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Direct Observation of Atomic Exchange During Surface Self-Diffusion

by

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B.S., University of New Mexico, 2012

M.S., Physics, University of New Mexico, 2016

DISSERTATION

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Dedication

For Brigitte, Cora, and Maxwell.

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Abstract

The diffusion of adatoms across the (100) plane of iridium has been previously inferred to occur by an exchange mechanism based on site mapping. This study provides the first direct observation that surface self-diffusion can occur by exchange. Iridium enriched to $\geq 93\%$ ^{191}Ir was deposited onto an atomically clean and smooth $\text{Ir}(100)$ plane as observed in an atom probe field ion microscope. Following thermally activated surface self-diffusion the adatom was field desorbed and mass analyzed. Observation of the ^{193}Ir isotope in one-half of the cases demonstrates conclusively that atomic exchange can occur during surface self-diffusion.

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Glossary

APFIM	Atom probe field ion microscope.
FIM	Field Ion Microscope.
MCP	Microchannel plate.
TOF	Time-of-Flight.
UHV	Ultrahigh vacuum.
fcc	Face-centered cubic
bcc	Body-centered cubic

Chapter 1

Introduction

The vapor phase growth of crystalline materials is widely used in many technological applications, ranging from the microfabrication of microprocessors to the development of biological sensors. Over the last decade such fabrication processes have been pushed to the near atomic scale where continuous films, several nanometers thick, are required and self-organization is of interest in creating features such as quantum dots and nanometer scale surface templates for patterning. Clearly technology is working toward manipulating atoms and creating functional devices such as transistors and memory at the atomic scale [1, 2]. Because of this, an understanding of the processes that occur during atom transport and the growth of crystalline materials at the atomic level has become of great technological importance.

The dynamics of the surface diffusion of adatoms, the nucleation and diffusion of clusters, and the impact of adatom-step interactions are several key phenomena governing mass transport and the resulting crystal growth. This importance has led to their study at the atomic level for over 50 years [3].

The majority of atomic level studies seeking to address the most basic processes, such as the surface diffusion of adatoms and whether atomic exchange with the

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substrate might occur during surface diffusion of an adatom, have been conducted using the field ion microscope (FIM) to study heterogeneous systems, i.e. an adatom of a different element than the substrate atoms. This is because the FIM, even when compared to the more recent scanning tunneling microscope and its cousins, remains adept at such atomistic studies [4]. However, like the scanning tunneling microscope, the FIM, in general, has difficulty distinguishing the chemical nature of individual atoms and thus is insensitive to detecting adatom exchange with the substrate if it were to occur in surface self-diffusion.

The first evidence for exchange during surface self-diffusion was reported by Bassett and Webber in 1978 using the FIM [5]. They studied the diffusion of *Pt*, *Ir*, and *Au* adatoms on *Pt*(110). A ball model of a face-centered cubic (fcc) (110) surface is shown in Fig. 1.1. The fcc (110) surface is corrugated, as shown in the cross-sectional view in Fig. 1.1. Based on a hard sphere hopping model where a diffusing adatom moves between binding sites and the lattice atoms are fixed in place, it was assumed that adatoms would undergo one-dimensional diffusion, i.e. along the channels, on this surface as long as temperatures were kept to a range that would not give the adatom the activation energy necessary to hop over the channel wall. This hypothesis proved to be true for *Au* adatoms. However, *Pt* and *Ir* adatoms were observed to undergo two-dimensional diffusion. The activation energy for cross-channel diffusion was expected to be significantly higher than for diffusion along a channel, but the authors found the activation energies for the two processes to be comparable. They suggested the possibility that other mechanisms of diffusion needed to be considered to explain their observations. One of the suggested mechanisms was a concerted displacement of the diffusing adatom and a lattice atom from the channel wall in which the lattice atom moved into the neighboring channel while the original adatom occupied the now vacant lattice site in the channel wall, though they gave no firm theoretical basis for this hypothesis. It is perhaps not too surprising to find that an atom in a channel wall, with less near-neighbor bonds than atoms in the bulk, might

Figure 1.1: A ball model of cross channel diffusion on face-centered cubic $Ir(110)$ showing a) a top and cross-sectional view of a W adatom, blue, at a site in the channel of the surface. b) Top and cross-sectional view of the adatom in a lattice site in the channel wall and the displaced Ir atom, red, in the neighboring channel.

interact in concert with a diffusing adatom and become displaced.

The first and only direct evidence of diffusion by exchange in a heterogeneous system was reported by Wrigley and Ehrlich [6] for W on $Ir(110)$. In these studies a W adatom was deposited on the channeled $Ir(110)$ surface. Again, if hard sphere hopping was the only diffusion process available, then the expected diffusion would be one dimensional. However, cross-channel diffusion was observed in several instances using both Ir and W adatoms. W adatoms that had apparently undergone cross-channel diffusion were mass analyzed using the atom-probe field ion microscope (APFIM) and identified as Ir indicating that the W adatom had exchanged location with an Ir substrate atom from the channel wall. Though this directly showed exchange in one heterogeneous case, the result should not be immediately extended to the homogeneous case. As Bassett and Webber found, a particular adatom/substrate combination may show distinct behavior from another combination.

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Atomic exchange during surface self-diffusion on FCC (100) surfaces has been inferred from previous theoretical studies and FIM-based experiments. The FCC (100) surface is smoother than the (110) surface and the possibility of exchange on a smooth surface was surprising. In a theoretical model of Al adatoms diffusing on $Al(100)$, Feibelman predicted that an adatom and a substrate atom could undergo a "concerted displacement" in which the adatom descends into the lattice and the substrate atom is displaced upward to the surface at a second near-neighbor site [7]. Though Feibelman explicitly used the trivalency of Al in his calculations, the search for evidence of exchange mechanisms on FCC (100) surfaces began. Experimental results consistent with surface self-diffusion by exchange of Ir and Pt adatoms on their respective (100) -type planes was provided by mapping the visitation sites of single adatoms [8, 9, 10, 11]. If adatoms diffuse by hopping over substrate adatoms, then the expected site visitation map would form a (1×1) net of the lattice sites. However, the sites visited by a single adatom always formed a $c(2 \times 2)$ net as shown in Fig. 1.2, consistent with a model of diffusion by exchange. Fig. 1.3 is a ball model illustrating the exchange mechanism on $Ir(100)$.

Additional evidence was inferred from the activation energies for the diffusion of different elemental adatoms on the $Ir(100)$ surface. Fu and Tsong [12] found that for Ir and Rh adatoms on the $Ir(100)$ plane the activation energy for diffusion of Ir (0.74 ± 0.02 eV) was lower than that for Rh (0.80 ± 0.08 eV). The authors note that these activation energies are reversed to the order expected for hard sphere hopping given that on $Ir(100)$ the cohesive energy of a Rh atom (5.75 eV/atom) is less than that of an Ir atom (6.94 eV/atom). They suggest that the existence of exchange diffusion for $Ir/Ir(100)$ may explain the lower activation energy. Although the $c(2 \times 2)$ map of visitation sites and measurement of activation energies for different elemental adatoms provides strong inferential evidence of exchange diffusion, there still remained no direct evidence for atomic exchange in surface self-diffusion.

Figure 1.2: a) A site map of the diffusion of an *Ir* adatom on the *Ir*(100) plane. The data was taken over 514 heating periods of 20 s each at a temperature of 257.5 K. The thin lines are the c(2x2) net and the bold lines are connect all lattice sites of the substrate. b) The frequency of visitation for each site is shown. Figure taken from [8]

In my studies of atomic exchange during adatom surface self-diffusion a source of adatoms that has been highly enriched in a particular isotope of the elemental substrate was used. This preserves the homogeneous chemical nature of the system and makes it possible to directly detect exchange diffusion. For example, if adatoms undergo exchange diffusion, then regardless of which elemental isotope is deposited, mass analysis of the adatoms following surface self-diffusion should show the natural isotopic abundance of the substrate. However, if adatoms undergo diffusion by hopping, then mass analysis of the adatoms following surface self-diffusion should show the isotopic abundance of the enriched adatom source. An APFIM is used to both observe the diffusion of adatoms on atomically clean substrates, and to identify the isotopic identity of adatoms that have undergone surface self-diffusion. The technique developed utilizing the enriched material may answer many questions that remain regarding surface self-diffusion in different atomic environments.

Chapter 2 discusses the theoretical background regarding the operation of the APFIM, namely field ionization and field evaporation. In addition, the basic the-

Figure 1.3: a) A top view and a cross-sectional ball model of an adatom deposited on $Ir(100)$ and b) diffusion by exchange on $Ir(100)$. Note that the visitation sites form a $c(2 \times 2)$ net of the substrate lattice.

ory used to analyze single atom diffusion is also discussed. Chapter 3 describes the APFIM, custom-built for surface self-diffusion studies, in detail and describes the operational procedures used to study surface self-diffusion, including the use of the enriched isotopic material. Chapter 4 presents the results of calibration experiments used to benchmark system performance. Surface self-diffusion experiments showing the first direct detection of atomic exchange are discussed in Chapter 5. The description of future investigations of diffusion in homogeneous systems, i.e. same-element adatom/substrate combinations, and the necessary modifications to the instrument are discussed in Chapter 6. Chapter 7 concludes by summarizing the important

Chapter 1. Introduction

findings of my research.

Chapter 2

Theoretical Background

In this chapter the physics underlying the operation of the APFIM and random walk diffusion of adatoms are presented. The physical process underlying the atomic resolution capability of the FIM is field ionization. The theory of field ionization and field ion microscopy are discussed first. Then experimental aspects required to generate large electric fields, the field ionization of gas atoms, and image interpretation are presented. The related phenomena of field evaporation and its use as the basis of time-of-flight spectroscopy are considered. The chapter concludes with a description of the general theory used to analyze the diffusion of single atoms on crystal surfaces.

2.1 Field Ionization

Field ionization is a process in which electrons in a gas atom tunnel through a potential barrier that has been deformed by an external electric field. The process was first predicted by Oppenheimer in 1928 for a single electron in a hydrogen atom [13]. Of particular interest in his work is the case where the gas atom is near a metal surface that provides electric field. Fig. 2.1 shows a potential energy diagram for

the outermost electron in the gas atom.

