INVESTIGATION OF HYDROGEN CHEMISORPTION ON THE TUNGSTEN (100) SURFACE

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Stephen Parker Withrow, Ph.D. Department of Physics University of Illinois at Urbana-Champaign, 1975

A new apparatus for surface studies has been constructed and placed in operation. The instrument incorporates a monoenergetic beam of electrons, a high resolution, high sensitivity electrostatic energy spectrometer : for electrons and ions, plus other hardware and electronics necessary to perform work function measurements, Auger electron spectroscopy, electron stimulated desorption of ions, low energy electron diffraction, and electron scattering energy loss measurements. It has been used to investigate geometric, energetic, and kinetic properties associated with the chemisorption of hydrogen on a single crystal tungsten (100) surface over a temperature range from 60° C to -150 $^{\circ}$ C.

Auger spectroscopy data indicate heating the crystal to 2200° K' is sufficient to clean the surface of carbon and oxygen. However, weak structure is observed between 475 eV and 520 eV. Possible sources of this structure have been considered.

The work function changes observed at both 60 $^{\circ}$ C and -150 $^{\circ}$ C as a function of exposure of the crystal surface to hydrogen are equivalent within experimental error. The full monolayer changes in work function with hydrogen adsorption are 0.98 eV and 0.92 eV at the two temperatures, respectively. Cooling the clean surface from 220 $^{\circ}$ C to -150 $^{\circ}$ C increases the work function ≈ 0.05 eV.

Hydrogen ions are desorbed from the dosed tungsten surface following electron impact. The distribution in energy of these ions has a Gaussian line shape, with a peak intensity at an ion energy of 3.0 eV and a full width at half maximum of 2.6 eV. The ion yield is found to be coverage dependent, reaching a maximum at work function changes of 0.18 eV and 0.11 eV for desorption at $60^{\sf o}{\sf C}$ and -150 $^{\sf o}{\sf C}$, respectively. The total desorption cross section for H⁺ from the β_2 hydrogen state is calculated to be $5x10^{-20}$ cm² at 60° C and 1.2×10^{-19} cm² at -150°C.

A new hydrogen binding state, labeled the fast state, has been observed and characterized using ESD techniques. This state is desorbable if the undosed crystal is cooled below room temperature. It is populated to a very low coverage, ${\ge}10^{-4}$ monolayer, by adsorption from the background of some species other than H_2 . The total desorption cross section, 10^{-17} cm², and energy distribution of the fast state are markedly different than for the β states.

LEED pattern changes, observed as a function of hydrogen coverage, are in good agreement with results published in the literature. The intensity of the c(2x2) pattern associated with the β_2 hydrogen state maximizes at a work function change with adsorption of 0.15 eV. LEED elastic intensity profiles have been obtained for several low index beams. These are compared to theoretical, microscopic model calculations and to published experimental profiles. A $c(2x2)$ LEED pattern is obtained if the crystal is cooled below room temperature. Attempts have been made to correlate the appearance of this pattern to changes in measurements taken in this low temperature range with other techniques. No significant bulk to surface diffusion of hydrogen was

found. No evidence was found from work function and electron scattering experiments to support the hypothesis that the low temperature, $c(2x2)$ pattern results from hydrogen on the surface. **In** addition, the fast hydrogen state is not believed to be responsible for the $c(2x2)$ pattern. LEED intensity profiles from the undosed, cold surface c(2x2) pattern and from the c(2x2) pattern associated with the β_2 hydrogen state are not identical, an indication that the atomic geometry responsible for the two patterns may not be the same.

Electron scattering energy loss spectra have been obtained as a function of hydrogen coverage for loss energies of $0 \text{ eV} \leq w \leq 40 \text{ eV}$. Hydrogen adsorption has a marked effect on the spectra. Fine structure in the data has been discussed and compared to photoemission data. Cooling the clean crystal below room temperature causes only a slight change in the energy loss spectrum.

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CHAPTER 1

MOTIVATION AND REVIEW OF LITERATURE

1.1 Introduction and Motivation

The experimental investigation of chemisorption of gases onto metallic surfaces has uncovered in the past decade a baffling complexity of adsorption geometries and binding state kinetics and energetics. A growing interest in surface phenomena, generated by the questions raised in these researches and by the long anticipated use of the answers, has led to the rapid development of new surface probing techniques and to an increase in the availability of new technologies compatible with surface research. Aided by the new technologies and techniques, chemisorption research has been undertaken on many different systems (system \equiv solid substrate + gas adsorbate) under a wide range of environmental conditions. Surface theoreticians have proposed microscopic and phenomenological models with which data have been analyzed and compared. A large experimental and theoretical literature in the field has resulted.

The study of adsorption on metal surfaces has among its primary objectives a detailed description of the physical geometry of the atoms in the surface layers and a quantitative understanding of electronic and chemical surface phenomena. While considerable progress has been made in documenting gas-surface phenomena, it has been only in the past three years that any credible claims to understanding specific surface overlayer geometries have been made.¹ At the same time, many basic questions involving system kinetics and energetics have not been adequately resolved.²

It has become apparent from the failure of the research effort to satisfy the above objectives and from seemingly conflicting data that adequate

characterization is basic to all surface experimentation. The need for such characterization has been strongly emphasized by disagreement between quasisimilar research performed at different locations. Small impurity concentrations, small changes in crystal orientation, minor temperature differences, etc. often have considerable effects on experimental measurements.

A corollary to the necessity of being able to characterize the surface is the importance of being able to control the surface characterization. In order to compare data, it is necessary to reproduce all experimental parameters accurately. The theory to which experimental data are compared is constrained by complexity to be based on ideal, clean substrates with a definable gas-surface interaction. It is desirable to be able to choose the adsorbate-substrate system and experimental parameters that can also be used with theoretical models. Of course, compromises are inevitable.

One approach in surface research has been to incorporate several experimental techniques into one apparatus. At the present time this approach is increasingly more common. A combination of surface sensitive probes offers many advantages. It provides for more checks of the data against results published in the literature. It allows for better characterization of the experimental parameters. It allows surface phenomena to be probed in more than one way in order to eliminate ambiguities and/or to reinforce conclusions. It eliminates the uncertainties that arise from data taken at different locations using the techniques separately, hence it allows better correlations between data taken using the different techniques.

In this study, several aspects of the chemisorption interaction of hydrogen with the low index (100) plane of single crystal tungsten, denoted

W(100), have been investigated. The choice of the tungsten-hydrogen system is motivated by several factors. The literature raises questions on the unusual state behavior observed when hydrogen adsorbs on W(100), questions which our apparatus is especially well-suited to study. In addition, the interaction of hydrogen with close packed planes of single crystal metals, including W(100), is of particular interest to theoreticians since hydrogen is the simplest molecular gas; as detailed in Sections 1.2.8 and 1.2.9 below, recent theories of chemisorption have been applied to the hydrogen-tungsten system. Tungsten was chosen as the substrate metal because of its relative ease of preparation and cleaning, and because the large body of literature on the hydrogen-tungsten system indicates wide interest in this interaction.

In particular, this research is concentrated in three areas. Tungsten, when cleaned and subsequently cooled to below room temperature, exhibits an anomalous centered $(2x2)$, denoted $C(2x2)$, low energy electron diffraction pattern. The possibility that this is caused by hydrogen diffusing from the bulk or adsorbing from the background has been investigated. Secondly, the room temperature and low temperature hydrogen adsorption binding states have been studied using electron stimulated desorption and electron spectroscopy. Finally, low energy electron diffraction has been used in an investigation of the atomic geometry of the clean tungsten surface and the geometry of one of the hydrogen binding states.

The remaining sections of this chapter summarize literature relating to this research. Chapter 2 details the construction and performance of the experimental apparatus. A presentation of the experimental data is made in Chapter 3. A discussion of the results is made in Chapter, 4. A summary,of

the research and conclusions from it are given in Chapter 5.

1.2 Review of Literature

1.2.1 Introduction

Experimental investigation of the adsorption of hydrogen on tungsten has been carried out using field emitter tips, macroscopic polycrystalline surfaces, and all the low index orientation single crystal faces, including W(100). From the wide range of results, it is clear that the substrate exerts a strong influence on the adsorption properties. The question has been raised whether adsorption models postulated from polycrystalline substrates can be extended even qualitatively to single crystal systems.³ Likewise, there are such sharp differences in the chemisorption behavior of hydrogen onto the different single crystal tungsten surfaces, that the specific physical process governing adsorption on each face appears to be unique to that face. This review will, therefore, be concerned for the most part with literature dealing with hydrogen adsorption on $W(100)$, the gas-substrate system used in this research.

The following data review is presented in subsections, each concentrating on a specific experimental technique or class of experiments. Subsection 1.2.7 includes some gas mixing literature which was considered relevant, and Subsection 1.2.9 gives a bibliography of some related chemisorption theoretical papers.

1.2.2 Thermal Desorption

One technique widely employed in investigation of the kinetics of gas adsorption has been thermal, or flash desorption. $4,5,6$ By monitoring the system

pressure changes of a species while rapidly heating the crystal, inferences can be made on the existence of binding states, adsorption energies and reaction order. Heating is accomplished by a focussed light beam^{7,8}, electron bombard m ent⁷, or ohmic losses⁹.

The strongest indication that hydrogen exhibits multiple state adsorption behavior on W(lOO) comes from flash desorption data. Tamm and Schmidt⁷ and Madey and Yates⁸ found, for room temperature adsorption, that two large peaks are observed in the plot of pressure of H_2 versus temperature. These peaks are centered at 450 $^{\sf o}{\rm K}$ and approximately 550 $^{\sf o}{\rm K}.$ Only hydrogen molecules are observed to be desorbed from the surface. Using desorption rate theory^{4,5,6}, the lower temperature (β_1) state is found to obey first order kinetics, the peak temperature being independent of initial coverage. The higher temperature (β_2) state obeys second order kinetics, the peak temperature moving down from approximately $580^{\sf o}{\rm K}$ to $550^{\sf o}{\rm K}$ as the initial coverage is increased.

In addition to the two main peaks, several small peaks comprising a total of less than 10 percent of the desorbed hydrogen are observed during a flash when the crystal is cooled to nitrogen temperature before hydrogen exposure. These states are believed to result from adsorption onto edges and other non- (100) crystal orientations.⁸

The dependence of the desorption energy, E_A , on coverage is weak, with $E_d^{\beta_1}$ = 25.2 kcal/mole⁸ and $E_d^{\beta_2}$ = 32.3 kcal/mole⁸. As would be predicted from this result, the β_2 state is largely populated before the β_1 state begins to fill. The ratio of the populations in the states at full coverage, n_{β_1}/n_{β_2} ' is 2.1/1.⁸ Jelend and Menzel¹⁰ point out that the cross section for electron

desorption (see Subsection 1.2.5) from the β_1 state is considerably smaller than that of the β_2 state, a result not predicted from the experimental flash desorption binding energies.

Tibbetts¹¹, using a stepped temperature flash desorption technique, has shown that hydrogen is bound to the surface of po1ycrysta11ine tungsten, W(110), and W(lll) with a distribution of binding energies ranging from 16.2 kcal/mole (0.7 eV) to 41.5 kcal/mole (1.8 eV) . Using this technique, desorption at a constant temperature from a distribution of states can be easily distinguished from desorption from a state with a unique binding energy. While he did not extend his work to $W(100)$, these results suggest that hydrogen does not bind to the surface at a few energies, but rather, with a range of binding energies. Tibbetts also shows that the determination of the order of the desorption process is difficult for adsorption into a range of binding energies.

In experiments using a combination of hydrogen and deuterium as room temperature adsorbates, the elemental composition of the desorbed β_1 and β_2 states shows complete isotopic mixing between the states, $7,8$ independent of the adsorption sequence or ratios. However, for low temperature adsorption, complete state conversion is not observed for all the additional small peaks. Where mixing is observed, atomic adsorption is suggested. Where mixing is not observed, molecular adsorption is inferred.

Some theoretical models indicate that multiple peak flash desorption spectra may be due to binding energy changes caused by adsorbate-adsorbate interactions 12 or order-disorder transactions during flash 3,13 rather than actual distinct multiple binding states under the adsorption conditions.

1.2.3 LEED and HEED

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Low energy electron diffraction, or LEED, refers to the coherent scattering of a monoenergetic, focused electron beam from the surface of a crystalline solid. Electrons in the energy range $0 < E < 300$ eV interact strongly with the ion cores and valence electrons of the solid. The inelastic mean free path is on the order of $10 \, \text{Å}$. As a consequence, electrons which are observed elastically have been backscattered within the first several surface layers in the solid, making LEED a surface sensitive probe. 14 , 15 The periodic translational symmetry of the surface leads to the momentum conservation laws

$$
\mathbf{k}_0^{\dagger} = \mathbf{k}_0 + \mathbf{g} \tag{1.1}
$$

$$
k_{\rm H} = (2mE/h^2)^{\frac{1}{2}} \sin \Theta \qquad (1.2)
$$

where k_{11} is the momentum parallel to the surface of the emerging electron and $k_{\rm H}$ is the parallel momentum of the incident electron. The vector g is a reciprocal lattice vector of the solid surface and ® is the polar angle of the incident beam. As a result of the conservation laws, the scattered electrons emerge in a series of beams, called a spot pattern, which is a manifestation of the surface symmetry. The beams are labelled by their corresponding g vectors. Information on the actual configuration of the surface ion cores is extracted from the plot of elastically scattered electron intensity versus incident energy, called elastic intensity profiles or I-V curves. 16,17

Changes in the LEED spot pattern resulting from hydrogen adsorption onto W(100) at room temperature have been reported by Estrup and Anderson¹⁸ and by Yonehara and Schmidt.¹⁹ As hydrogen is adsorbed at room temperature, the

($lx1$) pattern characteristic of clean tungsten changes into a weak $C(2x2)$ pattern at a hydrogen coverage, θ , of less than 0.05 monolayer (where $\theta = 1$ monolayer at a coverage of $2x10^{15}$ hydrogen atoms/cm² which is 2 hydrogen atoms for each surface tungsten atom). The $(1/2,1/2)$ spots become sharp and intense with increased hydrogen adsorption, reaching a maxima in intensity at approximately 0.15 monolayer 19 or θ = 0.25 monolayer. 18 (Coverage in both cases was determined by flash desorption.) The $(1/2,1/2)$ spots split into four new spots which move apart continuously, and upon further hydrogen adsorption, eventually form 1/3-order streaks at a coverage of \geq 0.35 monolayer.¹⁹ These in turn change at higher coverage into poorly developed 1/4-order features with the $(0,1/2)$ spots missing. Finally, near $\theta = 1.0$, all extra diffraction features are gone and the LEED pattern returns to a (lxl) symmetry. This series of LEED pattern changes is reversible with coverage.

For hydrogen adsorption at 195° K, the C(2x2) pattern develops, maximizes in intensity at $\theta \approx .18$, and splits into four beams similar to room temperature adsorption. However, the higher coverage LEED structures, third order streaks and fourth order spots, are not observed.¹⁹ At 78[°]K, adsorption of hydrogen produces half-order $C(2x2)$ spots that maximize in intensity at $\theta \approx 0.27$. Additional hydrogen adsorption beyond this causes the half-order spot intensity to decrease but with no splitting of the spots.¹⁹

If "clean" W(lOO) is allowed to cool below room temperature, a sharp and intense $C(2x2)$ pattern is observed even though total coverage due to the background of H₂ and CO is less than $\theta = 0.01$ as determined by flash desorption measurements. The intensity of these half-order beams can be altered by additional hydrogen adsorption or by various hydrogen and oxygen heat treatments. Yonehara and Schmidt¹⁹ have postulated that the extra spots may result from hydrogen, endothermally soluble in tungsten, diffusing to the surface. Possible alternative explanations include the reconstruction of the clean tungsten surface or impurity overlayer adsorption from the background. It should be noted that Plummer and Bell²⁰ saw no effects upon cooling their field emitter tip to 78 $\mathrm{^{0}K}$ that they could attribute to hydrogen diffusion to the surface.

Elastic intensity profiles for several beams have been measured by Estrup and Anderson¹⁸ and by Papageorgopoulos and Chen²¹ at room temperature. Estrup and Anderson reported profiles for $(0,0)$ and $(1/2,1/2)$ LEED beams out to 300 eV. The intensity variation for the $(0,0)$ beam was found to be independent of hydrogen coverage, a manifestation of the relatively weak scattering cross section of a hydrogen ion core relative to that of tungsten. The additional beams observed on adsorption would be expected to be more sensitive to the adsorbed overlayer. Estrup¹³ found the intensity of the $(1/2,1/2)$ beams for $H_2/W(100)$ and $D_2/W(100)$ to decrease as a function of temperature between $300\mathrm{^o\!K}$ and $600\mathrm{^o\!K}$ at a constant incident energy, but neither obeyed the Debye-Waller relation.²² Estrup interpreted this result to imply the adsorbed species are directly involved in the diffraction process.

¹⁹ Yonehara examined the tEED spot intensities as a function of temperature down to liquid nitrogen temperatures. His results are examined in the data discussion in Chapter 4.

The hydrogen-W{lOO) system has also been studied using high energy electron diffraction, or HEED.²³ This technique utilizes the strong forward scattering of high energy electrons in probing the surface by having the incident beam strike the solid at grazing incidence. The resulting diffraction

patterns are sensitive to the translational symmetry of the surface. As in LEED, a diffraction pattern with C(2x2) symmetry is observed during initial hydrogen adsorption. With further hydrogen exposure, the beams broaden, some splitting is observed, and eventually the half-order intensity decreases completely. The width of the observed half-order beams has been interpreted to indicate hydrogen initially adsorbs into a large number of small square or rectangular domains, each consisting of 20 to 25 atoms, with sides parallel to the [100J directions.

1.2.4 Electron Scattering, Field Emission, and Photoemission

The electronic structure of the surface layers of solids can be characterized by electron emission spectroscopies. Such techniques require a surface sensitive perturbation on the gas-solid system leading to an electron yield. A spectrometer is used to energy analyze the emitted or scattered electrons. In electron scattering $24,25$, a monoenergetic beam of electrons is directed onto a crystal. The inelastically scattered signal, containing quantitative information about electronic excitations at the surface, is measured as a function of energy loss. Field emission is a technique in which application of a high positive electric field to the surface lowers the potential barrier for electrons to tunnel out of the system.²⁶ The total energy distribution of electrons emitted as a result of the applied field contains spectroscopic data on the adsorbed species.^{27,28} Structure induced by the adsorbate in the elastic tunneling spectrum is thought to be a measure of the electronic density of states in the vicinity of the adsorbate. 29,30 The inelastic tunneling spectrum reveals discrete excitation energies in the

gas-surface system. In photoemission or photoelectron spectroscopy, an incident monochromatic light beam incident on the solid induces emission of electrons by interband transitions, with or without an inelastic scattering after the initial excitation. 31

The vibrational spectrum of hydrogen adsorbed on the tungsten (100) surface has been observed by Propst and Piper³² using inelastic low energy electron scattering and by Plummer and Bell 20 using field emission. Propst and Piper found two peaks in the energy loss distribution E_{primary} - $E_{\text{scattered}}$ at 135 meV and 69 meV for all coverages used up to saturation. These results are interpreted as indicating hydrogen atoms are multiply bonded to tungsten atoms. No losses near 550 meV 33 , the vibrational energy of molecular hydrogen, were observed. Plummer and Bell measured the total energy distribution of field emitted electrons from tungsten (100) as a function of coverage of hydrogen and deuterium at several temperatures. Discrete losses at 100 meV and 50 meV for deuterium, which correspond to the 135 meV and 69 meV vibrational losses observed by Propst and Piper, were evident for deuterium in the β_2 state. No discrete energy losses at 550 meV or 390 meV, the molecular vibrational levels of H_2 and D_2 respectively, were measured. Hence there was no observable molecular adsorption at room temperature.

Additional structure in the field emission total energy distribution is observed as a function of hydrogen adsorption. The clean surface spectrum has two peaks 0.4 eV and 1.5 eV down from the Fermi level which have been identified as high density of states associated with the surface. 34 As hydrogen (or deuterium) coverage increases between 0 and $5x10^{14}$ atoms/cm², i.e., while the β_2 state is filling, the surface states disappear and the field emitted

energy distribution changes from that of clean tungsten to a spectrum indicative of resonance tunneling through a level positioned 0.9 eV below the Fermi energy. There is a shoulder at -1.1 eV and an energy dependent background. With further adsorption up to saturation, this energy distribution, characteristic of the β_2 state, shifts to a broad level centered at 2.6 eV below the Fermi level. This is interpreted to indicate that the β_1 state does not adsorb "on top of" the β_2 state.

The photoemission results of Waclawski and Plummer³⁵ and Feuerbacher and Fitton 36 are in agreement with those obtained using the field emission technique. As hydrogen adsorbs on the surface, emission from the 0.4 eV surface state decreases. The level 0.9 eV down from the Fermi energy, as well as a level 5 eV down, remain unchanged by adsorption. At full coverage a strong peak at -2.5 eV is observed.

1.2.5 Electron Stimulated Desorption

Desorption of energetic ions and neutrals from a gas overlayer can be induced by electron bombardment. This process, termed electron stimulated desorption or ESD, $37,38,39,40$ is described below in the discussion of the data in Chapter 4. In brief, intensity and energy measurements of the ion yield can be interpreted in terms of the parameters characterizing the binding energy curve of the adsorbed state, and adsorption states can be classified by cross section for desorption, ion energy distributions, primary energy threshold for desorption, etc.

ESD has been employed to study adsorption kinetics for the hydrogentungsten (100) system. Madey⁴¹ obtained a coverage dependence yield of H^+ ions,

observing an ion signal during the initial stages of hydrogen adsorption that reached a maximum at a coverage of $\theta = 0.17$ and then decayed to zero yield after θ = 0.75; the maximum cross section obtained was 1.8×10^{-23} cm² at a primary electron energy of 100 eV. Tamm and Schmidt⁷ reported a maximum cross section for H^+ desorption of 10^{-21} $\rm cm^2$. Benninghoven, Loebach, and Treitz 42 and Jelend and Menzel 10 obtained qualitatively similar (to Madey) coverage dependencies on tungsten ribbons which were believed to be predominantly of (100) crystallites; the main difference between these results and Madey's is the observation of a residual signal at high hydrogen coverage.

The cross section results indicate that the β_2 state, even though it is more tightly bound than the β_1 state, provides more hydrogen ions upon electron impact. The cross section for ion desorption from the β_1 state is estimated⁴¹ to be less than 10^{-25} cm².

No energy distributions of the desorbed H^+ ions have been reported. The dependence of the desorption cross section on the primary electron energy has not been investigated. Jelend and Menzel¹⁰ found their results independent of temperature for temperatures above room temperature. No ESD results for temperatures less than 300° K have been reported.

1.2.6 Work Function

The work function is the minimum amount of energy required to remove an electron from a metal. 43 An adsorbate may alter the potential barrier for electrons at the surface and hence change the work function. Such is the case for hydrogen on W(100). Hydrogen adsorbs as an electronegative ion on W(100), thereby increasing the work function.

Using a retarding potential current-voltage technique, 44 Madey and Yates⁸ reported a linear relation between work function change and hydrogen coverage over the entire coverage range for adsorption occurring at a temperature of $> 300^\circ K$. Coverages were determined by flash desorption. Total work function change at one monolayer was found to be 0.90 eV, which corresponds to a constant dipole moment per adsorbed atom of 0.15 Debye (assuming a total coverage of $1.5 \text{x} 10^{15}$ atoms/cm²).

Estrup and Anderson¹⁸, using the retarding potential technique, and Plummer and Bell²⁰, using a field emission Fowler-Nordheim plot, 45 found a work function change versus coverage relationship which deviated only slightly from being linear, in near agreement with the results of Madey and Yates.⁸ Becker⁴⁶, using field emission and Armstrong⁴⁷, using a retarding potential technique, found a work function change for the $H_2/W(100)$ system of approximately 0.90 eV when $\theta = 1.0$. Hopkins and Pender 48 obtained an anomalously low value ⁴⁹ of 0.54 eV while Collins and Blott obtained a high value of 1.09 eV for the same coverage.

