MASTER**DEFECTS IN METAL CRYSTALS****Progress Report****for the Period May 1, 1979 to April 30, 1980****David N. Seidman****Cornell University****Ithaca, New York 14853****January 1980****Prepared for****THE U.S. DEPARTMENT OF ENERGY
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DEFECTS IN METAL CRYSTALS

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ABSTRACT

The objective of the present research effort is a broad investigation of the properties of crystal defects in metals and semiconductors. Attention during the past year has focused on fundamental properties of point defects (vacancies and self-interstitial atoms); aggregates of point defects (i.e., depleted zones); the range profiles of low-energy (< 1000 eV) implanted ^4He and ^1H in tungsten, the diffusive properties of ^4He and ^1H ; the adsorption kinetics and sticking coefficient of hydrogen on tungsten; the imaging of silicon by field-ion microscopy; the chemical analysis of ordered Ni_4Mo and GaAs - on an atomic scale - via atom-probe field microscopy; and the low-temperature isochronal recovery behavior of ion-irradiated Ni_4Mo and Pt_3Co . Heavy use was made of the high-resolution field-ion microscope and the atom-probe field-ion microscope.

Progress was made in the following areas:

- A. The Direct Observation of the Point-Defect Structure of Depleted Zones in Ion-Irradiated Metals (Dr. M. Current, D. Pramanik and B. Moser)
 1. Dependence of the Structure of Depleted Zones in Tungsten on Ion Energy (Dr. M. Current)
 - a. Visual Representations of the Point-Defect Structure of Depleted Zones.
 - b. Energy Dependence of the Number of Vacancies per Depleted Zone
 - c. Variation of the Properties of Depleted Zones with Reduced Energy (ϵ)
 - d. The Depth of Depleted Zones from the Irradiated Surfaces

- e. The Diameters of the Depleted Zones
- f. Vacancy Concentration in the Depleted Zones
- 2. The Properties of Near-Surface Depleted Zones in Tungsten and Sputtering (Dr. M. Current)
 - a. Visual Representations of the Depleted Zones in the Near-Surface Region
 - b. Number of Vacancies per Depleted Zone in the Near-Surface Region
 - c. Diameters of the Near-Surface Depleted Zones
 - d. Vacancy Concentration in the Near-Surface Depleted Zones
 - e. Sputtering Yields and their Relationship to Depleted Zones
- 3. The Vacancy Structure of Depleted Zones Produced in Platinum Irradiated by 20 keV Kr^+ or Pt^+ Ions (D. Pramanik)
 - a. General Experimental Problems Particular to the Study of Irradiated Platinum
 - b. Experimental Results for Irradiated Platinum Specimens
 - i. Results for 20 keV Kr^+ Ions on Pt:
 - Absolute number of Frenkel Pairs and Mean Damage Depth
 - ii. Spatial Arrangement of Vacancies and Vacancy Concentration
- B. Diffusion of Implanted Helium (4He) Atoms in Tungsten (Dr. M. Yamamoto)
- C. Atom-Probe Field-Ion Microscope Studies of Ordered Ni_4Mo and the Semiconductors GaP (Dr. M. Yamamoto)
 - a. Ordered Ni_4Mo
 - b. The Semiconducting Compound GaP
- D. Field-Ion Microscope Imaging of Silicon (Dr. G. Kimmel)
 - a. Specimens
 - b. Mounting the Specimen
 - c. Polishing

4. Vacuum and Baking Procedure
5. Results
- E. An In Situ Field-Ion Microscope Study of the Recovery Behavior of Ion-Irradiated Ordered Alloys - Ni_4Mo and Pt_3Co (J. Aidelberg)
 - a. Introduction
 - b. Experimental Details
 - c. Experimental Results
 - i. Control Experiments
 - ii. Isochronal Warming Experiments of Pt_3Co Alloy
 - iii. Isochronal Warming Experiments of Ni_4Mo
 - d. Discussion
 - i. Annealing Behavior of the Pt_3Co Alloy
 - ii. Annealing Behavior of the Ni_4Mo Alloy
 - e. Summary
- F. An Atom-Probe Field-Ion Microscope Investigation of Tungsten Irradiated with Very Low-Energy (100-500 eV) Hydrogen Ions (Dr. A. Macrander)
 - a. Introduction
 - b. Null Results at High Temperatures
 - c. Profiles Obtained Near 25 K
 - d. Qualitative Observations
 - e. Conclusions
- G. An Atom-Probe Field-Ion Microscope Study of Hydrogen Adsorption on the (110) Plane of Tungsten (Dr. A. Macrander)
 - a. Introduction
 - b. Standing Voltage Dependence
 - c. Adsorption Experiments
 - d. Conclusions

H. Atom-Probe Field-Ion Microscope System Improvements

(Drs. A. Macrander and M. Yamamoto)

a. Peripherals to the NOVA 1220 Minicomputer

b. Additions to the Goniometer

I. Segregation to Voids in Fast-Neutron Irradiated Refractory Metals and Alloys

J. The Recovery Behavior in Stages I, II and III of Proton-Irradiated Tungsten (Dr. R.S. Averback - Argonne National Laboratory)

K. Seminars and Meetings

Key Phrases and Words: Spatial arrangement of vacancies within depleted zones in ion-irradiated tungsten and platinum; dependence of the vacancy structure of depleted zones on the ion energy; vacancy concentration within depleted zones; diameters of depleted zones; the properties of near-surface depleted zones and their relationship to sputtering; depth profiles of low-energy (300 to 1000 eV) implanted ^4He in tungsten; diffusion of ^4He in tungsten between 90 and 120 K; atom-probe field-ion microscope studies of the chemistry, on an atomic scale, of ordered Ni_4Mo and the semiconductor GaP; field-ion imaging of silicon; the low-temperature isochronal recovery behavior (Stage I) of ion-irradiated ordered Ni_4Mo and Pt_3Co ; range profiles of low-energy (100 to 500 eV) hydrogen implanted in tungsten; diffusion of hydrogen in tungsten at low temperatures; the kinetics of the adsorption of hydrogen on the (110) plane of tungsten; and the sticking coefficient of hydrogen on the (110) plane of tungsten.

I. INTRODUCTION

During the past year several projects were completed and significant progress was made in other areas. A brief account of the work is given in Section II and the following personnel were involved:

Professor D.M. Seidman, Principal Investigator

Dr. J. Amano, Research Associate (left April 1979 to take a position as a staff scientist, Hewlett-Packard Corp., Palo Alto, California).

Dr. M. Current, Research Associate (joined October 1976)

Dr. A. Macrander, Research Associate (joined September 1977)

Dr. M. Yamamoto, Research Associate (joined June 1978)

Dr. G. Kimmel, Research Associate (joined July 1979)

J. Aidelberg, Research Assistant (completed Ph.D. degree and left September 1979 to join INTEL Corp., Santa Clara, California as a staff scientist.)

B. Moser, Research Assistant (joined September 1979)

D. Pramanik, Research Assistant (joined September 1977)

E. Roebig, Half-time Film Scanner (left February 1979)

C. Regal, Half-time Film Scanner (joined January 1979 and left May 1979)

J. Givot, Half-time Film Scanner (joined January 1980)

R. Whitmarsh, Technician (joined January 1968)

K. Perry, Undergraduate Assistant for the summer of 1979

C. Cole, Undergraduate Assistant for the summer of 1979

II. EXPERIMENTAL WORK

- A. The Direct Observation of the Point-Defect Structure of Depleted Zones in Ion-Irradiated Metals (Dr. M.I. Current, Mr. D. Pramanik, Ms. B. Moser)

The systematic study of the point-defect structure of depleted zones (DZs), in ion-irradiated tungsten, reported on in last year's progress report⁽¹⁾ has been continued during the 1979-80 contract year. In addition, we made a good deal of progress on a research program on the study of DZs in ion-irradiated platinum; the latter metal was chosen as a prototype face-centered cubic metal.

The subject of the point-defect structure of a DZ is basic to our knowledge of the radiation damage produced by a single primary knock-on atom (PKA). The field-ion microscope (FIM) is, at present, the only experimental technique capable of obtaining quantitative information on the point-defect structure of DZs. The only other "technique" capable of providing information about the detailed point-defect structure of a DZ is the computer simulation technique; this approach is a theoretical one and the results are sensitive to the interatomic potential employed, the physical assumptions made (e.g., a many-body calculation versus the binary-collision approximation) and the mathematical approximations used.