Figure 2.1: Electron potential energy as a function of distance for a gas atom near the surface of a metal at zero temperature. The electric field, F , distorts the potential well of the electron, I_0 is the first ionization energy of the gas atom, ϵ_F is the Fermi energy of the metal, Φ is the work function of the metal, e is the elementary charge, and x_c is the critical distance for ionization of the atom.

As the atom nears the metal surface the deformation of the electron's potential well is further enhanced from the free space value by the image effects of the atom near the metal surface. The deformation of the potential barrier allows the electron to tunnel through the now finite barrier into the metal surface. However, at distances closer than a critical value, x_c , there are no available states in the metal for the electron to occupy. From Fig. 2.1, an approximate expression for x_c is given by

$$x_c \approx \frac{I_0 - \Phi}{eF}. \quad (2.1)$$

At or beyond the critical distance the electron may tunnel into an available state in the conduction band of the metal, near or above the Fermi level ϵ_F .

The field required for the process is of the order $\sim 10^{10}$ V/m and the tunneling probability is highly sensitive to the electric field [14]. If the image terms are ignored and the barrier is approximated as a triangle then an analytical solution for the tunneling probability at the critical distance can be calculated and is given by

$$D(x_c) = \exp \left(-6.83 \frac{I_0^{3/2}}{F} \left(1 - 2.4 \frac{F^{1/2}}{I_0} \right)^{1/2} \right) \quad (2.2)$$

where I_0 is the first ionization potential of the atom in eV and F is the electric field in V/nm [14]. Fig. 2.2 is a plot of 2.2 with $I_0 = 24.6$ eV, the first ionization potential for *He*, and a representative value of $x_c = 0.45$ nm [15]. The tunneling probability increases by an order of magnitude when the field is increased from 20 to 35 V/nm.

While so far the surface of the metal has been assumed to be planar, in reality the surface is composed of atoms. The local electric field around the apices of atoms will be enhanced and the field around interstices will be reduced. The tunneling probability is then larger in regions directly above atoms protruding from the surface of the metal. This enhancement makes it possible to image surface atoms.

2.2 Field Ion Microscopy

The field ion microscope, invented by Erwin Mueller in 1951 [16], is an ingenious application of field ionization. Figure 2.3 shows a schematic diagram of the essential features of a field ion microscope.

Figure 2.2: Tunneling probability for an electron in an atom at the critical distance from a metal surface as a function of electric field strength.

To generate the high electric fields necessary to field ionize gas atoms a metal specimen is formed into a very sharp needle, called a tip. The tip apex is typically ~ 100 nm in diameter. Recall that the electric field of a spherical conductor goes as

$$F \sim \frac{V}{R} \quad (2.3)$$

where V is the applied voltage and R is the radius of the sphere. To account for the fact that the tip is, to a good approximation, a hemisphere at the end of a cone, the field at the apex takes the following form

$$F \sim \frac{V}{kR} \quad (2.4)$$

where k is called the field reduction factor and typically ranges between 5 and 7 [15]. As an example, for a tip of radius 100 nm, field reduction factor of 5, and a field

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Figure 2.3: Schematic diagram of a field ion microscope. A sharp metal tip is raised to a positive potential relative to its surroundings and ionizes gas atoms. The positive gas atoms are accelerated away from the tip and collected by the channel plates for image intensification. The diverging beams provide geometric magnification of the surface of the tip.

strength of 25 V/nm the necessary voltage is 12.5 kV, easily achievable by typical laboratory equipment. The high electric fields required for field ionization do limit the choice of materials to those that can withstand the stress caused by the field without undergoing catastrophic failure [17, 18, 19].

The tip is mounted on a cold finger and placed in an ultrahigh vacuum (UHV) system. The tip is cryogenically cooled and a noble gas, typically either *He* or *Ne*, is introduced into the vacuum system and acts as an imaging gas. Noble gasses are

Figure 2.4: a) A ball model of the hemispherical apex of a bcc $\langle 110 \rangle$ oriented tip where each ball represents an atom. b) The most protruding atoms have been marked with phosphorescent paint and illuminated with an ultraviolet lamp. c) Actual FIM image of a bcc $\langle 110 \rangle$ W tip.

chosen as the imaging gas to avoid chemical interaction with the tip.

The large electric field polarizes the imaging gas molecules and they are drawn to the surface. The imaging gas atoms undergo a series of hops as they interact with the surface becoming thermally accommodated and losing much of their lateral velocity because of the cryogenic cooling of the tip. The size scale of the tip apex is such that local protrusions of atoms are significant and they intensify the local electric field above their locations. As imaging gas atoms lose energy they are field ionized in regions where the local field is highest over the protruding atoms.

The high positive potential of the tip creates an electric field that accelerates the positive imaging gas ions away from the surface. Because of the thermal accommodation and the loss of lateral velocity, the trajectories of the ions as they are accelerated by the field are nearly normal to the surface. Furthermore, the region of ionization is localized to the area just above the most prominent surface atoms [14].

Fig. 2.4a shows a ball model of the apex of a hemispherical bcc $\langle 110 \rangle$ oriented tip. The edges of terraces are regions where atoms protrude the most. Therefore these

Chapter 2. Theoretical Background

are the regions where field ionization of imaging gas atoms is most likely to occur. The normal trajectories of the ionized imaging gas atoms will diverge as they travel away from the tip. A microchannel plate (MCP) and phosphor screen assembly is used to view the beams of ions at a distance of a few centimeters away from the tip. The diverging ions form a geometrically magnified image of the surface of the tip. The magnification is $\sim 10^6$ [15]. Fig. 2.4b shows the most protruding atoms painted with phosphorescent paint. Fig. 2.4c shows an actual image of a $\langle 110 \rangle$ oriented W tip in a FIM. The pattern is recognizable from the ball model.

Essentially, only the boundary atoms on the edge of the terraces are imaged in Fig. 2.4c. This is because at the field used to obtain the image, the local radii of curvature of the roughly flat terraces are not sufficient to field ionize imaging gas atoms. However, if a single atom is deposited on a flat terrace, i.e. a plane, then the enhancement of the field in the vicinity of the atom can be such that it is imaged in the FIM, as shown in Fig. 2.5. Such atomic resolution has made the FIM the instrument of choice for single atom diffusion studies for nearly 60 years [3].

2.3 Field Evaporation

Field evaporation is the electric field induced removal of an atom from the surface of a metal. When distinguishing between the field induced removal of a substrate atom and an adatom the terms field evaporation and field desorption, respectively, are employed by convention, though the physical process is the same. Field evaporation occurs when the potential applied to the tip is increased beyond that required for field ionization. There are two commonly encountered models to describe the phenomenon of field evaporation. The first is called the image hump model and was proposed by Erwin Mueller [20]. While the image hump model has the benefit of providing analytical expressions from which estimates of evaporation fields can be made, the

Figure 2.5: Single atom adsorbed onto the top of the $W(110)$ plane is clearly resolved in the FIM. The dark spot to the right is a defect in the phosphor screen.

charge exchange model is considered to be more physically realistic [15]. To explain the charge exchange model, consider the potential energy diagrams shown in Fig. 2.6. Fig. 2.6a shows the potential energy curves for an atom adsorbed onto a surface and for an ion near the surface. The curves are separated by the first ionization energy, I , minus the work function, ϕ , which is the energy gained by the electron removed from the ionized atom as it enters the metal surface. Fig. 2.6b shows that an electric field has the effect of lowering the ionic curve such that there is now an anticrossing at x_c with an activation energy for field evaporation Q [21]. Thermal agitation can then cause the atom to become field evaporated and leave the surface as an ion.

Figure 2.6: a) Potential energy curves showing the adsorbed, $M+A$, and ionic, M^-+A^+ , states. b) The adsorbed and ionic states in the presence of an electric field. The electric field lowers the ionic state such that it crosses the adsorbed state. Figure from [21].

This model is sufficient to explain the field evaporation of singly charged ions, but it does not account for experimental observations of multiply charged ions. However, Kingham showed that after atoms are field evaporated it is possible for them to undergo further field ionization as they depart from the metal surface [22]. Calculations of expected charge states as a function of electric field agree quite well with experiment [15]. Estimates of the charge states of field evaporated ions are important for time-of-flight mass spectroscopy as will be described shortly.

The thermally activated field evaporation rate, Φ_{evap} is typically modelled as an Arrhenius process

$$\Phi_{evap} = \nu_0 \exp\left(-\frac{Q}{k_B T}\right) \quad (2.5)$$

where ν_0 is the frequency of vibration of the atom on the surface, k_B is Boltzmann's

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constant, and T is the temperature of the surface [23]. This expression shows that there are two experimental parameters that affect the evaporation rate. Increasing either the electric field, and consequently lowering Q , or increasing the temperature both result in an increased field evaporation rate. Both parameters were adjusted to achieve field evaporation in the experiments described in this thesis.

In practice, the electric field is increased for field evaporation in one of two ways, by raising the standing d.c. voltage, $V_{d.c.}$, or by briefly applying a positive voltage pulse, V_{pulse} , in addition to the standing d.c. voltage, to the tip. Slowly raising the standing d.c. voltage is useful in preparing atomically clean surfaces. Controlled field evaporation of entire atomic layers of the substrate is possible when using this method. The substrate surface is then that of the bulk terminated structure. When voltage pulsing it is possible to controllably field evaporate only one to a few ions from the surface in a well defined time period. This is the technique employed for time-of-flight mass spectroscopy.

2.3.1 Time-of-Flight Mass Spectroscopy

Field evaporated ions are accelerated away from surface of the tip by the electric field. If a grounded shield having an aperture through which ions may travel is placed in front of the tip, then the ions drop through a known potential difference before entering a field-free drift region beyond the aperture. The energy acquired from the field is neV , where n is the ionization state of the atom, e is the elementary charge, and V is the total potential applied to the tip, i.e. $V = V_{d.c.} + V_{pulse}$. If the region of acceleration is much smaller than the overall distance traveled by the ion to the detector then the energy acquired by the ion can be equated to the classical expression for kinetic energy

$$neV \approx \frac{1}{2}mv^2 \tag{2.6}$$

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where m is the mass of the ion, and v is the velocity as it enters the field-free drift region. Because the ion is not accelerated in the drift region, the substitution $d/t = v$ is made in equation 2.6, where d is the tip to detector distance and t is the time of flight from the tip to the detector. Upon rearranging, the mass-to-charge ratio of the ion is given by

$$\frac{m}{n} = \frac{2eVt^2}{d^2}. \quad (2.7)$$

The distance from the tip to the aperture in the grounded shield is small enough that atoms evaporated by the pulse travel the distance before the pulse ends. A detector with single ion sensitivity, such as a microchannel plate, is placed at the end of the field-free drift region. The tip to detector distance, d , and the total applied voltage, V , are measured before hand. Then the time-of-flight, t , is measured and the mass-to-charge ratio of the ions is calculated. After the detection of many ions, a histogram of the calculated mass-to-charge ratios is created. The charge ratio of evaporated ions depends solely on the electric field and not on the particular isotope. Therefore, the mass spectrum generated in this fashion shows the elemental abundances of the constituent elements in the tip, as well as the isotopic abundances of a single element. Comparison of a single detection with the mass spectrum can then be used to identify the elemental and isotopic nature of the evaporated atom. All experiments in this thesis were performed on elemental tips and the isotopic identity of evaporated ions were determined by comparison with mass spectra.