1.2.7 Chemical Probes

Hydrogen adsorption has also been studied using a "chemical probe", i.e., by coadsorbing some additional, different gas with the hydrogen and observing the effect this additional species had on results obtained using techniques discussed in previous sections.

Yates and Madey⁵⁰ found using flash desorption that CO coadsorption onto a hydrogen monolayer displaces both the β_1 and β_2 binding states with near unity probability, in doing so initially replacing these states with a

less tightly bound hydrogen state. After high CO exposure, no hydrogen remains on the surface if the coadsorption is done at room temperature. At lower temperatures only about 10 percent of the hydrogen is desorbed. Jelend and Menzel $10,51$ found that the ionic and total desorption cross sections for hydrogen, the sticking probability, and bond strength of hydrogen are all affected by preadsorption of CO or oxygen. Yates and Madey³ found that N₂ slowly replaces preadsorbed hydrogen at temperatures greater than 300° C. Below 273[°]K the displacement of hydrogen by N_2 does not occur.

These results all show that small impurity concentrations of CO, N, and 0, if intentionally introduced, do affect the resulting hydrogen chemisorption properties. These experiments underscore the necessity of surface chemical characterization.

1.2.8 Chemisorption Models

Several models $7,18,19,52$ have been proposed to account for the experimental results from hydrogen chemisorption on W(100). Each of these models embodies some combination of the following three phenomenological assumptions. 1) The tungsten surface is ideal, planar, and free of contaminants. 2) There are available two types of adsorbates, namely hydrogen atoms and molecules. 3) There are three high symmetry, logical bonding sites⁵³ on a BCC (100) face, usually designated by the letters A, B, and C. These positions are A, a bridge site with 2 nearest neighbors and the hydrogen equidistant from two adjacent surface tungsten atoms, B, a four fold symmetric site with 5 nearest neighbors and the hydrogen located on a surface normal that passes through the center of a surface primitive unit cell, and C, the hydrogen located directly above a surface atom with one nearest neighbor. There are $2x10^{15}$ A sites/cm², and $1x10^{15}$ B or C sites/cm² on W(100).

The proposed models attempt to explain or at least be consistent with empirical results presented in Sections 1.2.1 through 1.2.7. A summary of salient features of the reported research includes a) a linear work function change with coverage, b) a saturation coverage of between 1.5 and $2.0x10^{15}$ H atoms/ cm^2 , c) a coverage dependent adsorption layer symmetry including a wellordered surface at low coverages, d) the appearance at low temperatures of a surface translational symmetry not equivalent to room temperature clean tungsten, e) adsorption into states which produces a two state thermal desorption spectrum with relative coverages in the two states of $n_{o} / n_{o} = 2:1$, f) a ~1 ~2 coverage dependence for the observed electronic structure, including the absence at high coverage of structure observed at low coverages, and g) no observed vibrational levels which correspond to free H_2 molecule.

Following is a short review of several proposed surface models.

Estrup and Anderson¹⁸ account for their LEED spot pattern results using a model wherein the hydrogen molecules dissociate upon adsorption and migrate initially to form islands of hydrogen atoms located at type A sites in a $C(2x2)$ structure. Dissociation is assumed since the $C(2x2)$ pattern maximizes at a coverage of 2.5×10^{15} molecules/cm² whereas without dissociation it would maximize at $5 \mathrm{x} 10^{15}$ molecules/cm 2 . Although type B or type C site adsorption could also produce the initial $C(2x2)$ LEED pattern, these sites are rejected because of the following. 1) There are only 1×10^{15} B or C sites/cm². This is not enough sites to accommodate a full monolayer coverage if all binding is atomic and if it is into equivalent sites as suggested by the linear work

function change with coverage. 2) While a complete 1/4-order LEED pattern is possible with type B or type C sites, it is not possible to produce a 1/4-order pattern with $(0,1/2)$ spots missing 54 using B or C sites. As the adsorption proceeds past a surface density of $5x10^{14}$ hydrogen atoms/cm² the adatoms continuously rearrange into "long period" superlattices with antiphase domains that produce successively the 1/2-order spot splitting, the 1/3-order streak (only partly ordered domains), the 1/4-order pattern and finally the (lxl) full coverage structure.

This model has been criticized for not accounting for the two observed binding states and for predicting a maximum in intensity of the half order spots at $\theta = 0.25$; these beams maximize at less than that coverage. In addition, the authors themselves questioned the idea of well-ordered superlattices.

In order to explain the relative intensity of the two states at satur**a**tion seen in flash desorption, n_{α} : n_{α} = 2:1, Tamm and Schmidt⁷ propose a $1 \frac{1}{2}$ model wherein the initial hydrogen adsorption is atomic and at B sites in a C(2x2) pattern. At full coverage the remaining B sites are filled with hydrogen molecules. B sites are chosen over C sites using molecular orbital ⁵⁵ arguments. A sites are rejected as there are too many to satisfy this model. This model satisfies the second order kinetics observed for the β_2 state and the first order kinetics observed for the β_1 state. In addition, it explains their saturation coverage of $> 3x10^{14}$ molecules/cm^{2.7} One weakness of this model pointed out by Tamm and Schmidt is that it is not obvious the model can account for the observed LEED and work function results. Also, no molecular vibrations have been observed.

Yonehara and Schmidt¹⁹ propose a three bonding state model that is more consistent with the low temperature LEED results. In their model, an additional state, labeled β_3 , is always present 'at the surface in A or B sites with a density of $5x10^{14}$ atoms/cm². This state orders on the surface at low temperatures to give the C(2x2) pattern observed. At room and higher temperatures, it goes into solution (or perhaps disorders), becoming invisible to LEED. In the type A site model, adsorption from the background fills in the remaining A sites sequentially with the β_2 and β_1 states. This model is similar to that proposed by Estrup and Anderson¹⁸ except that the β_3 state, although invisible to LEED at room and higher temperatures, occupies 1/4 of the type A sites. This model eliminates the stoichiometric objection to Estrup and Anderson's model. The model depends on the possibility of type A sites being occupied by states with considerably different properties. If the β_3 state occupies type B sites, β_2 state adsorption fills in the remaining type B sites and then β_1 hydrogen adsorbs into random, or possibly type C sites. This second model does not explain satisfactorily work function or LEED spot pattern experimental data.

Propst⁵⁶ found, using a point defect type calculation, that only a B-site model of adsorption would produce the observed vibrational energies of 69 meV and 135 meV. Park⁵⁷, using LEED intensity arguments, found that only adsorption into sites with 4-fold symmetry on the (100) surface (type B or type C sites) would be consistent with broadening and splitting of the half-order beams while the integral beams remain sharp.

Madey and Yates⁸ offer a critique of several of the proposed models.

No adsorption geometry adequately accounts for all the observed data. It is possible that surface hydrogen mobility, adsorbate-adsorbate interactions, tungsten surface reconstruction, and other surface phenomenon must be better understood before this system can be adequately characterized.

1.2.9 Theoretical Treatment

Several theoretical treatments of hydrogen-tungsten chemisorption phenomenon have been reported in the literature, as discussed below.

The most elementary, geometric models⁷, 18, 19, 52 already have been mentioned in Section 1.2.8. Grimley⁵⁸ considers the hydrogen on W(100) system ⁵⁹ in an Anderson-Hamiltonian formalism. Anders and Hansen obtain the relative bonding energies of hydrogen chemisorbed at the three high symmetry adsorption sites of $W(100)$ using an extended Huckel molecular orbital theory. Their results indicated a preference for hydrogen adsorption at type C sites. Schrieffer 60 offers a review on the theory of chemisorption, in which he concludes the Hartree-Fock approximation to the Anderson model for hydrogenmetal adsorption is invalid. Newns , using the same approximation, also shows the one-electron HF theory to be invalid. Schrieffer and $Gomer$ study the exchange interaction between the adatom and the solid which results from the nonorthogonality of the adatom and solid wave functions. Smith, Ying, and Kohn⁶³, ⁶⁴ investigate the hydrogen-metal chemisorption problem by requiring complete self-consistency between the three-dimensional electrostatic potential used and charge density obtained. They calculate electron scattering, resonance levels, and ground state vibrational frequency. Jennings and McRae $^{\rm 65}$, using a multiple scattering LEED theory (but neglecting inelastic collision

damping) show that there can be half-order beams of high intensity in the $_{2}^{\text{u}-\text{W}}$ system even though hydrogen is a weak scatterer. Weinberg 66 applies a bondenergy bond-order model of chemisorption to the hydrogen-W(100) system and predicts binding energies for the molecular state and atomic state of hydrogen on $W(100)$ to be 26.2 kcal/mole and 32.2 kcal/mole, respectively.

1.2.10 Literature Summary

Some conclusions can be drawn concerning the state of understanding of the hydrogen-tungsten system and in particular the $H_2/W(100)$ system.

Despite considerable research, experimental uncertainties still exist in the $H_2/W(100)$ interaction. It is still not clear if hydrogen adsorbs as a molecule. The preponderance of evidence, from electron scattering vibrational levels, field emission, and H_2-D_2 gas mixing flash desorption measurements indicates most hydrogen probably adsorbs atomically. Multiple state behavior is exhibited. It is not known, however, if this observed state behavior is a result of distinct hydrogen-tungsten interactions; it is believed that, to a large extent, it is driven by coverage dependent adsorbate-adsorbate interactions. There is no model that can successfully incorporate the measured work function, flash desorption, and ESD parameters. The adsorption sites are not known. Total coverage at one monolayer is between 1.5x10 15 and 2x10 15 atoms/cm 2 , which is more than the number of surface tungsten atoms/ cm^2 in the (100) face. LEED results at different temperatures indicate a possible temperature dependence for the adsorption of hydrogen on $W(100)$. Particularly confusing is the anomalous LEED result obtained at low temperatures for the clean surface. Only small adsorption temperature dependencies are found **in** sticking probability

work function changes, and flash desorption results.

1.3 Review of Experimental Techniques

As indicated in Section 1.1, this research has been undertaken in an attempt to characterize more fully the hydrogen-W(lOO) interaction. A multitechnique spectrometer has been used. Chapter 2 gives a discussion of the instrument. This instrument is capable of making work function, Auger electron spectroscopy, electron scattering, ESD (including a pulsed time-of-flight mode), and LEED measurements. These techniques, except AES, have been well-reviewed as referenced previously (work function $^{43,44},$ AES $^{67,68},$ ES $^{24,25},$ ESD 3,37,38,39,40 LEED 15,16,17). Their use in this research can be summarized as follows: work function changes are a measure of adsorption coverage. Auger electron spectroscopy has been used to characterize the contamination of the experimental surface. ES and ESD are sensitive probes of surface and adsorption parameters. Time-of-flight has been used to determine the ion species desorbed. LEED has been used here to indicate the orientation of the surface and to attempt to take initial data useful in calculation of overlayer geometries. A more detailed discussion of these techniques as used in this research is given in Section 3.2.

A discussion of the instrument constructed and used for this research is given in Chapter 2. Sections 3.1 and 3.2 deal wIth organization and experimental procedures. Experimental data are presented starting with Section 3.3. A discussion of the data and conclusions from the research are given in Chapter 4.

CHAPTER 2

EXPERIMENTAL APPARATUS

2.1 General Description

The apparatus used in this research is designed to probe an experimental macroscopic crystal with several surface sensitive techniques. It combines an electron gun which focuses a monoenergetic beam of electrons onto the crystal, a new high resolution electrostatic spectrometer capable of energy analysis of electrons and ions, a low energy electron diffraction (LEED) system, and a crystal manipulator. The crystal manipulator allows positioning of the experimental sample and provides sample cooling, heating, and electrical biasing. Also included in the apparatus are a mass spectrometer and a gas handling system. System electronics allow the spectrometer to perform work function, electron energy loss spectroscopy, electron stimulated desorption, Auger electron spectroscopy, and low energy electron diffraction measurements. The spectrometer can be operated over a wide range of primary electron energies and currents, and analyzer pass energies. It can be biased in both electron and ion pass modes, and in a pulsed time-of-flight mode for species identification. An external spot photometer is used for LEED intensity measurements. The instrument is housed in an ultrahigh vacuum chamber. A schematic diagram of the overall system is given in Figure 2.1. The construction and performance characteristics of each of the components are discussed in the following sections of Chapter 2.

2.2 Vacuum System and Magnetic Shielding

The requirement that the experimental surface has to remain clean

Figure **2.1.** Schematic diagram of mu1titechnique **apparatus.**

while making measurements necessitates housing the apparatus in an ultrahigh vacuum chamber. A commercial, Varian vacuum chamber and pumping station have been used. Ultrahigh vacuum was achieved in several steps; after the chamber was rough pumped down to 10^{-2} Torr using cryosorb pumps, main system pumping was accomplished using a 400 liter/sec ion pump and a titanium sublimator. After a bakeout of 24 hours at temperatures up to 270 $^{\circ}$ C to outgas the system walls, the system pressure read about $1x10^{-10}$ Torr, as measured with a Bayard-Alpert ion gauge. The pressure decreased somewhat during the first weeks of spectrometer operation after bakeout. The final system background pressure was less than $8x10^{-11}$ Torr, or below the x-ray limit of the gauge. When operating in the Auger mode, the background rose to $1x10^{-10}$ Torr, presumably because of the large currents involved. A mass spectrometer scan indicated that the main components of the background were H_{2} , CO, CO₂, and H_{2} O. The ion gauge, which can affect the composition of the background, was turned off while taking data, except if noted otherwise.

In an electrostatic deflection analyzer such as used here, magnetic fields can introduce spurious results. In order to reduce the earth's magnetic field in the region of electron or ion trajectories, three concentric cylinders of Eagle AAA ultrahigh nickel steel alloy magnetic shielding are placed around the spectrometer. The shielding is mounted on a stainless steel and ceramic support which rests in a groove in the inside wall of the vacuum chamber. This shielding is electrically isolated so it can be floated at any desired voltage. The ambient magnetic field in the target region is less than 5 milliGauss.

The region inside the shielding and below the spectrometer (the region shown in Figure 2.14) is referred to in this work as the experimental chamber. There are apertures cut in the magnetic shielding which allow the crystal to be put in (and out of) the experimental chamber. Apertures also allow line-of-sight access to this region of the gas dosing jet, mass spectrometer, and allow the crystal to be viewed.

2.3 Electron Gun and Gun Electronics

The electron gun provides the incident, focused electron beam used in all the surface probing techniques. Figures 2.2 and 2.3 show a schematic drawing of the electron gun and a photograph of the gun assembled and disassembled. The gun is a modified version of a gun designed by Peria. 69 The comporients of the gun are a thermal cathode or source of electrons, three electrodes, and four deflection plates. The cathode is a Philips Metalonics Type M barium calcium aluminate impregnated tungsten emitter. The cathode was generally operated at 875 $^{\circ}$ C, with the heating accomplished indirectly with a tungsten filament behind the heater. The electrons emitted are focused into a beam by two lenses; the crossover formed by the lens action of the control grid and first anode is focused onto the target by a second lens formed by the first anode and second anode. The incident primary beam thus formed can be deflected along two axes in the target face by means of deflection plates located at the entrance to the drift tube.

The gun's electronic circuitry is shown in Figure 2.4. Three 6 V lead storage batteries in series power the cathode heater through an integrated circuit voltage regulator. The gun electrodes are biased using a resistor chain voltage divider circuit. This arrangement scales the gun's lenses, thus keeping the beam focused as the primary beam energy is changed by varying the

Figure 2.2. Schematic diagram of electron gun.

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Figure **2.3.** Photograph of electron gun assembled and disassembled.

Figure **2.4.** Diagram of the electron gun's biasing circuitry.

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gun power supply, a Kepco BHK-2000 supply. The gun can be operated in two modes. In the accelerating mode *(ace.* mode) the second anode is biased more positive than the first anode. With this biasing, the gun has been operated from 30 V to 1825 V primary energy. In the decelerating mode (dec. mode) the first anode is biased more positive than the second anode. This allows for higher field gradients at the cathode surface, resulting in higher currents at lower energies. In the dec. mode the gun can be operated from $10 \,$ V to $200 \,$ V.

A spatial profile of the primary beam was taken using a two grid retarding field analyzer mounted on the target manipulator at the position of the target. Electrode bias settings that optimized the beam line shape were determined over the gun's energy range. These results are summarized in Figure 2.5. The spatial full width at half maximum of the spot intensity is less than 0.25 mm at 1825 V, less than 0.75 mm at 100 V (dec. mode) and about 2.5 mm at 10 V. The energy width of the primary beam can be estimated by retarding the primary beam between the drift tube and target. At $E_{\text{pri}} = 100$ eV, the current to the target goes from 90% maximum to 10% maximum over a retarding voltage of $\Delta V \le 0.360$ meV. This is an upper estimate on the energy spread in the primary beam. A lower limit would be the thermal spread of the cathode, \approx 2kT, or about 200 meV.

2.4 Energy Spectrometer

A schematic diagram of the spectrometer used in this research to energy analyze electrons and ions is given in Figure 2.6. The spectrometer's operation can be summarized as follows. Electrons and ions, originating at the target with some energy distribution, are accelerated or decelerated to the

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Figure 2.5. Spatial characteristics of primary electron beam. Top panel - Full width at half maximum of beam as a function of primary energy. Bottom panel - Line shape of beam at several primary energies.

Figure 2.6. Schematic diagram of energy spectrometer.

pass energy of the spectrometer by three spherical sector grids prior to entering the spherical analyzer section of the instrument. (An annular slot cut in the LEED screen which is located between the grids and the spherical analyzer allows particles to pass into the analyzer.) Energy selection is accomplished by a combination of two electrostatic deflection analyzers. The first is a high resolution spherical deflection analyzer. This is backed by a cylindrical mirror-type electrostatic analyzer, referred to in this work as the cylindrical or tandem analyzer. Particles that pass through the spectrometer impinge on the first dynode of a high gain electron multiplier. The output signal of this multiplier is detected using the electronics discussed in Section 2.5.

The spectrometer is constructed mainly of 304 stainless steel which has been hydrogen and vacuum fired to reduce residual magnetism to less than 5 milliGauss. Most interior surfaces have been rhodium plated to eliminate surface charging problems. Final design dimensions used in the spectrometer are listed in Table 2.1. Refer to Figure 2.7 for a diagram of the variables used in this table.

The emission angle at the target of the central trajectory that passes into the spectrometer is 35° . The entrance aperture (slot) accepts particles that originate within $+0.045$ radians of this central ray, making a total solid angle accepted of 0.32 steradians.

The spherical electrostatic deflection analyzer section is a spherical velocity selector of the type first investigated by Purcell.⁷⁰ The analyzer is designed to focus an object spot of electrons or ions originating at the front surface plane of the target onto the first energy resolution

TABLE 2.1 FINAL DESIGN DIMENSIONS FOR SPECTROMETER

SPHERICAL ANALYZER

- 1. Inner sphere radius, $r_1 = 3.42$ cm
- 2. Outer sphere radius, r_2 = 4.19 cm
- 3. Radius of central ray, $a = 3.81$ cm
- 4. Emission angle of central ray, $\theta = 35^{\circ}$
- 5. Angular range of accepted rays, 32.44° 37.56°
- 6. Angle subtended between entrance and exit planes of spherical analyzer section, $\Phi = 51.66^{\circ}$
- 7. Acceptance solid angle of spectrometer, 0.32 steradians
- 8. Diameter of first $E.R.A., D = 0.25 cm$
- 9. Distance of target from "center" of spherical analyzer, $P = 6.65$ cm
- 10. Distance of first E.R.A. from "center" of spherical analyzer, $Q = 13.28$ cm

CYLINDRICAL ANALYZER

- 11. Distance from first E.R.A. to entrance diaphram, $S = 3.30$ cm
- 12. Distance between entrance and exit diaphrams, $T = 3.99$ cm
- 13. Distance from exit diaphram to second E.R.A., U = 3.30 cm
- 14. Inner cylinder radius, $R_1 = 0.099$ cm
- 15. Distance from second E.R.A. to electron multiplier, $V \approx 2.54$ cm
- 16. Radius of entrance aperture, $R_2 = 0.99$ cm
- 17. Radius of repulsion electrode, $R_3 = 3.30$ cm
- 18. Radius of exit aperture, $R_A = 0.93$ cm
- 19. Width of exit aperture, $G = 0.37$ cm
- 20. Diameter of second $E.R.A.$, $E = 0.44$ cm
- 21. Width of entrance aperture, $F = 0.53$ cm

Figure 2.7. Schematic diagram of particle trajectories in spherical analyzer section. Spatial configuration of tandem cylindrical analyzer section also shown.

aperture, or image plane. The spatial configuration of the analyzer is such as to give maximum reduced dispersion according to the relations derived by Purcell. The magnification of the source at maximum reduced dispersion is 2. Diaphrams at the entrance and exit apertures of the spherical analyzer are designed to minimize problems caused by the fringing fields as discussed by Herzog.⁷¹

Initial tests using only the spherical analyzer indicated electrons that scattered from the interior surfaces could be passed through the first energy resolving aperture over a range of analyzer pass energies. To eliminate this erroneous signal, a second, low resolution cylindrical mirror-type electrostatic analyzer was designed and constructed by P. Luscher.⁷²

Electrons or ions that pass through the first energy resolving aperture at the correct energy are deflected by the repulsion electrode of the cylindrical analyzer and pass through the second energy resolving aperture. This signal impinges on the first dynode of the electron multiplier. Trajectory tracing calculations indicated that the cylindrical analyzer would eliminate the scattered signal if this second analyzer had a full width energy resolution, $\Delta E/E_{pass}$ = 0.28 where E_{pass} is the energy of the particle executing the correct, central trajectory through the spectrometer. This is not a stringent design requirement.

The energy resolution of the spectrometer is defined as the ratio, $\Delta E/E_p$, where ΔE is the width of the line shape passed as the spectrometer is scanned in pass energy for a monochromatic source of particles with energy E_p . For the spectrometer configuration here, the energy resolution is determined by the resolution achieved in the high resolution spherical analyzer section,

at least down to low pass energies. Line shape broadening effects in the spherical analyzer originate from three sources: 1) the finite diameter, D, of the first energy resolving aperture, 2) the finite radius, R, of the source disk, and 3) the use of a finite range of emission angles of particles from the crystal surface which can enter and be passed by the spectrometer. This third source of line broadening results from the spherical analyzer having imperfect second order focusing at the first energy resolving aperture. The effect on the line shape of the finite range of emission angles goes as the square of the acceptance half width, which, in this analyzer is small. In the calculation of energy resolution below, the third source of line broadening will not be considered.

A numerical value for the energy resolution for the spectrometer used in this research can be calculated. To do so it is necessary to derive an expression for $\Delta E/E_p$ in terms of the diameter D and radius R given above. In the calculation below, these two sources of line broadening will be considered independent, and the effective line shape and energy resolution from each will be calculated separately. Following an analysis by Purcell, an energy resolution can be expressed in terms of the velocity resolution, $\beta_{\texttt{i}}.$ β . is defined by

$$
v_{i} = (1 \pm \beta_{i}) v_{pass} \tag{2.1}
$$

where v_{pass} is the velocity of a particle which the analyzer passes along the central trajectory when set at E_{pass} , and v_i is the velocity of a particle with slightly different energy, E_i . (For convenience, E_{pass} and v_{pass} will be shortened to E_p and v_p in the following discussion. Lower case subscripts are

used to distinguish this derivation from the defined energy resolution above.) A resolution can be calculated as follows:

$$
\Delta E_{1p} = E_1 - E_p = \frac{1}{2} m (v_1^2 - v_p^2)
$$
 (2.2)

Using Equation 2.1 this becomes

$$
= E_p (\pm 2\beta_1 + \beta_1^2)
$$
 (2.3)

For β_1 small,

$$
\frac{\Delta E_{1p}}{E_p} \approx \pm 2\beta_1 \tag{2.4}
$$

If the line shape width ΔE is written as

$$
\Delta E = E_{\text{max}} - E_{\text{min}} = (E_{\text{max}} - E_{\text{p}}) + (E_{\text{p}} - E_{\text{min}}) \qquad (2.5)
$$

then the energy resolution can be expressed as

$$
\frac{\Delta E}{E_p} = 2(\beta_{max} + \beta_{min})
$$
 (2.6)

D and R can be related to β_{max} and β_{min} as shown below.