In the present program of studies the emphasis has been on determining: (1) the average number of vacancies produced by an ion incident with a given amount of energy; (2) the spatial arrangement of vacancies within a DZ for an ion of a given mass; (3) the change in the spatial arrangement of vacancies within a DZ as a function of the mass of the irradiating ion at constant bombardment energy; (4) the vacancy concentration within DZs; and (5) the arrangement of self-interstitial atoms (SIAs) within and around the DZs. Heavy use has been made of the OR TEP program⁽²⁾ to provide three-dimensional and stereo-displays of the vacancy structure of individual depleted zones and the arrangement of SIAs with respect to the depleted zones.

1. Dependence of the Structure of Depleted Zones in Tungsten on Ion Energy (Dr. M.I. Current)

The principal emphasis in recent years, of the studies of DZs at Cornell, has been the systematic investigation of the effect of ion mass on the properties

of the structure of DZs, created by the slowing down of single ions in tungsten FIM specimens. In these studies, the ion energy was kept fixed at 30 keV while the mass of the irradiating ions (M_1) was varied between 183.8 amu (W^+) to 39.9 amu (Ar^+). To complement these studies a similar investigation was made of the DZ structures created by single Kr^+ ($M_1=83.8$ amu) ions with energies ranging from 15 to 70 keV.

A useful parameter for the discussion of these two systematic studies was the Linhard, Scharff and Schiott⁽³⁾ reduced energy (ϵ) where

$$\epsilon = \left[\left(\frac{M_2}{M_2 + M_1} \right) E_1 \right] / \left[Z_1 Z_2 e^2 / a_{t-f} \right],$$

M_1 and Z_1 are the mass and atomic number of the projectile ion, E_1 the kinetic energy of the projectile ion, M_2 and Z_2 are the mass and atomic number of the target ($M_2=183.8$ amu and $Z_2=74$ for tungsten), e is the charge on an electron and a_{t-f} is a Thomas-Fermi screening length (typically $\sim 8 \times 10^{-2}$ Å). As shown in fig. 1., the range of ϵ values covered by the Kr^+ ion studies was nearly the same as that for the earlier 30 keV work ($10^{-2} \lesssim \epsilon \lesssim 10^{-1}$). We were thus able to check, in detail, many of the proposed scaling relationships suggested by theory for the properties of the DZs, as well as having a convenient parameter with which to organize the experimental results.

a. Visual Representations of the Point Defect Structure of Depleted Zones

After the detailed mapping of the positions of vacancies found in the FIM specimen, the relative coordinates of the vacancies were entered into a standard format data list and transformed into a single coordinate system based on the principle cubic axes of the tungsten lattice. Another standard format listing was then prepared with the Nova 1220 computer - in our laboratory - for transfer of this data to the Materials Science Center Computing Facility at Clark Hall. At this facility a visual representation of the relative vacancy positions was computed with a version of the OR TEP program⁽²⁾ which we had modified to accommodate our special requirements. Examples of these OR TEP visualizations

Figure 1: Variation of the projectile energy (E_1) and reduced energy (ϵ) for the irradiations used to study the structure of depleted zones (DZs) in tungsten at 15 K.

for four of the eight DZs created by Kr^+ ions, which were mapped in atomic detail, are shown in figs. 2 to 5.

b. Energy Dependence of the Number of Vacancies per Depleted Zone

As was the case for the 30 keV studies, the most directly determined property of the DZs, found in the FIM specimens, was the number of vacancies (ν) in the DZ. Both the irradiations and pulse field evaporation of the FIM specimens were all carried out near 10 K; this temperature was below the onset of long-range self-interstitial atom (SIA) motion (~ 30 K), thus the values of ν can be compared to the various theoretical estimates of the number of atoms displaced during the slowing down of the energetic projectile in the tungsten lattice in the absence of any extensive recombination of Frenkel pairs. The variation of the ν with E_1 is shown in fig. 6 for the thirty DZs which were analyzed to date in this laboratory. This included eight DZs created by Kr^+ ions, a single DZ created by a 45 keV Xe^+ ion, the two DZs created by 20 keV W^+ ions mapped by Beavan et al.,⁽⁴⁾ as well as the extensive results from irradiations with different 30 keV ions.

The experimental results were in agreement with the expression for ν developed by Robinson and Torrens⁽⁵⁾ (ν_{R-T}) which took into account the screened potential nature of the projectile-target interactions, as well as the fraction of the projectile energy which was lost in inelastic processes did not contribute to the permanent displacement of target atoms from their lattice sites. The simple hard sphere estimate of the number of displacements per projectile proposed by Kinchin and Pease⁽⁶⁾ (ν_{K-P}) overestimated the observed value of ν by $\sim 50\%$. Both of these estimates were based on a minimum threshold energy (E_d) for displacement of the target atoms. We employed the E_d value measured by Maury et al. of 43 eV for electron damage in tungsten.⁽⁷⁾ An estimate by Lucasson of the number of displacements (ν_L) created by energetic projectiles, which was based on an average threshold energy of ~ 110 eV and a lower displacement efficiency than the Robinson-Torrens value, clearly underestimated the observed results - at all ion

DZ 14b

Figure 2: Computer-generated isometric view of DZ14a which was created by a single 30 keV Kr⁺ ion in tungsten. DZ14a contained 238 vacancies. Those vacancies which were in first-nearest neighbor sites (~ 2.7 Å apart) are connected by a short bar.

Figure 3: Computer-generated isometric view of DZ8a, which was created by a single 45 keV Kr⁺ ion; it contained 298 vacancies.

Figure 4: Computer-generated isometric view of DZ9b, which was created by a single 60 keV Kr^{+} ion; it contained 398 vacancies.

Figure 5: Computer-generated isometric view of DZ13a which was created by a single 70 keV Kr^{+} ion; it contained 378 vacancies.

Figure 6: The number of vacancies per DZ (ν) as a function of the projectile energy (E_1) for DZs in tungsten. Also shown were the theoretical estimates of the average number of defects created by a single ion proposed by Kinchin and Pease ($\langle \nu \rangle_{K-P}$) Robinson and Torrens ($\langle \nu \rangle_{R-T}$) and Lucasson, ($\langle \nu \rangle_L$).

energies-by about a factor of four.

c. Variation of the Properties of Depleted Zones with Reduced Energy (ϵ)

According to the theory⁽⁹⁾ for the stopping of energetic particles in amorphous solid targets, the stopping power of the target-due to elastic collisions between the projectile and target atoms - has a common functional form, independent of the particular projectile-target combination when the ion energy is expressed in terms of the quantity ϵ (see section 1). Since the total stopping power of the target is dominated by this elastic component for our irradiations, we expected that the properties of the DZs - which depend on the spatial extent of the energy deposited in the target as the ion slowed down-to exhibit some common behavior when they are compared as a function of ϵ . The principle examples of these properties which scale with ϵ are: (1) the depth of the DZs below the irradiated surface; (2) the spatial extent of the DZ; (3) to some degree - the average vacancy concentration; and (4) the separation of large clusters of vacancies within the individual DZs.

d. The Depth of Depleted Zones from the Irradiated Surface

In the present experiments the extent of the disruption of the lattice structure, when an ion hit the FIM specimen, was sufficiently great that all of the ion impacts within the volume of the specimen produced a recognizable region of damage. Thus even in the cases where the DZs were detected in (hkl) planes with high artifact vacancy concentrations and therefore were not mapped out in detail, these DZs were counted and included in the total ion dose in the specimen. In addition the depth of these DZs, from the irradiated surface, was determined even though the detailed atomic structure of these DZs could not be analyzed. The depth (R), along the direction of the ion beam from the irradiated surface, for 38 DZs and one dislocation loop as a function of ϵ is shown in fig. 7. Also exhibited is the calculated mean depth of damage ($\langle x \rangle_D$) for an amorphous target with $M_2 = 184$, $Z_2 = 74$ and a density of 19.3 gm cm^{-3} (tungsten). The wide range of R values (fig. 7) demonstrated that the DZs analyzed in these studies -

were sampled from the full range of ion damage depths. Approximately 65% of the DZs were within one standard deviation of the mean (dotted line in Fig. 7) which was consistent with the slightly skewed Gaussian nature of the elastically deposited energy distribution. The distribution of all of the R values, normalized by the corresponding calculated $\langle x \rangle_D$ values, had a mean value of 1.0 and a standard deviation (first moment) of

$$\frac{\Delta R}{\langle x \rangle_D} = 0.8.$$

The normalized standard deviation of the calculated damage distribution was typically of the order of

$$\Delta X / \langle x \rangle_D = 0.75.$$

So the distribution of depths of the observed DZs was in excellent agreement with the first two moments of the calculated elastically deposited energy distribution.