2.4 Atomic Diffusion

An atom adsorbed on a surface may undergo lateral movements while still remaining bound to the surface. The potential minima the atom moves between are typically

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interstices defined by the arrangement of surface atoms. For the crystal surfaces of metals studied in this thesis, the interstices form a well defined surface net of binding sites [24]. Surfaces prepared by field evaporation in the FIM are ideal for studying atomic diffusion for several reasons. The surface is atomically smooth, free from contaminants, and the surface is essentially the bulk terminated structure of the lattice.

Diffusion of adatoms on metal surfaces are modeled as random walks. The diffusion may be one or two-dimensional. All experiments discussed in this thesis were performed with surfaces on which the adatoms underwent two-dimensional diffusion. The relevant diffusion coefficient, D , for following the mean squared displacement of a single atom, rather than a collection of atoms, is called the "tracer" diffusion coefficient, defined by the following equation

$$\langle r^2 \rangle = 4Dt \quad (2.8)$$

where $\langle r^2 \rangle$ is the mean-square displacement and t is the time over which diffusion occurs [25]. From diffusion theory (see for example [26, 27]) the mean-square displacement is,

$$\langle r^2 \rangle = l^2 N. \quad (2.9)$$

where l is the jump length, and N is the number of jumps in the time interval. The number of jumps in the time interval can be estimated from transition state theory (see for example [28]) as follows

$$N = 2\nu t \exp\left(\frac{S}{k_B}\right) \exp\left(-\frac{E_a}{k_B T}\right) \quad (2.10)$$

where ν is the vibrational frequency of the atom, t is the time interval, S is an activation entropy, and E_a is the activation energy. Substituting expression 2.10 into 2.9, and comparing with 2.8 we see that

$$D = 2l^2 \nu t \exp\left(\frac{S}{k_B}\right) \exp\left(-\frac{E_a}{k_B T}\right). \quad (2.11)$$

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The expression for D is typically simplified as

$$D = D_0 \exp \left(-\frac{E_a}{k_B T} \right) \quad (2.12)$$

where D_0 is called the diffusion prefactor.

In diffusion experiments of single adatoms on metal surfaces the temperature is measured and the mean-square displacement is determined from FIM images. The determination of the mean-square displacement from FIM images is not trivial. The local magnification changes as a function of the local radius of curvature, which means the magnification over a single crystal plane is not constant. Accurate determination of the mean-square displacement requires hundreds of diffusion periods and the location of the adatom must be precisely determined after each period. Then the location of adatom binding sites is compared with the known arrangement of the binding sites of the plane to correct for variations in magnification and the mean-square displacement can be determined [29, 30].

If the process is repeated at several temperatures, an Arrhenius plot can be made from the data with the following equation

$$\ln \left(\frac{\langle r^2 \rangle}{4t} \right) = -\frac{E_a}{k_B T} - \ln(D_0). \quad (2.13)$$

This equation is a line with a slope of $-E_a/k_B$ and an intercept of $\ln(D_0)$. Typical values for a few representative elements and planes are shown in Table 2.1. Activation energies are typically in the range of 0.1 to 1 eV and the diffusion prefactors are typically within one order of magnitude of 10^{-3} cm²/s.

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Adatom/ Substrate(Plane)	Activation energy (eV)	Diffusion prefactor (cm^2/s)	Reference
<i>Ir/Ir(100)</i>	0.74 ± 0.02	$7.30 \times 10^{-3 \pm 0.5}$	[12]
<i>Rh/Ir(100)</i>	0.80 ± 0.08	$2.09 \times 10^{-3 \pm 1.5}$	[12]
<i>Ir/Ir(111)</i>	0.289 ± 0.003	$3.5(\times 1.4^{\pm 1}) \times 10^{-4}$	[31]
<i>W/W(110)</i>	0.92 ± 0.05	2.6×10^{-3}	[32]

Table 2.1: Activation energies, diffusion prefactors, and references are listed for four adatom/substrate combinations.

Chapter 3

Experimental Apparatus and Procedures

This chapter gives a general description of the experimental apparatus and experimental procedures used in single atom diffusion studies.

3.1 Atom Probe Field Ion Microscope

3.1.1 FIM Operation

Experiments were carried out in an all-metal, ultrahigh vacuum atom probe field ion microscope. The background pressure of the system was in the low to mid 10^{-10} Torr range after baking the system at $\sim 200^\circ$ C for two days. The instrument is shown in Fig. 3.1.

Two viewports were used, one for photographing of the FIM image and the other for entry of a laser beam into the system. The system was rough pumped by a

Figure 3.1: Photograph of the custom-built atom probe with the major components labelled.

turbomolecular pump, and then ultrahigh vacuum was achieved with an ion pump. A titanium sublimation pump was used to maintain low background pressures during FIM experiments when the ion pump was valved off from the system.

Substrates for the atom probe are made into a needle form using electrochemical polishing. First, a ~ 1 cm, section of the specimen material was cut from 0.005" diameter, polycrystalline wire. This section was spot welded to a 0.010" diameter molybdenum support loop.

Electrochemical polishing of metals has been thoroughly studied for use in transmission electron microscopy foils [33]. The same polishing techniques are used to form metal wire into needle tips. The solutions used for electrochemical etching depended on the substrate being prepared. The solution used for *Ir* was a 1:1 ratio

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by weight of molten KOH and $NaNO_3$. This solution was placed inside of an iron crucible. The sides of the crucible were covered with fire brick and heated using a Bunsen burner as shown in Fig. 3.2a. The temperature of the solution significantly affected the etching of the tips. Rough etching was done using ~ 7 V a.c. with the solution completely melted, a temperature of $\sim 1000^\circ$ C. The end-form is typically jagged and irregular as seen through a 100x optical microscope in Fig. 3.3. Final polishing was done at a lower temperature. This was done by lowering the burner output and allowing the solution to cool until a solid layer of material just began to form on the edges of the surface, as in Fig. 3.2b. At these lower temperatures the polishing is done at 2-3 V a.c. and the sharpness of the tip is checked repeatedly in an optical microscope. The process for Rh was identical except the solution was 4:1 $NaNO_3$ and $NaCl$ by weight and the rough etching was done at 5 V a.c. and the final polishing was done at 3 V a.c.

The solution used for W was a room temperature 5N solution of $NaOH$. The process for creating the tip blank was the same as described above. The tip was submerged and etched at 5 V a.c. until the end of tip was observed to dissolve. The rest of the tip dissolved rapidly after the end of the tip blank begins to dissolve. The process was judged by eye and the tip blank was pulled out of the solution when the length of the remaining tip was ~ 5 mm.

Tips were mounted to a liquid nitrogen cold finger for cryogenic cooling and manipulation. The cold finger had four Kovar electrical feedthroughs, two of which were not used. For ease of installation, spring coils were installed on the Kovar feedthroughs, as shown in Fig. 3.4. The coils were made from 0.005" diameter tungsten wire. The wire was coiled around a cylindrical form, bent 90° , and mounted on the Kovar feedthroughs. The ends of the molybdenum support loop were inserted into the coils and held in place by tension. This allowed for fine orientation of the tip prior to mounting on the system. While the apex of the tip is not fully visible in

Figure 3.2: a) Side view of the bunsen burner and fire brick used to heat the KOH and $NaNO_3$ solution. b) View of the tip mounted on the Mo support loop undergoing final polishing as the sides of the solution begin to cool.

an optical microscope small deviations in the wire's alignment with the apex could still be seen. The orientation of the tip could be fine tuned by adjusting the support loop's position in the coils.

An aluminum grounding shield with a 3 mm diameter aperture was placed ~ 4 mm in front of the tip. The shield serves to terminate the electric field created by the tip thereby creating a field-free drift region in the rest of the system.

In previous atom probe designs a goniometric stage was used to keep the tip to detector distance constant while still being able to adjust the orientation of the tip [34, 35]. We opted to use a different method to reduce the complexity of construction of the instrument, while still being able to manipulate the tip. The cold finger on which the tip is mounted is attached to welded bellows as shown in Fig. 3.1. Steel

Figure 3.3: a) 200x magnified view of the rough etched tip showing the jagged end form. b) 100x magnification of the tip after final polishing. The apex of the tip is too fine to be fully resolved in the optical microscope.

tabs were welded to the flange of the bellows. Clearance holes were drilled into the steel tabs to allow a 5/16" diameter threaded rod to run through. The rod is anchored into threaded holes drilled and tapped in a 4.5" to 6" reducer flange on the main body of the system. Nuts on the threaded rod support the steel tabs and allow the position of the cold finger, and thus the tip, to be manipulated. Fig. 3.5 shows a top view of the tabs used to align the tip. The tab on the right side of Fig. 3.5 is aligned with the axis of the drift tube. The two tabs on the left are 135° away on either side from the first tab. This method of tip manipulation changed the tip-to-detector distance, which was calibrated when accumulating mass spectra.

A single Hamamatsu model F1942 3" diameter microchannel plate provided image intensification for FIM imaging. The MCP was operated at 1 kV and the phosphor screen at 5 kV. The phosphor screen in the imaging plate assembly had a small spot of phosphor removed in the center. This spot was aligned with the axis of the drift tube and was used to align adatoms with the drift tube detector. It is visible in FIM images (see for example Fig. 2.5). The steel tab system mentioned above was manipulated until the image of the desired adatom was aligned with the dark spot,

Figure 3.4: Photograph of the tip mounted on the cold finger in the APFIM. The tip, Kovar feedthroughs, tungsten mounting coils, grounded shield, and deposition source are shown.

and hence with the axis of the drift tube. An angled front-silvered mirror mounted behind the channel plate allows for photography through a viewport. The MCP and the mirror were mounted to a rotary motion feedthrough that allowed them to be rotated 90° , similar to the atom probe design of Chambers and Ehrlich [35]. Ions field evaporated from the tip then have a clear line of sight to the drift tube.