Line shape broadening due to the finite diameter, D, of the first energy resolving aperture (1st ERA) can be calculated from the velocity dispersion given by $Purcell$ ⁷⁰

$$
y_2 = 2\beta a (1 - \cos \Phi + (x_{20}/a) \sin \Phi)
$$
 (2.7)

$$
= 9.00 \beta \tag{2.8}
$$

Refer to Figure 2.7 for a definition of the variables in these equations.

Assume a current, $j(\beta)$, emanating from the center of the target along x_1 with energy distribution

$$
j(\beta) = 1 \tag{2.9}
$$

All of this current crosses the plane of the 1st ERA at a position, d, given by

$$
d = y_2 / \cos \delta = 9.00 \beta / \cos \delta \qquad (2.10)
$$

A lst ERA of diameter D will pass all the current for which $y_2 \leq y_2$, leading to the relation for the limiting values of β

$$
\left| y_{2}/\cos \delta \right| \leq D/2 \tag{2.11}
$$

$$
-\frac{D\cdot\cos\delta}{2\cdot9.00} \le \beta \le \frac{D\cdot\cos\delta}{2\cdot9.00}
$$
 (2.12)

The energy resolution due to a finite 1st ERA is then calculated from Equation 2.6 to be

$$
\frac{\Delta E}{E_p} \text{ (1st ERA)} = 2 \cdot [.053D + .053D] = 0.212D \tag{2.13}
$$

For $D = 0.25$ cm $(0.10$ in) this evaluates to

$$
\frac{\Delta E}{E_p} \text{ (1st ERA)} = 0.021 \tag{2.14}
$$

The line shape of the current distribution resulting from the finite 1st ERA is a unit function for the allowable β values (Equation 2.14), since all the current $j(\beta)$ is passed by the 1st ERA and $j(\beta)$ is a unit function in β .

The above line shape and resolution have been obtained, effectively, by varying the energy of the signal current (via Equation 2.9), rather than

using a monochromatic current source and varying the pass energy as initially used in defining the spectrometer resolution. That the results given in Equation 2.14 are the same as would be obtained from a more complicated calculation using a monochromatic current source can be seen by considering a monochromatic source $v_1 = (1 + \beta_1)v_p$ and noting that it will be deflected to the edge of the 1st ERA by a pass energy E_p .

Line shape broadening and an energy resolution due to a finite radius to the source disk can be determined in a manner analogous to that used above. Consider a point source of particles at the 1st ERA that travel back through the analyzer. Such reverse trajectories would cross the target plane at a position

$$
y_1/\cos \theta = \rho \tag{2.15}
$$

where for these reverse trajectories, using Equation 2.7

$$
y_1 = 4.91 \text{ B} \tag{2.16}
$$

 ρ being a variable representing the radius at which these trajectories cross the plane of the target. *p* is analogous to d in the earlier calculation. Using reciprocity, particles emanating from a position on the target at radius *p,* with a velocity corresponding to S, will cross the plane of the 1st ERA at the axis. For a source of radius R, the line width is found, by using the arguments leading up to Equation 2.11, to be

$$
-\frac{R \cdot \cos \theta}{4.91} \le \beta \le \frac{R \cdot \cos \theta}{4.91} \tag{2.17}
$$

For a spot size $2R = 1$ mm (0.039 in.), the energy resolution due to a finite source disk is

$$
\frac{\Delta E}{E_p} \text{ (source)} = 2[0.17R + 0.17R] \tag{2.18}
$$

$$
\frac{\Delta E}{E_p} \text{ (source)} = .013 \qquad \text{for } 2R = 1 \text{ mm.}
$$
 (2.19)

At low primary energies, for which the beam spot size is greater than 1 mm, the above broadening and resolution due to spot size are correspondingly larger.

The line shape associated with a finite source disk is linearly proportional to β . The functional dependence of source current on β , which essentially determines the line shape due to the finite source, is not given by Equation 2.9. Rather, it can be obtained by assuming uniform emission over the area of the source, knowing that β and the radial position at the source, p, are linearly related by Equation 2.16, and using the area relation

$$
dA_{\rho_1} \approx 2\pi \rho_1 \Delta \rho \tag{2.20}
$$

$$
\mathbf{J}_{\mathbf{p}_1} \propto \mathbf{d}\mathbf{A}_{\mathbf{p}_1} \tag{2.21}
$$

If the current from the source with velocity $(1 + \beta)v_p^{\dagger}$ that passes the 1st ERA is designated $J'(\beta)$, then

$$
J'(\beta_1) = J_{\rho} \cdot \delta(\rho - \frac{4.91 \cdot \beta_1}{\cos \theta})
$$
 (2.22)

$$
J'(\beta_1) \propto 2\pi \cdot \frac{4.91 \cdot \Delta p}{\cos \theta} \cdot \beta_1 \tag{2.23}
$$

From Equation 2.23, the line shape of the current due to finite source is seen to be linearly related to β .

$$
40\,
$$

The overall resolution of the instrument can be approximated by the sum of the two resolutions calculated above, which is approximately 2%. Experimentally, the resolution of the spectrometer is measured as the full width at half maximum (FWHM) of the elastic peak. The bottom panel of Figure 2.8 shows the FWHM of the elastic peak as a function of the spectrometer pass energy. At 90 eV, the experimental energy resolution is

$$
\frac{\Delta E}{E_P} = \frac{FWHM}{E_P} = \frac{2}{90} = .022
$$
 (2.24)

which is close to the theoretical calculations.

The effective resolution of the spectrometer can be greatly increased by retarding the beam using the three grids located between the target and spherical analyzer. This can be seen by repeating the calculation of Equation 2.24 using data from Figure 2.8 at a lower energy. The measured effective energy resolution of the spectrometer varies between 2.2 percent and 0.6 percent as the elastic peak is retarded by 10 percent to 90 percent of its initial value. Over this same range, the intensity decreases almost 98 percent. Hence increased resolution is obtained at the expense of signal intensity. This is shown in the top panel of Figure 2.8. The solid curve in the top panel is the transmission function of the spectrometer for a primary beam of 100 eV. The transmission function shows the fractional decrease in signal passed by the spectrometer as a function of pass energy of the spectrometer. The data points were taken by retarding the 100 eV elastic peak between the grids until it was passed by the spectrometer. The transmission function is the ratio of the peak signal intensity passed by the spectrometer at E_{pass} to the peak

Figure 2.8. Top panel - Transmission function of spectrometer. This function was obtained by retarding the 100 eV elastically scattered electron signal between the spectrometer grids and then measuring the ratio of the peak signal intensity passed by the spectrometer to the peak signal passed at $E_{pass} = E_{nri} = 100$ eV. Bottom panel - Full width at half maximum of $\frac{p+1}{p+1}$ elastically scattered electron signal passed by the spectrometer when the 100 eV signalis retarded using the grids to an energy E_{pass}

signal passed at $E_{pass} = E_{pri} = 100$ eV. The dotted line in Figure 2.8 indicates the transmission function for $\frac{\Delta E}{E}$ = constant for a monochromatic point source. Deviations from the straight line are due: 1) to the nonidea1 elastic peak (i.e. finite breadth) and spectrometer geometry, 2) to field penetration at the grids as a function of the retarding potential (which was varied to obtain the graph), and 3) to the varying response of the electron multiplier as a function of the voltage of the electrons incident on the multiplier. For the data presented here, electrons were incident on the multiplier with an energy equal to the pass energy of the spectrometer. The bottom panel of Figure 2.8 shows the experimental full width at half maximum of the elastic peak as a function of pass energy. (in this case, pass energy ⁼ (100 eV - retarding voltage)).

The energy spectrometer has been operated successfully in both the electron and ion pass modes, over a pass energy range from 2 eV to 400 eV. The spectrometer is normally operated at a fixed pass energy, and, ideally. fixed energy resolution. Energy sweeps are made by retardation (acceleration) of electrons or ions between the first (screen grid) and third (tEED grid) grids prior to entering the spherical analyzer section of the spectrometer. The third grid, which was added primarily to eliminate charging problems associated with the LEED screen (see Section 2.6), also improved the effective resolution; this improvement is due to decreased field penetration of the applied retarding (accelerating) potential since the retarding (accelerating) can be done over a 50 percent longer distance. In addition the third grid is made of smaller mesh which also reduces field penetration.

The spectrometer is supported vertically from the electrical feedthrough turret, as shown in Figure 2.9. This assembly attaches at the top of the main vacuum chamber (see Figure 2.1), and can be removed completely wired, independent of other parts of the instrument.

The electron multiplier is an EMI model 9643/4B detector, with 17 BeCu venetial blind dynode stages.

2.5 Spectrometer Electronics

Figure 2.10 shows a schematic diagram of the electronic circuitry used for taking electron energy loss spectroscopy, electron stimulated desorption, and Auger electron spectroscopy measurements. Some details, for example capacitors used to eliminate noise and some switches used to change from one mode to another, are not shown. Only the most common biasing arrangement used in this work will be discussed.

In the electron pass mode, (including Auger measurements), the LEED grid, LEED screen, Herzog diaphrams, driftspace and center electrode of the cylindrical analyzer are grounded. Energy sweeps of the spectrometer are made by varying the retardation or acceleration voltage applied between the three grids. A variable frequency, variable height, floating sawtooth generator 73 plus a variable d.c. offset bias are summed at the inverting input of a Kepco OPS-2000 operational power supply, the output of which biases the three grids through a resistor chain. When the output signal from the multiplier is being detected using a phase sensitive detector, a 3 kHz sinusoidal signal is also fed into the summing junction. V_T , the target bias with respect to the screen grid, is zero in the electron pass mode. The spherical analyzer deflecting

Figure 2.9. Photograph showing support of spectrometer from electrical feedthrough turret.

Figure 2.10. Circuit diagram of the spectrometer electronics for operation in the electron pass and ion pass modes.

electrodes and the repulsion electrode of the cylindrical analyzer are scaled using a resistor chain powered by a second OPS-2000 operational amplifier power supply. The voltage scaling for these electrodes was determined from particle trajectory calculations. The voltage applied to the repulsion electrode using this resistor chain can be varied using a potentiometer; this adjustment can, in effect, vary the resolution of the cylindrical analyzer. The OPS-2000 supply also biases the outer electrodes of the analyzer deflection plates by means of a separate resistor chain. The inner electrodes of these deflection plates are fixed at the potential of the analyzer's Herzog diaphrams. The ripple voltage on the output of both operational power supplies is less than 20 meV at 100 eV.

Electrons impinge on the first dynode of the multiplier with an energy equal to the pass energy of the spectrometer plus a voltage equal to $(R_m/(36M) + R_m)$)V_M where R_m is shown in Figure 2.10 and V_M is the voltage across the multiplier. In the synchronous detection mode, V_M was varied between 1100 V and 1700 V. In the pulse counting mode the voltage was normally set at 2800 V. The output of the multiplier, after being passed by an isolation capacitor, is either pulse counted with a ratemeter or is detected using a PAR HR-8 phase sensitive detector. The reference signal for the HR-8 is either 3 kHz when taking dN(E)/dE distributions (see Section 3.2.4 and Appendix B) or Auger data, or 6 kHz when taking $d^2N(E)/dE$ distributions.

When the spectrometer is operated in the ion pass mode, the polarity of the biasing on the analyzer deflecting electrodes is switched, In addition the positive pole of the electron mUltiplier supply is grounded. This biasing arrangement causes the ions to impinge on the multiplier at an energy

 $E_{pass} + V_{M}$, which was usually 3040 kV. In the ion pass mode the spectrom eter is generally operated at E_{pass} = 40 eV. This requires an acceleration of the ions between the screen and LEED grids, since the initial ion energies are between 0 eV and 10 eV. In addition to accelerating between the grids, the ions were normally accelerated between the target and screen grid, using $V_T^{},$ in order to facilitate interpretation of the data, as discussed in Section 3.2.5.

The electronic circuitry for operating the analyzer in the time-offlight mode is identical to that just described for the ion pass mode, except a pulsed voltage is applied to the retarding grid. Figure 2.11 shows a schematic of this arrangement. Unlike continuous operation, in this mode ions can enter the analyzer only during the "on" pulse. In the lower part of Figure 2.11, the energy of an ion is shown as a function of its position in the spectrometer, with the pulse on and off.

In the work function mode, the target is fixed at ground potential through a picoammeter. Retardation of the incident current is accomplished by driving the drift tube positive in voltage.

2.6 LEED Display System

The low energy electron diffraction (LEED) system consists of a phosphor-coated screen, located at the entrance to the spherical analyzer, and three grids. The screen, a 109.6° stainless steel sector (of which approximately a 98° sector is visible), was coated with a P-1 phosphor. The first two grids are constructed of 50 mesh, rhodium-coated stainless steel. The LEED screen and these two grids are operated as a standard two grid LEED

Figure 2.11. Circuit diagram of the spectrometer for operation in the time-of-f1ight mode.

system, with the retarding grid biased to pass only electrons elastically scattered from the target and with the LEED screen accelerating voltage normally set at 5000 V. Slots cut through the screen allow electrons and ions to pass into the spectrometer. Initial operation of the instrument indicated that charging of the LEED screen caused a significant perturbation on electron trajectories below 100 eV. The third grid, a 100 mesh stainless steel spherical sector, is located 0.050 cm in front of the LEED screen to alleviate this problem.

An aluminum-coated glass plate mirror located below the spectrometer reflects the LEED screen through a 6 \pm h.ch window in the chamber wall (see Figure 2.1). LEED spot intensities are measured through this window using a Gamma Scientific Model 2000 telephotometer.

2.7 Crystal Manipulator Assembly

The crystal manipulator assembly is shown schematically in Figure 2.12 and a photograph is given in Figure 2.13. The assembly is designed to provide thermal and electrical control of the target, while allowing the target face to be rotatable between the gas dosing port, the LEED screenenergy spectrometer position, and the quadrupole mass spectrometer. This rotation is indicated in Figure 2.14. The manipulator assembly is composed of a commercial Physical Electronics specimen manipulator, a long shaft which supports the rotary electrical connections, a liquid nitrogen dewar and aluminum foil strap to provide target cooling, and a target mounting assembly.

The long shaft of the manipulator assembly is constructed of different materials, as follows: $A1_{2}0_{3}$ for electrical isolation (Figure 2.12, Figure 2.12. Schematic diagram of the target manipulation and thermal control system showing: (1) kovar-glass-kovar dewar insulation, (2) Miniconflat flanges, (3) Physical Electronics Industries specimen manipulator, Model 10-501M mounted on 8 inch o.d. Conflat flange, (4) six 5 kV - 150 A electrical feedthroughs, (5) clamp assembly, (6) $A1_2O_3$ rod, (7) molybdenum spring,
(8) stainless steel electrical connectors, (9) electrical connection (1 shown), (10) $A1_2O_3$ spacers, (11) Pyrex plates, (12) molybdenum, (13) 0.01" wall stainless tube, (14) Pyrex tubes, (15) tantalum rods, (16) copper rod, (17) vacuum chamber wall, (18) liquid nitrogen dewar, (19) 0.01" wall stainless tube, (20) copper radiation shield, (21) strap-to-dewar clamp, (22) crystal support, (23) 12 pole heater, (24) strap-to-copper rod clamp, (25) aluminum foil strap, (26) pancake heater supports, (27) thermocouple, (28) crystal, (29) pancake heater, (30) tanta~ lum section, (31) molybdenum section, (32) molybdenum-to-copper rod clamp assembly.

 $\overline{}$

Figure 2.13. Photograph of crystal manipulator. The retarding field analyzer used to characterize the primary electron beam is shown mounted on the manipulator in place of the tungsten crystal mounting assembly. \mathcal{L}_4

Figure 2.14. Schematic of the experimental chamber of the apparatus (see Section 2.2 for a discussion of the experimental chamber). Rotation of the crystal is indicated by the dotted line.

no. 6), molybdenum rod (no. 12), 304 stainless steel tubing for thermal isolation (no. 13) and copper rod (no. 16). Six electrical leads, separated by glass discs (no. 11), wind around the shaft. (This configuration allows for rotary motion of the shaft while still providing electrical control at the target.) The electrical leads then enter glass tubing parallel to the shaft and end up at the target mounting assembly. For clarity, only one of these leads is shown in Figure 2.12.

An aluminum foil strap (no. 25) made of 150 pieces of 2.54 cm $x \approx 25.4$ em x 0.0025 cm foil connects the liquid nitorgen reservoir to the copper rod end of the manipulator shaft. This provides conduction cooling to the target. A copper radiation shield (no. 20) is constructed around the strap. This cooling system is sufficient to cool the target from flash temperatures to approximately -150° C in 5 minutes.

The tungsten single crystal target is supported 0.95 cm above a tantalum and molybdenum right angle mount (nos. 30, 31) on one 0.038 cm diameter tungsten wire. The wire was spot-welded to the back face of the tungsten disc prior to its final electropolishing. The target is heated by electron bombardment of its back face from a tungsten pancake heater (no. 29). The target can also be heated by conduction through its support wire using a 25 watt, 12 pole, 25L6 RCA heater which is mounted inside the tantalum part of the right angle mount as shown dotted in Figure 2.12 (no. 23). Using this heater the target temperature can be varied between -20 $^{\sf o}{\rm C}$ and -150 $^{\sf o}{\rm C}$. Tungsten and tungsten-26% rhenium thermocouple leads, .0076 cm in diameter, are spotwelded to the side of the target. The thermocouple wires are each supported by being fed along the axis of a tungsten wire helix (not shown in Figure

2.12). The helices are made of .025 cm diameter wire and are spot-welded to supports near the center of the molybdenum part of the right angle mount. Calibration of the thermocouple was made out of the vacuum chamber using a copper-constantan reference thermocouple. The calibration procedure is described in Appendix A, and the calibration is given in Figure A.1.

2.8 Crystal Preparation and Cleaning Procedures

The experimental sample is a single crystal tungsten disc, cut from a (100) oriented tungsten rod using a diamond impregnated stainless wire in a string saw. The tungsten rod, supplied by Metals Research Ltd., was taken from the purest 7.5 cm of a triply zone refined 25 cm length.

Both the front and back surfaces of the disc were polished using, in succession, 15 micron, 3 micron, and 1 micron alumina. After being mechanically polished, the crystal was e1ectropo1ished using a 1% NaOH solution. The final dimensions of the target disc are 0.033 cm (.013 in) thick and approximate1y 0.80 cm in diameter.

After the final electropolish the orientation of both the front and back surfaces was checked using an x-ray diffractometer and was determined to be within 0.10° of the (100) face. A back reflection Laue picture of the final surface showed sharp, well-defined beams, indicating a high degree of crystalline order.

The target was cleaned initially by heating to at least $2200 \mathrm{\textdegree K}^{74}$ in a $1 \mathrm{x} 10^{-6}$ Torr oxygen atmosphere for 9 hr to remove carbon. The choice of temperature and time were somewhat arbitrary, as there is considerable debate in the literature as to the proper method for cleaning tungsten for surface

research.⁷⁴ A standard method⁷, 18, 23 has been to heat the target to some temperature above $1100^{\sf o}{\rm K}$ (commonly above 2000 $^{\sf o}{\rm K}$) in an oxygen environment for times varying up to 200 hr or more. This process is generally followed by a high temperature degassing in ultrahigh vacuum. However, there is evidence that if the temperature is held above 2000° K, bulk carbon will not diffuse to the surface.⁷⁵ The possibility of thermal etching must also be considered.⁷⁴

For the tungsten used in this research, the amount of contamination on the surface was determined using Auger spectroscopy. Figure 2.15 is an Auger spectrum taken from a dirty surface showing the Auger peaks resolved in our system. Carbon, oxygen, and tungsten peaks are seen clearly. Also shown in Figure 2.15 are theoretical Auger transition energies for C, O, and W^{6} with the relative theoretical strengths of the transitions indicated by the normalized height of the lines. In Figure 2.16 are shown Auger spectra taken after different crystal treatments or under different experimental conditions. Curve a shows the spectrum taken after saturating the surface with CO. Note the carbon and oxygen peaks. There is no measurable carbon peak after a flash, as seen in curve b. Structure does remain between 475 eV and 525 eV. It is doubtful that this structure is a result of oxygen contamination, since there are normally three oxygen Auger peaks, with the 490 eV oxygen peak stronger than the 475 eV oxygen peak; in this spectrum, no 490 eV peak is observed. In order to reduce any oxygen contamination, the target was heat treated to 2200 $^\circ$ K in a hydrogen atmosphere of 5x10 $^{-7}$ Torr for 4 minutes. 74 The structure above 475 eV is seen to remain unchanged, as seen in curve c. This is a further indication that this structure is not oxygen, Curve d shows that sitting in a 400 eV, 4 μ A primary beam, close to typical operating

Figure 2.15. Auger electron spectrums obtained at different instrument sensitivities from dirty tungsten crystal. Also shown in upper part of figure are theoretical Auger transitions for tungsten, carbon, and oxygen calculated by Coghlan and Clausing⁷⁶. Heights of the lines represent relative theo retical strengths of the transitions.

Figure 2.16. Comparison of Auger electron spectrums taken over the energy range 200 eV to 550 eV under different experimental condition,

conditions, for 25 minutes causes only a slight change in the slope of the curve at the energy at which the carbon peak occurs. (Note that curve d was taken with a primary beam of 1700 eV after the crystal had been sitting in the lower energy beam for 25 minutes.) The absence of the carbon peak in curve d means that the crystal surface is not contaminated from the gun while taking measurements. After bombarding the target for 10 minutes with a primary beam of 1700 eV and 21 $_{\text{u}}$ A, typical Auger spectroscopy beam conditions, a carbon peak is observed, as shown in curve e. Using the peak to peak height of the 272 eV carbon peak obtained near CO saturation as an indication of carbon monolayer coverage, the electron gun in the Auger mode is seen to deposit approximately 0.13 monolayer of carbon in 10 minutes.

From the above results, it is concluded that the tungsten surface could be flashed clean, and that no carbon or oxygen contamination is deposited during most experimental measurements. Some carbon is deposited when operating in the Auger mode. Two unexpected, small peaks are observed between 475 eV and 525 eV. Identification of the source of this weak structure could not be made with certainty, although two possible causes are worth noting. The unexpected structure could be tungsten Auger transitions. Theoretically, several relatively strong tungsten peaks have been predicted at 477 eV and 486 eV and also between 510 eV and 520 eV. However, no observations of tungsten transitions in this energy range have been reported in the experimental literature. A second possible source of this structure might be chromium. There is considerable chromium in the spectrometer's stainless steel parts and chromium Auger peaks occur at 489 eV and 529 eV. However, if it is assumed that Auger spectroscopy is sensitive to one percent of a monolayer, it would

require surface coverages of 10^{13} chromium atoms/cm² or more to yield these peaks. It is extremely unlikely that either 1) a concentration of chromium this large could diffuse to the tungsten surface from the stainless parts, or 2) enough chromium could be sputtered (at the ambient pressure) into the background from the stainless parts and subsequently adsorb onto the surface. A spark vaporization mass spectroscopy analysis of a tungsten sample cut from the same boule as the tungsten used in this research revealed no chromium, thus eliminating the possibility of a bulk chromium concentration in the crystal. Hence, although the weak structure corresponds to some degree to chromium Auger lines, it is believed that the crystal is not contaminated with this element. In an Auger spectrum taken between 500 eV and 900 eV (not shown) some additional very weak structure was seen, but none of it could be attributed to any specific element.

In this research the crystal was always flashed to $> 2200^{\circ} K^{77}$ for 30 seconds prior to experimentation. Any reference to a clean tungsten surface means that this procedure has been followed.

The crystal surface exhibited what appeared to be furrows, which increased in density during the course of the research. Because the coolest part of the crystal during a flash, that region next to the tungsten wire support, remained visibly polished and flat, it is believed that the uneven appearance was temperature related.

