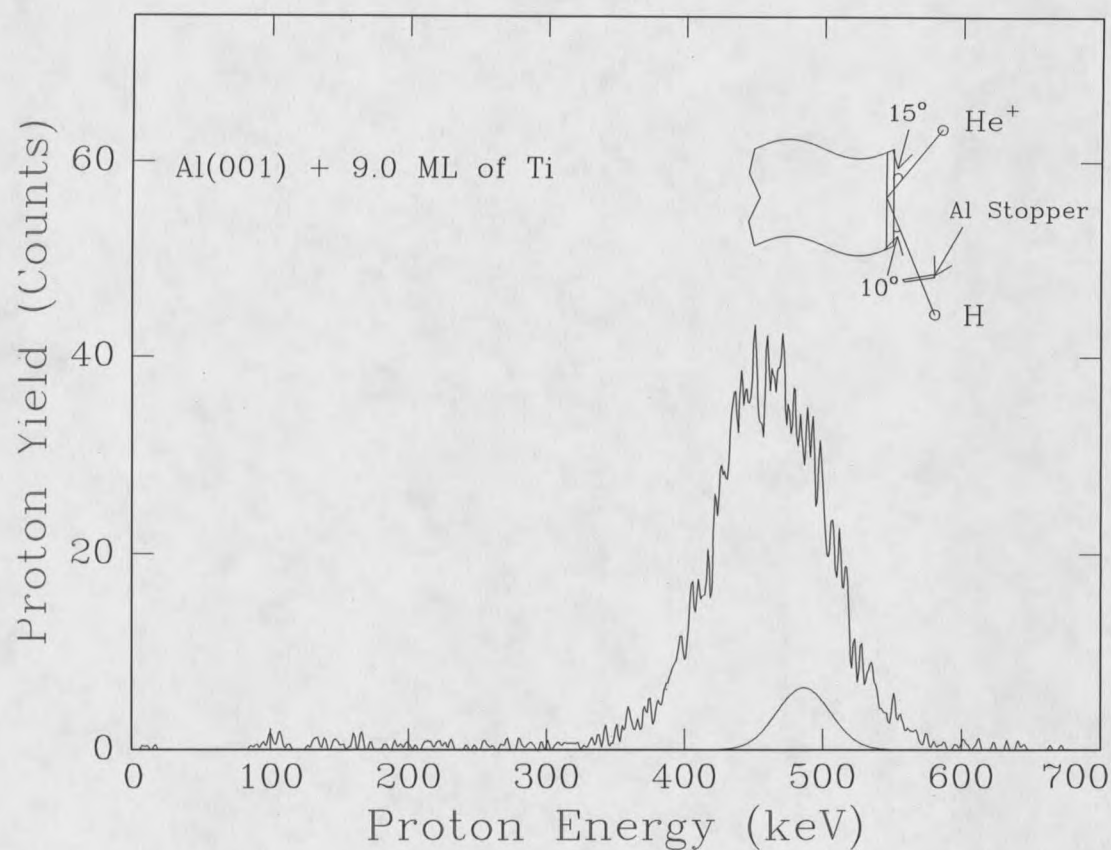


Figure 6.1 Proton recoil spectrum from Ti/Al(001). The Ti film, 9 ML in thickness, has been exposed to 5500 L of H₂. The peak area corresponds to a hydrogen uptake of 13 ML. The Gaussian peak indicated in the figure is the expected yield from 1 ML of hydrogen adsorbed on the surface.