3.1.2 Atom Probe

A voltage pulse was applied to the tip and the superposition of the pulse voltage and the standing d.c. voltage initiated field evaporation of ions from the tip. The pulse was provided by a Microwave Associates model 961 KV nanosecond pulse generator.

Figure 3.5: Top view of the steel tabs used for specimen manipulation.

The pulser utilizes a mercury wetted reed to achieve pulse rise times of ~ 1 ns. A charging line was used to provide a 40 ns pulse width. The pulse output is known to have a sharp overshoot at the leading edge of the pulse typically lasting ~ 5 ns due to reflections of the pulse in the system, as shown in Fig. 3.6. The pulse overshoot proves to be desirable for atom probe operation because field evaporation occurs preferentially during the overshoot and the evaporated atoms are allowed to acquire the full energy provided by the pulse before entering the field free drift tube [36, 15].

The pulse entered the system through a custom built voltage feedthrough shown in Fig. 3.7. The standing d.c. voltage was applied to the tip through a 10 M Ω resistor that protected the voltage source from current spikes and the voltage pulse. The pulse entered the system through a 2.8 nF 20 kV capacitor. A General Radio GR874 model CT-3 10% signal pickoff sent an attenuated signal of the voltage pulse to a Tektronix DPO 4054 oscilloscope and triggered a sweep. A 50 Ω load terminated the pulse line.

Figure 3.6: 40 ns pulse showing the characteristic overshoot at the leading edge.

The atom probe detector is a set of two Hamamatsu model F1942 3" diameter microchannel plates arranged in a chevron configuration. The chevron configuration increases the signal from a single atom detection and prevents a phenomenon called ion feedback where residual gas atoms inside the channels are ionized by the electrons emitted during a detection and are accelerated back to the input side of the channel plate where they hit the channel wall producing a second burst of electrons that can be mistaken for a second ion detection [15]. The chevron MCPs were operated at 1.5 kV and their phosphor screen (P47) at 5 kV. The open area ratio of the MCP was 0.60, meaning that a given ion had a 60% chance of striking an active channel. It is possible to apply a small positive voltage bias, ~ 15 V, to the input side of the MCP

Figure 3.7: a) Picture of the voltage feedthrough with the components labeled. b) Schematic of the connections in the voltage feedthrough.

and draw electrons emitted during an interchannel strike back into an active channel to increase the detector efficiency[37]. This method was applied during various single ion detection experiments. The phosphor screen installed with the chevron MCPs was capacitively coupled by a $500\ \text{pF}$ $20\ \text{kV}$ capacitor to an Ortec model VT120 preamplifier. The millivolt signals from the the screen [15] were amplified and an impedance matched signal sent from the preamplifier to the oscilloscope. The timing system for the atom probe is shown in Fig. 3.8.

3.2 Deposition Source

The isotopically enriched material was received from the distributor as a fine powder. Fig. 3.9 shows an image of the W powder taken with a scanning electron microscope. The grains were $<10\ \mu\text{m}$ in size. The enrichment levels were 93.14% for the ^{191}Ir

Figure 3.8: Schematic of the electrical timing system used in for time-of-flight mass spectrometry.

material and 95.10% for the ^{180}W material. Powder has a large surface area for the adsorption of atmospheric gasses. To test for contamination the ^{180}W material was tested using energy-dispersive x-ray spectroscopy. The resulting spectrum is shown in Fig. 3.10. The primary contaminant was O . Therefore the material required outgassing *in situ* to remove as many contaminants as possible.

The powder was suspended from a tungsten loop made from 0.011" diameter wire attached to electrical feedthroughs, shown in Fig. 3.11. The powder was cleaned by running current through the tungsten coil and heating the powder to $\sim 1600^\circ\text{C}$, as measured using an optical pyrometer. It was formed by wrapping the wire around a 0.0625" cylindrical form three times. The coil was spot welded to the electrical feedthroughs on the linear motion feedthrough. A drop of ethyl alcohol was placed inside the coil and held there by capillary action. A small amount of enriched powder was scooped up using the tip of a metal syringe and deposited into the alcohol. As the alcohol dried, the powder adhered to the tungsten support loop and the flange

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holding the entire deposition setup was quickly attached atom probe. If the alcohol dried completely the powder was very unstable to shocks and could be lost from the loop entirely. Once the flange was bolted onto the atom probe the system was pumped out with a turbomolecular pump. Once vacuum in the 10^{-5} Torr range was reached, current was run through the loop until the powder became incandescent. The exact temperature reached was not measured, but the color was observed by eye to be dull red. The purpose of the initial heating was to sinter the material together. After sintering, it was quite stable to shocks and movement with the linear motion feedthrough used to position the powder in front of the tip for deposition. The process used to deposit the material onto the tip is described in the next section.

Figure 3.9: Scanning electron microscope image of the enriched ^{180}W powder.

Figure 3.10: EDS analysis of the *W* powder showed that *O* was the primary contaminant.

3.3 Experimental Procedure for Diffusion Studies

The general experimental procedure for single atom diffusion studies was as follows. The cold finger was maintained at 78 K by liquid nitrogen. The tip was annealed by Joule heating to remove surface contamination and to remove irregularities that may persist after the polishing process. The isotopic adatom deposition source was also outgassed at $\sim 1600^\circ\text{C}$. The system was valved off from the ion pump and the Ti sublimation pump maintained low background pressure. Research grade (99.9999%) helium imaging gas was allowed into the system through a leak valve. The imaging

Figure 3.11: Deposition source installed in the atom probe. The enriched ^{191}Ir powder is sintered to the W support loop.

gas pressure for FIM operation was 5×10^{-5} Torr. The pressure was decreased during atom probe mass analysis to 5×10^{-6} Torr to reduce detection noise. The tip voltage was slowly raised until a FIM image was visible on the channel plates. Estimates of the best imaging voltage, i.e. the voltage at which there was maximum contrast between atoms, were made by eye, which usually only results in an error of 1-2% [15]. The tip surface as prepared by the annealing procedure was a thermally equilibrated surface and, in general, not atomically smooth. Field evaporation of the first few atomic layers of the tip left an atomically smooth and clean surface, which was stabilized by the cryogenic cooling of the tip [38]

Deposition was accomplished by heating the isotopically enriched powder using

Figure 3.12: The optical setup used to heat the deposition source and substrate. Path 1) was used for heating the deposition source and path 2) was used to heat the substrate.

a focused 1064 nm laser beam from a IPG Photonics model YLR-100 variable power ytterbium fiber laser. The laser included a red guide beam laser that could be used with the 1064 nm beam off. The guide beam was used to coarsely align the beam onto the deposition source without heating the powder. The temperature necessary for reasonable deposition was determined by vapor pressure curves [39]. For example, for *Ir* to have a vapor pressure of $\sim 10^{-6}$ Torr requires a temperature of 1900° C. Fig. 3.12 shows the configuration of the optical elements. The laser output was directed at a front silvered mirror. The laser had two orientations after the first mirror. For heating the deposition source the first path shown in Fig. 3.12 was used,

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and the second orientation was used to heat the tip, as will be described shortly. The beam was reflected from a coated infrared mirror through a 20 mm focal length plano-convex lens and a quartz viewport. The lens was used to focus the beam onto the deposition source. The beam could be focused very precisely and a small, well-defined region of the powder could be raised to the desired temperature. Fig. 3.13 shows the result of a test of the laser focus using unenriched W powder in which a small region of the powder was vaporized while leaving the surrounding material intact.

Figure 3.13: A test using unenriched W powder determined that the laser could be focused tightly and a localized region of the deposition source could be raised to temperatures necessary for deposition. In this test the laser vaporized a small area of the powder while leaving the surrounding area intact.

The deposition source was observed with an optical pyrometer, which served two purposes. First, the powder could be heated at low laser power to temperatures below those required for deposition, but high enough that the focused beam could be seen as a small, incandescent spot on the material visible through the magnified and filtered view of the pyrometer. The beam position could then be finely adjusted to heat any region of the deposition source. Second, once the beam position had been ideally placed the temperature reached by the powder could be verified with the pyrometer filament. Heating the source for 10 s at a distance of ~ 6 cm from the tip typically resulted in the deposition of between one and ten adatoms on the plane

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of the specimen, as observed using the FIM. The imaging field was carefully raised to field evaporate all but one of the deposited adatoms. The position of the adatom was photographed and the imaging voltage was turned off.

To initiate diffusion the tip temperature needed to be raised to ~ 250 K for *Ir(100)* experiments and ~ 380 K for *W* experiments. The tip was heated using the same laser used for deposition. To do this, the lens was removed from the beam path and the mirror was adjusted so that the apex of the tip was illuminated with the guide beam, shown as path 2) in Fig. 3.12. The tip was then illuminated with the 1064 nm beam and the beam placement was verified using an infrared viewer. It has been shown that FIM tips heated by a continuous wave laser reach the final temperature on μ s time scales [40]. Because the tip was not incandescent during heating, the optical pyrometer could not be used to determine the tip temperature. In principle the temperature could be calculated from measuring the mean-square displacements of many jumps of the deposited adatom. Given the known activation energies and diffusion prefactors for the planes studied in my experiments, however, this was impractical because of the time required to make such measurements. In practice, the laser power was adjusted until the adatom underwent a diffusion jump of one to a few lattice spacings. Based on previous studies of the activation energy for diffusion of *Ir* on the *Ir(100)* surface [12], this corresponds to a temperature of ~ 250 K. The average laser power was ~ 10 W (as indicated by the instrument control panel) and the heating period was typically 10 s. The tip was imaged again after heating. If the adatom had not undergone diffusion, determined by comparing photographs before and after heating, then the heating process was repeated until diffusion occurred.