2.9 Gas Handling System

The gas handling system used to obtain adsorption overlayers is shown in Figure 2.17. Research grade hydrogen (impurity level less than 2

Figure 2.17. Schematic drawing of gas handling system.

ppm) is admitted from a glass flash into a pyrex manifold and stainless steel reservoir. Reservoir pressure was kept near 50 microns, as read using a thermocouple gauge. From the reservoir, hydrogen is admitted into the vacuum system through a 1.26 cm diameter tube by opening valve A, Figure 2.17, or is admitted as a gas jet by opening valve B. The jet is formed as hydrogen effuses through a small orifice at the end of a 0.63 cm dia tube.^{78,79} Leaking hydrogen through the 1.26 em diameter tube increases the background and is used when hydrogen is to be adsorbed from the background. The jet can be used with the target rotated in front of the gas dosing port for rapid overlayer adsorption with a low hydrogen background pressure. The gas jet is designed so that only that fraction of the effusing gas which will strike the target is allowed to pass through an aperture in a skimmer. The rest of the gas jet is reflected back from the skimmer and out of the experimental chamber. When the target is rotated up to face the spectrometer, the gas jet, if left on, passes out of the experimental chamber through holes in the opposite side of the magnetic shielding.

The gas manifold and reservoir can be pumped down to less than 1 micron using a liquid nitrogen cryosorb pump.

2.10 Mass Spectrometer

A quadrupole mass spectrometer, Varian Residual Gas Analyzer Model 974-0003, is mounted on a vacuum chamber port, opposite the gas jet port. In this research it was used for vacuum chamber leak testing and determination of the components of the background pressure.

CHAPrER 3

EXPERIMENTAL PFGCEDURE AND RESULTS

3.1 Introduction

The experimental data taken on the hydrogen- $W(100)$ system are presented in this chapter. The apparatus used in obtaining the data has been discussed previously in Chapter 2. A further explanation of experimental procedures used in measuring parameters follows in Section 3.2. The experimental results are presented in the remaining sections of this chapter. A general discussion of the data is given in Chapter 4, and a summary of the research is given in Chapter 5.

3.2 Experimental Procedure

3.2.1 Work Function and Coverage Measurements

Contact potential measurements, in this case the difference between the work functions of the target and of the cathode **in** the electron gun, are measured using a retarding potential technique. $43,44$ The primary, or incident, electron beam current is retarded between the electron gun drift tube and the target. The measured current to the target goes to zero at a retarding voltage, V ^R, given by

$$
V_R = (\varphi_{\text{cath}} + V_{\text{sc}} - \varphi_W) + E_{\text{pri}} \tag{3.1}
$$

where φ _{cath} is the cathode work function, φ_W is the W(100) work function, V_{sc} is the potential due to space charge immediately in front of the cathode, and E_{pri} is the applied potential between the cathode and the drift tube. Changes
in the work function of the target, $\Delta \varphi_{\text{tr}}$, are calculated by measuring changes in V_R , ΔV_R . From Equation 3.1, a change in V_R is found to equal

$$
\Delta V_R = -\Delta \varphi_W \tag{3.2}
$$

with the assumptions of constant $\varphi_{\rm cath}$, $V_{\rm sc}$, and $E_{\rm pri}$. The assumptions used are reasonable since the cathode is in thermal equilibrium and since it is exposed to very small changes in the ambient during the measurements. The applied potential E_{pri} can be maintained constant.

A typical retarding potential curve is given in Figure 3.1. The electron current to the target, the ordinate in this figure, is given by

$$
I_T = I_{pri} - I_{sec}(E_{pri}, N)
$$
 (3.3)

where I_{pri} is the current incident on the target from the electron gun and I_{sec} (E_{pri} ,N), the secondary current, represents the electron current leaving the target surface. This secondary current is a function of both primary electron energy and hydrogen coverage.⁴⁷ Because of the dependence on coverage, the intensity and line shape of the retarding potential curves change somewhat upon adsorption.

In determining $\Delta V_{\rm p}$, or equivalently, the target work function change, a retarding potential curve taken from the clean tungsten surface and a curve taken after hydrogen adsorption are normalized at a position on the curve where the target current begins to falloff sharply (position A in Figure 3.1). The work function change is then measured as the voltage difference between the two curves at half the normalized height.

Changes in the work function of 0.01 eV can be resolved. The

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Figure 3.1. Retarding potential curve, showing the current to the target as a function of the difference in applied potential between the electron gun cathode and the target. The curve is shifted in energy with changes in hydrogen coverage, due to changes in the target work function, $\Delta\varphi$. $\Delta\varphi$ is measured as the difference between two retarding curves at the height A/2.

measurement was sensitive to target rotation position because of the retarding field in the target region. However, with the target positioning stop used, the retarding potential curve could be repeated with an accuracy better than 0.02 eV after rotating the target. Since the work function change is the difference between two such curves, the error in the measurement is $\lesssim 0.04$ eV.

Changes in hydrogen coverage are monitored by changes in the work function of the tungsten surface. No experimental attempts have been made to calibrate the measured work function change to an absolute change in the coverage of atoms/surface area. Such a calibration requires an accurate measure of system pumping speed or dosing flux. However, as discussed in Section 3.4, such a calibration can be made using results from the literature.

3.2.2 Primary Electron Beam Energy and Current Measurements

The total electron beam current incident on the target, I_{pri} , is measured by biasing the target at a potential of +45 volts with respect to the surrounding experimental chamber. Tests indicated that the current measured in this manner is within 3 percent of the total current leaving the electron gun, which is also I_{pri}. The current leaving the gun is measured by summing electron currents to the target, grids, LEED screen, magnetic shielding, analyzer Herzog diaphrams, and front shield plate. This current sum measurement of I_{nri} was more difficult to make experimentally than biasing the target at +45 volts.

The primary electron energy, E_{pri} , refers to the energy of the incident electrons referenced to the vacuum level. The primary energy is measured between the cathode and drift tube of the electron gun. A contact potential correction between the gun's cathode and the target of between

-1.7 eV and -2.2 eV has been applied to the measured primary energy given in the data. This correction is found by using the measured cut off potential $V_{\overline{R}}$ and Equation 3.1. The spread in the correction is a result of the change in space charge, and hence change in $V_{\rm sc}$, which occurs when the potential gradient at the cathode is altered by changing the voltage on the control grid. The control grid voltage determines the potential fields in the region of the cathode surface and hence affects the emitted current and space charge.

3.2.3 Target Temperature Measurement

Prior to taking any data, the target was cleaned by rapid electron bombardment heating (flashing) at $> 2200^{\rm o}$ K for 30 seconds. Figure 3.2 shows the temperature of the target versus time from end of flash, with and without liquid nitrogen in the dewar. Residual heat in the crystal supports due to previous flashes does affect the temperature versus time curves somewhat. The higher temperature data were normally taken starting 3 to 4 minutes after flashing, at a target temperature of 60° C + 15°C. Data taken under these conditions are sometimes referred to as room temperature, or higher temperature data. Low temperature data were taken starting 4 to 5 minutes after flashing, when the target temperature was less than -145° C.

3.2.4 Electron Scattering and Auger Measurements

The electron scattering data consists of the electron signal emanating from the target in the acceptance solid angle of the spectrometer following impingement of the primary electron beam on the target. An energy distribution of these electrons is taken by fixing the pass energy of the spectrometer at E_{mass} and sweeping a retarding or accelerating voltage between the screen grid and LEED grid as described previously in Section 2.5. The output current of

Figure 3.2. Temperature of the tungsten crystal versus time elapsed since a crystal flash. The upper curve represents the temperature versus time relation when there is no crystal cooling. The lower curve shows this relation when there is liquid nitrogen in the cooling dewar.

the electron multiplier, $N(E)$, is pulse counted or, as discussed below and in Appendix B, synchronously detected.

N(E) is proportional to the electron current originating at the target with energy between E and $E + dE$ and with momentum in the acceptance solid angle of the analyzer. This distribution consists of rapidly varying true secondary and characteristic loss structure interpretable in terms of transitions and collective oscillations in the target, plus a smoothly varying background. In order to separate the structure from the background, the energy distribution is electronically differentiated using a technique proposed by Harris. 67 As shown in Appendix B, a signal proportional to the first or to the second derivative of $N(E)$ is obtained by synchronously detecting the appropriate harmonic of the output of the electron multiplier. The relation between the electron signal, $N(E)$, and the synchronously detected signal can be seen from Equations B.4 through B.9. In these equations, it is assumed a peaked structure, $G(E)$, being investigated can be represented by a Gaussian centered at E_0 with standard deviation σ . The detected first harmonic of N(E) has structure which has a peak-to-peak height proportional to $G(E_{0\pm} \sigma)$. The detected second harmonic of $N(E)$ has structure at $E_{\overline{O}}$ proportional to $\texttt{G(E}_{\texttt{\tiny O}})/\sigma^2$. In addition, there is a contribution to the detected signal from the background. Since the background, which can be represented by a polynomial in energy, is slowly varying, the higher order terms which remain in the differen tiated signals are small.

The first derivative mode has been used in taking Auger data, as is commonly done. The second derivative mode has been used in taking electron scattering characteristic energy loss measurements.

3.2.5 Ion Measurements

 $H⁺$ ions, desorbed from the crystal following electron impact, could be detected by the spectrometer when operated in the ion pass mode. It was found convenient to operate the instrument at a pass energy of 40 eV in this mode; operation at a lower pass energy, while increasing the resolution, decreased the already weak signal intensity. Since the ions have between 0 eV and 10 eV energy when desorbed, acceleration between the target and spectrometer was necessary. An accelerating voltage V_{acc} (the output of an OPS-2000 power supply) was applied between the screen grid and the entrance to the spectrometer. In addition, a second accelerating voltage, V_T , was applied between the target and the screen grid. This latter voltage was needed in order to energetically separate the ion signal which originated at the target from a background signal produced by 1) ions electron desorbed from the screen grid and/or other surfaces in the experimental chamber and 2) ionization of the background. The ions that passed into the spectrometer were accelerated into the first dynode of the electron multiplier. The output pulses of the multiplier were amplified and then counted with a ratemeter.

Prior to taking ion data, the target was flashed and allowed to cool to the experimental temperature. It was then exposed to hydrogen, with the hydrogen coverage being monitored using work function measurements. Ion energy distributions were taken by fixing E_{pass} and V_T , and sweeping the accelerating voltage V_{acc}. Desorption curve measurements, which are a measure ment of the decrease of the ion signal in the electron beam, were taken by fixing V_{acc} , V_T , and E_{pass} , and monitoring the ion signal as a function of time.

The kinetic energy of the detected ions is equal to the spectrometer pass energy, E_{pass}, minus the acceleration of the ions between the target and spectrometer, $V_{acc} + V_T$, plus a contact potential correction term due to the difference in work functions of the clean target and surfaces of the spectrometer. The pass and acceleration energies are chosen for each experiment. The contact potential difference between the tungsten target and the rhodium coated stainless steel surfaces of the spectrometer is less than 0.15 eV. This was determined using a retarding potential measurement between the target and screen grid. Dosing the target with hydrogen did not change the work function of the grid. Hence it is assumed that 0.15 eV can be used for the correction at all target hydrogen coverages. Since this correction is on the order of the error in the measurement, it has not been made in the data.

The analyzer is operated in a time-of-f1ight mode by applying a pulsed voltage to the retarding grid. Figure 2.11 shows a schematic of this arrangement. Incident ions can enter the analyzer only during the pulse. By measuring the path length $d = ab$ (see Figure 2.11) from the retarding grid to the electron multiplier, knowing the pass energy, E_{pass} , of the spectrometer, and experimentally measuring the time for the entering species to traverse the distance d, the mass of singly-charged ions passing through the analyzer can be calculated using the following formulation of the distance equals velocity times time equation.

$$
m = \left[t / \int_{a}^{b} \frac{dx}{\sqrt{2E(x)}} \right]^2
$$
 (3.4)

The flight time is measured by making a trace on an oscilloscope of both the pulse applied to the retarding grid that allows ions to pass into the spectrometer and also the output pulses of the linear amplifier. The flight time t is the time difference between these two signals, minus the transmission time of the pulse from the first dynode of the electron multiplier to the oscilloscope. This transmission time is estimated to be several hundred nanoseconds.

The data taken in this research is presented in the remaining sections of this chapter.

3.3 Ion Species Identification

The ion species desorbed from the tungsten crystal by electron impact are identified using a time-of-flight technique, as described above. For these measurements, the spectrometer was set to pass 40 eV ions. A total acceleration voltage, $V_T + V_{acc}$, of 37.0 eV was applied between the crystal and the entrance to the spectrometer. Hence, the energy of the ions originating at the crystal surface and passed by the spectrometer was 3 eV. (3 eV corresponds to the maximum in intensity of the ion energy distribution given in Section 3.5.) Figure 3.3 shows an oscilloscope trace obtained when operating in the time-of-flight mode. The trace was taken by applying a $2.2 \text{ }\mu \text{ sec}$ pulse to the retarding grid (duty cycle of $2x10^4$ pulses/sec). This is the large pulse at the left in the figure. Several output pulses from the linear amplifier can be seen approximately 4μ sec after the retarding grid pulse. These are pulses that have been produced by the electron multiplier following ion impingement onto the first dynode. Taking into consideration the transmission time, the experimental flight time is $3.7\,\mu$ sec. Using Equation 3.4

Figure 3.3. Oscilloscope trace showing the pulses observed when operating the spectrometer in the time-of-flight mode. The 2.2 μ sec trace at the left is the "analyzer on" pulse applied to the retarding grid (duty cycle of $2x10^4$ pulses/sec). During this pulse, ions pass into the spectrometer. Several output pulses from the linear amplifier, resulting from ions striking the electron multiplier, can be seen delayed by their flight time in the spectrometer and the pulse transmission time from the $\mathcal{A}^{\mathcal{X}}_{\mathcal{A}}$, and \mathcal{X} multiplier to the oscilloscope. The output pulses have been enhanced for reproduction purposes.

with the analyzer pass energy of 40 eV, a path length of 0.29 m, and a time of 3.7 μ sec, the mass of the desorbed ions is calculated to be 1.4 amu. The uncertainty in this calculation is estimated to be ≈ 0.5 amu. Sources of error include the estimate of transmission time and the uncertainty in the time difference read from the oscilloscope trace. In adqition, over part of the path length (the region between the retarding and LEED grids and in the cylindrical analyzer) the ions have less than 40 eV energy. Hence from this calculation alone it is not possible to identify the ions as H^+ . However, in experiments in which the length of the retarding grid pulse was shortened to \approx 1 μ sec, flight times that differed by >1 usec could be distinguished on the oscilloscope. The calculated flight time for ions of mass one is 3.3μ sec and for ions of mass two is 4.6μ sec, or 1.3μ sec longer. Thus H⁺ could be resolved from H_2^+ ions. The ions detected in the time-of-flight experiment of Figure 3.3 have been identified as H^+ . For certain spectrometer biasing conditions, pulses appear on the oscilloscope $1.5\,\mu$ sec later than the H⁺ pulses. The ions causing these pulses have been identified as having mass two.

When oxygen is adsorbed on the surface, the signal pulses on the oscilloscope occur approximately 13.5 μ sec after the retarding grid pulse. This is in good agreement with the expected flight time for 0^+ ions.

In addition to the H^{\dagger} ions observed after adsorbing hydrogen from the jet, H^+ ions were unexpectedly desorbed by electron impact from the undosed tungsten surface upon cooling the crystal to below 0° C. Possible sources for the hydrogen desorbed under these conditions are discussed in Chapter 4.

If E_{pass} is set at 40 eV, V_T set at 0 eV, and V_{acc} varied above 40 eV, no ions originating at the crystal surface can be passed by the spectrom

eter. However, with these biasing conditions both H^+ and H_2^+ ions are observed. This ion signal has to originate at the walls of the experimental chamber from a ESD process and/or from the ambient. Both the H^+ and H_2^+ signals increased when H_2 was admitted into the background from the gas handling system, an indication that at least part of the signal originates from ionization in the background. It is not easy to determine the intensity of the H^+ or H_2^+ desorbed from the chamber walls. However, it is possible to show that ionization of ambient H_2 could be a serious noise problem. The cross section for electron impact ionization of H₂ to H₂⁺ is 4.8x10⁻¹⁷ cm² and of H₂ to H⁺ is 2.2×10^{-17} cm² for 400 eV electrons. 80 An electron current of 1×10^{-6} A at 400 eV would produce about 1.1×10^{13} H₂⁺ ions per cm³-Torr-sec and 5×10^{12} H⁺ ions per cm³-Torr-sec. Thus it is reasonable to assume that at the background pres sures here a sizable ion signal is produced, although most of it undoubtedly is not detected. In the ESD experiments performed here it was desired to detect only ions produced at the surface of the crystal. It has been possible to bias the spectrometer such that this is the case. Almost none of the extra signal has the correct energy to pass through the spectrometer when V_r is held several volts positive and when V_{acc} is kept less than $E_{pass} - V_T$.

3.4 Work Function Results

Work function changes resulting from hydrogen adsorption have been monitored as a measure of hydrogen coverage. Figure 3.4 shows the tungsten surface work function change as a function of exposure to hydrogen. The crystal was at 60° C for this experiment. To obtain this data, the crystal was rotated into the gas jet, dosed for a measured time, and then rotated back to a position in front of the spectrometer where a retarding potential curve was

Figure 3.4. Change in work function, $\Delta\phi$, of a room temperature tungsten (100) surface resulting from hydrogen adsorption. $\Delta\varphi$ is plotted versus exposure of the crystal surface to hydrogen. For comparison, the results reported by Madey^{8,20} are also shown. Exposures for the data taken here have been determined by normalizing the measured adsorption time to Madey's absolute exposure at a work function change, $\Delta \varphi$, of 0.41 eV.

Figure 3.5. Comparison of work function changes at
60^oC and -150^oC resulting from hydrogen
adsorption onto tungsten (100).

 \bar{z}

Figure 3.6. Change in the work function of the undosed tungsten (100) surface versus crystal temperature for the temperature range -150° C to versus crystal comperature for the temperature range -150 C to
220^oC. The ordinate in the graph represents the work function at temperature T measured with respect to the work function at 220° C. The data was obtained in three separate experimental runs, indicated by different symbols, as discussed in the text.

taken. This procedure was followed repeatedly without closing the jet in order to assure a constant hydrogen flux (mole/ cm^2 -sec) from the jet onto the crystal face. An incident primary electron current of $2x10^{-8}$ A at a primary energy of 100 eV was used. The saturation coverage work function change, $\Delta\phi_\mathtt{max}$, is 0.98 \pm 0.04 eV. For comparison, results obtained by Madey and Yates 8 for the work function change resulting from adsorption of hydrogen on W(lOO) are given in Figure 3.4. Absolute exposures for the data taken here have been obtained by normalizing the dose time to Madey and Yates' exposure at a work function change of 0.41 eV. Using this normalization, good agreement between their results and the data obtained here is found.

The work function change of the tungsten surface as a function of hydrogen exposure was also measured when the crystal was at -150° C. The data are given in Figure 3.5. The procedure used in obtaining the 60° C data was followed in taking these data. The maximum work function change at this low.temperature is 0.92 + 0.04 eV.

The dependence of the work function on crystal temperature is shown in Figure 3.6. The work function is seen to decrease 0.05 eV as the temperature is raised from -150° C to 220[°]C. The data in this figure were obtained in a series of retarding potential curve measurements taken at different crystal temperatures. The temperature was varied by radiation heating the crystal on its back face using the pancake heater. It was found impossible to take decent retarding potential curves when the crystal was heated more than about 150° C above its initial temperature. As the current through the pancake heater was increased, electron emission from this heater also increased. This emission current interfered with the retarding potential measurement when it became a

fraction of the incident current. The three different symbols in Figure 3.6 represent data taken when the initial temperature prior to heating was -150° C, -135° C, and 50° C. The change in work function with temperature was reversible.

work function change has been reported. 8 Assuming this result and using the In this research, no attempts have been made to measure absolute coverages. Coverages are defined in terms of $\mu\varphi$, the measured work function change. As discussed in Section 1.2.6, a linear relation between coverage and room temperature data taken here, coverage and work function can be described by the expression

$$
\theta = 1.02 \Delta \phi \tag{3.5}
$$

where $\Delta\varphi$ is measured in eV. θ represents coverage in fraction of a monolayer. A monolayer is assumed to be $2x10^{15}$ H atoms/cm².⁸ Estimates of coverage in this work will be made by measuring work function changes and using Equation 3.5. However it should be noted that the data will be presented in terms of the measured quantity $\Delta\varphi$, and therefore are not dependent on any assumptions made relating coverage and work function.

3.5 H^+ Ion Desorption Measurements

The electron stimulated desorption of H^+ ions from the W(100) surface has been studied under different experimental conditions. Detection of the ion signal has been discussed in Section 3.2.5. The results follow below.

$3.5.1$ H⁺ Ion Energy Distribution

Ions desorbed from a surface by electron impact have a characteristic distribution in energy. This distribution is dependent on the adsorption states from which the ions originate. In the simple models used to describe this phenomena, changes in the observed energy distribution, except some intensity

changes, result from changes in the adsorption states. Hence, this measurement can be used to characterize the states from which ions are desorbed. A theoretieal discussion of the ion energy distribution is given in Appendix C.

Figure 3.7 shows the energy distribution of H^+ ions electron desorbed from W(100) using a primary beam current of $1x10^{-6}$ A at an energy of 400 eV. This current was sufficiently low such that the energy distribution was obtained without desorbing the hydrogen coverage to any extent. The choice of 400 eV for the primary energy was, to some extent, arbitrary, although it was found that below 400 eV the ion signal was weaker and the measurements required more time to take. To obtain the data, the crystal was flashed and then allowed to cool several minutes to 60° C. It was then dosed with hydrogen from the jet until a work function change of 0.18 eV, corresponding to a substantial coverage in the β_{2} state, was measured. The distribution was obtained by scanning $v_{\rm acc}$ while holding V_{τ} at 4 volts. The distribution has an intensity maximum at 3 \pm 0.5 eV and a full width at half maximum of 2.6 eV. No correction to the energy scale has been made for the target-spectrometer contact potential difference, since this amounts to only 0.15 eV, which is smaller than the accuracy in the measurement. A small part of the detected ion signal, which did not originate at the crystal surface, has been subtracted out. The amount of this contribution was determined by monitoring the ion signal from the flashed, undosed surface. This extra signal amounted to no more than 10 percent of the total signal, and was entirely on the low side of the energy distribution.

For comparison, the energy distributions of H^+ ions produced by electron impact of gas phase hydrogen 81 and hydrogen-covered polycrystalline tungsten 82 are included in Figure 3.7. All three curves have been normalized to the same peak intensity. The three curves have characteristically different

Figure 3.7. Energy distribution of H^+ ions from a tungsten (100) surface after adsorption of hydrogen. Hydrogen coverage for this measurement corresponds to a work function change of 0.18 eV (approximately 0.19 monolaygy). For comparison, the energy distribution reported by Nishijima⁰² of H^T ions des orbed from hydrogen covered poly crystalline tungsten is given. Also shown is an ion energy distribution obtained by Hagstrum⁸¹ from gas phase hydrogen. The three distributions have been normalized at their peak intensities.

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distributions in energy.

Energy distributions of H^+ ions taken at different hydrogen coverages are shown in Figure' 3.8. Experimental conditions for these measurements were the same as used to obtain the previous figure. There is no change in peak position or line shape as a function of coverage, except for heavy dosings where the distribution appears to be slightly broader. The maximum intensity is a function of coverage, as discussed below.

Figure 3.9 shows a series of ion energy distributions taken after adsorption from the jet with the target temperature approximately -150 $^{\sf o}$ C. For these data the target was flashed and allowed to cool 5 minutes before adsorption. All other experimental conditions were identical to the corresponding $60\rlap{.}^\circ\text{C}$ data. The distributions peak at 3 eV (except at high coverage where the peak appears to be slightly higher) and have full widths at half maxima of 2.6 eV, identical to the results found for 60° C adsorption. The high energy tail of these low temperature distributions appears to be somewhat wider than the corresponding higher temperature data, however.