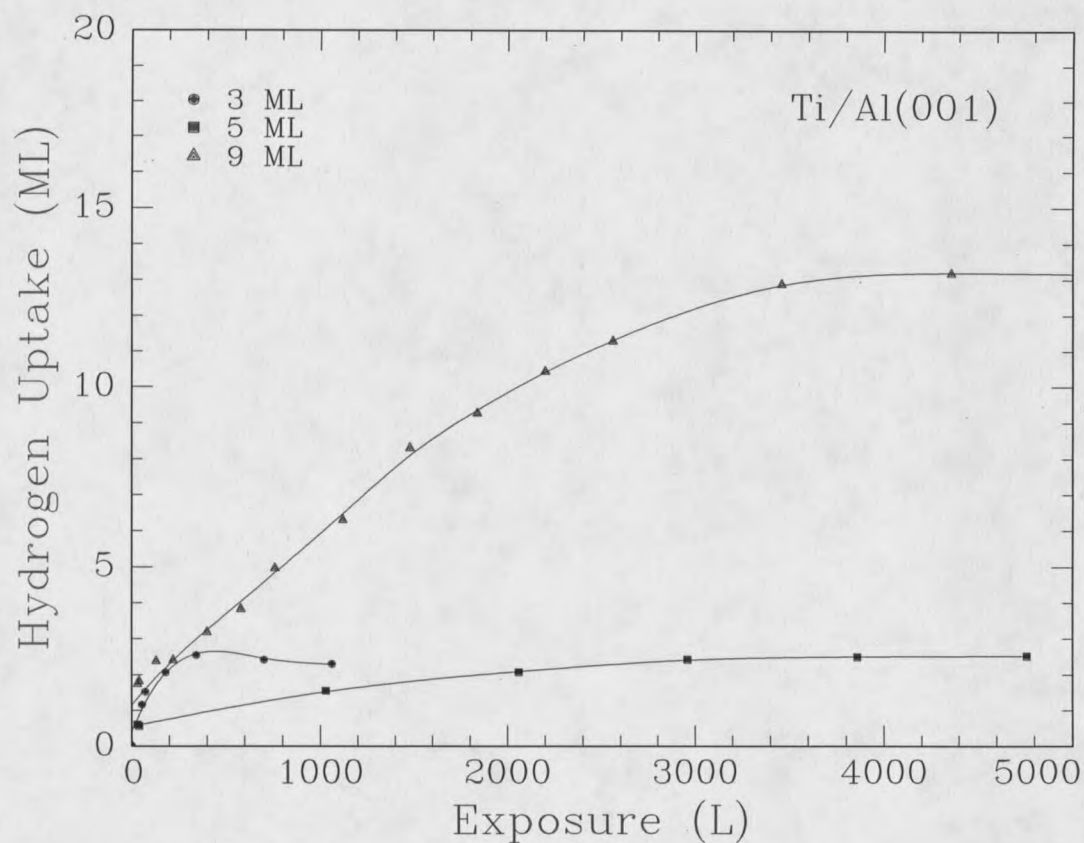


Figure 6.2 Hydrogen uptake of 3 ML, 5 ML and 9 ML Ti films deposited on the Al(001) surface as a function of exposure to H_2 gas. The uptake of both *fcc* films saturates at 2.5 ML. Uptake in the 9 ML thick film saturates at 13 ML of hydrogen.

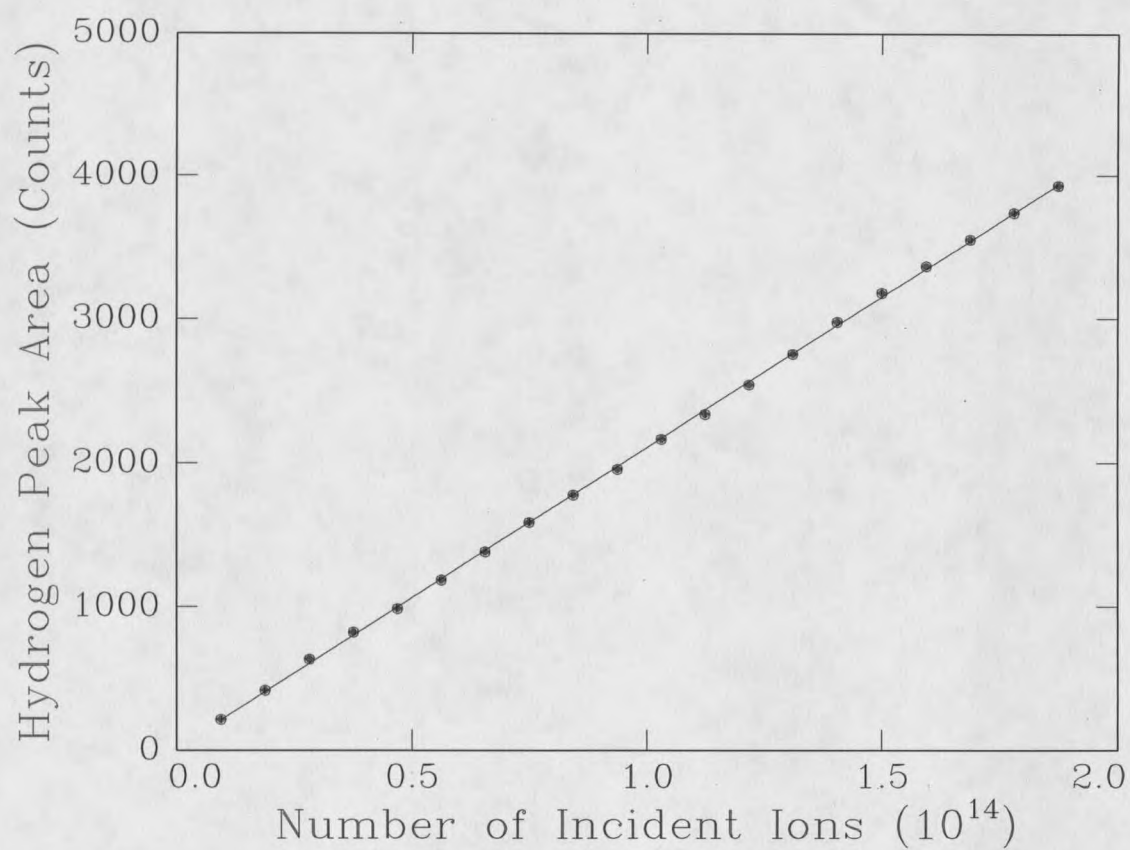


Figure 6.3 Proton recoil yield as a function of sample dose. There is no indication of hydrogen depletion in our experiments.

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