Once diffusion was observed, the adatom was mass analyzed. To do so the tip position was adjusted until the adatom of interest was aligned with the dark spot on the FIM phosphor screen, as mentioned in section 3.1.1. The new position of the

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adatom was photographed and the imaging MCP was turned off and rotated to allow access to the drift tube. The chevron MCP was turned on and the adatom position identified and any final adjustments to the alignment with the chevron detector were made. The imaging gas pressure was reduced from 5×10^{-5} Torr to 5×10^{-6} Torr. The d.c. imaging voltage, $V_{d.c.}$, and the pulse voltage, V_{pulse} were adjusted so the pulse fraction, defined as $V_{pulse}/(V_{d.c.} + V_{pulse})$ was ~ 0.18 . The sum of the d.c. and pulse voltages was the evaporation voltage for the adatom on the plane and was estimated from the required voltage for the onset of evaporation of boundary atoms from the central plane. The choice of pulse fraction affects the leading edge of the voltage pulse. Higher pulse voltages from the Microwave Associates pulser corresponded to a larger overshoot at the leading edge of the pulse, as described in section 3.1.2. For a given evaporation voltage, it was found that a larger overshoot decreased the rate of multiple detections in a single pulse as only the adatom on the plane, and not atoms from the surrounding substrate, would evaporate under these conditions.

Voltage pulses were applied to the tip until the adatom was observed to desorb as seen on the chevron MCP. The imaging plate was rotated back into place and a photograph was taken of the surface to check for the evaporation of surrounding substrate material that could potentially have evaporated and also entered the drift tube. If the surrounding substrate was intact and only the adatom had been desorbed, then the imaging MCP was turned off and rotated out of the way. Mass analysis of the substrate was then performed. The purpose of mass analyzing substrate atoms was to acquire enough detections to form a mass spectrum to calibrate the detection of the adatom.

In general, the need to calibrate the mass spectrum in an atom probe arises from a number of processes. Errors in the measurement of the d.c. voltage, the measurement of the tip-to-detector distance, and a timing delay due to finite propagation

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time of signals in the electronics system all affect the conversion of time-of-flight measurements to mass-to-charge ratios. Another factor affecting accurate calibration of the atom probe's mass spectrum is the pulse factor [41]. There are reflections of the voltage pulse in the system because the tip constitutes an unterminated transmission line. The reflections can add constructively to the voltage reaching the apex of the tip. Many atom probe calibration procedures exist to account for the pulse factor [41, 15, 23]. The calibration is only correct for a finite range of masses, e.g. a calibration for the W^{3+} range will give incorrect results when applied to He [42]. The calibration is important if the purpose of the experiment is the identification of unknown elemental constituents of a tip, however, in all the experiments described in this thesis the constituent elements were all known. The errors in measuring the voltage and distance for a given tip position, the timing delay, and the pulse factor should be consistent between voltage pulses [41, 23]. To determine the isotopic identity of an adatom it was sufficient to compare the single detection to a mass spectra created with the same parameter configuration used during the desorption of the adatom.

Mass analysis continued until no further material could be evaporated. Often, this was not sufficient to generate a mass spectrum. To induce additional field evaporation the tip was pulsed while heated by the laser. The laser was set to the lowest possible power during this heating. If evaporation still ceased while voltage pulsing during laser heating and more data was needed, then additional material was deposited onto the tip from the deposition source. This approach inherently skewed the relative isotopic abundances found in the mass spectra, as will be discussed in Chapter 5, but the location of the mass peaks was the feature of interest and was not affected by the detection of isotopically enriched material. After acquiring a mass spectrum with identifiable peaks, the detection of the single desorbed ion from the central plane was compared and the isotopic identity of the desorbed adatom was deduced.

Chapter 4

APFIM Calibration Experiments

This chapter describes the results of experiments used to ensure the proper operation of the APFIM and to benchmark system performance. The primary performance parameter that was determined was the mass resolution of the APFIM, which is the system's ability to distinguish between two closely spaced mass peaks.

Two elements were used to test APFIM performance, *Rh* and *W*. *Rh* was used initially because it is monoisotopic and hence useful for testing the functionality of the instrument and determining mass resolution from a single peak. *W* was the second element chosen for system calibration. *W* has five naturally occurring isotopes and was used to test the APFIM's ability to distinguish between the isotopes of a single element, which are closely spaced in a mass spectrum. Of the five *W* isotopes, ^{180}W has the lowest relative abundance, $<1\%$, and is available in at enrichment levels of $\geq 95\%$. This isotope was also used to test the deposition method for enriched material.

4.1 Mass Resolution

In section 2.3.1 energy considerations were used to derive the expression for the mass-to-charge ratio of field evaporated ion

$$\frac{m}{n} = \frac{2eVt^2}{d^2}. \quad (4.1)$$

In practice the total evaporation voltage and the flight distance are known and the time-of-flight of the ions is measured. The average FWHM of the output pulse of the preamplifier, discussed in section 3.1.2, is 5 ns. As an example of the time resolution required by the instrument, consider a typical evaporation voltage of 8 kV. The difference in the calculated flight times of the doubly ionized ^{191}Ir and ^{193}Ir isotopes is 34 ns. The preamplifier peaks and the corresponding measured flight times should be well resolved for each individual isotope. The conversion to the mass-to-charge ratio is done later during data analysis. Small errors in the measured applied voltage and distance will introduce errors in the mass-to-charge ratio calculation, but they are consistent between evaporation pulses if the applied voltage and distance are held constant[15].

The largest variation occurs in the measured values of the flight time of evaporated ions. The spread in measured values arises because of the probabilistic nature of field evaporation. In the ideal case atoms are evaporated at the peak of the overshoot of the pulse, shown in Fig. 3.6. The remainder of the pulse allows them to acquire the full energy $neV = ne(V_{d.c.} + V_{pulse})$ prior to entering the field-free drift region. This results in the fastest possible measured flight time for the ion. It is possible, however, for the atom to field evaporate at any point during the pulse [23, 43, 42]. If the atom evaporates prematurely during the time the pulse is rising, or if it evaporates late in the pulse and the accelerating voltage ends before the ion enters the field-free drift

region, then the energy acquired by the ion will be less than neV , i.e. it will have an energy deficit compared to ions that evaporated at the peak of the overshoot. These energy deficient ions cause a tail in the measured flight times. A histogram of flight times for a single mass species of a given ionization state will show a sharp leading edge, corresponding to ions that are fully accelerated by the electric field, and a gradually decreasing tail that is the result of the energy deficient ions. When the mass-to-charge ratio is calculated the mass spectra show the same features as the time spectrum [15]. Fig. 4.1 shows a time spectrum where the peak shows the leading edge and the energy deficient tail.

Figure 4.1: Time spectrum of Rh showing the energy deficient tail characteristic of time-of-flight mass spectroscopy using the atom probe.

The temperature of the tip also impacts ion energy deficits. Ion energy deficits

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increase with increasing tip temperature because field evaporation is a thermally activated process. Typically the temperature of the tip was held at 78 K by thermal contact with liquid nitrogen in the cold finger. However, during the collection of ions to generate some mass spectra the tip was heated to initiate additional field evaporation at a given voltage. The increased temperature of the tip likely caused an increase in ion energy deficits. This will be discussed further in the next chapter.

The mass resolution of an atom probe is a measure of the spread of the mass peaks in the spectra and is defined as $\Delta m/m$, where Δm is the width of the peak at a given height, and m is the mass of the ion. The choice of what height to measure Δm varies between researchers, but commonly given values are the full width at half maximum (FWHM) and full width at tenth maximum (FWTM) [42].

The spread of the peaks in a mass spectrum affects the ability of the APFIM to identify individual atoms. If the tails of mass peaks do not go to zero before the next peak in a series, then the leading edge of the next peak is a convolution of the leading edge of that peak and the energy deficient tail of the previous peak. If the spread is too large, then the mass peaks will blend together and the individual isotopes are not resolvable. It was therefore necessary to show that the APFIM had the capability to distinguish the five W^{3+} mass peaks and the two Ir^{2+} mass peaks, the ionization states being chosen because they are the most commonly occurring ionization states for the respective elements at the fields used in the experiments described in this thesis [15, 23, 22].

4.2 *Rh* Experiments

Rh is a platinum group metal with atomic number 45. It has a face-centered cubic lattice structure and the only naturally occurring isotope is ^{103}Rh . The most commonly encountered charge state is Rh^{2+} [15, 23], therefore the expected mass-to-charge ra-

tio is ~ 51.5 . Two tip orientations occurred in approximately equal frequency after tip etching, (100) and (111) . There was no preference for tip orientation in early experiments because the mass resolution of the system was the desired measurement. No dependence of the mass resolution on the tip orientation was noted in these experiments, as expected.

Fig. 4.2 shows a Rh mass spectrum. Using the FWTM mass resolution protocol, the mass resolution of the system was found to be $\sim \frac{1}{41}$. To test the single atom sensitivity of the system a Rh adatom was deposited on the (111) plane, as shown in Fig. 4.3. The adatom was desorbed and a single signal was detected on the oscilloscope, as shown in Fig. 4.4. The width of the peak in a single detection is ~ 0.25 Da, corresponding to a spread for a single ion detection of $\sim 1/200$.

Figure 4.2: Mass spectrum of Rh used to determine the mass resolution of the system.

Figure 4.3: *Rh* adatom on the *Rh(111)* plane after deposition. The atom was aligned with the drift tube and mass analyzed.

To test that isotopically enriched material could be deposited and detected as expected, a ^{180}W deposition source enriched to $\geq 95.10\%$ was installed in the system. The procedure described in section 3.2 was used to ensure clean deposition. The laser was aligned and focused on the source. An average laser power of 12 W heated the tip to $\sim 2600^\circ\text{C}$, resulting in the deposition of an adatom onto the boundary of a *Rh(111)* plane, as shown in Fig. 4.5. The adatom was aligned and mass analyzed. Fig. 4.6 is a FIM image of the adatom using the chevron MCPs before and after desorption. Fig. 4.7 shows the detector signal from the pulse that desorbed the atom from the boundary, converted to mass-to-charge ratio. There were two peaks in the signal. Analysis of the two peaks indicates that one was *Rh* and one was ^{180}W ,

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without assuming the mass-to-charge ratio of the first peak. To see this recall that the mass-to-charge ratio for ions is given by

$$\frac{m}{n} = \frac{2eVt^2}{d^2}. \quad (4.2)$$

Let $M \equiv m/n$ and let subscript 2 denote the longer flight time and subscript 1 denote the shorter flight time. The ratio of the mass-to-charge ratios is then

$$\frac{M_2}{M_1} = \frac{t_2^2}{t_1^2}. \quad (4.3)$$

Taking the ratio of the squares of the flight times,

$$\frac{t_2^2}{t_1^2} = \left(\frac{4.223 \mu\text{s}}{3.91 \mu\text{s}} \right)^2 = 1.665 \quad (4.4)$$

Figure 4.4: *Rh* adatom detection showed the necessary single ion sensitivity for surface self-diffusion studies. The signal near zero is noise pickup from the pulse line.