e. The Diameters of the Depleted Zones

The spatial extent of the DZs was determined by sampling the standard deviation of the distribution of vacancies along the thirteen $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ type directions in the tungsten lattice. The largest value of the standard deviation was denoted as σ_1 and the average of the standard deviations along directions perpendicular to the largest extension was called σ_2 . The volume of the DZ was then approximated as an ellipsoid with principal radii equal to σ_1 and σ_2 . An average DZ diameter was then calculated as

$$\langle \lambda \rangle = 2 [\sigma_1 (\sigma_2)^2]^{1/3}.$$

The values of $\langle \lambda \rangle$ as a function of ϵ are shown in Fig. 8. Also shown for comparison are the calculated diameters based on the second moments of the elastically deposited energy distributions parallel and perpendicular to the beam direction $\langle \Delta x \rangle_D$ and $\sqrt{\langle y^2 \rangle_D}$, respectively; where

$$\langle D \rangle = 2 [\langle \Delta x \rangle_D \langle y^2 \rangle_D]^{1/3}.$$

TUNGSTEN

Figure 7: Measured depth (R) from the irradiated surface to the center of the DZ along the ion beam direction, as a function of ϵ for DZs in tungsten. Also shown were the calculated mean damage depth ($\langle x \rangle_D^{TRIM}$)-shown as a solid line - and the calculated damage depths at one standard deviation from the mean (shown as dotted lines).

The second calculated diameter ($\langle D_g \rangle$) included the contraction factors (δ)- suggested by Sigmund, Scheidler and Roth⁽¹⁰⁾ - as an estimate of the smaller volume damaged by the impact of a single ion, as compared to the average over a large number of ion impacts which were used in the calculation of $\langle \Delta x \rangle_D$ and $\sqrt{\langle y^2 \rangle}_D$. It was clear that both the values of $\langle D \rangle$ and $\langle D_g \rangle$ overestimated the spatial extent of a DZ produced by a single ion in tungsten.

The mean free path length between large transfer energy collisions-within the DZs-was determined by the spacing of the major fluctuations in the radial distribution functions^(11,12). These distances corresponded to the average spacings between the large clusters of vacancies within the DZs; for example, see the OR TEP drawing of DZ14b in fig. 2. The values of the mean free path lengths were similar to the average DZ diameters determined by the measured standard deviations of the vacancy distributions along the principal axes. This implied that the development of the structure was controlled by a few large angle and large energy transfer collisions between the projectile ion and the target atoms.

f. Vacancy Concentration in the Depleted Zones

The concentration of vacancies within a DZ is a direct measure of the density of energy deposited by the projectile ion, above transferred energies of the order of E_d (43 eV). The deposited energy density is not a property that scaled exactly with ϵ . However, in the range of ϵ spanned by these studies, the values of the calculated vacancy concentration was case c_v^* , were not much different for the 30 keV ion and the Kr^+ ion irradiations. Therefore, ϵ is also a convenient experimental parameter for organizing the data for the measured vacancy concentrations ($\langle c_v \rangle$).

The vacancy concentration was determined for each DZ by dividing the total number of vacancies in the DZ by a rectangular volume which included all of the vacancies and was fitted closely around the DZ employing a series of rectangular slabs whose sides were normal to the $\langle 100 \rangle$ directions.

Figure 8: Measured diameters ($\langle \lambda \rangle$) as a function of ϵ for DZs in tungsten. Also shown were the theoretical estimates of the DZ diameters calculated from transport theory ($\langle D \rangle$ and $\langle D_\delta \rangle$).

The measured values of $\langle c_v \rangle$ as a function of ϵ are shown in Fig. 9. The values of $\langle c_v \rangle$ ranged from $\sim 20\%$ for the 20 and 30 keV self-ion irradiations to $\sim 2\%$ for the 30 keV Ar^+ ion and 60 keV Kr^+ ion irradiations. Also shown are the calculated vacancy concentrations using $\langle v \rangle_{R-T}$ as an estimate of the number of defects produced by a single ion and a volume based on $\langle D_\delta \rangle$, where

$$c_v^* = \frac{0.30 \langle v \rangle_{R-T} \Omega_0}{(4\pi/3) (\langle D_\delta \rangle / 2)^3},$$

Ω_0 is the atomic volume, and the factor 0.30 was the fraction of area within one standard deviation of the central maximum of a Gaussian distribution. These calculated concentrations give a reasonable account of the observed trends in the data, although the variations between the results for the individual DZ is quite large.

Shown on the right-hand margin of Fig. 9 is the calculated density of deposited energy, $(\mathcal{E}_0)$ which varied from 20 eV atom⁻¹ for the self-ion irradiations to 2 eV atom⁻¹ for the $\epsilon \approx 10^{-1}$ indications.

2. The Properties of Near-Surface Depleted Zones in Tungsten and Sputtering (Dr. M.I. Current)

Following many of the in situ ion irradiations, DZ regions were found which extended up to and included segments of the initial surface of the FIM specimen. Atoms which were located near the surface of the specimen and were displaced by the slowing down of the irradiating ions could be expected to be ejected from the target. This was the initial stage of surface erosion under ion bombardment or sputtering. The FIM is a particularly sensitive tool for the study of these near-surface DZs since the field-evaporation process allows the experimentalist to study the surface of atoms in successive atomic planes which are spaced $\sim 0.5 \text{ \AA}$ apart. The near-surface region was therefore carefully examined with a high degree of depth resolution.⁽¹²⁾

Figure 9: Vacancy concentration (c_v) as a function of ϵ for DZs in tungsten. Also shown was the calculated average concentration (c_v^*) based on the Robinson - Torrens formula for v and transport theory estimates for the size of a DZ for a single projectile ion.

We mapped out seven such near-surface DZs, which were created during the course of the 20 and 30 keV ion irradiations. Examples of near-surface DZs were examined for W^+ , Kr^+ , Cu^+ and Ar^+ ion bombardments.

a. Visual Representations of the Depleted Zones in the Near-Surface Region.

Figures 10 to 12 exhibit OR TEP graphic visualization of the positions of vacancies within DZs, which contained a portion of their volume in the near-surface region. DZ2c is exhibited in Fig. 10; it was created by the impact of a single 30 keV W^+ ion and contained 123 vacancies. Forty-five of these vacancies were detected within $3 \text{ \AA}$ of the irradiated surface-the near-surface region-and they are indicated by solid circles. The bond connecting any two vacancies is the first-nearest neighbor bond. The depth of the region we defined as the near-surface region was determined by the depth to which an atom was visible in a ball model of the (hkl) planes used in analysis of the DZs. This geometrically defined near-surface region extended between three and six atomic layers below the first layer imaged and it was between 2 to $3 \text{ \AA}$ in thickness. We would expect that an atom displaced from a site in the near-surface region-which is characterized by less than the full number of first nearest neighbors-would have a high probability to be ejected from the irradiated surface as a sputtered atom.

The OR TEP visualization of DZ7b, which was created by a single 30 keV Cu^+ ion, is shown in Fig. 11. DZ7b contains 200 vacancies of which 51 were found in the near-surface region. The breakup of the DZ into distinct clusters of vacancies is clearly evident in DZ7b.

The OR TEP visualization DZ10a which was created by the lightest ion used in this study - a 30 keV Ar^+ ion - is shown in Fig. 12. It contained 192 vacancies of which 70 were within the near-surface region. The more diffuse nature of the vacancy distribution ($c_v = 1.8\%$) for this light ion irradiation is evident.

Figure 10: Computer-generated isometric view of DZ2c, which was created by a single 30 keV W^+ ion; it contained 123 vacancies, of which 45 were within the near-surface region (within ~ 2.5 Å of the irradiated surface); the latter vacancies were indicated by solid circles.