After flashing the target to 2200° K and allowing it to cool five minutes to a temperature of \langle -145^oC, hydrogen ions can be detected without dosing the surface from the jet. An energy distribution for this signal is shown in Figure 3.10. A time-of-flight measurement confirmed that the observed signal is indeed H⁺ ions. The energy distribution peaks at 2.5 + 0.5 eV, with a full width at half maximum of 5.8 eV. The peak intensity of the ion signal obtained without dosing depends on the previous history of the sample and on the experimental parameters as discussed in Section $3.5.4$. This intensity change is indicated by arrows in Figure 3.10. For this measurement, the

Figure 3.8. Comparison of energy distributions of H^+ ions desorbed from a 60°C tungsten (100) surface after adsorption of hydrogen to different coverages. Coverages are given in terms of measured work function changes $\Delta\varphi$.

Comparison of energy distributions of H^+ ions desorbed from a
low temperature (-150°C) tungsten (100) surface after adsorption Figure 3.9. of hydrogen to different coverages. Coverages are given in terms of measured work function changes $\Delta\phi$.

Figure 3.10. Energy distribution obtained from a flashed but undoged tungsten (100) surface which has been cooled to -150°C. For comparison, the energy distribution of H^+ ions from the tungsten (100) surface after dosing with hydrogen is shown by the dashed line. The two distributions are normalized at their maximum intensities. The intensity of the ion signal from the undosed surface changes as a function of sample history, as discussed in the text. This is indicated by the arrow.

primary energy was 400 eV. A relatively low incident electron current of $1x10^{-7}$ A was used so that the coverage in the surface state being probed would not be strongly depleted during the measurement. This state has a high desorption cross section, as calculated in Chapter 4, and hence depletion is a possibility. It should be noted that the same energy distribution is obtained from the low temperature state using a beam current of 2×10^{-6} A. The latter high current measurement reflects the distribution in energy of H^+ ions desorbed from the fast state when its coverage is in "equilibrium" as discussed in Section 3.5.2.

The intensity of the ion signal desorbed from the surface at both 60° C and -150° C is strongly coverage dependent. In Figure 3.11 is plotted the intensity of the 3 eV H^+ ion signal as a function of work function change upon adsorption of hydrogen. The signals from the 60° C and -150° C surfaces have maximum intensities at work function changes of 0.18 eV and 0.11 eV, respectively. This difference indicates that adsorption at the low temperature differs somewhat from that at 60° C. At higher hydrogen coverages, the ion signals decrease to less than 15 % of their peak intensities, indicating that the cross section for ion desorption decreases as the β_1 state fills. The reason for this decrease is not well understood, although Madey 41 has sug+ \cdot gested that it results from a coverage dependent rate of reneutralization of the ions produced by the incident beam. At near monolayer coverages the 3 eV ion signal increased somewhat.

The data in Figure 3.11 are normalized at the peak intensity. The absolute maximum yields at the two temperatures are the same within 25 %. Also shown normalized at the peak intensity are Madey's intensity versus coverage data 41 for hydrogen adsorbed on W(100) at room temperature. The

Intensity of the 3 eV H^+ ion signal from the tungsten $(1007)^{-1195}$ Figure 3.11. surface as a function of the change in work function resulting from hydrogen adsorption. Data for adsorption at 60° C and $7\frac{150^{\circ}}{150^{\circ}}$ C are plotted. For comparison, the results obtained by Madey⁴ from a room temperature tungsten (100) surface are included.

maximum in his ion signal occurs for the same coverage as the maximum in the room temperature data taken here. His results are more sharply peaked, however. This difference may be due to the different conditions under which the two sets of data were obtained. Madey's results represent ions desorbed in a narrow cone. normal to the surface whereas the spectrometer used here collected only those ions desorbed from the surface at 35° + 2 $1/2^{\circ}$. Madey also used a lower primary energy.

3.5.2 Desorption Curve Measurements

The H^+ ion signal is observed to decrease with time if a primary electron beam current of sufficient intensity per surface area is used. A theoretical description of this measurement, referred to as a desorption curve, is given in Appendix C. It can be shown that the expected ion signal decreases to an equilibrium value. The rate of decay of the desorption curve and the equilibrium value are used to calculate parameters characteristic of the adsorption state being probed.

Figure 3.12 shows the decay of the 3 eV H^+ ion signal from tungsten (100) initially covered with hydrogen to a work function change of 0.10 eV. The temperature of the crystal for this measurement was 60° C. An incident current of $5x10^{-6}$ A (a current density of $2.5x10^{-3}$ A/cm²) at a primary energy of 400 eV was used. The decrease in ion yield is seen to be quite slow. The equilibrium value shown in this figure, i_{H} + , was estimated from the equil analysis of the data in Chapter 4.

As noted above, H^+ ions could be desorbed from a cold but undosed tungsten (100) surface. The desorption curve for this undosed state is shown in Figure 3.13. For this data, the crystal was flashed and allowed to cool 5 minutes to -150 $^{\circ}$ C. Then the incident electron current was turned on (see

Figure 3.12. Change in the H^+ ion current during electron bombardment of a 60° C tungsten (100) surface. Hydrogen was initially adsorbed to a coverage of 0.10 monolayer.

Change in the H[†] ion current during electron
bombardment of a flashed but undosed tungsten
(100) surface cooled to -150°C. Figure 3.13 .

Section 3.5.4 for a discussion of how the current was controlled) and the ion signal decay monitored. The signal is seen to undergo a rapid decay. It reaches its equilibrium value in several minutes, in sharp contrast with the desorption curve obtained after hydrogen dosing at room temperature. An in cident current of $1x10^{-6}$ A (a current density of $5.1x10^{-4}$ A/cm²) at a primary energy of 400 eV was used to take the desorption curve from the undosed, cold surface. This current density is only 20 percent of the value used for the room temperature data of Figure 3.12. It was found convenient to use this smaller value since the decay of the ion signal was so rapid. Additional desorption measurements on this fast decaying, or "fast" state, are given in the following two sections.

A desorption curve obtained after dosing the cold tungsten (100) surface with hydrogen is shown in Figure 3.14. The data were taken using a primary current of $3x10^{-6}$ A (a current density of 1.5x10⁻³ A/cm²) at a primary energy of 400 eV. The surface was dosed to a work function change of 0.07 eV. Initially there is a rapid decay of the ion signal which is similar to the desorption curve obtained from the fast state. Following this initial decay, the signal continues to fall for a time but at a much slower rate of decay. This desorption pattern, different than either of the desorption curves given in Figures 3.12 or 3.13 , can be described in terms of simultaneous desorption from two adsorption states. This is discussed further in Chapter 4.

3.5.3 Temperature Dependence of the Fast State H^+ Ion Signal

The ion yield from the flashed but undosed tungsten (100) surface has been studied as a function of temperature. These data were obtained by continuously monitoring both the tungsten temperature and the 3 eV H^+ ion

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Figure 3.14. Change in the H^+ ion current during electron bombardment of a -150°C tungsten (100) surface. Hydrogen was initially adsorbed to a coverage of 0.07 monolayer.

signal following a crystal flash. The current for this measurement was $1x10^{-6}$ A (a current density of $5.1x10^{-4}$ A/cm²). The primary energy was 400 eV. As can be determined from the previous section, this current density was such that the electron beam caused Significant perturbations on the hydrogen state during the measurement. None the less, several conclusions can be inferred from the intensity versus temperature data presented in Figure 3.15. The ion signal from the fast hydrogen state is strongly temperature dependent. The H⁺ intensity is seen to increase sharply below approximately -50^oC. The results are reversible with temperature; the ion signal decreases if the crystal is heated and the signal returns to its original intensity when the crystal cools back down.

Several mechanisms could be responsible for the appearance of a H⁺ ion signal below room temperature. For example, a temperature dependent bulk to surface diffusion of hydrogen could produce a desorbable hydrogen state. Likewise, adsorption from the background might produce desorbable H^+ only below room temperature. In order to better understand the fast state, some additional measurements were made as described in the following section.

3.5.4 Additional Measurements on the Fast State

Additional experiments were performed to further elucidate the nature of the low temperature fast state. Experiments were made to determine the source of hydrogen which populates this state. The effect of co-adsorption of hydrogen from the jet with this state was probed. In addition, the possibility that the appearance of the state was related to surface contamination was investigated. Possible correlations between the fast state hydrogen and the low temperature LEED phenomena described in Section 1.2.3 were probed.

Intensity of the 3 eV H^+ ion signal from the
flashed but undosed tungsten (100) surface as Figure 3.15. a function of tungsten temperature.

In these measurements it was desired to study the appearance of the fast state H^+ ion signal without the complicating effects of simultaneous, significant depletion of this hydrogen state with the primary electron beam. This possibility exists since the cross section for electron desorption of the fast state is high, as shown in Chapter 4. It was found that a measure of the change of coverage in the fast state could be obtained in experiments in which the electron beam was turned off for short times. During the time the gun was off, referred to as "adsorption times", the fast state populated. The increase in the coverage in this state during the adsorption time could be monitored by taking a desorption curve right after the adsorption time. The change in coverage is assumed proportional to the difference $i_{\text{u}}+ - i_{\text{H}}+$ \int initial \int ^Hequil where i_{tr} + is the ion intensity immediately after turning the gun back on initial and i_{H} + has been discussed above. The difference i_{H} + - i_{H} + will equil $\begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix}$ equil $\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}$ equil ${}^{\text{a}}$ equil ${}^{\text{b}}$ equil ${}^{\text{b}}$ referred to as Δi_{H}^{+} (adsorption time). The rate of increase in coverage of the fast state is assumed proportional to Δi_{H} +(adsorption time)/adsorption time.

To turn the gun off, the control grid was biased 6 volts negative with respect to the cathode. This method of controlling the gun current kept the cathode temperature constant during the adsorption time while at the same time no current could reach the crystal. The primary beam could be turned off (or subsequently back on) in fractions of a second. No effects on the observed measurements could be attributed to this biasing procedure.

The change in the population of the fast state has been monitored as a function of the tungsten crystal temperature. Figure 3.16 shows the results of a series of measurements, each done at a different crystal temperature, in

Figure 3.16. The quantity $i_{\text{initial}} + \n i_{\text{equil}}$, measured
from desorption curves from the fast state, as a function of crystal temperature.
which the above procedure has been used with adsorption times of 150 seconds. From the desorption curves taken following the adsorption times the quantity Δi_H^+ (adsorption time) has been calculated. This quantity is plotted versus the crystal temperature in Figure 3.16. The quantity Δi_H^+ (adsorption time), i.e., the fast state signal, is small and less than 5 % of the maximum signal when the temperature of the tungsten crystal is higher than 0° C. Below 0° C the change in population in the fast state during the adsorption time increases as the temperature decreases. This temperature dependence is in agreement with the the results of Figure 3.15 which was taken continuously with a high primary current as the crystal was cooled after a flash. Thus the procedure used to obtain Figure 3.16 appears reasonable.

The rate of population of the fast state can be an indication of the source of hydrogen, as discussed in Chapter 4. The rate of population of this state has been investigated as a function of adsorption time using the procedure given above. Figure 3.17 shows a plot of the quantity $\Delta i_{\rm H}^{\text{+}}$ (adsorption time) versus adsorption time. From the figure it is concluded that the rate of popUlation is constant in time, at least for coverages of the fast state obtained in 26 minutes.

The effect of co-adsorption of hydrogen from the jet on the fast state has been probed. The purpose of these measurements has been to determine if hydrogen (H_2) from the gas dosing system is the source of the fast state. In a series of measurements, the cold crystal surface was dosed with hydrogen and then an ESD ion signal monitored until it reached equilibrium. Following this, the fast state was allowed to populate during an adsorption time of 150 seconds. Finally a desorption curve from the co-adsorbed fast

Figure 3.17. The quantity i_{rf} \ldots $\frac{1}{n+1}$, measured from inc quantity $H_{initial}^+$ H_{equal}^+ , measured
desorption curves from the fast state, as a function of adsorption time. "Adsorption time" is defined in the text.

state and dosed hydrogen states was taken. In Figure 3.18 the quantity Δi_{μ} +(adsorption time) calculated from these desorption curves is plotted versus work function change due to adsorption from the jet. For low doses of hydrogen ($\Delta \varphi < 0.10$ eV) there is almost no change in the quantity $\Delta I_H^+(adsorption$ time), i.e., the rapid decay of the ion signal characteristic of the fast state is observed. However, preadsorption of hydrogen from the jet clearly affects the ion signal from the fast state for $\Delta \phi \leq 0.10$ eV. The signal is decreased for hydrogen coverages in the β_1 state, in qualitative agreement with the data presented in Figure 3.11.

For Δp < 0.10 eV, the change in coverage in the fast state during adsorption times of 150 seconds is seen to be independent of the amount of hydrogen in the dosed, or β_2 state. This result was used in a series of experiments in which the rate of population of the fast state was measured at different hydrogen background pressures. The flux (molecules per cn^2 per second) of H_2 onto the surface from the background is directly proportional to the partial pressure of hydrogen. If H_2 is the source of the fast state, changing the background pressure would be expected to have an effect on the measured change in coverage in the fast state, as long as the total adsorption is lower than about 0.10 monolayer (which corresponds to a work function change of 0.10 eV). For the data in Figure 3.18, the background pressure of hydrogen was less than $7x10^{-11}$ Torr (the Bayard-Alpert gauge pressure). In a series of experiments this hydrogen pressure was raised by letting gas in from the the gas handling system for times ranging from one to two minutes. While the pressure was raised, the electron gun was turned off so that simultaneous adsorption into the fast state and the β_2 state could take place. The

Figure 3.18. The quantity i_{Ht} 1nitial desorption curves from - i_{Ht}
the low temperature hydrogen
the low temperature hydrogen dosed surface, as a function of work function change, $\Delta \varphi$. $\Delta \varphi$ results from hydrogen coverage.

total hydrogen coverage in the β_2 state was kept below 10 percent of a monolayer. Desorption curves were then taken and the quantity $\Delta \mathbf{i}_\text{H}^+$ (adsorption time) calculated. An interesting result was obtained. It was found that the coverage in the fast state was unrelated to the background pressure of H₂, and hence, unrelated to the total impingement of H_2 . Even though experiments were made in which the background pressure was varied over two orders of magnitude, the change in coverage in the fast state during equal adsorption times was always the same. Hence it is concluded that the fast state is not populated by hydrogen added to the background from the gas handling system.

It was found, however, that the fast state signal intensity could be correlated to a pressure reading under certain experimental conditions. Normally during flashing, the crystal manipulator was rotated so that the tungsten crystal faced away from the entrance to the spectrometer (a rotation of 180° from the crystal position shown in Figure 2.14). This normal flashing position is referred to as the "down" position. The crystal could also be flashed while it was in the "up" position, or facing the spectrometer. It was observed that when the crystal was flashed in the up position, an increase in the ion signal from the fast state could be obtained over that measured when the crystal was flashed in the down position. This unexpected result suggested that the fast state might be correlated to a thermal, instrumental effect. Radiation heating from the crystal raised the temperature of the surrounding experimental chamber surfaces. If the crystal is close to the surfaces during a flash, as for example when flashed in the up position, the heating is greater. One consequence of greater heating would be an enhanced thermal desorption from the surfaces and a higher pressure in the experimental

chamber. Hence, the incident flux of gas thermally desorbed from the chamber surfaces would be increased. Unfortunately, the best test of this hypothesis, a measurement of the temperature of the surfaces in the experimental chamber, could not be made. However, an interesting pressure related result could be obtained when the x-ray current in the Bayard-Alpert gauge (which is equivalent to approximately $7x10^{-11}$ Torr pressure) was nulled out so that ambient pressure increases at the gauge of as little as $0.5x10^{-12}$ Torr could be easily detected. It was observed that during a crystal flash when the crystal was in the up position the gauge pressure showed a maximum pressure burst of approximately $3x10^{-10}$ Torr. This was higher than the pressure burst when the crystal was flashed in the down position, a strong indication that some surfaces in the experimental chamber became hotter during an up flash. When the crystal was flashed in the down position, the pressure fell quickly after the flash was terminated to the nulled, or equilibrium level. However, after a flash in the up position, the pressure fell to a quasi-equilibrium level which was higher than the true equilibrium pressure by as much as $2x10^{-12}$ Torr. The quasiequilibrium pressure was dependent on the number of previous flashes in the up position and on how long after flashing the pressure was read. Once the crystal had been flashed in the up position, the pressure remained elevated for several hours, slowly decreasing to the equilibrium level. It should be noted that these pressure increases are read outside the experimental chamber. The actual pressure increase in the experimental chamber, and hence the increased gas flux at the crystal surface, can only be estimated to be pro-

The magnitude of the pressure increases following a flash in the

portional to the gauge pressure.

up position was linearly related to both the change in coverage of the fast state during the adsorption time and to the desorption curve equilibrium level. This can be seen from the data presented in Figure 3.19. The lower panel shows the results of a series of measurements in which desorption curves were taken after letting the fast state populate for adsorption times of 150 seconds. The ordinate in the lower panel is Δi_{H} + (adsorption time). The abscissa in the figure is the increase in pressure over the equilibrium pressure as a result of flashes in the up position. The change in ion yield is seen to be directly proportional to the observed pressure increase. The top panel shows the equilibrium ion signal observed for the desorption curves, plotted versus the same pressure increase as the lower panel. A direct proportionality between the equilibrium ion signal and the pressure increase is seen. These two linear results would be expected if the fast state populated as a result of adsorption from the background. This is discussed further in Chapter 4. On the other hand, no dependence of the fast state ion signal on background pressure would be expected if the source of the hydrogen were bulk to surface diffusion. Thus, while there may be hydrogen on the surface which is not desorbed by incident electrons, it can be concluded from this measurement that the fast state is populated by adsorption from the ambient.

A possible explanation for the fast state is suggested by the work of Jelend and Menzel.⁵¹ They found that co-adsorption of oxygen or CO with hydrogen leads to the κ hydrogen state which has similar characteristics as the fast state observed here. The possibility that impurities are on the surface in the temperature range in which the fast state is observed has been investigated using Auger electron spectroscopy and electron stimulated desorption in Figure 3.19. Lower panel - The quantity i_{rf} + - i_{rf} + , measured from desorption curves from the fast state, as a function of gauge pressure change. The fast state populated during adsorption times of 150 seconds. The pressure change results from flashing the tungsten crystal while it is in the "up" position. Upper panel - Equilibrium ion current, $i_{H_{\text{equil}}^{+}}$, measured from the desorption curves taken for the data in the lower panel.

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the time of flight mode. In order to test for these elements, the flashed tungsten surface was cooled with the gun turned off, allowing the fast state to populate. Total adsorption times of up to 15 minutes were used, times in which a strong fast state signal could be obtained. However, no carbon or oxygen Auger peaks were observed and no desorbed oxygen or carbon ions that could be attributed to the fast state were monitored with ESD. Hence any oxygen or CO present on the surface would have had a coverage below the detection sensitivity of the techniques used, or less than approximately 1 percent of a monolayer. It can be noted here that coverage calculations given in Chapter 4 indicate the fast state hydrogen coverage is well below $1 \text{ %}.$

3.6 Low Energy Electron Diffraction Data

The low energy electron diffraction (LEED) system used here has been described previously in Section 2.6. LEED data has been optained using hydrogen coverage, crystal temperature, and primary electron energy as variable parameters, as described below.

The symmetry of the LEED spot pattern has been noted as a function of hydrogen coverage at room temperature. Results from these observations are in good agreement with previously reported research (see Section 1.2.3). Half order diffraction spots become visible with initial hydrogen coverage. The intensity of the half order spots maximize at a coverage corresponding to $\Delta \varphi = 0.15$ eV at a primary energy of 115 eV. Additional adsorption causes the half order spots to split into four poorly defined spots. This pattern, upon further adsorption, becomes blurred. At full coverage, a (lxl) pattern is observed. Figure 3.20 shows a photograph of the LEED pattern observed from a clean room temperature tungsten surface and also the $c(2x2)$ LEED pat-

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Figure 3.20. Photograph of LEED screen, showing a clean (lxl) pattern and a c(2x2) pattern. Models of possible surface atom configurations for the LEED patterns are also shown.

tern that occurs with a hydrogen overlayer in the β_2 state.

When the crystal is cooled to below room temperatures, half order spots are visible without any dosing of the crystal from the gas system.

Graphs of LEED spot intensity versus primary electron energy, called elastic intensity profiles, are shown in Figures 3.21, 3.22, and 3.23 for the $(1,0)$, $(1,1)$, and $(1/2,1/2)$ diffraction beams. A normally incident primary electron beam was used in these measurements. Data were taken at two temperatures, 60° C and -150° C, for both the clean surface and for hydrogen adsorbed on the surface to a coverage corresponding to a $_{\Delta\phi}$ of 0.15 eV. This coverage corresponds to the maximum in intensity for the 115 eV half order beams. All observable, equivalent beams show the same line shape and peak positions. There are some intensity differences between equivalent beams, probably due to an uneven phosphor coating of the LEED screen, particularly near its edge. Small misalignments might also affect the intensities. The effect of hydrogen adsorption on the intensity profiles is seen to be small, except above 100 eV in the $(1,1)$ beam profile and below 50 eV in the $(1/2,1/2)$ beam profile. Some small shifts (< 2 eV) in the energy positions of the peaks are observed as a function of coverage but not as a function of temperature.

The intensities of the $(1/2,1/2)$, $(1,0)$, and $(1,1)$ spots have been measured as a function of crystal temperature for the clean (flashed) surface. These results are presented in Figures 3.24 and 3.25 using a semilogarithmic scale. The data were obtained by continuously monitoring both the tungsten temperature and the intensity of the beams following a crystal flash. Primary energies of 115 eV for the $(1/2,1/2)$ beam, 110.5 eV and 67 eV for the $(1,0)$ beam, and 113 eV for the $(1,1)$ beam and currents of 1.0×10^{-6} A were used. The

Figure 3.21. Elastic intensity profiles for the $(1,0)$ beam from both clean and hydrogen covered tungsten (100) surfaces. Profiles have' been taken at 60° C and -150° C. A work function change, $\Delta \varphi$, of 0.15 eV corresponds to hydrogen adsorbed in the β_2 state.

Figure 3.22. Elastic intensity profiles for the $(1,1)$ beam from both clean and hydrogen covered tungsten surfaces. Profiles have been taken at 60° C and at -150°C. A work function change, $\Delta \varphi$, of 0.15 eV corresponds to hydrogen adsorbed in the β_2 state.

Figure **3.23.** Elastic intensity profiles for the (1/2,1/2) beam from both clean and hydrogen covered tungsten surfaces. Profiles have been taken at 60° C and at -150°C. A work function change, $\Delta\varphi$, of 0.15 eV corresponds to hydrogen adsorbed in the β state.

Figure 3.24. Temperature dependence of $(1,0)$ and $(1,1)$ LEED beams from a flashed tungsten (100) surface. Primary energies used are indicated on the graph.

Figure 3.25. Temperature dependence of the $(1/2,1/2)$ LEED beam from flashed tungsten (100) surface. A primary electron energy of 115 eV was used.

intensities of the $(1,0)$ and $(1,1)$ beams are seen to increase exponentially (linearly on the semilogarithmic scale) as the temperature is lowered. The intensity of the $(1/2,1/2)$ order beam also increases as the temperature is lowered. Down to approximately -75° C the rate of increase with temperature is greater than that for the integral order beams. Below -75° C the intensity changes at about the same rate as the integral order beams. The results are reversible with temperature.

In Sections 3.5.3 and 3.5.4 a hydrogen ion signal has been reported from the flashed surface. LEED measurements have been made to ascertain if this ion yield from the fast state could be correlated to the intensity of the LEED spots. After flashing the crystal, the photometer signal from the $(1/2,1/2)$ beam was measured as the crystal cooled to -150°C. Then the incident electron current was turned off for 300 seconds in order to allow the fast state to populate. When the electron current was turned back on, the photometer signal immediately returned to the same intensity as obtained prior to turning off the incident current. There was no decay in the photometer signal that could be correlated to the desorption curve phenomena seen with the ion signal. The intensity of the photometer signal from the $(1,0)$ and $(1,1)$ beams, as well as from the background, was monitored using this same procedure. In no case was there any structure observed in the photometer signal that could be correlated to the rapid decay in the fast state ion yield.