Chapter 4. APFIM Calibration Experiments

and comparing with the ratio of M_i for the first two isotopic species of W^{3+} , 60 Da for $^{180}W^{3+}$ and 60.6 Da for $^{182}W^{3+}$, gives $60/51.5 = 1.650$ and $60.6/51.5 = 1.1779$, indicating that the adatom detected with a Rh atom was ^{180}W , as expected. This proved the capability of the laser ablation method for deposition of the isotopically enriched material onto FIM tip substrates.

Figure 4.5: a) A clean $Rh(111)$ plane. b) A W adatom incorporated into the boundary of the plane immediately after deposition.

Figure 4.6: FIM images from the chevron MCPs a) with the W adatom aligned and b) the plane boundary showing the adatom has been desorbed.

Figure 4.7: Detection of a Rh atom and a W adatom deposited from the enriched source during a single pulse. The Rh^{2+} detection is at $m/n=51.5$. Red lines are located at the expected m/n values for the W^{3+} spectrum. Comparison shows that the detected W atom was ^{180}W , as expected.

4.3 W Experiments

W has atomic number 74 and a body-centered cubic crystal structure. Only the (110) tip orientation is observed in etched W tips. Several experiments were conducted with W . The primary two that are discussed here are a test of the ability of the APFIM to distinguish the closely spaced mass peaks from the isotopes of a single element and a test of the laser for use in adatom diffusion. The five naturally occurring W isotopes and their relative natural abundances are listed in Table 4.1.

^{180}W	^{182}W	^{183}W	^{184}W	^{186}W
0.135%	26.41%	14.4%	30.64%	28.41%

Table 4.1: Naturally occurring isotopes of W and their relative atomic abundances [44].

Fig. 4.8 shows a mass spectrum of W generated with the APFIM. Although the tails of the mass peaks overlap somewhat with the rise of the next peak in the series, the location of the peaks themselves are distinguishable. The identification of individual atoms of ^{182}W and higher masses is difficult because there is not complete certainty that the location of the single atom detection is not an energy deficient ion from the previous isotope. Fortunately, the lowest mass isotope, ^{180}W , is available at enrichment levels of $\geq 95.10\%$ [45]. Thus, in any experiment that seeks to identify the deposited adatom, the ^{180}W should be readily identifiable, even if it is energy deficient up to the leading edge of the ^{182}W peak.

The laser was used to heat the substrate to initiate diffusion. Fig. 4.9a shows an adatom deposited on the $W(110)$ plane. The substrate was heated by the laser at ~ 10 W for 10 s between Fig. 4.9a-d. Each time the substrate was heated the adatom underwent diffusion over several lattice spacings. Only four are shown in Fig. 4.9, but the adatom underwent a total of thirty-two jumps before being lost from the

Figure 4.8: Mass spectrum of W^{3+} showing peak overlap and distinct peaks. The expected m/n for the W^{3+} peaks are marked with red lines.

plane. The loss of the adatom may have been premature field evaporation as the imaging voltage was raised, or it may have diffused over the step edge. The reason that the adatom stayed on the plane for so many heating periods is because of a reflective barrier potential near the edge of the plane known as the Ehrlich-Schwoebel barrier [46, 47]. Barriers to descent and the possibility of additional mechanisms of descent over step edges will be discussed further in Chapter 6. The long series of jumps of a single adatom showed that the laser could controllably heat the substrate to temperatures required for diffusion studies. The boundary of the $W(110)$ plane becomes mobile at 400 K [48]. The observation of some slight boundary change in combination with the number of heating periods compared to the data in [48] gives a rough indication that the temperature of the tip was between 370 and 400 K. This is above the temperatures needed to initiate diffusion on Ir surfaces, ~ 260 K, thus proving the laser capable of tip heating for all substrates.

Figure 4.9: a) W adatom deposited on the $W(110)$ plane. b)-d) the adatom has changed position after a 10 s heating period at 11 W of laser power. The temperature was likely in the 370-400 K range.

Chapter 5

Direct detection of atomic exchange on *Ir/Ir(100)*

5.1 Introduction

The diffusion of single atoms on crystal surfaces is a fundamental process governing crystal growth and the resulting technical applications. The importance of surface diffusion and its effect on the macroscopic qualities of crystals was recognized as early as 1932 by Langmuir and Taylor [49, 50]. Studies of the diffusion of single adsorbed atoms on crystal surfaces would have to wait for the invention of the FIM. In 1966 Ehrlich and Hudda used the FIM to study the motion of *W* adatoms on several *W* surfaces [46]. Studies of single atom diffusion were continued and the model of diffusion used was that of hard sphere hopping of an atom between binding sites [51].

It was not until 1978 that the work of Bassett and Webber indicated that alternative mechanisms of diffusion were possible [5]. In their study they found that *Ir* and *Pt* adatoms on the FCC *Pt(110)* plane underwent two-dimensional diffusion, in contrast to *Au* atoms that only underwent diffusion in one-dimension. A ball model

of the FCC (110) plane is shown in Fig. 1.1. The surface is corrugated and the Au adatoms underwent diffusion along the channels in the $[1\bar{1}0]$ direction. Estimates of the activation energy based on hard sphere hopping for the cross-channel diffusion observed for Ir and Pt adatoms are higher than those for diffusion solely along the direction of the channels, but the experimental values in the study were found to be comparable to the activation energy for the diffusion of Au . The authors proposed a model for diffusion in which a Pt lattice atom in the channel wall spontaneously diffuses into a channel, leaving a vacancy for the diffusing adatom to occupy. However, no mechanism for the spontaneous creation of the vacancy was proposed [5].

The first direct observation of the concerted movement of a diffusing adatom and a lattice atom in a channel was presented by Wrigley and Ehrlich for a W adatom diffusing on the $Ir(110)$ plane [6]. Ir also has an FCC structure. Cross channel diffusion was observed after the deposition and diffusion of a W adatom. Using an APFIM the authors found that the atom in the neighboring channel after the observation of cross-channel diffusion was indeed an Ir atom, indicating that the W adatom had moved into a lattice site in the channel wall.

The possibility of exchange diffusion on smoother surfaces than FCC (110) was proposed by Feibelman and Peter in 1989 and was published in 1990[7]. In this study density functional theory calculations showed that for surface self-diffusion in the FCC system $Al/Al(100)$ diffusion by exchange was more energetically favorable than diffusion by hopping. The argument made by the author is that a concerted movement of the adatom and a substrate adatom would maintain more chemical bonds during the process. If diffusion only proceeded by exchange then a site map of adatom visitation sites would form a $c(2 \times 2)$ net of the lattice structure, as shown in Fig. 1.3. Although the author explicitly invokes the trivalency of Al in his calculations, he expresses the importance of chemical considerations in the diffusion mechanism on other FCC (100) surfaces, such as on $Ir(100)$ [7].

A possible explanation for the exchange mechanism on other FCC (100) surfaces was presented by Kellogg, Wright, and Daw in 1991 [52]. In their experiments the authors observed the diffusion of *Pt*, *Pd*, and *Ni* atoms on *Pt(100)*. They found that *Pt* adatoms diffusing on this surface formed the c(2x2) net predicted by Feibelman, while the *Pd* adatoms diffusing on the same surface formed a (1x1) net of the substrate lattice. It seemed likely that *Pt* diffused by exchange, while *Pd* diffused by nearest neighbor hopping. Using embedded atom calculations, the authors hypothesize that surface relaxations induced by the adatom on the atoms surrounding it may initiate the exchange mechanism for FCC (100) surfaces.

Experimental studies of surface self-diffusion of *Ir/Ir(100)* began with the work of Chen and Tsong [8]. The site map of the *Ir* adatoms did form a c(2x2) net of the substrate lattice, as predicted. More detailed work by Fu and Tsong confirmed that the site map was a c(2x2) net of the substrate lattice, in contrast to the site map of *Rh* adatoms diffusing on *Ir(100)* which formed (1x1) net of all available binding sites [12]. In the same study the authors also determined the activation energy and the prefactor for diffusion for single adatoms of both *Ir* and *Rh* diffusing on the *Ir(100)* plane. Estimates for the activation energy based on hard sphere hopping the two adatoms indicate that *Rh* adatoms should have a lower activation energy than *Ir* adatoms because *Rh* has a lower cohesive energy (5.75 eV/atom) than *Ir* (6.94 eV/atom). The actual order was found to be reversed with *Ir* having an activation energy of 0.74 ± 0.02 eV and *Rh* having an activation energy of 0.80 ± 0.08 eV. These facts are consistent with a model of surface self-diffusion by a different mechanism than hard sphere hopping.

The evidence from these studies is consistent with a model of surface self-diffusion by the exchange of an adatom with a substrate atom, but the evidence remains inferential. This chapter reports the first direct observation of surface self-diffusion by an exchange mechanism.

5.2 Isotopically Enriched ^{191}Ir

To determine the mechanism of surface self-diffusion on $Ir(100)$, a reliable way of "labeling" Ir adatoms is necessary. The FIM has been used to distinguish the movement of adatoms in heterogeneous systems [53], but it is incapable of directly identifying whether or not exchange has occurred. The APFIM has been used to directly observe exchange diffusion in heterogeneous systems as mentioned in the previous section, but to date has not been used to study the homogeneous case. However, the APFIM is fully capable of studying surface self-diffusion in conjunction with the use of isotopically enriched material. The two naturally occurring isotopes of Ir , ^{191}Ir and ^{193}Ir , have relative atomic abundances of 37.3% and 63.7% respectively [54].

In the experiments reported in this thesis, an enriched source of ^{191}Ir was used for deposition. The enrichment level of the source was 93.14% [55]. If one assumes that diffusion on the $Ir(100)$ surface occurs by hopping, then the isotopic abundances of the adatoms detected using the APFIM following surface self-diffusion should be the same as the source, 93.14% ^{191}Ir and 6.86% ^{193}Ir . If one assumes that adatoms undergo diffusion by exchanging with substrate atoms, then several possibilities exist. The probability to deposit a ^{191}Ir atom onto the surface is 0.9314, and the probability to deposit a ^{193}Ir atom is 0.0686. The substrate is composed of a mixture of the two isotopes, each occurring with their natural atomic abundance. Therefore, the conditional probability of detecting ^{191}Ir after exchange is 0.37 and the probability for detecting ^{193}Ir is 0.63, regardless of which isotope is deposited first, and therefore the abundances of the detected adatoms would match the abundances of the substrate atoms. Fig. 5.1 shows a tree diagram summarizing the probabilities of detecting ^{191}Ir and ^{193}Ir after deposition from the enriched source.