Note that the angle of incidence at the point of impact of the ion beam on the irradiated surface of the FIM specimens was rather large ($\sim 60^\circ$), so that all of these near-surface DZs are examples of sputtering at a glancing angle.

b. Number of Vacancies per Depleted Zone in the Near-Surface Region

The number of vacancies per DZ (ν) for the six near-surface DZs created by 30 keV ions is shown as a function of M_1 in Fig. 13. Also indicated in this figure are the range of observed values for ν , for the 30 keV DZs which were found in the bulk of the FIM specimens and the theoretical estimates of ν which were used for comparison in section A1.b. The average value of ν ($\langle \nu \rangle$) for the near-surface DZs was 148 vacancies per DZ; this value compared favorably with the observed average value for the bulk DZs (183) and the estimates from the Robinson-Torrens formula (~ 200). As with the bulk DZ results, there was no distinct trend in the values of ν for the range of M_1 used in this experiment.

c. Diameters of the Near-Surface Depleted Zones

The measured average DZ diameters ($\langle \lambda \rangle$) for the seven near-surface DZs are shown as a function of ϵ in Fig. 14a. All of the values of $\langle \lambda \rangle$ for the near-surface DZs were within the range of values found for the bulk DZs (see Fig. 8) and were generally somewhat smaller than the estimates of the DZ dimension ($\langle D_\delta \rangle$) based on the distribution of elastically deposited energy.

d. Vacancy Concentration in the Near-Surface Depleted Zones

The measured values of $\langle c_v \rangle$ for the seven near-surface DZs are shown in Fig. 14b. Here, as in the comparisons with measured values of ν and $\langle \lambda \rangle$, the values of $\langle c_v \rangle$ for the near-surface DZs were in general agreement with results for DZs which were found in the bulk of the FIM specimens.

e. Sputtering Yields

If all of the vacancies observed in the near-surface region were created by the ejection of tungsten atoms from the surface of the FIM specimen, then the number of vacancies in the near-surface region per DZ (ν_{ns}) provided a measure of the degree of fluctuation of the sputtering yield. The fraction of DZs with

Figure 11: Computer-generated isometric drawing of DZ7b which was created by a single 30 keV Cu^+ ion; it contained 200 vacancies, of which 51 were in the near-surface region (solid circles).

Figure 12: Computer-generated isometric drawing of DZ10a, which was created by a 30 keV Ar^+ ion; it contained 192 vacancies, of which 70 were in the near-surface region (solid circles).

Figure 13: The number of vacancies (ν) in the near-surface DZs, for $E_1 = 30 \text{ keV}$, as a function of projectile mass (M_1). Also shown were the range of values of ν for the 30 keV DZs found in the bulk of the specimens and the theoretical estimates of the average number of defects created by a single projectile based on the theories of Kinchin and Pease ($\langle \nu \rangle_{\text{K-P}}$) Robinson and Torrens ($\langle \nu \rangle_{\text{R-T}}$) and Lucasson ($\langle \nu \rangle_{\text{L}}$).

Figure 14a: Measured diameter ($\langle \lambda \rangle$) for the near-surface DZs as a function of ϵ . Also shown were the range of values of λ for the DZs found in the bulk of the specimens an estimate of the size of the DZs produced by a single ion ($\langle D_0 \rangle$) based on transport theory.

Figure 14b: Vacancy concentration ($\langle c_v \rangle$) for the near-surface DZs as a function of ϵ . Also shown were the range of values of $\langle c_v \rangle$ for the DZs found in the bulk and an estimate of the average vacancy concentration (c_v^*) based on the Robinson-Torrens estimate for v and the transport theory estimates of the size of a DZ produced by a single ion.

v_{ns} near-surface vacancies for the 30 keV irradiations, as a function of v_{ns} is shown in Fig. 15. While the majority ($\approx 60\%$) of the DZs were produced within the bulk of the FIM specimens and contained no near-surface vacancies, the peak in values of v_{ns} , for $v_{ns} > 0$, is ≈ 45 vacancies per DZ. This is ≈ 2.5 times greater than the average of $\langle v_{ns} \rangle = 18$ vacancies per ion. The measured value of $\langle v_{ns} \rangle$ compared favorably with the calculated average sputtering yields for 30 keV W^+ , Kr^+ or Cu^+ ions at 60° incidence on tungsten, which ranged from 19 to ≈ 14 atoms per ion.

3. The Vacancy Structure of Depleted Zones Produced in Platinum

by 20 keV Kr^+ or Pt^+ Ions (D. Pramanik)

a. General Experimental Problems Particular to the Study of Irradiated Platinum

We have performed a systematic study of the radiation damage created in platinum irradiated with 20 keV Kr^+ or Pt^+ ions. All the irradiations were carried out at 60 K and the FIM specimens were maintained at this temperature throughout the pulse-field evaporation process. This temperature was above the temperature at which the long-range migration of SIAs commenced and therefore there may have been both correlated and uncorrelated recombination of Frenkel pairs.⁽¹³⁾ Attempts to pulse field-evaporate platinum specimens below 60 K were made but the rate of fracture of specimens was almost 100% after irradiation, so that no data on the vacancy structure of DZs could be obtained. Even at 60 K, we were limited to the bombardment of specimens with ions having energy ≤ 20 keV, as the rate of fracture rose sharply with ion energy and almost 100% of the tips fractured for ion energies greater than 30 keV. In the case of 20 keV ions, the rate of fracture, after irradiation was found to be closely related to the stress and annealing history of the platinum specimens. The platinum wire used in the experiments was 99.999 wt. % pure and was obtained from Engelhardt Industries. The wire was given a 9 hr. recovery anneal at $450^\circ C$ by the company. Specimens prepared from the as-received wire presented no problems in the imaging and pulse field-evaporation

Figure 15: The fraction of DZs with ν_{ns} vacancies in the near-surface region as a function of ν_{ns} . Note that the majority (~63%) of the DZs had no vacancies in the near-surface region. The average number of near-surface vacancies was ~18 vacancies per incident ion.

processes, prior to irradiation but all of them fractured, after irradiation, when the first few layers were pulse field-evaporated. The best results were obtained with wire that had been annealed in air at 1100°C for 24 hours. Even then ~50% of the specimens fractured before a sufficient number of layers had been field evaporated. The importance of keeping the wire free from stress became clear, when a wire annealed - as above - was work-hardened by merely straightening a small length. FIM specimens prepared from this length fractured at once after bombardment with ions having an energy as low as 10 keV, before even one or two layers were field-evaporated. The high rate of fracture of platinum specimens compared to tungsten specimens after irradiation appeared to be related to the nature of the defects created in the platinum. At an ion energy of 20 keV, dislocation loops were produced in the region of the specimen that was subjected to high elastic stresses caused by imaging electric-field. Under the effect of these stresses some of the loops may have glided to subgrain or grain boundaries and thus led to fracture which was initiated at the grain boundaries. Even in tungsten specimens, the rate of fracture was found to increase rapidly when dislocation loops were produced inside the specimen.

b. Experimental Results for Irradiated Platinum Specimens

The results for the 20 keV Kr^+ or Pt^+ ion irradiations of pure platinum showed that the primary state of damage due to 20 keV ion bombardment at 60 K, could be classified into three basic morphological types: (a) depleted zones (DZs); (b) compact vacancy clusters or voids; and (c) dislocation loops. The voids can be considered to be DZs with a very high vacancy concentration, and we have classified them as such pointing out the void-like nature where it was pertinent. It is a generally accepted view that the dislocation loops were produced from DZs that had a high local value of c_v and had collapsed into lower-energy dislocation loops. The presence of dislocation loops alongside with DZs - in the same specimen - at temperatures where it is known that the long-range migration of vacancies was impossible supports this view point.

In the case of the 20 keV, Kr^+ ion bombardments we were able to detect seven DZs (this included void-like DZs)-in planes that had a low-artifact density - and we analyzed them completely[†]. In addition, we have observed three other defects, that we tentatively classified as dislocation loops by virtue of the contrast effects obtained in the FIM images. We hope to determine the character of the loop by comparing the experimentally observed field evaporation sequences of the FIM image with computer-simulated FIM patterns for loops under various planes. All the dislocation loops were observed near the initial surface of irradiated FIM specimens.