3.7 Electron Scattering Data

The electron signal backscattered from the crystal has been observed as a function of hydrogen coverage and crystal temperature, using synchronous

detection of the second harmonic of the energy distribution $N(E)$, as discussed in Appendix B and in Section 3.2.4.

Figure 3.26 shows the characteristic loss structure for electrons scattered from a clean, room temperature tungsten (100) surface and also from this surface after dosing with hydrogen. The abscissa in this figure represents electron loss energy, w, where $0 \in V \le w \le 40 \text{ eV}$. A primary energy of 110 eV and a primary current of $1x10^{-6}$ A were used to take these data. Since for tungsten true secondary structure extends out to 60 eV, 25 there is no overlap of secondary and characteristic loss structure down to losses of 50 eV when operating at 110 eV primary energy. The data of Figure 3.26 were taken in the second derivative mode in order to suppress the background. The data were taken at a spectrometer pass energy of 30 eV with a 1 volt peak to peak oscillation on the retarding potential.

Coverage dependent changes in the spectra are seen. The peak at $w = 2.5$ eV in the clean spectrum decays as the hydrogen coverage in increased. At the same time, the narrow peak at 4 eV becomes broader and a peak grows at a loss energy of 7.5 eV. The structure at 21.0 eV in the clean spectrum moves down in loss energy as hydrogen adsorbs. Below $w = 30$ eV very little change in the spectra as a function of hydrogen coverage is observed.

Figure 3.27 shows characteristic loss structure for electrons scattered from a tungsten surface cooled to -150° C. The data were taken using the same electron gun and spectrometer operating conditions as used for the data of Figure 3.26. The low temperature, clean spectrum is nearly identical to that obtained at the higher temperature. The only change is a slight enhancement of the shoulder at about 4.5 eV. Changes in the clean spectrum with

Figure 3.26. Characteristic electron energy loss spectra from a 60[°]C tungsten (100) surface. Data are given for the clean surface and for hydrogen adsorption up to near monolayer coverages. A primary energy of 110 eV and a spectrometer pass energy of 30 eV were used to obtain the spectra. The second derivative of the spectra, taken with a modulation voltage of 1 volt peak to peak, is shown.

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Figure 3.27. Characteristic electron energy loss spectra from a -150° C tungsten (100) surface. Data are given for the clean surface and for hydrogen adsorption up to near monolayer coverage. A primary energy of 110 eV and a spectrometer pass energy of 30 eV were used to obtain the spectra. The second derivative of the spectra, taken with a modulation voltage of 1 volt peak to peak, is shown.

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hydrogen adsorption are identical to those seen for adsorption at the higher temperature.

Loss spectra were also taken for $0 \text{ eV} \leq w \leq 10 \text{ eV}$ from the flashed but undosed cold surface after turning off the electron gun for 10 minutes. These measurements were made to see if the fast state hydrogen would affect the loss measurements. No changes in the electron loss spectrum from those taken immediately after cooling the flashed crystal were found.

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A discussion of the data presented in this chapter follows in Chapter 4.

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CHAPTER 4

DISCUSSION OF RESULTS

Hydrogen chemisorption on single crystal tungsten (100) has been probed in this research using complementary surface sensitive techniques. Auger measurements have been given in Section 2.8. Work function, ESD, LEED, and electron scattering results have been given in Chapter 3. A discussion of this data is presented here.

4.1 Auger Electron Spectroscopy Measurements

The chemical composition of the surface layer has been characterized under experimental condition using Auger electron spectroscopy. The procedures used have been previously described with the spectrometer electronics, Section 2.5. The Auger data have been given and discussed in Section 2.8. A brief summary of these results follows.

Tungsten, carbon, and oxygen Auger transitions have been observed using this technique. It can be seen from Figure 2.16 that after flashing the cryst.l to $2200^{\sf o}{\rm K}$, no structures attributable to carbon or oxygen Auger elec trons remain in the Auger spectrum. The Auger measurement is estimated to be sensitive to approximately 1 percent coverage. Operation of the electron gun in the high current, high voltage Auger mode results in a slow deposition of carbon from the background. Since the Auger mode is used to chemically characterize the surface, the net effect of this beam related contamination is an overestimation of the carbon impurity concentration at the surface.

Some weak structure in the Auger spectra from the flashed surface occurs between 475 eV and 525 eV. No definite conclusions regarding the

origin of these peaks can be made. The possibility that the structure results from transitions in tungsten and/or other elements is discussed in Chapter 2. ⁸³ It is worth noting that Watts, Jones, and Hopkins recently published an Auger spectrum from a flashed W(lOO) surface in which weak structure can be seen at approximately the same energies as the unidentified structure observed here. This similarity lends support to the hypothesis that the peaks are tungsten Auger transitions. However, it does not rule out other possibilities. The similarity of the data indicates, at least, that if the structure in question results from some contaminate, the problem is not unique to the apparatus here. It should be emphasized that work function, ESD, and LEED data taken here are in good agreement with the literature; any possible contamination has not had a noticeable effect on the measurements.

4.2 Work Function Results

Retarding potential work function measurements have been taken as a measure of hydrogen coverage. Plots of work function changes versus exposure to hydrogen are presented in Figures 3.4 and 3.5. Adsorption of hydrogen at $60^{\sf o}{\sf C}$ yields a maximum work function change of 0.98 \pm 0.04 eV. This is within 10 percent of 0.90 eV, the most consistent monolayer coverage work function change reported in the literature for the H₂ on W(100) : $8,18,46,47$ As argued by Armstrong, 84 agreement with the values from the literature is an indication of good (100) orientation. This is because the work function of a faceted surface is a weighted average over the work functions of the facets. 44 Since hydrogen adsorption increases the work function of the (100) face far more than the expected facet orientations, a

faceted (100) surface would have a lower full coverage work function change than a true (100) surface.

Hydrogen adsorption onto W(lOO) at low temperatures increases the work function by $0.92 + 0.04$ eV at full coverage. This is slightly lower than the room temperature maximum increase, although within experimental error the two measurements are the same,

The increase in work function with hydrogen coverage can be interpreted using a simple model in which each adsorbed hydrogen atom acts as a negative dipole at the surface. The work function change on adsorption, $\Delta\varphi$, can be shown⁴³ to equal the total added dipole moment at the surface divided by the permittivity. Using this and assuming a hydrogen coverage of $2x10^{15}$ atoms/cm² for a $\Delta\phi_{\rm max}$ of 0.98 eV, the average dipole moment per adsorbed hydrogen atom is calculated to be -0.13 Debye. This result can be compared to a theoretical account of the dipole moment of a hydrogen ion adsorbed onto metal surfaces given by Smith, Ying, and Kohn. 63 Their calculation indicates that in order to observe a negative dipole moment, the hydrogen ion must be closer than $0.61 \stackrel{\text{O}}{\text{A}}$ to the top plane of substrate ion cores. This would be an upper estimate of the proximity of the hydrogen atoms to the tungsten substrate. The minimum theoretical dipole moment per adsorbed hydrogen ion obtained by Smith et al. 63 is $\text{-}1\text{x}10^{-2}$ a.u. (1 a.u. equals 2.4 Debye). This value is lower than the observed value of -0.13 Debye by a factor of 5.

Cooling a clean tungsten (100) crystal from 200° C to -150° C results in a work function increase of approximately 0.05 eV, as shown in Figure 3.6. This is an average change with temperature, $d\varphi/dT$, of 1.4x10⁻⁴

 eV° K. The temperature dependence of work function for tungsten in this temperature range has not previously been reported. However, temperature dependent changes in work function of this magnitude have been reported for Cu, Ag, Na, and $K^{85,86}$ and have been described theoretically $85,86$ in terms of both a thermal expansion of the crystal lattice and a temperature dependence of the crystal electronic structure. The work function change observed here is quantitatively in agreement with experimental data for other elements and with a theoretical model that describes the temperature dependence solely in terms of intrinsic properties of a clean metal surface. While perturbations on the crystal surface, such as gas adsorption from the background or bulk to surface diffusion can reasonably be expected to affect the work function, it is not necessary to invoke these causes to explain the changes seen on cooling the crystal.

4.3 Electron Stimulated Desorption Results

Under electron bombardment, H^+ ions can be desorbed from the hydrogen dosed tungsten (100) surface and from the low temperature undosed surface. The theory that describes this ESD process was first proposed by Redhead³⁷ and by Menzel and Gomer.³⁸ A discussion of their model, including a derivation of the energy distribution of ions from the surface, is given in Appendix C. In addition, a discussion of the ESD phenomena in terms of surface kinetics is also given in this appendix.

ESD has been used to study the hydrogen-tungsten (100) system at crystal temperatures from slightly above room temperature to -150° C. Energy distributions of H^{\dagger} ions, desorption curves, and ion yield versus temperature. and coverage data have been obtained.

4.3.1 Room Temperature Results

The energy distribution of H^+ ions desorbed from room temperature W(lOO) is given by the solid curve in Figure 3.7. The distribution has a Gaussian line shape, with a peak intensity at an ion energy of 3.0 ± 0.5 eV and a full width at half maximum of 2.6 eV. The line shape of the energy distribution remains virtually unchanged as a function of hydrogen coverage, at least to near saturation coverage, as shown by the curves in Figure 3.8. Near full coverage, the distribution appears to broaden somewhat. This latter change requires further study which has not been done here.

From Equation C.l of Appendix C, the energy distribution of the desorbed ions is given by the expression

$$
f(V(x_i)) = -N\sigma_{ex} |\varphi_G(x_i)|^2 \frac{P(x_i)}{\frac{dV(x)}{dx}|_{x_i}}
$$
 (4.1)

where x is the coordinate normal to the surface. Ions that start at $x = x$ _i desorb with energy V. N is the surface density of hydrogen atoms adsorbed in the ground state, $\sigma_{\rm ex}$ is the cross section for electron induced excitation of hydrogen from the ground state to the ionic state, $|\varphi_{G}(x_i)|^2$ is the probability density of hydrogen at x_i' , $P(x_i')$ is the probability that an ion starts from the position $x_{\underline{i}}$ and escapes from the surface as an ion, and $dV(x)/dx\Big|_{X_i}$ is the slope of the ion-metal interaction evaluated at x_i . The line shape of the energy distribution depends on the metal-neutral interaction $V_c(x)$ via φ_c and depends on the ion-metal interaction $V(x)$ via $P(x)$ and the slope $dV(x)/dx$.

One manifestation of multistate adsorption, in which $V_G(x)$ and $V(x)$ are dependent on the binding state, is a change in the experimentally observed energy distribution. Multistate adsorption has been observed with ESD for some systems, for example, as a function of oxygen coverage on W(100).²⁵ A similar result might be expected for hydrogen adsorption on W(100) since two states, β_1 and β_2 , are seen in thermal desorption spectra. However, from the ion energy distribution line shapes for hydrogen on $W(100)$, no evidence of multistate adsorption as a function of coverage is seen. The line shapes of the energy distribution curves are the same at hydrogen coverages corresponding to both thermal desorption states. Hence, coverage dependent interactions, which have been proposed to account for the thermal desorption results and other phenomena reported for this system, are not observed using this technique.

Another conclusion to be drawn from the energy distributions is that the ions originate at an energy position which remains constant with respect to the Fermi level of the tungsten, independent of hydrogen coverage. A shift of nearly a volt in the work function is observed as hydrogen adsorbs. However, the ion energy distribution, which would be sensitive to changes of this magnitude if it shifted with the work function, remains fixed in energy.

The decay of the room temperature 3 eV H^+ ion yield is shown in Figure 3.12. A theoretical account of the desorption curve measurement has been given in Appendix C. From that discussion, it is seen that a semilogarithmic plot of i_{H} + $-i_{H_{equil}^+}$ versus time yields a straight line. The total desorption cross section of the adsorption state being probed can be

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determined from the slope of the straight line, $-\frac{1}{\tau}$, where τ is given by

$$
\tau = \frac{e}{j_e^{\alpha^t} (E_{\text{pri}})}
$$
 (4.2)

 j_e is the current density used to obtain the desorption curve and e is the unit of electric charge.

The discussion of the desorption process leading to Equation 4.2 is based on the assumptions that the total desorption cross section and the hydrogen sticking probability are independent of hydrogen coverage N. The validity of these assumptions for the hydrogen on tungsten (100) systems should be examined. An indication that the ionic cross section is independent of N for low coverages can be gotten from data presented in Figure 3.11. The H⁺ ion yield versus work function change is nearly linear for $\Delta\varphi$ < 0.1 eV. If coverage is linearly related to work function change, as shown by Madey, $^{\text{8}}$ then the ion yield is directly proportional to N in this low coverage region. A direct proportionality between ion yield and coverage satisfies Equation C.5 only if the ionic desorption cross section Q^{\dagger} is not a function of coverage. In a series of experiments it has been observed that the equilibrium ion yield, which is proportional to the ratio q^+/q^t as given by Equation C.8, is independent of N for low coverages. Since Q^+ and an expression proportional to Q^+/Q^t are both independent of N, it is assumed that Q^t is also independent of N.

The dependence of the sticking probability on coverage has been reported in the literature for the hydrogen-tungsten (100) system. Tamm and Schmidt⁸⁷ found s(N) to be independent of N for coverages of less than 15

percent. Madey 41 found s(N) to be proportional to (1-N/N $_{\tt max}$). Hence, the assumption that the sticking probability is independent of N appears valid to within \approx 10 percent for low coverages. For coverages less than 10 %, the analysis in Appendix C of the desorption curve measurements can be applied to the data.

A semilogarithmic plot of $i_{\mathbf{u}^+}$ - $i_{\mathbf{u}^+}$ for the desorption curve ~quil shown in Figure 3.12 is given in Figure 4.1. The equilibrium level has been chosen approximately 5% lower than the ion intensity obtained after monitoring the decay curve 30 minutes (the final recorded data) since it appeared from the data the signal was still slowly decreasing. In addition, with this correction the data give a better fit to the predicted straight line. From the slope of the line, $-1/\tau$, and Equation 4.1, a q^t (400 eV) of $5x10^{-20}$ cm² is calculated. Without making the 5% correction in i_{H^+} , the best visual $\mathop{\text{[equil]}}$ straight line fit to the data gives a q^t (400 eV) approximately three times larger. Because the initial hydrogen coverage for this data was 0.10 monolayer, this cross section represents the total desorption cross section from the β , hydrogen adsorption state, i.e., represents Q_{o}^{t} (400 eV). For 2 coverages corresponding to the β_1 state, the assumptions leading up to Equation 4.2 are not valid, and no attempt has been made to calculate Q_2^t . The value obtained for $\operatorname{q}_\mathsf{o}^\mathsf{t}$ (400 eV) is somewhat larger than the cross section results reported by Menzel and Gomer³⁸ for hydrogen desorption from a field emitter tip, and is a factor of 10 lower than reported by Jelend and Menzel 10 for desorption from a tungsten ribbon. The latter researchers corrected for readsorption effects, which would partly explain their higher value. The value of φ_{β}^{t} (400 eV) found here is over three orders of

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Figure 4.1. Semilogarithmic plot of the quantity i_{H^+} - $i_{H^+_{equil}}$ as a function of time. The data are measured from the desorption curve given in Figure 3.12.

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magnitude smaller than the total cross section found by Jelend and Menzel $^{\rm 51}$ for hydrogen coadsorption with either carbon monoxide or oxygen. This is a verification that these contaminants are not present to any great extent.

4.3.2 Low Temperature, Fast State Results

If the tungsten crystal was flashed to 2200° K and subsequently allowed to cool below room temperature, H^+ ions could be desorbed from the surface. The state from which this hydrogen is desorbed has been labeled the "fast" state. Experiments have been made to characterize the energetics and kinetics of this undosed state and also to address the important question of the origin of the hydrogen which is desorbed. These data are discussed below.

The energy distribution of H^+ ions desorbed from the fast state, shown in Figure 3.10, is considerably broader than the distribution obtained after room temperature hydrogen dosing into the β states. The peak intensity is somewhat lower in energy, 0.5 eV, than the peak obtained from the β states. The distribution has a tail extending up several electron volts on the high energy side, It should be noted that the same energy distribution line shape could be obtained from the state at any position on its desorption curve; that is, the broad distribution is not an anomalous result reflecting a depletion of the hydrogen fast state during the measurement. A low primary current of $1x10^{-7}$ A was used to take the distribution in Figure 3.10 so that electron desorption effects were minimal. From a comparison of energy distributions, as given in Figure 3.10, it is possible to conclude that the fast state is a separate state from the β states.

This conclusion is supported by cross section calculations below.

The intensity of the ion yield from the fast state is temperature dependent. As shown in Figures 3.15 and 3.16, the ion yield increases as the temperature is lowered. This phenomena is reversible. Using the assumption that the ion yield is proportional to coverage, it is concluded that the fast state coverage is a function of temperature.

The desorption curve obtained from the undosed tungsten (100) surface has been measured and is given in Figure 3.13. The decay time is seen to be extremely rapid compared to the analogous measurement taken after hydrogen dosing at room temperature. A semilogarithmic plot of i_{H}^+ - $i_{H_{\tt equil}^+}$, measured from the data in Figure 3.13, is given in Figure 4.2. The total desorption cross section for the fast state, $Q_f^t(400\,\text{eV})$, calculated from the slope of the straight line in Figure 4.2, is 1×10^{-17} cm 2 . This is nearly three orders of magnitude higher than Q_{β}^{t} (400 eV).

Since Q_f^t (400 eV) is on the same order of magnitude as the cross section obtained for hydrogen desorption from carbon monoxide or oxygen contaminated surfaces, $\frac{51}{1}$ the possibility that the fast state results from surface contamination has been examined. No direct evidence was obtained to support such a hypothesis. No carbon or oxygen peaks were observed in Auger electron spectra from the cold surface. It is estimated that these spectra were sensitive to 1 percent of a monolayer coverage. No carbon or oxygen ions that could be attributed to the fast state phenomena were observed in time of flight measurements. It might be noted that Jelend and Menzel observed the high cross section state, labeled ν , at room temperature after simultaneously adsorbing hydrogen plus CO or oxygen. Almost no fast state

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Figure 4.2. Semilogarithmic plot of the quantity i_{H^+} - i_{H^+} as a function of time. The data are measured from $\frac{n}{2}$ the desorption curve given in Figure 3.13.
hydrogen was detected here above 0° C. Jelend and Menzel 10 did not observe any H⁺ ion yield from a cleaned surface if cooled to -13° C. Since the H⁺ signal is weak at that temperature, it is possible their apparatus did not detect it. It is also possible that they did not populate their surface with hydrogen by cooling. In any case, it's not possible to make any simple correlations between the fast state and the contamination related κ state. However, as discussed below, the equivalence of the two states cannot be ruled out.

It is of interest to determine the origin of the hydrogen which populates the fast state, There are several possibilities. This state could populate as a result of adsorption from the background. Alternatively, hydrogen, since it is endothermically soluble in tungsten, 88,89 might diffuse from interstitial sites to surface sites as the temperature of the crystal is lowered. A discussion of these phenomena has been given in Appendix C. The latter suggestion has been offered as a possible explanation of the c(2x2) LEED pattern observed on cooling. In addition, a combination of these two processes could be occurring.

Experiments have been performed in which the coverage in the fast state has been monitored as a function of both adsorption time and system background pressure. If the source is external, the dependence of N on adsorption time and ambient pressure can be determined by solving Equation C.4. For the case of no incident electron beam ($j_e = 0$) and if the sticking probability is assumed constant with coverage (probably a good assumption since the change in coverage due to adsorption from the background would be extremely small at the experimental ambient pressures), then the change in

coverage in the fast state would be expected to be linearly related to the time during which adsorption occurs, i.e., linearly proportional to the variable "adsorption time." Furthermore, for a fixed adsorption time, the coverage would be expected to be linearly proportional to the partial pressure of the populating species.

If the hydrogen source is bulk to surface diffusion, a calculation of the dependence of coverage in the fast state on time and background pressure is considerably more involved. $^{40}\,$ Several points can be made, however, from the discussion in Appendix C. The time dependence of N, due to diffusion, could be similar to that expected from background adsorption, i.e., linear with adsorption time. However, background pressure doesn't enter into the diffusion process. If the fast state phenomena is only diffusion related, the coverage N would be expected to be independent of background pressure. This is different than the expected coverage dependence for adsorption from the background.

The rate of populating the fast state has been measured by turning off the electron gun for various time intervals (setting $j_e^{}$ = 0), referred to as adsorption times, and observing the build up of the ion signal while the gun is off. The increase in the fast state is then assumed proportional to the increase in the ion yield, i_{ut} , \cdots i_{ut} , when the electron gun is $H_{\text{initial}}^{\text{T}}$ $H_{\text{equil}}^{\text{T}}$ turned back on. The dependence of the population rate on adsorption time is shown in Figure 3.17. N is found to be linearly related to adsorption time. As discussed above, this time behavior can reasonably be expected to be observed for either an external or an internal source.

The rate of population of the fast state has also been observed as

a function of hydrogen pressure admitted to the background from the gas handling system. As discussed in Section 3.5.4, the rate of population did not depend on the impingement rate from the hydrogen background. Hence, it is concluded that hydrogen from the gas handling system does not populate the fast state. This does not rule out external adsorption, however. Other sources of hydrogen in the ambient, such as H^+ , H, H₂ in an excited state, or hydrogen from a simple compound such as H_0 could be the source.

Although the population of the fast state was not affected by the background pressure of hydrogen (H_2) from the gas handling system, there is evidence that this state does result from adsorption from an external source. This conclusion is based on experiments in which the Bayard Alpert gauge sensitivity was increased by nulling out the x-ray limiting current. Changes in the background pressure on the order of $2x10^{-12}$ Torr were observed experimentally if the crystal was flashed while it was facing the spectrometer. One explanation of this observation is that a flash in the up position warms experimental chamber surfaces, most likely the grids and electron gun drift tube. The resulting pressure increase occurs because of an increased rate of thermal desorption from these surfaces. The linear dependence of the equilibrium current, i_{Hequil} , with pressure change, as found experimentally and shown in the top panel of Figure 3.19, is expected if external adsorption populates the fast state, This can be seen from Equation C.9. Likewise, the rate of change of coverage in the fast state is seen to be proportional to the pressure change in the lower panel of Figure 3.19. This is also expected for external adsorption. If bulk to surface diffusion were the source of the hydrogen, no dependence on pressure would be expected. Hence Figure 3.19

indicates that hydrogen becomes desorbable because of adsorption from the background. It is not possible to say what species is adsorbing.

An interesting calculation that can be made from the current nulling experiments is an estimate of the coverage in the adsorption state responsible for the fast state hydrogen ions. Since the relation

$$
\frac{\dot{I}_{H}^+}{\Delta \dot{I}_{H}^+} = \frac{P}{\Delta P}
$$
 (4.3)

can be obtained easily from Equation C.9 and since Δi_{tri} is on the same $^{\rm H}$ equil order as $i_{H_{\text{equil}}^+}$, the background partial pressure that populates the undosed state is on the same order of magnitude as ΔP , or about $1x10^{-12}$ Torr. The coverage N, at equilibrium, can now be obtained by setting Equation C.4 equal to 0. At a pressure of 10^{-12} Torr, the impingement rate of hydrogen molecules, for example, is $1.5 \mathrm{x} 10^9$ molecules/cm 2 -sec $^-$ and the impingement rate of other species would be of this same magnitude. Assuming a sticking probability of 1, a total desorption cross section of 10^{-17} cm² as calculated, and a current density of 5.1×10^{-4} A/cm², the surface coverage in the fast state would be \approx 10 $^{-11}$ atoms/cm 2 or 10 $^{-4}$ monolayer. This calculation depends on the assumption that the pressure change at the crystal face in the experimental chamber is the same as measured at the gauge. Experiments performed in which the crystal was rotated to the down position after flashing in the up position indicated that the flux of the populating species at the surface was about twice as great when the crystal faced the spectrometer than when it faced down. Since the pressure at the bottom of the experimental chamber should

be about the same as the gauge pressure, the calculated coverage could be low by 50 percent. It should be noted, however, that this is still 50 times *too* low to amount to 1 percent of a monolayer.