Figure 5.1: Probability tree diagram showing the probabilities to detect ^{191}Ir and ^{193}Ir given the deposition of a particular isotope, assuming that the deposited adatom exchanges with substrate atoms.

5.3 Experimental results

The experimental procedure used to study surface self-diffusion is described in section 3.3. Fig. 5.2a shows an Ir adatom deposited on the surface. Fig. 5.2b shows the adatom's displacement due to thermally activated surface self-diffusion. Diffusion of a few boundary atoms can also be seen, which is expected because boundary atoms begin to diffuse along the step edge at lower temperatures than those required for adatom diffusion across the Ir(100) plane [11]. Following diffusion, the adatom was field evaporated and mass analyzed. Measurements of six adatoms show that after surface self-diffusion one-half were ^{191}Ir and one-half were ^{193}Ir as shown in Fig. 5.3a, which approximately matches the natural abundances of the substrate. The probability that this is the result of the deposition of three ^{193}Ir atoms in six trials with hard sphere hopping on the surface can be calculated. The deposition of

Figure 5.2: FIM image showing (a) ^{191}Ir adatom deposited on the $\text{Ir}(100)$ surface. (b) The adatom following displacement by thermally activated surface self-diffusion.

adatoms from the source are independent events as they do not rely on the previous deposition. There are only two outcomes from deposition for Ir , hence the deposition of adatoms constitutes a Bernoulli trial [56]. The Binomial distribution can therefore be used to calculate the probability of depositing $k = 3$ ^{193}Ir atoms in $n = 6$ trials. Let a successful trial be the deposition of a ^{193}Ir atom with a probability of $p = 0.0686$, and a failure be the deposition of a ^{191}Ir atom with probability $q = 0.9314$. Then we find the probability from the Binomial distribution

$$P(3) = \frac{n!}{k!(n-k)!} p^k (1-p)^{n-k} = \frac{6!}{3!3!} 0.0686^3 \cdot 0.9314^3 = .0052 \quad (5.1)$$

This means that it is highly improbable that the adatoms are undergoing diffusion by hopping and the measured abundances show conclusively that Ir adatoms diffusing on the $\text{Ir}(100)$ plane do so by atomic exchange. Fig. 5.3a shows the adatom mass spectrum with the noise subtracted.

Fig. 5.3b shows the calibration spectrum used to identify the adatom mass.

There are two features to note. First, because the removal of adatoms was done in the presence of the helium imaging gas, additional peaks appear in the mass spectrum corresponding to the doubly charged helide compound $IrHe^{2+}$ for each isotope as expected from previous studies [57]. Second, the isotopic abundances of the Ir species match the natural abundance of the substrate, as expected. The $IrHe$ species show a larger proportion of the ^{191}Ir helide. This is likely due to the fact that in order to collect enough ions for a mass spectrum following the detection of a desorbed adatom additional ^{191}Ir atoms were deposited from the enriched source and desorbed in the APFIM. It is interesting to note that only the proportion of the helide species of ^{191}Ir is enhanced.

The precise uncertainty associated with the measured time of flight of each individual ion is difficult to determine. Ideally, hundreds of measured flight times of adatoms deposited on and desorbed from the top of the central plane under identical conditions would determine the total fraction of energy deficient ions, and therefore the probability that any given ion would be energy deficient. However, this is impractical because the evaporation voltage ranged over several hundred volts and because of the time required to perform such calibrations. In practice, the choice of pulse fraction and careful estimation of the voltage for the onset of evaporation were made to increase the probability that the evaporation of an adatom from the central plane only occurred during the overshoot on the leading edge of the voltage pulse, as discussed in section 3.3. The probability for field evaporation is exponential in the applied electric field. The pulse fraction was chosen to be ~ 0.18 , which for a typical evaporation voltage of 8 kV corresponds to $V_{d.c.} = 6.5$ kV and $V_{pulse} = 1.5$ kV. An overshoot on the order of 100 V at the leading edge of the voltage pulse should be sufficient to ensure that evaporation occurs only during the overshoot. Empirically, in cases where one or two ions were evaporated and detected from a single pulse, the mass-to-charge ratio was always reasonably close to an expected value. If two ions were detected after a single pulse was applied, then the ratio of the squares of the

flight times was calculated, as mentioned in section 4.2, and no significant deviations from expected mass-to-charge values were noted.

The direct observation of diffusion by exchange in surface self-diffusion confirms the hypotheses of several previous studies and underscores the need for deeper consideration of diffusion processes. While Ir remains a commonly used element in technical applications, such as in catalysts [58], and the confirmation of diffusion by exchange allows models of self-diffusion on $Ir(100)$ to focus on that mechanism in calculations, it highlights the fact that the chemical nature and interaction of diffusing adatoms and surfaces cannot be neglected. Such interactions give rise to unexpected mechanisms of atom transport. If a combination of exchange diffusion and surface hopping occur, then site mapping may not give any indication of the exchange process and may be much more prevalent than current evidence indicates. Surface self-diffusion is the most fundamental system of adatom diffusion and the determination of different mechanisms of adatom movement in this fundamental case warrant further research.

Figure 5.3: a) Mass spectrum of the adatoms observed following deposition of ^{191}Ir and subsequent surface self-diffusion. The detections of ^{193}Ir show that the deposited ^{191}Ir adatoms underwent atomic exchange during surface self-diffusion. b) Mass spectrum used to calibrate the atom-probe.

Chapter 6

Future Work

The method of using isotopically enriched material described in this thesis can be used to investigate a number of unanswered questions regarding surface self-diffusion. Prior to describing these experiments, necessary modifications to the APFIM to improve system performance for these experiments are discussed.

6.1 APFIM Improvements

This section describes two major improvements to the APFIM that allow the study of additional diffusion phenomena. The first improvement is finer temperature control, which is achieved by using Joule heating and resistance thermometry. The second is the installation of a rotatable aperture in the drift tube.

6.1.1 Temperature Control

Using the same laser for heating the deposition source and for heating the tip necessitated moving the beam often during an individual experiment. The exact placement

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on the deposition source was determined using the optical pyrometer as described in Chapter 3. There was uncertainty about the exact beam placement when moving the laser to the tip for heating. The guide beam and the infrared viewer did aid in positioning of the beam, but it was difficult to get the laser to the exact orientation that had previously been used for heating. Additionally, if the tip was moved then incidence of the beam on the tip changed. This resulted in only a coarse control of the temperature. Coarse control was sufficient to initiate diffusion of adatoms, but finer control will be needed when investigating the descent of adatoms over step edges.

The conventional approach to heating tips in FIM studies of adatom diffusion utilized Joule heating and resistance thermometry to directly measure the temperature of the tip [32, 59]. In this approach fine wire leads are spot welded to the *Mo* support loop on each side of the tip. These potential leads are used to determine the resistance of the loop using Ohm's law. Current is run through the loop causing Joule heating and a rise in the resistance of the loop. A feedback circuit adjusts the current to raise the loop to a known temperature accurate to within a few K for any desired time interval [38].

The use of the laser for tip heating was chosen over this approach to maintain a $50\ \Omega$ impedance as close to the tip as possible. This is because the end of the tip constitutes an unterminated transmission line and reflections of the evaporation pulse distort its shape at the apex of the tip [36]. The potential leads would be connected to the two unused Kovar feedthroughs mentioned in chapter 3. The effect of the additional connections on the shape of the voltage pulse reaching the tip was unknown.

To utilize the Joule heating method, studies would be necessary to determine a voltage feedthrough design that preserves the shape of the pulse to the degree necessary for APFIM experiments. Direct measurement of the pulse shape reaching

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the apex is possible using field emission. Field emission, in a basic sense, is field ionization in reverse. A large negative potential is applied to the tip. This distorts the potential energy barrier in which electrons in the metal are trapped. It is then possible for electrons to tunnel through the potential barrier into free space [14]. The shape of the pulse reaching the tip can be determined by measuring the field emission characteristics of the tip during the voltage pulse, as described by Panitz and Walko [36].

The potential leads would be attached and a different high voltage feedthrough connector would be constructed for the cold finger to attach the feedback circuit to the tip. The connector would be removed during pulsing so the only additional connections to the tip would be the potential leads and the two additional Kovar feedthroughs. The shape of the pulse reaching the apex of the tip with the additional connections would have to be measured to ensure that the pulse shape would not be distorted to an unusable shape. The signal pickoff on the voltage hood is insufficient for this purpose because it measures the pulse before it enters the system and reflects from the tip.

6.1.2 Rotatable Aperture

In the initial configuration of the APFIM a 0.6" diameter aperture was installed at the entrance of the drift tube in addition to the small aperture in the grounded shield in front of the tip. The purpose of the aperture was to allow the passage of a field evaporated adatom into the drift tube while precluding any possible off-axis field evaporated ions from entering the drift tube. The aperture worked for this purpose, but it was found that the collection of mass spectra was hindered by the presence of the aperture. During the removal of substrate material to generate calibration spectra, only a small area of the tip was aligned with the drift tube. Combined with

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the low evaporation rates mentioned in Chapter 3 this made it difficult to acquire sufficient data for an accurate mass calibration.

The aperture was removed for the *Ir* experiments to allow for the collection of enough ions to create a mass spectrum. The drawback of the removal was an increase in the rate of multiple detections from a single pulse during the desorption of adatoms that had undergone diffusion. Multiple detections from a single pulse did not allow for unequivocal identification of the desorbed adatom and the experiment would have to be repeated to address this issue.

An aperture mounted to a rotary motion feedthrough could be placed at the entrance to the drift tube. The aperture could be in place to reject off axis ions during the desorption of adatoms, reducing the rate of multiple detections. It could then be rotated 90° during the collection of atoms for mass spectra.

6.2 Future *Ir* Experiments

There are a number of experiments that could be performed on many different planes of *Ir*. This section is divided into sections describing possible future experiments on two planes, *Ir*(100) and *Ir*(111).