We have compared our experimental results with the corresponding values obtained from a computer simulation program based on Biersack's and Haggmark's TRIM program.⁽¹⁴⁾ The program simulates the trajectory traversed by a single ion of mass M_1 and atomic number Z_1 and energy E_1 , through an amorphous target material composed of atoms of mass and atomic number M_2 and Z_2 , respectively. It followed the trajectories of all recoil atoms with energies above the threshold energies and kept account of the positions of the vacancies formed, as the ion energy was dissipated through a series of recoil events. Thus we were able to simulate the effects of individual ion hits and calculate the various quantities of interest - for individual cascades - such as number of vacancies per cascade, mean size and depth of cascade, etc.⁽¹⁵⁾ The analytical results from the radiation damage theory of Winterbon, Sigmund and Sanders⁽¹⁶⁾ pertain to quantities that are the net effect of a large number of overlapping cascades, which results in some problems in comparing the theoretical predictions with quantities that we can measure for DZs produced by a single ion (see Section A.1.f).

[†] We have analyzed these DZs for:

- (a) number of vacancies;
- (b) spatial arrangement of vacancies;
- (c) mean depth of damage; and
- (d) mean vacancy concentration.

In the case of 20 keV Pt⁺ bombardments of Pt we were able to detect two depleted zones in planes that had a low artifact defect-density. We have completed a count of the total number of vacancies in each DZ but have not yet completed the total analysis of these DZs. In addition, we observed one defect that was tentatively identified as a dislocation loop.

b 1. Results for 20 keV Kr⁺ on Pt: Absolute Number of Frenkel Pairs
and Mean Damage Depth

In Table 1 we have summarized the results of the mean damage depth, measured from the surface along the direction of the incident beam.

Table 1: Results for Depleted Zones Produced in Platinum
Specimens by 20 keV Kr⁺ Ions

Name of Depleted Zone	Depth from the Surface (Å)	Number of Vacancies (v)
DPKr 1	2	154
DPKr 2	27.6	155
DPKr 3	39.6	209
DPKr 4	*	116
DPKr 5	45	291
DPKr 6	5	85
DPKr 7	15	282
Average		184±79

*Difficult to measure because angle of incidence ~ 90° for this case.

The mean number of defects obtained from the computer accumulation of 50 cascades, produced by 20 keV Kr^+ ions incident normally on platinum, was 182 ± 11 , assuming a single threshold energy of 36 eV⁽⁸⁾. This mean value was very close to the value obtained from the Robinson-Torrens version of the Kinchin-Pease formula:

$$\langle v \rangle = 0.84 \frac{\langle E_1 - \hat{Q} \rangle}{2E_d} ,$$

where E_1 was equal to 20 keV and $\langle E_1 - \hat{Q} \rangle$, which is the amount of energy available for nuclear displacements, was taken from the tables of Winterbon⁽⁹⁾ which were in turn based on a Linhard-Scharff⁽¹⁷⁾ electronic stopping formalism. This indicated the convergence of the two theoretical approaches, the analytical and computer simulation models.

We have simulated on the computer, the formation of cascades when the projectile was incident at various angles to the surface and have confirmed the above observation. At 60° the average number of defects became

$$\langle v \rangle = 144 \pm 35.$$

A cascade with as little as 12 vacancies, and one with 32 were obtained in the computer simulation indicating the degree of fluctuation caused by the loss of energy through the surface. We can thus account for the smaller number of vacancies of DPkr 4 and DPkr 6 (especially since both were close to the surface).

The mean depth of damage for 20 keV Kr^+ on Pt and incident normally to the surface was obtained from the computer simulations to be

$$34.45 \pm 23.7 \text{ \AA}$$

All the depleted zones we have found were within this distance. The structure of the DZ should not be dependent on the depth at which it was located as the development of the cascade was independent of the position at which the large-energy recoils, that initiated the cascade took place. This will be true as long as the various properties of the material-involved in the radiation damage process are the same all the way up to the surface. We have confirmed this with the computer simulations.

Since the damage profile - referred to in the analytical theories - represents the net damage due to large number of ion hits, we compared the net damage profile due to the seven cascades with theoretical results. We counted the number of vacancies in 5 Å thick slabs parallel to the surface, for each of the cascades DPKr 1 to DPKr 7, and summed up the total number of vacancies in each slab for all the DZs. The total number of vacancies counted was 1285. Let $n_v(x)$ equal the number of vacancies in one such slab at a distance x , measured normal to the surface, i.e., along the direction $[hkl]$ that was perpendicular to (hkl) .

$$n_v(x) = \alpha F_D(x) \Delta x \quad (1)$$

where $F_D(x)$ is the damage energy deposited between x and $x+\Delta x$ (here we take $\Delta x = 5 \text{ Å}$), and where α is a constant. If Δx is large enough we would expect the proportionality to be given by a Robinson-Torrens type formula with

$$n_v(x) = \frac{50.8 F_D(x) \Delta x}{2E_d} \quad (2)$$

Since $F_D(x) \Delta x$ is the total energy going into recoil in the volume - represented by Δx - we expect that the recoil distribution within this volume would be the same as that within the cascade volume as a whole.

If N is the total number of vacancies created and $\hat{E}$ is the total damage energy then

$$N = 50.8 \frac{\hat{E}}{2E_d} \quad (3)$$

thus from (2) and (3) we should have

$$f_v = \frac{n_v}{N} = \frac{F_D(x) \Delta x}{\hat{E}}$$

In other words, if we plot the fraction of vacancies as a function of distance then the curve (or histogram) should be the same as the damage profile measured in terms of the fraction of the total deposited damage energy as a function of depth.

Note that this is not exactly the same as the damage profile talked about in analytical theories which consider the damage deposited as a fraction of the total incoming energy, though the shape of the profiles will be the same. This distinction is important only in as much as it is necessary to match the calculated profiles to our experimental damage profiles, using the number of vacancies without using any scaling factors. We have obtained the theoretical damage profile using the TRIM program for 10^3 20 keV Kr^+ ions incident at 60° and 70° to the surface of an amorphous platinum target.[†] The TRIM results are more useful than the analytical results - especially at the high angles of incidence we are dealing with - since a substantial fraction of the incoming energy was lost through the surface either due to backscattering of the incident projectile or the loss of energetic recoil atoms through the surface. The TRIM program takes this loss into account whereas the analytical theory does not consider this loss through the surface. In fact for 70° incidence, 42.6% of the 20 keV projectiles were backscattered. The TRIM results for 70° incidence agreed quite well with the experimental damages profile: see Fig. 16.

The excellent agreement between the experimental results and the profiles expected on the basis of binary-collision approximation indicated that the current level of understanding of ion-solid interaction - for the present situation - is adequate.

We end this section with a brief comment on the problem of sputtering which is closely related to the problem of radiation damage. According to Sigmund's theory,⁽¹⁸⁾ sputtering is caused by the intersection of a cascade with the surface and the sputtering yield per ion should be closely related to the damage energy deposited near the surface. On the basis of this and the previous comments linking the vacancy distribution to the damage profile, it is possible to obtain an estimate of the sputtering yield from our results.

[†] The average angle of incidence experimentally was 70° . In fact for five out of the seven DZs the angle of incidence was $\sim 70^\circ$. In one case it was 54° and the other case it was 85° .

Figure 16: Comparison of experimental and computer simulation damage profiles.

It was assumed that all the vacancies contained within in a certain characteristic depth (d) were caused by atoms that had left the target, i.e., were sputtered. We adopted the criterion of Current and Seidman ⁽¹²⁾ which assumed that the only atoms that left the surface were those visible when looking at a ball model of the surface; this criterion yielded a value of d equal to $2.5 \text{ \AA}$ for the planes on which we observed vacancies. The criterion of Sigmund yielded a d value of $5 \text{ \AA}$. For $d = 2.5 \text{ \AA}$ we measured the total number of vacancies within this depth [near surface vacancies (NSV)] to be 373 out of 1285 vacancies. Since there were seven DZs, each created by one incident ion, we obtained an average sputtering yield (S) per ion to be

$$S = \frac{373}{7} = 53$$

For $d = 5 \text{ \AA}$ the total number of NSVs was 481 and the sputtering yield was then $S = 69$. Experimentally the value of S has been determined to be 111 for 20 keV Kr on Pt, which is also approximately close to the value obtained from Sigmund's formula. This yield was for normal incidence. Both experimentally and theoretically the sputtering yield should increase with increasing angle of incidence according to the relation

$$\frac{S(\theta)}{S(\theta=0)} = (\cos\theta)^{-f}$$

where $f \approx 1.7$ for $\theta < 70^\circ$. Thus we would expect that

$$\begin{aligned} S(\theta = 70^\circ) &= 11 \times (\cos 70^\circ)^{-1.7} \\ &= 68, \end{aligned}$$

which is within 25% of the value we obtained from the count of NSVs. The FIM data also indicated the degree of fluctuation involved. The highest number of NSVs - for $d = 2.5 \text{ \AA}$ - was found for DPKr 1 and was 118, the lowest number was for DPKr 2 and was 9.