From the above discussion, it can be concluded that the fast state is related to both the temperature of the crystal and to the background pressure of some unidentified species. It is not possible to determine if this state is a separate state from the μ hydrogen state previously reported even though it appears under different circumstances. In fact, since the coverage in the state is so low, Auger spectroscopy would not be sensitive to any contamination of this same magnitude. The possibility of undetected contamination accompanying the fast state cannot be ruled out. It is possible that the adsorbing species does not contain hydrogen as such, but rather, is a species which promotes a small amount of surface hydrogen (from the background or diffusion) to the fast state. It can also be concluded that since coverages less than 1 percent of a monolayer would not be expected to strongly alter the LEED spot symmetry, the half order spots seen on cooling do not arise from the fast state.

4.3.3 Low Temperature, Dosed Surface Results

ESD measurements have been made on the low temperature tungsten crystal after dosing with hydrogen from the jet. Energy distributions at different coverages of hydrogen are given in Figure 3.9. The distributions

are seen to have a peak at 3 ± 0.5 eV, in agreement with the peak positions in the data obtained from the $\bm{\beta}$ states at $60^{\sf o}{\rm C}$. However, the energy distri butions are somewhat broader than the higher temperature data. The fast state yields a broad energy distribution, and it is possible that the results of Figure 3.9 represent simultaneous desorption from both the fast state and the β states. This hypothesis can be tested by analyzing a desorption curve from the low temperature, dosed surface. If two states with different cross sections are being desorbed, then a semilogarithmic plot of the desorption curve should be the sum of two straight lines. The quantity i_{H^+} - $i_{H^+_{equil}}$, measured from the data of Figure 3.15, is plotted in Figure 4.3. The curve can be separated into two straight line segments from which total desorption cross sections of 1.6×10^{-17} cm² and 1.2×10^{-19} cm² are calculated. These cross sections correspond within $+$ 60 percent to the calculated values of Q_f^t (400 eV) and Q_{β}^t (400 eV). Hence, it is concluded that at low temperatures the fast state and S-like states co-adsorb.

It should be noted, however, that the interaction of hydrogen from the jet with the tungsten surface at low temperatures is not exactly the same as at $60^{\rm o}{\rm C}$. This can be seen from the plot of 3 eV ion yield versus work function change given in Figure 3.11. At both 60° C and at -150° C the results are qualitatively similar; the ion yield increases steeply with initial hydrogen adsorption, reaches a maximum and then decreases to less than 15 percent of the maximum value with additional hydrogen adsorption. Hence it is assumed that a similar phenomena is occurring at both temperatures. However, the work function change at maximum intensity for the low temperature measurement was found to be repeatedly lower by 0.07 eV than the

Figure 4.3. Semilogarithmic plot of the quantity i_{H^+} - i_{H^+} as equil a function of time. The data are measured from the desorption curve given in Figure 3.14.

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peak intensity for measurements taken at 60° C. If the expression relating coverage to work function change, Equation 3.5, is valid at both 60° C and at -150° C, then the 0.07 eV shift would represent a dosed coverage difference of 7 % of a monolayer. The ion yield at the low temperature would maximize at a dosed coverage of 11 %, which is 40 % lower than the coverage for the maximum ion yield at the higher temperature. If the decrease in ion yield for higher hydrogen coverages arises from interactions between adsorbed atoms, these calculations suggest that the interactions observe .a different coverage dependence at the two temperatures. Alternate explanations are possible for the measured difference. Equation 3.5 may not be valid at both temperatures. It is possible that the work function change per adsorbed atom is smaller at the lower temperature, and the dosed coverages are the same at the ion yield maximas. It is also possible that hydrogen not visible in ESD or electron loss spectroscopy measurements, but capable of interacting with dosed hydrogen, diffuses to the surface at the low temperature. This latter alternative, while a possible explanation for the LEED phenomena, would raise many questions as to why such hydrogen is not detectable with other techniques.

4.4 Low Energy Electron Diffraction Measurements

Low energy electron diffraction measurements made on the clean and hydrogen dosed tungsten (100) surface have been presented in Section 3.6. The symmetry of the LEED patterns has been noted as a function of hydrogen coverage and crystal temperature. Elastic intensity profiles for three LEED beams are given in Figures 3.21 through 3.23. LEED beam intensities as a function of temperature have been monitored. These are given in Figures 3.24 and 3.25.

General agreement between symmetry patterns seen here and those published in the literature 18 , 19 is good. The (1x1) LEED pattern

characteristic of clean tungsten at room temperature changes into a c(2x2) pattern with initial hydrogen adsorption. With further adsorption, the LEED pattern splits into four spots, becomes blurred, and finally at full coverage returns to a (lx1) pattern. When the crystal is cooled to temperatures. below room temperatures, half order spots become visible without any dosing of the crystal from the gas system.

The intensity of the room temperature half order spots maximizes at a coverage corresponding to $\Delta \varphi = 0.15$ eV, or 0.15 monolayer using Equation 3.5. This is close to the 0.16 monolayer coverage at which Yonehara and Schmidt¹⁹ found these beams to maximize. Estrup and Anderson¹⁸, on the other hand, observed sharp and intense half order LEED spots at a coverage of 0.29 monolayer. The coverages reported here were calculated from work function changes using the linear relation between work function change and coverage obtained by Madey by a flash desorption technique. In both other experiments 18 , 19 coverage was measured directly using flash desorption. The c(2x2) pattern is associated with the β_2 adsorption state. The structures proposed to account for this state, as given in Section 1.2.8, predict that the maximum of the half order spots should occur at 0.25 monolayer coverage (one monolayer being $2x10^{15}$ atoms/cm²). Estrup and Anderson's measurement is closest to this coverage. While it is not known why there is such a large discrepancy between the results, it should be noted that determination of coverage using flash desorption techniques is difficult, with large uncertainties in pressure gauge calibration and system volume. The results given here in terms of $\Delta\phi$ should be considerably more accurate.

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Elastic intensity profiles for the $(1,0)$, $(1,1)$, and $(1/2,1/2)$ LEED beams are given in Figures 3.21 through 3.23, respectively. The profiles were taken at $60^{\sf o}{\rm C}$ and -150 $^{\sf o}{\rm C}$ from both a clean tungsten surface and a surface dosed with hydrogen to 0.15 monolayer. (This coverage corresponded to the observed maximum in the half order pattern.) As seen in these three figures, corresponding clean room temperature and low temperature profiles are nearly identical. Adsorption of hydrogen to a coverage of 0.15 does cause some changes in the clean profiles, with the same changes being observed at both temperatures. Hydrogen adsorption considerably enhances the 42 eV peak observed in the $(1/2,1/2)$ profile and shifts it in energy approximately + 1 eV. Adsorption also leads to a change from a single peak to a double peaked structure of decreased intensity in the $(1,1)$ profile above 100 eV. Adsorption causes very little change in the $(1,0)$ profile line shape above 60 eV, although the 65 eV, 83.5 eV, and 110 eV peaks are lowered in energy approximately 1.5 eV, 0.5 eV, and 1.5 eV respectively. Between 30 eV and 60 eV there are some adsorption effects on the profiles.

These elastic intensity profiles can be compared to corresponding data previously reported in the literature. In Figure 4.4 a comparison is made between clean surface $(1,0)$ and $(1,1)$ profiles taken here and reported by Wei.⁹¹ The agreement is good, except in the energy range below 50 eV. This poor agreement below 50 eV is also true for the $(0,0)$ beam which is not compared here. The low energy discrepancies may be caused by the ambient magnetic field present in Wei's target region. In fact, it is surprising that the data agrees as well as it does considering the different experimental conditions under which the two sets of data were obtained. Figure 4.5

Figure 4.4. Comparison of $(1,1)$ and $(1,0)$ elastic intensity profiles from the clean tungsten (100) surface. .
Data includes profiles taken here at 60°C and -150° C and results reported by Wei 94 .

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Figure 4.5. Comparison of $(1/2,1/2)$ elastic intensity profiles from tungsten (100) surface after hydrogen adsorption into the β_2 state. Data includes profiles obtained here and results reported by Estrup and Anderson¹⁸ and Papageorgopoulos and Chen²¹.

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shows a comparison of elastic intensity profiles for the $(1/2,1/2)$ beam taken after hydrogen adsorption. From the general appearance of the data, Estrup and Anderson's profile 18 appears shifted up in energy about 5 eV with respect to the profile taken here. This suggests the possibility of a discrepancy in the energy measurement. The line shapes are similar, however, although Estrup and Anderson found one well-defined peak around 75 eV whereas in this work a peak at 67 eV and an additional shoulder between 85 eV and 90 eV is seen: Papageorgopoulos and Chen²¹ did not observe the large peak below 50 eV nor the double peaked structure above 100 eV reported by both other researchers. These discrepancies could easily be due to a residual magnetic field in the work of Papageorgopou1os and Chen. It can be concluded from these comparisons that control over experimental conditions is crucial for the reproduction of data.

Information on the actual configuration of the surface ion cores can be extracted from a sufficient set of elastic intensity profiles. $^{16}\cdot^{17}$ Although the data base is small here, a preliminary analysis of the clean tungsten data has been conducted by Duke, using a microscopic, quantum-field theory formalism of low energy electron diffraction.¹⁶ In this formalism, a model for the electron-solid interaction is used in an attempt to match theoretical line shape predictions to experimentally observed elastic LEED intensity profiles. An important feature of this microscopic approach is the strong interactions between the incident electron and valence electrons in the solid. The inelastic mean free path, $\lambda_{\rm ee}^{\vphantom{\rm e}}$, is about 3-8 $^{\vphantom{0}0}_{\vphantom{0}}$ for most materials for electron energies of $30 \le E \le 200$. As a consequence, electrons which are observed elastically have been backscattered within the first

several surface layers of the solid and hence, LEED elastic profiles are surface sensitive. Elastic backscattering of the electrons is described by short range, electron-ion core interactions. Information on the configuration of the surface ion cores is extracted from the elastic energy profiles by varying parameters in the theory and obtaining the best fit to the data. Theoretical analysis of elastic energy profiles from tungsten at energies above 100 eV is computationally difficult because of the large number of phase shifts needed to describe the electron-ion core scattering. Hence the experimental profiles were taken only for energies $E_{\text{pri}} \leq 125$ eV.

Comparisons of theoretical and experimental elastic intensity profiles for the $(0,0)$, $(1,0)$, and $(1,1)$ beams are given in Figure 4.6. The theoretical fit to the experimental data was made by taking an inelastic mean free path, λ_{ee} , equal to 8 Å and an inner potential V_1 , which represents the real part of the electron-electron interaction¹⁶ equal to 8 eV. The agreement in peak position is good for the $(1,0)$ beam in the range 25 eV \leq E \leq 125 eV and for the (1,1) beam in the range 60 eV \leq E \leq 100 eV. The theoretical and experimental line shapes of the $(1,0)$ beam show remarkable agreement, but the line shapes of the $(1,1)$ beam do not fit as well. For the (0,0) beam, the theoretical profile is not similar to the experimental plot except for the peak at 117 eV. Most of this discrepancy for the $(0,0)$ beam probably arises from the differences in theoretical and experimental incidence and aximuthal angles used to obtain the profiles. The theoretical profile was calculated assuming a primary electron beam normally incident; $experiments$ $ally$, this is not possible with the spectrometer used here since the (0,0) beam would not be visible on the LEED screen under these conditions.

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Figure 4.6. Comparison of theoretical and experimental elastic intensity profiles for clean tungsten (100) surface. Theoretical results have been calculated by Duke.

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Data has been obtained for the temperature dependence of clean elastic intensity profiles. No differences in the clean surface $(1,0)$ and (1,1) profiles taken at 60° C and -150 $^{\circ}$ C are seen even though the LEED pattern symmetry changes from a (lx) pattern to a $c(2x2)$ pattern. Apparently these two elastic intensity profiles are not sensitive to the scattering geometry changes that are manifested in the LEED pattern change.

It has been speculated $19,92$ that the extra half order spots may result from hydrogen on the surface. As shown above, the $(1,0)$ and $(1,1)$ profiles don't change even though the half order spots appear on cooling. This may not be surprising if the extra spots seen on cooling the undosed crystal are related to hydrogen on the surface. The cross section for hydrogen backscattering is very weak^{92,93} compared to scattering from tungsten. While a priori it is not necessarily true that the addition of a weak scatterer will have little effect on intensity profiles, this does seem to be the case for hydrogen adsorption onto tungsten. Adsorption of hydrogen has no effect on the $(0,0)$ profile from tungsten $(100)^{18}$ and it was found here that adsorption of hydrogen has very little effect on the (1,0) beam profile out to 0.15 monolayer coverage as can be concluded from Figure 3.21. On the other hand, it is true that adsorption of hydrogen did alter the $(1,1)$ beam. A second explanation for the extra spots seen on cooling the crystal is that they result from a tungsten surface reconstruction. No theoretical calculations have been performed which would indicate how reconstruction would affect the intensity profiles. The sensitivity of the profiles to an hypothesized surface atom reconstruction could be determined from calculations similar to those leading to the theoretical profiles given in Figure 4.6. Such a

theoretical calculation would be of interest as it would help evaluate how much credence should be given to a reconstruction hypothesis.

More than one atomic geometry may be associated with a given surface translational symmetry, i.e. associated with the same LEED spot pattern. Different geometries, however, would be manifested via differences in the intensity profiles associated with the same spot pattern.¹ After hydrogen adsorption to 0.15 monolayer at 60° C and -150°C, both the LEED pattern symmetry, c(2x2) and the elastic intensity profiles are the same. Thus this data would indicate hydrogen adsorbs into the same surface atomic geometry at the two temperatures. A comparison of elastic intensity profiles from the undosed and hydrogen dosed cold surface is given in Figure 4.7. The LEED pattern for both conditions has a c(2x2) symmetry. The profiles are not the same, particularly the $(1,1)$ profile above 100 eV and the $(1/2,1/2)$ profile below 50 eV. Hence the atomic geometry responsible for the two sets of profiles may be different, even though the observed pattern symmetry, $c(2x2)$, is the same.

The intensity dependence on temperature of the LEED beams has been observed. The intensity of integral order beams monitored from the clean surface increases with decreasing temperature as shown in Figure 3.24. The exponential temperature dependence obtained is predicted $22,95$ from a kinematic treatment of electron scattering in which thermal vibrations are included via an effective Debye-Waller factor. Experimental Debye temperatures, θ_{D} , can be calculated from the slopes of the straight lines in Figure $3.24.^{22,96}$

For the (1,0) beam taken with a primary energy of 110.5 eV, θ_{n} is calculated to be 280° K.⁹⁷ This is on the order of the Debye temperature for bulk tungsten 98 and higher than the Debye temperature of 183° K found by

Figure 4.7. Comparison of experimental $(1,0)$, $(1,1)$ and $(1/2,1/2)$ elastic intensity profiles from a cold tungsten (100) surface for hydrogen adsorption in the fast state (undosed surface) and in the β_2 state.

Estrup 13 for the (1,0) beam for intensities taken between 600 $^{\circ}$ K and 800 $^{\circ}$ K. The Debye temperature for the $(1,1)$ beam is calculated to be 410° K. The values of θ_D found here seem to be anomalously high, since calculations⁹⁵ indicate that the surface Debye temperature should be lower than the bulk Debye temperature.

The temperature dependence of the half order beam is not the same as found for the integer order beams. Figure 3.25 shows that the intensity of this beam increases at different exponential rates over two temperature regions. Down to about -75° C the intensity increase is exponential but with a steeper temperature dependence than observed with the integer order beams. Below -75° C the intensity increases at approximately the same exponential rate as the integer order beams. This same result is found at primary energies of both 42 eV and 115 eV. The effect is reversible with temperature. Yonehara and Schmidt¹⁹ measured the temperature dependence of the half order beams and fit their results to a straight line on a linear scale. However, for the data they took immediately after flashing to 2500 $^{\text{o}}$ K, an exponential dependence as found here appears to be as good, if not better, fit.

Below -75 \degree C, the half order beam intensity increases at approximately the same exponential rate as the integer order beams. This suggests that in this lower temperature region, the intensity increase can be explained by the Debye-Waller factor. However, between 100° C and -75[°]C, it is not known why the $(1/2,1/2)$ spots appear and then increase in intensity so strongly.

The intensity dependence on temperature of the $(1/2,1/2)$ beam below 0° C can be compared to the temperature dependence of the fast state H⁺ ion intensity. These data are given in Figures 3.12 and 3.25. Because the

 $H⁺$ ion yield from the fast state also increases with decreasing temperature, a possible correlation between the appearance of this ion signal and the appearance of the half order beams is suggested. It is tempting to hypothesize that the fast state is adsorbed into a $c(2x2)$ array and hence half order spots are produced on cooling. However, this connection probably cannot be made. For one thing, the estimated coverage of the fast state is several orders of magnitude below a coverage reasonably expected to exert an influence on the LEED pattern. In addition, while the fast state has a high total desorption cross section, with the ion signal decaying rapidly after turning on the electron gun, no evidence of this type of behavior is found for the LEED spot intensities if a corresponding experiment is made. A depletion of the fast state in the electron beam does not affect the half order LEED spot intensities. Finally, in the region below -75°C, the ion signal increases reversibly with temperature at a steep rate, while the LEED spot intensity increases reversib1y at a slow rate, i.e., the intensity correlation is not good in this range. These arguments do not refute the possibility that the half order spots are a hydrogen phenomena. They strongly indicate, however, that a correlation cannot be made between the hydrogen ions observed from the undosed surface and the appearance of the half order spots, aside from the obvious result that they both occur over the same temperature range. It would appear more reasonable to suggest that the formation of a $c(2x2)$ scattering symmetry on the surface, via reconstruction or some other mechanism, provides a binding site into which a species from the ambient can adsorb and, subsequent1y, be desorbed. The identity of that species is not known.

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4.5 Electron Scattering Results

Energy loss spectra for electrons scattered from the clean and hydrogen covered tungsten (100) surface are given in Figures 3.26 and 3.27. The second derivative mode has been employed in order to suppress background as discussed in Appendix B. Data have been presented for energy losses between 0 and 40 eV for a primary electron beam energy of 110 eV.

Several general comments can be made. A comparison of the clean spectra taken at the two temperatures shows they are nearly identical. The only difference is a slight enhancement in the low temperature data of the shoulder at $w = 7.5$ eV (barely evident in the figures). It might be noted that adsorption of hydrogen produces as peak at 7.5 eV, and the small change in the low temperature spectrum near this energy may be an indication of a small hydrogen coverage. An attempt was made to observe effects of the fast state on the clean spectrum. After cooling the crystal the fast state was allowed to populate by turning the gun off for adsorption times of 10 minutes. The spectrum taken after preparing the crystal in this way was identical to those obtained immediately after cooling. Hence fast state hydrogen does not perturb the electronic structure, unlike β state hydrogen. This result is not surprising because of the very low coverages calculated for the fast state from the desorption measurement.

Hydrogen adsorption into the β states perturbs the clean surface loss spectrum. The same changes are observed at both 60° C and -150° C. The most dramatic changes that occur with increasing coverage are the growth of a 7.5 eV loss, the movement down in loss energy of the structure at 21 eV in the clean spectrum, and the annihilation of the peak at 2.5 eV. In addition, the loss peak at 10.7 eV decreases in intensity somewhat.

Definite changes in the loss spectra are seen (for example, at $w = 7.5$ eV) for work function changes of 0.03 eV. This is a coverage of only 3 percent hydrogen, At coverages corresponding to a work function change of 0.15 eV, the 7.5 eV peak is well-developed and the 21 eV structure has moved down \approx 1 eV. While hydrogen is adsorbing at room temperature from 0 to 15 percent of a monolayer, half order spots develop in the LEED pattern. As noted before, half order spots also develop in the LEED pattern by cooling the crystal to -150° C. However, electron loss measurements from the cold, flashed surface don't show any changes that correspond to hydrogen on the surface. Thus no correlation can be drawn, using electron loss measurements, between the half order patterns obtained by hydrogen dosing and by cooling the crystal.

Interpretation of the structure in the energy loss spectra taken here is nontrivial. Although the data incorporates information on the electronic structure of the surface and near surface region, i.e. represents bulk and surface single particle transitions and collective oscillations, both theoretical and experimental complexities arise in attempting to extract electronic structure from the data. While the electron energy loss has been measured with high resolution, information on the momentum transfer, \vec{q} , involved in the electron solid inelastic interaction is not retained since 1) the analyzer integrates over a wide range of \overrightarrow{q} 's and 2) the backscattered electron has undergone at least two collisions - an inelastic scattering with an accompanying momentum transfer which is not enough to turn the electron around and an elastic scattering which does. Hence the analyzer is expected to be sensitive to loss mechanisms which are well-defined in energy but relatively independent of momentum transfer. Transitions satisfying these

conditions are possible in tungsten. Luscher has shown²⁵ that at least one relatively flat and narrow d-band in tungsten located near the Fermi level acts as the final state for electron excitations involving core electrons. This d-band may be operative as a final state for transitions involving valence and adsorbate electrons as well.

The structure at 21.0 eV and 25.5 eV has been identified²⁵ as resulting from surface and bulk plasmons, Adsorption of hydrogen increases the energy of the surface plasmon but does not affect the energy of the bulk plasmon.

The energy losses at 38.1 eV, 34.6 eV, and 32.4 eV remain constant as a function of hydrogen coverage. These losses correspond in both relative strengths and separation in energy to tungsten core electron excitations from the 5p and 4f (doublet) levels found in x-ray photoemission 99 at 36.9 eV, 33.3 eV, and 31.1 eV below the Fermi level. A comparison of these photoemission values to the energy losses observed here would indicate the position of the final state operative in the energy loss measurements is 1.3 eV above the Fermi level.

It would be convenient to use this value, 1.3 eV, for the final state energy in interpreting the rest of the sharply peaked structure arising from electron transitions. There are difficulties with such an approach, however. The data being compared in calculating the final state energy location have been obtained with two techniques that perturb the adsorbateplus-solid system in distinctly different ways. The observed energy losses in electron scattering are strongly influenced by interband oscillators, electron screening and relaxation effects, and these perturbations are not

constant as a function of loss energy. Hence, extension of the 1.3 eV value in interpreting data at other loss energies may not be valid. None the less, using the 1.3 eV final state, the peaks in the clean ELS spectrum at 2.5 eV and 4.0 eV would correspond to peaks in the photoemission spectra at 1.2 eV $(2.5 \text{ eV} - 1.3 \text{ eV})$ and at 2.7 eV $(4.0 \text{ eV} - 1.3 \text{ eV})$, respectively. There is no obvious correspondence between these peaks and structure seen in clean surface photoemission spectra.^{35,36} The structure changes on adsorption in the ELS spectra for $0 \text{ eV} \le w \le 4 \text{ eV}$ may reflect the sharp photoemission loss which appears at 2.5 eV as hydrogen coverage increases. The strong 7.5 eV energy loss which appears in the ELS spectra as hydrogen adsorbs onto the crystal would correspond to structure in photoemission data near 6.2 eV $(7.5 \text{ eV} - 1.3 \text{ eV})$. Recently, photoemission peaks at 5.2 eV and between 6.8 eV and 7.8 eV have been reported. 100 From these comparisons it can be seen that quantitative interpretation of the fine structure in the energy loss measurements cannot be made with this simple model.

CHAPTER 5

SUMMARY AND CONCLUSIONS

An experimental apparatus for surface research has been designed, constructed, and successfully placed in operation. It incorporates the necessary hardware and electronics for performing several complementary surface probing techniques, including Auger electron spectroscopy, retarding potential work function measurements, low energy electron diffraction, electron energy loss spectroscopy, and electron stimulated desorption of ions. System electronics allow the instrument to be easily switched between the techniques. The apparatus has been used to study the chemisorption of hydrogen on a tungsten single crystal surface over the temperature range $60^{\sf o}{\rm C}$ to -150 $^{\sf o}{\rm C}$.