6.2.1 *Ir*(100) Experiments

Additional investigations of the *Ir*(100) plane are possible with the current system, though they would be greatly aided by the improvements mentioned above. *Ir*(100) has been shown to reconstruct to an ordered, quasi-hexagonal (1x5) orientation when heated to temperatures of ~ 1500 K for short durations [60]. FIM investigations of the reconstructed surface have only been concerned with imaging the reconstructed

Figure 6.1: Annealed $Ir(100)$ surface after field evaporation showing some row structure, indicating the reconstruction of the surface.

surface and not with the diffusion of adatoms on the reconstructed surfaces [61, 62, 63]. Although the reconstructed surface does form a hexagonal net, the plane is not flat because of the underlying square lattice of the bulk substrate. The deformation that is caused by forming the hexagonal structure causes buckling in ordered troughs ~ 0.5 Å in height. The predicted difference in the distance from the surface between the elevated atoms and the "lower" atoms is 0.5 Å. This difference in height is enough to cause significant contrast in FIM images [63].

No studies of adatom diffusion on the reconstructed surface have been reported.

With the addition of the temperature control to the APFIM, self-diffusion studies could be performed. The activation energy, diffusion prefactor, and site map of adatom binding sites could be determined. Site mapping would give initial indication of the possibility of exchange diffusion. The quasi-hexagonal surface has more near neighbors than the unreconstructed surface and hence a higher coordination number. Given that models of exchange diffusion propose that the coordination number is an important consideration, it would be interesting to see if a diffusing *Ir* adatom still undergoes exchange on the reconstructed surface. Furthermore, it would be interesting to see if the corrugation of the surface causes the diffusion to be one or two dimensional. Regardless of the results of site mapping adatom visitation locations, the exchange process could, of course, be examined directly utilizing enriched isotopes.

6.2.2 *Ir*(111) Experiments

In addition to atomic exchange as adatoms diffuse across a surface, the exchange mechanism has been observed as an adatom diffuses over a step edge. A ball model of the descent of an adatom by exchange is shown in Fig. 4.2. Wang and Ehrlich studied the descent of *W* adatoms from the *Ir*(111) plane [53]. In their studies of descending *W* adatoms they first prepared a cluster of 12 *Ir* atoms. They determined that *Ir* atoms consistently required a $\sim 5\%$ higher voltage to be evaporated from the edge of the cluster than *W* atoms. The difference in evaporation voltage allowed the determination of the mechanism of descent for *W* adatoms. A *W* adatom was deposited onto the (111) oriented cluster of 12 *Ir* atoms. Heating to 220 K initiated diffusion of the adatom over the step edge, determined by observing a protruding boundary atom in a FIM image. The voltage required to evaporate the boundary atom corresponded to the measured value required to remove an *Ir* adatom from the boundary, indicating that the *W* adatom had undergone descent by exchange.

Figure 6.2: Ball model showing two possibilities for the diffusion of an adatom over a step edge. in a) the adatom descends directly over the edge and in b) the adatom exchanges with a lattice atom.

No dependence on the crystallographic direction of descent was found for the small cluster.

Interestingly a crystallographic dependence for the mechanism of descent was found for a W adatom descending from larger clusters. Fig. 4.3 shows a ball model of a 29 atom (111) cluster. The left and right edges differ from each other. The right boundary of the cluster is a $\{100\}$ type facet and is called an A type step. The left boundary of the cluster is a $\{111\}$ type facet and is referred to as a B type step. Using the same method of distinguishing the chemical identity of an adatom by its evaporation field Wang and Ehrlich found that on clusters of sizes in the tens of atoms range, a W adatom descended directly over A type steps and descended over a B type step by exchange.

The isotopically enriched method is capable of directly determining the mechanism of descent for $Ir/Ir(111)$. The two types of steps can be prepared for these studies. Field evaporation can be used to prepare a (111) plane of the desired size. The tip is then annealed at 500 K for ~ 30 s which reorders the cluster into a hexag-

Figure 6.3: Ball model showing the A and B type steps on $Ir(111)$. In a) the atom descends directly and in b) the adatom descends by exchange.

onal shape with distinguishable A and B type steps[64]. The heating circuit would be useful in these types of experiments where control of the temperature to create a reliable difference of 15 K is required. Fig. 4.4 shows an example of the hexagonal reordering of a plane accomplished by heating an $Ir(111)$ oriented tip in the APFIM used in this thesis.

6.3 Future W Experiments

The experiments described for Ir can also be carried out on W . The very low natural abundance of the ^{180}W increases confidence that any detection of the isotope is due

Figure 6.4: $Ir(111)$ plane a) prior to annealing at ~ 500 K and b) after annealing the boundary outline has become hexagonal.

to deposition from an enriched source. The diffusion mechanism of W adatoms on $W(110)$ could be determined. If W adatoms diffuse by a combination of exchange and hopping then previous site mapping studies would not indicate exchange at all. Repeated detections of ^{180}W after initiating diffusion across the $W(110)$ plane would quickly indicate that W adatoms diffuse by hopping and vice versa.

The descent of adatoms over step edges can also be investigated. Fig. 6.5a shows a deposited adatom on the $W(110)$ plane. After a 10 s heating period the adatom has descended and been incorporated to the boundary in Fig. 6.5b. It is possible that the exchange mechanism seen by Wang and Ehrlich for the descent of W adatoms on $Ir(111)$ could be operative here. The use of isotopically enriched material is capable of determining the mechanism of descent over step edges.

W has a narrow temperature range over which descent over the edge is reasonably probable and the boundary is stable. If the temperature is ~ 470 K the average number of heating periods required for the descent of an adatom over the step edge is 21.5 as reported by Wang and Tsong [48]. They reported an average number of 7.3

Figure 6.5: $W(110)$ plane with a) a deposited adatom from the enriched W source. b) The adatom has descended over a step edge during thermally activated surface self-diffusion.

jumps for adatom descent at 390 K. At 400 K the boundary atoms become mobile and the descent of an adatom during the motion of boundary atoms precludes the identification of the descended adatom. Fig. 4.6 is a FIM image before and after laser heating showing the mobility of the boundary atoms. Therefore the fine temperature control provided by the circuit described in section 6.1.1 is necessary for the study of adatom descent on $W(110)$.

Figure 6.6: $W(110)$ plane a) after field evaporation and b) after annealing to ~ 400 K the boundary atoms have become mobile and the shape of the boundary has changed.

Chapter 7

Conclusion

An APFIM capable of studying surface self-diffusion was constructed. Benchmarks of the system's performance show its suitability for the study of single atom diffusion on metal surfaces. The APFIM has single ion sensitivity and allows for the identification of an individual surface adatom. The instrument has sufficient mass resolution to determine the location of the five mass peaks of W . Although the peaks are not fully separated, the determination of the leading edge of each peak is sufficient for adatom identification.

A procedure for cleaning and depositing isotopically enriched material was developed. The use of the enriched material is crucial to the study of surface self-diffusion. The enriched material, both Ir and W arrived from the manufacturer in a powder form. The enriched material was tested for contaminants and O was found to be the primary contaminant in W . Suspending the powder on a W coil and sintering *in vacuo* stabilizes the powder for use as a deposition source for diffusion experiments. The use of a W coil also allows the powder to be cleaned by Joule heating before each experiment. The coil is mounted to a linear motion feedthrough which allows the deposition source to be positioned for deposition. Deposition is achieved by laser

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heating. The focusing of the laser heats a localized region of the powder to temperatures suitable for the evaporation of material and the ablated material is deposited onto a tip.

The use of isotopically enriched material has allowed the direct observation of atomic exchange during surface self-diffusion for the first time. Previous studies of the *Ir(100)* system presented observations that were consistent with a model of diffusion by exchange, but the evidence remained inferential. In the experiments a single ^{191}Ir atom was deposited onto the *Ir(100)* surface. The substrate was heated by illuminating it with an infrared laser. Heating the substrate initiated thermally activated surface self-diffusion. Atomic resolution imaging with the FIM confirmed the movement of the adatom. After diffusion, the adatom was mass analyzed by time-of-flight mass spectrometry. Of six detected adatoms, half were ^{191}Ir and half were ^{193}Ir . The probability of this abundance occurring in the absence of an exchange mechanism is determined by the binomial distribution to be $P = 5.2 \times 10^{-3}$. Given such a low probability for the deposition of three ^{193}Ir atoms in six trials, the measured isotopic abundances of the adatoms that had undergone diffusion represent the direct detection of atomic exchange. This conclusively shows the exchange mechanism of diffusion for surface self-diffusion on the relatively smooth *Ir(100)* plane, which has, since initial studies in 1990, only been inferred. Theoretical models of diffusion have been reported by several authors and at best show qualitative results for the preference of exchange over hopping for *Ir/Ir(100)*. Future theoretical work should focus on the exchange mechanism for surface self-diffusion on this plane.

The use of isotopically enriched material allows the investigation of a number of unanswered questions in surface self-diffusion. First and foremost, the self-diffusion mechanism of other homogeneous systems can be determined. If a combination of exchange and hopping occur then site mapping would give no indication that the exchange mechanism is occurring. The process may be more prevalent than

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previously thought.

Other types of experiments are also possible. The reconstructed $Ir(100)$ plane shows slight corrugation. The isotopic technique can investigate whether this changes the preference for diffusion by exchange. On $Ir(111)$ the exchange mechanism of step descent has been shown for the heterogeneous case of $W/Ir(111)$. The existence of the exchange mechanism in the homogeneous case has been hypothesized, and may be determined directly using the isotopic technique.

Additionally, all of these experiments can be repeated on W surfaces. W is particularly suited for these studies because of the natural scarcity of the ^{180}W isotope, which is available at 95% enrichment levels. The scarcity of the isotope reduces the number of trials necessary to gain confidence in the result of surface self-diffusion experiments. The mechanism of diffusion across various high and low index planes of W and the dependence on the crystallographic direction of adatom motion can be investigated.

These future studies require some modification to the system. The addition of a temperature control circuit to accurately raise and hold the temperature of the substrate for well defined time intervals will be useful. The temperature of the substrate is particularly important for the investigation of W systems. The inclusion of a rotatable aperture at the entrance to the drift tube of the APFIM will aid in the reduction of multiple detection events during the identification of a single adatom, while still allowing for the collection of many ions for the generation of mass spectra to compare the adatom to. The inclusion of these two relatively simple elements should allow the system to answer additional questions that have been unresolved for nearly 40 years.

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