DPKr 3 was a DZ that appeared to have the normal number of vacancies, and was reasonably well inside the tip so that we disregarded any effects of the surface. What was interesting was that the number of vacancies was still of the

order (in fact greater) than the Robinson-Torrens value, inspite of the fact that the SIAs were mobile. As mentioned earlier we would have expected that this would have led to the recovery of some of the defects. The fact that recovery was negligible seems to indicate that the SIAs were separated so far away from the DZs, that during their long-range migration they were annihilated at the surface rather than at the DZs. In the case of three-dimensional diffusion the probability that an SIA will eventually return to its origin is less than ~ 0.35 .⁽¹⁹⁾

b 2. Spatial Arrangement of Vacancies and Vacancy Concentrations

In Table 2 we summarized the vacancy concentrations data for all the DZs

TABLE 2: Vacancy Concentration Data for all the Depleted Zones

Name of Depleted Zone	$\langle c_v \rangle$ in at.%
DPkr 1	4.47
DPkr 2	1.7
DPkr 3	3.7
DPkr 4	2.53
DPkr 5	7
DPkr 6	11.53
DPkr 7	10.77

The first four DZs have an average c_v of 3 at.%, which was approximately the density expected from the Computer simulations. The fluctuation in c_v was of the order expected from the variations expected in the shape and elastically-deposited energy distribution for individual cascades. The remaining three DZs exhibited high vacancy concentrations, which may indicate collapse after formation of the DZ.

The quantity c_v is not a good indication of the spatial distribution of the vacancies in a DZ as the local density of atomic displacements may vary considerably within the DZ volume. We generated three-dimensional OR TEP representations of all the DZs, and calculated the number of vacancy clusters of different sizes within the DZ, which gave a detailed picture of the vacancy structure of the cascade. Figures 17 to 23 are the OR TEP representations of the seven DZs whose

Figure 17: A Computer-generated isometric drawing for DPKr 1.

Figure 18: A Computer-generated isometric drawing for DPKr 2.

Figure 19: A Computer-generated isometric drawing for DPKr 3.

Figure 20: A Computer-generated isometric drawing for DPKr 4.

Figure 21: A Computer-generated isometric drawing for DPKr 5.

Figure 22: A Computer-generated isometric drawing for DPKr 6.

Figure 23: A Computer-generated isometric drawing for DPKr 7.

characteristic properties are listed in Tables 1 and 2. The information pertinent to these DZs is as follows:

Fig. 17 DPkr 1: There were 33 monovacancies, six clusters of divacancies, and one each of four, 47 and 58. The OR TEP representations showed that the majority of the vacancies were clustered within the first few atomic layers from the surface.

Fig. 18 DPkr 2: There were 89 monovacancies, 12 clusters of divacancies, two clusters of trivacancies and one each of 6, 14 and 16. This DZ was rather extended and somewhat diffuse, as was indicated by the low vacancy concentration.

Fig. 19 DPkr 3: There were 69 monovacancies, 11 clusters of divacancies, four of trivacancies, two of four and one each of 5, 6, 7, 24, 26 and 30. This DZ seemed to be similar with respect to the number of vacancies, size and mean depth of the average DZ that we obtained in the computed simulation work.

Fig. 20 DPkr 4: The number of monovacancies was 61, there were 9 clusters of divacancies, two of six and one of seven and 17. The DZ was relatively diffuse. The ion responsible for this DZ was incident almost at a grazing angle, and it was not surprising that we did not find a fully developed DZ.

Fig. 21 DPkr 5: There were 53 monovacancies, 10 clusters of divacancies, one of 3, 5, 8 vacancies and one jumbo cluster of size 182. The OR TEP representation showed that a large fraction of the clusters were within the first few layers of the surface.

Fig. 22 DPkr 6: There were 19 monovacancies and one big cluster of 65 vacancies. This DZ was classified as a void.

Fig. 23 DPkr 7: There were 41 monovacancies, five clusters of divacancies, two of three and one jumbo cluster of 224 vacancies. Almost all the vacancies were in one big cluster so that the DZ was

effectively a void. The OR TEP showed that it had a platelike structure.

B. Diffusion of Implanted Helium (^4He) Atoms in Tungsten (Dr. M. Yamamoto)

Recently the fundamental properties of light gases (H and He) in metals have been investigated in our group.⁽²⁰⁾⁻⁽²²⁾ In this section the low-temperature diffusion of interstitial helium (^4He) atoms in tungsten are described.

The experimental method was fundamentally the same as that for ^3He diffusion in tungsten. Typical experimental conditions were as follows: (a) total ion dose was 3×10^{15} ions cm^{-2} ; (b) implantation temperature was between 60 and 120 K; (c) the ion source pressure was $\sim 10^{-5}$ Torr; (d) atom probe pressure was $\sim 10^{-7}$ Torr; (e) total implantation time was 20-30 minutes; and (f) the diffusion times employed were between 30 to 90 minutes.

In order to check for the possible occurrence of ^4He events in unimplanted specimens a number of control experiments were performed. Fig. 24 shows the result of a control experiment performed at 60 K. A total of two ^4He events were found after probing to a depth of $210 \text{ \AA}$. These ^4He atoms were detected near the surface within the first three (110) planes. The results shown for the control experiments in Fig. 24 implied that there were very few errors in the actual experiments. Also shown in Fig. 24 is an integral profile for a ^4He implantation, at 60 K, parallel ($\pm 5^\circ$) to the [110] direction; this integral profile was used as a reference standard.

Figure 25 shows a composite range profile for 300 eV ^4He implanted in tungsten at 60 K. The measured mean range ($\bar{x}$) and standard deviation or straggling (Δx) were 41 and $32 \text{ \AA}$, respectively. The work of obtaining the initial distribution function, from the Edgeworth expansion, by using this range profile is in progress. The diffusion coefficient of ^4He at different temperatures, will be determined by varying systematically the diffusion time at these temperatures.

In Fig. 26 the normalized integral profile for 300 eV ^4He implanted at 110 K is shown. At 110 K the integral profile has changed significantly in comparison

Figure 24: A normalized control integral profile for an unimplanted tungsten specimen and the integral profile for a 300 eV ^4He implantation at 60 K as a standard reference.

Figure 25: A composite range profile for 300 eV ^4He implantations at 60 K. The range profile contains a total of 305 ^4He atoms. The tungsten specimens were implanted parallel to the [110] direction.

Figure 26: A normalized integral profile for 300 eV ^4He implantations at 110 K, and at 60 K as a standard reference.

to the standard reference integral profile for a 60 K implantation; therefore, ^4He is mobile at 110 K. Diffusion experiments at various temperatures between 60 and 120 K, are in progress.

C. Atom-Probe Field-Ion Microscope Studies of Ordered Ni_4Mo and the Semi-Conductor GaP (Dr. M. Yamamoto)

In preparation for studies on problems related to defects in ordered alloys and semiconductors, preliminary experiments on ordered Ni_4Mo and the compound GaP - which is semiconducting at room temperature - were performed employing the atom-probe FIM technique.

1. Ordered Ni_4Mo

The mass spectrum, number of events versus mass-to-charge ratio, for ordered Ni_4Mo is shown in Fig. 27. The probed plane was the $(211)_{\text{BCT}}$ fundamental plane. The spectrum consists of essentially Ni^{+2} , Mo^{+2} and Mo^{+3} . The charge states of Ni and Mo in ordered Ni_4Mo were slightly different from those in pure Ni or Mo; Ni^{+1} , Ni^{+2} , Mo^{+2} , Mo^{+3} , Mo^{+4} were observed for pure Ni and Mo, respectively. No differences were detected for the charge states of Ni and Mo when analyzing the $(211)_{\text{BCT}}$ fundamental plane, and the $(200)_{\text{BCT}}$ and $(101)_{\text{BCT}}$ superlattice planes. In Fig. 28 a histogram of the Ni^{+2} and Mo^{+3} events, which overlapped, is shown. The peaks associated with the five naturally occurring isotopes of Ni (Ni^{58} , Ni^{60} , Ni^{61} , Ni^{62} , Ni^{64}) and the seven naturally occurring isotopes of Mo (Mo^{92} , Mo^{94} , Mo^{95} , Mo^{96} , Mo^{97} , Mo^{98} , Mo^{100}) are readily distinguishable from one another. A histogram of the Mo^{+2} spectrum is shown in Fig. 29. The peaks associated with the seven isotopes of Mo are easily distinguishable from one another.