The instrument combines an electron gun with an energy spectrometer, a LEED display system, and a crystal manipulator. The electron gun is capable of focusing a monoenergetic electron current of up to 21 μ A onto a macroscopic sample, The gun has been operated from 5 eV to 1800 eV. The high resolution, high sensitivity spectrometer consists of a retarding field analyzer in series with two electrostatic deflection analyzers. The energy resolution of the spectrometer is 2.1% without using the retarding field analyzer. This can be improved to less than 1% under some conditions by applying a retarding field. The spectrometer output can be detected using a watemeter or using modulation techniques. The instrument has been used to analyze electron and ion signals from the sample and to determine the charge to mass ratio of desorbed ions. The experimental sample, a tungsten crystal which has been polished to within 0.1° of the (100) face, is mounted on the

end of a crystal manipulator. The manipulator is used to position the sample, as needed. A two grid LEED display system has been used to study LEED pattern symmetry. The intensities of LEED spots have been monitored with a spot photometer.

The chemical composition of the surface layer has been characterized under experimental conditions using Auger electron spectroscopy. The Auger spectrum obtained after flashing the crystal to 2200° K is free of carbon and oxygen Auger structure. The electron gun could be operated under normal experimental conditions without contaminating the surface, but a carbon Auger peak appears if high gun currents and voltages are used. This effect can be taken into consideration when interpreting the data. Some weak structure in the Auger spectra from the flashed surface is seen between 475 eV and 525 eV. It is not possible to conclusively determine if this structure results from Auger transitions in tungsten or from some other source.

Retarding potential work function measurements have been made as a reproducible measure of hydrogen coverage. Adsorption of hydrogen onto the tungsten (100) crystal at 60° C yields a maximum work function change of $0.98 + 0.04$ eV. This is in good agreement with previously reported values. The work function change with exposure to hydrogen for the tungsten sample at -150 $^{\circ}$ C was found to be the same, within experimental accuracy, as found at higher temperature. The maximum work function change at -150° C is 0.92 \pm 0.04 eV. Cooling the flashed crystal from 220[°]C to -150[°]C resulted in an increase in the work function of approximately 0.05 eV. An intrinsic (clean surface) temperature dependence of this magnitude appears reasonable from theoretical considerations.

The time-of-flight technique employed for mass analysis was found to work well. Ion species H^+ and 0^+ , as well as H_2^+ , have been identified. Relative intensities of the ion yields could only be estimated with this technique as instrumented. H^+ ions are electron desorbed from the surface after adsorption of hydrogen. In addition, H^+ ions could be desorbed from the surface after a flash if the crystal was cooled below room temperature. No $_{12}^+$ ions were desorbed from the crystal. However, $_{12}^+$ and $_{1}^+$ ions, produced by ionization of the background and also by ESD from surfaces in the experimental chamber, were detected under certain operating conditions. This signal could be separated from the ions originating at the crystal surface by biasing the crystal several volts positive with respect to the spectrometer.

The distribution in energy of H^+ ions electron desorbed from a 60^oC tungsten (100) surface has been observed. The distribution has a normal line shape, with a peak intensity at $3.0 + 0.5$ eV kinetic energy and a half width of 2.6 eV. No evidence of distinct β_1 and β_2 adsorption states was found in the energy distribution line shape; the distribution is the same for coverages corresponding to both the β_2 adsorption state and the β_1 plus β_2 adsorption states. The intensity of the H^+ ion signal is coverage dependent. The dependence found here is in agreement with previously reported work. The maximum in intensity of the ion yield occurs for a work function change of 0.18 eV. The total desorption cross section for hydrogen ions from the β_{2} state is $5x10^{-20}$ cm².

An H^+ ion signal can be desorbed from the undosed (100) surface if the crystal temperature is lowered below room temperature. This represents a previously unreported hydrogen adsorption state. Experiments in which the pressure was carefully monitored indicate that this hydrogen results

from adsorption onto the crystal from the background. However, the state, labeled the fast state, is <u>not</u> populated by the adsorption of H_2 from the gas handling system. The adsorbing species that populates the fast state is not known. Hydrogen coverage in the fast state is estimated to be >10^{-4} monolayer, which is an extremely small coverage. The fast state hydrogen desorbs with a broad energy distribution which has a peak intensity at $2.5 + 0.5$ eV kinetic energy and a tail extending up to >9 eV. The total desorption cross section for H⁺ from this state is high, $1x10^{-17}$ cm². This is on the same order of magnitude as the cross section for desorption of the n hydrogen state. However, no evidence of CO or oxygen, contaminants which are associated with the μ state, was found. The techniques used to chemically characterize the surface were sensitive to about 1 percent of a monolayer, so these two contaminants could have been present at coverages less than 1 percent.

Hydrogen (H_2) dosed onto the low temperature surface co-adsorbs with the fast state in a separate, β state. This can be concluded from energy distribution and desorption curve measurements. The maximum ion yield obtainable from the low temperature surface occurs for a work function change of 0.11 eV. This is 0.07 eV lower than the maximum in the ion yield from the room temperature, hydrogen dosed surface. This difference may indicate that the mechanism responsible for the decrease in ion yield as the β_1 state fills is operative at a lower hydrogen coverage at low temperatures. An alternative possibility is that hydrogen coverage at the low temperature can not be measured by the same expression relating coverage to work function change as used at the higher temperature.

Low energy electron diffraction pattern changes, observed as a function of hydrogen coverage on the room temperature surface, are in agreement with those reported in the literature. The surface translational symmetry is strongly coverage dependent. The maximum in the c(2x2) pattern associated with the β_2 state occurs at a work function change of 0.15 eV for room temperature adsorption. If the crystal is flashed to $\approx 2200^{\circ}$ K and then cooled below room temperature, the (lxl) pattern characteristic of the clean surface changes into a $c(2x2)$ pattern. Since H^+ ions can be electron desorbed from the flashed surface if the crystal is cooled to this same temperature range, and since the β_2 state hydrogen is known to produce a c(2x2) pattern, it has been suggested that the low temperature c(2x2) LEED pattern may result from hydrogen on the surface. However, no evidence was found to support this hypothesis. The ions desorbed from the cold surface did not originate from the β_2 state, but from a distinctly different state, labeled the fast state. It is questioned whether the low coverage in the fast state is sufficient to produce half order LEED spots. There is no indication from the ELS measurements that hydrogen has diffused to the surface from the bulk. Electron energy loss spectra show almost no change on cooling the crystal below room temperature. These spectra are sensitive to electronic structure changes resulting from hydrogen adsorption of as little as 3 percent of a monolayer. The $(1,0)$ and $(1,1)$ LEED beam intensity profiles taken from the undosed surface are not changed by cooling the crystal. It would be of interest to compare this experimental result to theoretical elastic intensity profile calculations from both a normal and a reconstructed tungsten surface. This would help determine if reconstruction is a viable explanation for the cold surface,

c(2x2) phenomenon.

Low energy electron diffraction elastic intensity profiles for several beams have been reported from the clean tungsten (100) surface and from this surface dosed with hydrogen in the β_2 state. These profiles have been compared to published data where possible. Careful control over experimental parameters is essential in order to obtain agreement between the data. The clean surface intensity profiles have been compared to preliminary theoretical calculations. While fair agreement can be obtained, both experimental and theoretical problems must be solved before a reliable calculation of atomic geometry for the hydrogen overlayer can be made. A comparison of experimental profiles for the low temperature undosed and hydrogen dosed c(2x2) patterns suggests that the atomic geometries responsible for these identical patterns are not the same.

Electron scattering energy loss spectra have been presented as a function of hydrogen coverage. Changes in the electronic structure at the surface resulting from hydrogen adsorption are observed. Structure due to the surface and hulk plasmons are identified, and peaks due to tungsten Sp and 4f core level transitions can be identified by comparison to published photoemission data. Interpretation of other structure in the spectra requires more study.

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APPENDIX A

A tungsten, tungsten-26% rhenium thermocouple spot-welded to the side of the crystal is used to measure target temperatures. The thermocouple was calibrated against a copper-constantan standard. A low temperature, freezing slush of isopentane (2-methylbutane) was made in a dewar by adding liquid nitrogen. (Isopentane freezes at -159.89° C.) The solution was allowed to slowly warm up to room temperature over three hours, during which a semistatic calibration was made. The reference junction was kept in a slush of distilled ice water. The calibration is shown in Figure A.I.

Using an identical technique, a tungsten-S% rhenium, tungsten-26% rhenium thermocouple was also calibrated, as shown in Figure A.2. This thermocouple does not have an inflection point in the range 0° to -195 $^{\circ}$ C, and it is eight times more sensitive over the temperature range 0° to -150 $^{\circ}$ C than the tungsten/tungsten-26% rhenium thermocouple. A tungsten-S% rhenium wire should spot-weld to tungsten more readily than a pure tungsten wire. Thus, because of its increased sensitivity and ease of attaching to the tungsten crystal, a tungsten-S% rhenium, tungsten-26% rhenium thermocouple appears a better temperature sensor for low temperature research on tungsten.

In the apparatus used, the wires associated with the target manipulator, including the thermocouple leads, wind around the manipulator shaft to provide rotational motion. In order to get the .76 mm (.003 in) diameter thermocouple wires to wind smoothly around the shaft, it was found necessary to spring load them by turning a short segment of the wires into a 16 mm diameter spring. Unfortunately, the tungsten-5% rhenium wire available proved too brittle to turn into a spring and, thus, could not be used.

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Figure A.l. Calibration curve for W-5% *Re/W-26%* Re thermocouple.

 \mathcal{I}

Figure A.2. Calibration curve for W/W-26% Re thermocouple.

APPENDIX B

When operating the spectrometer in the electron mode at an effective pass energy E, the output current of the electron multiplier, N(E), is proportional to the electron current originating at the target with energy between E and $E + dE$ and with momentum in the acceptance solid angle of the analyzer. An energy distribution of the electron signal from the target can be measured by sweeping the effective pass energy of the instrument. This distribution consists of rapidly varying true secondary and characteristic loss structure interpretable in terms of electron transitions and collective oscillations in the target, plus a smoothly varying background. In order to separate the structure from the background, the energy distribution is electronically differentiated using a technique proposed by Harris. 67 A small sinusoidal oscillation is applied to the effective pass energy of the spectrometer, so that the energy of the electrons passing through the spectrometer oscillates around the instantaneous d.c. pass energy E_i . If the detected current N(E) is expanded in a Taylor's series around the energy $E_{\textbf{i}}^{\text{}}$, where the sinusoidal oscillation is $E-E_i = K \sin \omega t$, the first four terms are

$$
N(E) = N(E_{i}) + K \frac{dN(E)}{dE} \Big| \sin \omega t + \frac{K^{2}}{4} \frac{d^{2}N(E)}{dE^{2}} \Big|_{E=E_{i}} (1 - \cos 2\omega t)
$$
 (3.1)
+ $\frac{K^{3}}{24} \frac{d^{2}N(E)}{dE^{2}} \Big|_{E=E_{i}} (3 \sin \omega t - \sin 3\omega t) + ...$

Rearranging

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$$
N(E) = N(E_i) + \dots + \left(K \frac{dN(E)}{dE}\right) + K^3 \text{ term} + \dots \text{ } \text{sin wt}
$$
\n
$$
+ \left(\frac{K^2}{4} \frac{d^2N(E)}{dE^2}\right) + K^4 \text{ term} + \dots \text{ } \text{ } \text{cos 2wt} + \dots
$$
\n
$$
E = E_i
$$
\n
$$
E = E_i
$$

The coefficients of the sin wt and cos 2wt terms are found to be proportional respectively to the first two derivatives of N(E) providing K is small enough such that the higher order terms in K can be dropped. Under this assumption, a signal proportional to the first or second derivative of N(E) is obtained by synchronously detecting the appropriate harmonic of the output.

If a peak structure in the output signal is represented by a Gaussian, $G(E)$, centered at E_0 , and the background represented by a polynomial in E, B(E), then N(E) and the first two derivatives of N(E) evaluated at E^{o} become

$$
N(E) = B(E) + G(E)
$$
 (B.3)

N(E) = a + bE + cE² + ... +
$$
\frac{d}{\sigma(2\pi)^{\frac{1}{2}}}
$$
 e $\frac{-\frac{1}{2}(E-E_0)^2}{\sigma^2}$ (B.4)

$$
N(E=E_0) = a + bE_0 + cE_0^2 + \frac{d}{\sigma (2\pi)^{\frac{1}{2}}}
$$
 (B.5)

$$
\left. \frac{dN(E)}{dE} \right|_{E=E_{\text{O}}} = b + 2cE_{\text{O}} + \dots 0 \tag{B.6}
$$

$$
\frac{d^2N(E)}{dE^2}\Big|_{E=E_0} = 2c + \dots \frac{-d}{\sigma(2\pi)^{\frac{1}{2}}} \frac{1}{\sigma^2} \approx \frac{-1}{\sigma^2} G(E_0)
$$
 (B.7)

from the structure G(E). Extremum points in dN(E)/dE occur at $(E - E_0)^2 = \sigma^2$, From Equation B.6, the first derivative evaluated at $E_{\overline{O}}$ has no contribution if the background terms of order 3 or greater are not considered. Using this result in Equation B.6 gives

$$
\frac{dN(E)}{dE}\Bigg|_{E=E_0+\sigma} = b + 2c(E_0+\sigma) + \dots + \frac{-d(\sigma)}{\sigma(2\pi)^{\frac{1}{2}}}e^{-\frac{1}{2}} \qquad (B.8)
$$

The relation between the original signal, $N(E)$, and the synchronously detected signals can be seen from Equations B.4 through B.8. There is some background suppression in both modes. If N(E) is slowly varying, the higher order background terms that remain are small. The peak to peak height of the first harmonic signal is

$$
\frac{dN}{dE}\Bigg|_{E=E_0+\sigma} - \frac{dN}{dE}\Bigg|_{E=E_0-\sigma} = 4c\sigma + \dots - \frac{2d\sigma}{\sigma(2\pi)^{\frac{1}{2}}} e^{-\frac{1}{2}} \approx -2\sigma G(E-E_0+\sigma) \tag{B.9}
$$

The intensity of the second harmonic signal, evaluated at E_0 , is approximately proportional to $\frac{1}{\sigma^2} G(E_o)$. Hence, using the stated assumptions, the detected first and second harmonics of N(E) contain structure which is directly proportional to G(E).

The first derivative mode has been used in taking Auger data, as is commonly done. The second derivative mode has been used in looking at electron scattering energy loss measurements.

APPENDIX C

The process of desorption of ions from a surface by electron bombardment is referred to as electron stimulated desorption. The theory to account for this phenomenon was independently proposed by Redhead $^{37}\,$ and by Menzel and Gomer.³⁸ A brief explanation of their model follows.

In Figure C.l, schematic potential energy diagrams are given for the metal plus ground state adsorbate $(M + A)$ and metal plus ionic state $(M + A⁺)$ as a function of separation distance, x, of the adsorbing atom or ion from the metal surface. These two curves are labeled $V_G(x)$ and $V(x)$ for the ground state and ionic state, respectively. The nature of these interactions has been described 37 , 81 and several interaction calculations for hydrogen on metal surfaces have been given^{59,63}. The zero in potential energy in Figure 4.1 is defined as the energy of the ion A^+ at rest at infinity from the surface of M. The nucleus of the chemisorbed adsorbate is located at the minimum in the ground state potential energy curve. The wave function $\varphi_G(x)$ of the adsorbate in the ground state on the surface is shown centered at a position, x_i , which corresponds to the minimum in energy of V_{G} . V_{G} determines $\varphi_{\text{G}}(x)$. Vertical transitions from the ground state to the ionic state (labeled 1 in the diagram) are induced by incident electron bombardment of the surface. Secondary electrons leaving the surface also can cause such transitions. Once excited, the ion is subjected to a repulsive force and moves away from the surface (indicated by 2). The ionized adsorbate can be neutralized as it leaves the surface and hence desorb as a neutral (indicated by 3), or it can be de-excited back to the ground state and not desorb (indicated by 4). Ions

Figuze C.l. Schematic diagram of adsorbate-metal interactions, showing the transitions involved in the theory. of electron stimulated desorption.

that originate at $x = x_i$ leave the surface with energy $V(x_i)$. The energy distribution of the desorbed ions, $\mathrm{f(V(x_{i}^{,}))}$, is determined by the reflection 80 of the probability density distribution $|\phi_{G}(x_i)|^2$ through the ionic state energy curve. This can be given by the expression

$$
f(V(x_i)) = -N \sigma_{ex} |\varphi_G(x_i)|^2 \frac{P(x_i)}{\frac{dV}{dx}|_{x = x_i}}
$$
 (C.1)

where N is the number of species A adsorbed in the ground state per unit area, $\sigma_{\rm ex}$ is the cross section for excitation of the species A from the ground state to the ionic state (transition 1), $\varphi_G(x)$ is defined above, and $P(x_i)$ is the probability that an ion starts from the position $x = x_i$ and moves away from the surface without being neutralized. $P(x_i)$ can be given by 37,38,81

$$
P(x_i) = \exp\left(-\int_{x_i}^{\infty} dx \frac{R(x)}{v(x)}\right)
$$
 (C.2)

where $R(x)$ is the rate that the ions produced at the surface by electron impact are reneutralized. $v(x)$ is the velocity of the ion at a distance x from the surface. This depends explicitly on $V(x)$ as shown by Equation C.3 for an ion of mass M and charge q.

$$
v(x) = \left(\frac{2q(V(x_1) - V(x))}{M}\right)^{\frac{1}{2}}
$$
 (C.3)

Additional complexities, for example multiple initial and ionic states or electron induced state conversion, can be added to this simple mo'del.

The mass transport occurring at the surface during an ESD measurement can be described in a kinetic treatment which relates the observed ion signal to physical parameters characteristic of the experimental conditions. The change with time of the surface coverage per area of an adsorbate, dN/dt, is given by the rate of arrival of the adsorbate onto the surface minus the rate of desorption from the surface. In the simplest formulation of these processes, only adsorption from the background and desorption due to electron bombardment need be considered. The electron stimulated desorption flux of ions is assumed proportional to the electron current density, j_e , and to the surface coverage per unit area, N. The proportionality constant is the total desorption cross section $Q^t(N,E_{\text{pri}})$. $Q^t(N,E_{\text{pri}})$ is, in general, a function of both the coverage and the primary electron energy. For the simple model given above, the total desorption cross section is the sum of the ionic, Q^+ , and neutral, Q^n , desorption cross sections. The adsorption rate is equal to the striking rate times the sticking probability, s(N), which in general is a function of the coverage. The time dependence of N can now be written as

$$
dN/dt = s(N)\gamma P - \frac{j_e Q^C(N, E_{pri})N}{e}
$$
 (C.4)

where P is the partial pressure of the adsorbing species and γ is a constant equal to the number of molecules that strike unit area of the surface per unit time and pressure.

The measured electron stimulated desorption yield of A ions, i_{A^+} , is assumed proportional to the incident current i_e , the coverage of A per unit area, N, and the detection efficiency of the instrument G. The proportionality constant is the ionic desorption cross section $Q^+(N, E_{\text{pri}})$. (Since the only adsorbate being considered in this work is hydrogen, the subscript A will be replaced by H.) This relation for i_{H^+} can be written

$$
i_{H}^+ = i_e Q^+(N, E_{pri}) NG
$$
 (C.5)

Equation C.4 can be solved for N in closed form under certain simplifying assumptions. The dependence of the cross section on primary energy does not affect the form of the solution (if the primary energy is kept constant). Then $\operatorname{q}^{\operatorname{t}}$ can be written $\operatorname{q}^{\operatorname{t}}(\operatorname{E}_{\operatorname{pri}})$ if the cross section can be shown to be independent of coverage. This is not the case in general, so its validity for each metal-adsorbate system has to be examined. This is done in the text for H_2 adsorbed on W(100), so the assumption will be assumed here. Likewise, the sticking probability will be assumed independent of N. Equation C.4 can now be solved to yield

$$
N = N_{i}e^{-\frac{t^{2}}{T}} + \frac{es_{Y}P}{j_{e}^{0}}\frac{1 - e^{-\frac{t^{2}}{T}}}{r},
$$
 (1 - e^{-\frac{t^{2}}{T}}), (C.6)

N_i is the initial hydrogen coverage at $t = 0$ and τ is given by

$$
\tau = \frac{e}{j_e q^t (E_{pri})}
$$
 (C.7)

Combining Equations C.5 and C.6 gives for the H^+ ion yield

$$
\mathbf{i}_{H}^{+} = \mathbf{i}_{H_{equil}^{+}}^{+} + (\mathbf{i}_{H_{i}^{+}} - \mathbf{i}_{H_{equil}^{+}}^{+}) e^{-\frac{\langle \frac{t}{\tau} \rangle}{\tau}}
$$
(c.8)

where i_{H}^{+} is the initial ion yield at $t = 0$ and i_{H}^{+} is given by H_{equi1}^{+}

$$
i_{H_{equil}^{+}} = \exp PAG \frac{Q^{+}}{Q^{+}}
$$
 (C.9)

Equation C.8 shows that the H^+ yield decreases with time to a saturation value $i_{\text{tr}}+$. This decay of the ESD ion yield with time, is .
equil called a desorption curve. A semilogarithmic plot of $i_{H}^{+} - i_{H^{+}}^{+}$ versus time should yield a straight line, the slope of which is $-1/\tau$. From this slope and the definition of τ , the total desorption cross section characterizing the hydrogen binding state can be calculated.

If the hydrogen source is bulk to surface diffusion, a calculation of the dependence of coverage in the fast state on time and background pressure is considerably more involved. 40 Conceptually, such a diffusion process can be considered in two steps: 1) the diffusion of hydrogen from the bulk to just inside the surface or to a "near surface layer", and 2) the jumping from this configuration to surface sites. Diffusion from the bulk to the near surface layer could be described by Fick's law. If N' is the concentration of hydrogen in the near surface layer and N the surface concentration of hydrogen, then the time dependence of $N + N'$ due to bulk diffusion can be written as

$$
\frac{d(N+N')}{dt} = D \frac{dn}{dx}
$$
 (C.10)

where D is the diffusion constant for hydrogen in tungsten and dn/dx is the concentration gradient of hydrogen just inside the surface. The coverage, N, in surface sites will change as a result of hydrogen jumping from the near

surface layer to the surface, and vice versa. The rate of jumping to the surface, $d(N)/dt$, can be assumed proportional to the concentration, N' , and to some function, f(N), which describes the availability of surface sites. The diffusion rate to the surface from the near surface layer would also be exponentially dependent on an activation barrier energy, $E_{h,s}$. The reverse flux from the surface to the near surface layer can be written in an equivalent form. An expression for the change in surface concentration with time due to diffusion to and from the near surface layer can be written as

$$
\frac{dN}{dt} = C_{bs} N' e^{-E_{bs}/kT} f(N) - C_{sb} e^{-E_{sb}/kT} g(N')
$$
 (C.11)

The first term on the right-hand side represents the rate of diffusion from the near surface layer to the surface, and the second term represents the rate of diffusion from the surface back to the near surface layer. c_{hs} and c_{sb} are constants. E_{sb} and $g(N')$ correspond to E_{bs} and $f(N)$, respectively. A term representing depletion of the surface state due to incident electron bombardment, similar to the second term on the right of Equation C.4, could be added in Equation C.11. This has been omitted since only the case $j_e = 0$ will be considered here. In principle, an expression for N can now be obtained by solving Equations C.lO and C.ll. A general solution is not easily obtained. However, it is evident that the time dependence of N due to diffusion could realistically be similar to that expected from background adsorption. For example, for the isothermal case, if N' is assumed constant and $f(N)$ assumed equal to $(1 - N/N_{max})$, assumptions that are reasonable for small coverages, it can be shown from Equation 4.4 that N increases

exponentially in time to an equilibrium value. For N small this solution would be approximately linear in time, the same result obtained for the time dependence of background adsorption. However, background pressure doesn't enter into the above diffusion calculation. If the fast state phenomena is diffusion related, N would be expected to be independent of background pressure. This is different than the expected coverage dependence for adsorption from the background.

VITA

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