Figure 30 shows the number of field-evaporated Ni plus Mo atoms versus the cumulative number of field-evaporation pulses for the $(211)_{\text{BCT}}$ plane. Each step in Fig. 30 corresponds to the removal of one $(211)_{\text{BCT}}$ plane from the surface of the specimen. This step-like feature was also observed for the $(200)_{\text{BCT}}$ and $(101)_{\text{BCT}}$ superlattice planes.

Figure 27: The mass spectrum of ordered Ni_4Mo .

Figure 28: The Ni^{+2} and Mo^{+3} portion of the spectrum shown in Figure 27.

Figure 29: The Mo⁺² portion of the spectrum shown in Figure 27.

Figure 30: The pulse field-evaporation behavior of the (211)_{BCT} plane, giving the cumulative number of Ni plus Mo atoms versus the cumulative number of field-evaporation pulses.

The analysis of the composition in each layer of the $(211)_{\text{BCT}}$ fundamental plane and $(200)_{\text{BCT}}$ and $(101)_{\text{BCT}}$ superlattice planes is in progress. This information will be used to determine the mechanism of field-evaporation of ordered alloys.

2. The Semiconducting Compound GaP

A GaP tip was prepared by chemical polishing in a solution of HNO_3 : HCl (1:3). Next the GaP specimen was imaged in the atom-probe FIM and developed to an end form in pure H_2 gas at 78 K to obtain a clear image; it was analyzed at room temperature because field evaporation was easier at this temperature. The background pressure during probing was $\sim 10^{-9}$ Torr. Mainly hydrogen gas was used for imaging; this gas also made the process of field-evaporation easy. The region examined was the $\{111\}$ plane and the pulse fraction was 15%; this fraction was the ratio of the pulse voltage to the evaporation voltage.

Figure 31 shows the mass spectrum for a GaP specimen; the region analyzed was the $\{111\}$ plane. The spectrum consists of essentially Ga^{+1} and P^{+1} ions. Figure 32 is a plot of the cumulative number of Ga plus P atoms as a function of the cumulative number of field-evaporation pulses for the $\{111\}$ plane. The abscissa is proportional to the time elapsed during the evaporation process, therefore the slope of the curve is proportional to the field-evaporation rate. It is clear from this figure that the field-evaporation behavior was step-like and that the field-evaporation rate of the Ga atoms - from the $\{111\}$ plane - was greater than this same quantity for the P atoms. This step-like behavior is consistent with the zinc-blende type structure of GaP, that is, for the $\{111\}$ plane the chemistry is such that one $\{111\}$ plane consists wholly of P atoms and the following $\{111\}$ plane consists only of Ga atoms - this chemical behavior of the $\{111\}$ plane repeats itself periodically throughout the lattice crystal.

Figure 33 is a plot of the number of P atoms versus the number of Ga atoms. The ratio of Ga to P atoms, from one $\{111\}$ layer to the next $\{111\}$ layer,

Figure 31: The mass spectrum of the compound semiconductor GaP.

Figure 32: The pulse field-evaporation behavior of the (111) plane, giving the cumulative number of Ga plus P atoms versus the cumulative number of field-evaporation pulses (constant pulse duration).

Figure 33: The cumulative number of P atoms versus the cumulative number of Ga atoms for the compound semiconductor GaP.

was approximately equal to two. The expected value of this ratio was unity because of the chemistry of the {111} planes of the zinc-blende type structure. This discrepancy is not presently understood; research is in progress to understand our observations.

Figure 34 is a plot of the frequency of occurrence of atoms as a function of the number of atoms detected per field evaporation pulse; the upper value to the latter quantity was eight since our digital timer has eight channels. The average field-evaporation rate ($N_{\text{ions}}/N_{\text{pulse}}$) for the data in Fig. 34a and 34b was 0.01 and greater than 0.02, respectively. The quantity N_{ions} was the total number of As plus P ions detected and the quantity N_{pulse} was the total number of field-evaporation pulses; the pulse frequency was constant at a value of 60 Hz. For $N_{\text{ions}}/N_{\text{pulse}}$ equal to 0.01 the frequency of occurrence of atoms decreased approximately exponentially as a function of the number of atoms detected per field evaporation event. When the ratio $N_{\text{ions}}/N_{\text{pulse}}$ exceeded 0.02 the frequency of occurrence was approximately a constant for one to eight atoms detected per field-evaporation event. In particular, note that there were 281 and 349 events for the detection of one and eight atoms, respectively. This implied that for $N_{\text{ions}}/N_{\text{pulse}} > 0.02$ a number of atoms were most likely undetected. This statement is consistent with the observation that the phosphorous atoms evaporated in both the singly and doubly-charged states, so that many of the heavier - and therefore slower moving - Ga ions were undetected. It is clear from our observations that the detection of all the pulse field-evaporated ions requires that $N_{\text{ions}}/N_{\text{pulse}}$ be less than 0.01.

However, inspite of the above problems, the results on GaP are important from the point of view that even in a semiconductor it is possible to field-evaporate on an atomic layer-by-layer basis, so that it should be possible to investigate defect topics if the conditions of field-evaporation are correctly chosen.

Figure 34: Frequency of occurrence of atoms as a function of the number of atoms per field evaporation event for two different values of the ratio N_{ions}/N_{pulse} .

D. Field-Ion Microscope Imaging of Silicon (Dr. G. Kimmel)

Over the past thirteen plus years (since early 1966) we have worked on many different problems in the areas of point defects and radiation damage in metals employing the field-ion and atom-probe microscope techniques^(23,24). It is now my feeling that we should extend the direction of the research toward the study of defects in semiconducting materials using these two techniques in conjunction with various electron microscope techniques. On the field-ion microscopy side there have been a number of successful experiments on the imaging of semiconductors (silicon, germanium, gallium arsenide, gallium phosphide and β -silicon carbide), as well as the chemical examination of these materials by the atom probe technique (25-30). This work has concentrated, so far, on developing techniques for obtaining good field-ion images and understanding the physical nature of the field ionization and field evaporation processes for semiconductors^(31,32). It has also been shown very recently⁽³³⁾ that atoms from a silicon specimen, in the insulating state, can be pulsed desorbed employing six nanosecond wide pulses from a nitrogen laser. This exciting new discovery will allow semiconducting materials to be analyzed in situ, at cryogenic temperatures, while they are in the insulating state. Only one application of the capability of examining semiconductors has been made to date; this is a study, by Sakurai et al.⁽³⁴⁾, of hydrogen chemisorption on silicon surfaces employing an atom probe. It seems that it is now possible to apply all this background knowledge⁽²⁵⁻³⁴⁾ to the study of defects in semiconducting materials using the field-ion microscopy technique. We would also complement the field-ion microscope imaging work with direct lattice resolution transmission electron microscope research and the atom probe studies with analytical electron microscopy techniques⁽³⁵⁾.

Since in the past our main experience has been with the imaging of metals a special effort was made to achieve high resolution images of silicon. Therefore, we reconsidered every step in the process of obtaining FIM images. In the next few subsections we present the details of our study.

A. Specimens

We obtained - from Dr. J. Patel of Bell Laboratories - single crystal specimens in the form of whiskers; they were grown by the Vapor-Liquid-Solid (VLS) technique.⁽³⁶⁾ These whiskers were very long and narrow - 0.25 mm diameter - and they had an electrical resistivity, at room temperature, of 3000 Ω cm; their diameter was uniform and the electrical resistivity was constant along the length of each whisker. We also examined a second type of whisker, which was obtained from Dr. A.J. Melmed of the National Bureau of Standards (Gaithersburg, Maryland).[†] This whisker was grown by the chemical vapor deposition (CVD) technique and it had a diameter of ~ 0.5 mm and an electrical resistivity in the range of 10^2 to 10^4 Ω cm.

b. Mounting of the Specimen

Since silicon is very brittle at room temperature, it was found to be impossible to hold it in place employing a screw as we normally do for metal specimens. To solve this problem we used indium as a solder. A small amount of indium was inserted into the copper specimen holder through the screw hole. The screw was used as a piston to force the indium to flow toward the orthogonal hole which received the silicon whisker. Next the whisker was inserted in the hole and the copper specimen holder was heated with a solder gun until the indium melted and flowed completely into the hole around the whisker. While the indium was still molten the screw was advanced until its head was below the outer surface of the copper specimen holder; the screw did not apply any mechanical pressure on the whisker. As soon as the solder gun was removed from its contact with copper specimen holder the indium solidified and the specimen was fixed in place. If the whisker failed to make a right angle with the specimen holder the indium was remelted and the whisker adjusted until it was in the proper position.

[†] We are grateful to Dr. Melmed for his kind cooperation and for helpful advice concerning the imaging of silicon.

c. Polishing

The whiskers were polished to a sharp point by chemically polishing them in a solution of hydrofluoric acid and acetic acid (1:1 ratio by volume)*. The whiskers were moved up and down, in the vertical plane, during the polishing process employing a specially constructed stand. The polishing process was observed with a pair of binoculars and the whisker was removed from the solution when a sharply pointed tip was observed.

d. Vacuum and Baking Procedure

The standard procedure in our laboratory is to bake the FIM to obtain a background pressure of $(0.2 \text{ to } 2) \times 10^{-9}$ Torr. Since we used indium as a solder it was necessary to be certain that the temperature of the copper specimen holder did not exceed 130°C during the course of a bakeout. This condition necessitated some changes in the wiring of the platinum resistance thermometer, so that the temperature inside the FIM could be monitored continuously during the course of a bakeout.

e. Results

It was not found possible to achieve a well developed end-form in the presence of either helium gas or helium-air mixtures; the air was admitted through a varian leak valve to a partial pressure of 5×10^{-5} Torr. In view of this situation we used the procedure suggested by Melmed and Stein.⁽²⁵⁾ This involved the introduction of pure hydrogen gas to a gauge pressure of 3×10^{-5} Torr. At this pressure of hydrogen the silicon field-evaporated readily and an end form was obtained. Figure 35 shows an image of Si, obtained employing H_2 as the imaging gas, at a specimen temperature of 30 K and a voltage of 11 kV; the pole at the center of the image is 111.

* Since hydrofluoric acid attacks glass it was found necessary to use a plastic cylinder to hold the polishing solution.

Figure 35: Silicon whisker imaged at 30 K in an atmosphere of H_2 at a pressure of 3.5×10^{-5} torr and at a potential of 11 kV. The central pole is a (111) plane.

E. An In Situ Field-Ion Microscope Study of the Recovery Behavior
of Ion-Irradiated Ordered Alloys - Ni_4Mo and Pt_3Co (J. Aidelberg)

a. Introduction

Isochronal warming experiments of the type described by Seidman^(24,37) were performed on the ordered Ni_4Mo and Pt_3Co alloys. In this experiment the FIM specimen was irradiated in situ, in UHV, in the absence of an electric field. This procedure removed the question of the role played by the imaging electric field (E_i) during the point-defect production-stage. After the specimen was irradiated at a given temperature (T_i) the specimen was re-imaged and then warmed isochronally at a prescribed rate ($\dot{\delta}$), and the FIM images of the surface were simultaneously recorded. The surface of an FIM specimen served as an excellent sink for mobile point defects and the arrival of an SIA was detected as an extra bright-spot(s) which appeared on the surface of an FIM specimen.

During the isochronal warming stage the value of E_i was about $4.4 \text{ VA}^{-1/2}$.⁽³⁸⁾ The effect of E_i was to subject the tip to a negative hydrostatic pressure (p) which was approximately given by the expression $E_i^2/8\pi$.⁽³⁹⁾ This p dilated the lattice and changed the enthalpy of migration (Δh_{li}^m) of an SIA by an amount of $p\Delta v_{li}^m$ which is related to the internal energy change of migration (Δu_{li}^m) through the expression⁽⁴⁰⁾

$$\Delta h_{li}^m = \Delta u_{li}^m - |p|\Delta v_{li}^m = \Delta u_{li}^m - E_i^2\Delta v_{li}^m/8\pi. \quad (1)$$

Therefore, the effect of E_i was to reduce the value of Δh_{li}^m by an amount of $E_i^2\Delta v_{li}^m/8\pi$, which implied that the diffusivity (D_{li}) of an SIA in the stressed state was enhanced and made the SIA mobile at a temperature where in the absence of E_i it would be immobile. The effect of E_i on the value of D_{li} for tungsten⁽⁴¹⁾ and platinum⁽⁴²⁾ SIAs has been studied in detail in our laboratory. These studies showed that the upper limit of Δv_{li}^m , in both cases, was of the order of $(2-3) \cdot 10^{-2}$ atomic volume (Ω_a); thus the value of Δu_{li}^m was reduced by less than 0.02 eV.

In the present work we did not study the effect of E_i on D_{11} but in view of the above results we assumed that the migration processes of the SIAs were affected very little by E_i . Although a downward shift of our data by ~ 7 K as a result of the $p\Delta v_{11}^m$ effect was possible. ⁽²⁴⁾

It is emphasized that the FIM isochronal warming experiment can only detect the SIAs which undergo long-range migration and cannot detect SIAs which recover as a result of close-pair recombination. In addition, because of the progress of image formation of ordered alloys, only one migrating atomic species can be detected, i.e., Pt in Pt_3Co and Mo in Ni_4Mo . But this does not necessarily mean that the recovery spectrum obtained was a result of the migration of only one atomic species. The diffusion process occurred via an interstitialcy mechanism in which both species may have been involved. Thus, even though only one atomic species can be detected, its arrival at the surface of the FIM specimen may have been a result of the migration of both species.

There are six geometrically possible stable interstitial configurations in the fcc lattice. ⁽⁴³⁾ Theoretical calculations ⁽⁴⁴⁾ of the formation energy (U_{11}^f) of a single SIA in pure Cu(fcc) indicated that the most stable configuration was the [100] split interstitial. There are three configurations in which a single atom is distinguished as the interstitial: the octahedral, crowdion and tetrahedral configurations. In the other three configurations, the split interstitials, the extra atom is accommodated by sharing a site with another atom. These split configurations are sometimes referred to as [100], [110] and [111] dumbbells.

The situation in ordered alloys is more complicated than in pure metals because each of the different atoms which constitute the alloy can become an interstitial. There are two sublattices, one for each species, in a binary ordered alloy; an atom from either sublattice can be displaced to an interstitial position. This doubles the number of geometrically possible configurations as compared with a pure metal. Thus, there are twelve geometrically possible con-

figurations for the SIA in binary ordered alloys. Of the possible split interstitials, i.e., two atoms with different chemistry share one atomic site. The mixed [100] dumbbell was recently discovered in dilute Al alloys.⁽⁴⁵⁾ Interstitialcy migration of most of the interstitial configurations involves the migration of both atomic species which constitute the alloy. At present⁽⁴⁶⁾ there are no calculations of the relative values of the migration and formation energies of interstitials in ordered alloys. Because interstitialcy migration in ordered alloys has not experimentally been demonstrated we will compare the recovery behavior of the ordered alloys to the recovery behavior of the component elements of the alloys.

b. Experimental Details

The experiments were performed in the FIM that was attached to the Hill-Nelson sputtered metal ion source.⁽⁴⁰⁾ The irradiations were performed in situ at a pressure of $1 \cdot 10^{-9}$ Torr in the FIM. The total fluence employed was about $(2-10) \cdot 10^{12}$ ions cm^{-2} of either 30 or 60 keV Kr^+ or Xe^+ ions and the flux of ions at the specimen position was about $3 \cdot 10^{10}$ ions $\text{cm}^{-2} \text{sec}^{-1}$.

Since the main reason for performing these experiments was to determine the temperature at which the radiation damage distribution would not change as a result of the migration of SIAs, we irradiated the specimens at the lowest temperature that could be achieved in the FIM, i.e., $T_i \leq 6$ K. At this temperature the only imaging gas that could be used without extensive condensation was helium. Therefore we used helium as the imaging gas even though at high temperatures (70 K for Pt_3Co and 90 K for Ni_4Mo) the FIM images disappeared. The imaging voltage was maintained at a value which was 10% below the BIV characteristic of T_i to prevent continuous field-evaporation of the specimens at high temperatures. After an irradiation, the temperature of the FIM specimen was raised at a δ of $\approx 2 \text{ K min}^{-1}$ while the surface was photographed continuously at a rate of 40 frames min^{-1} which corresponded to 20 frames K^{-1} . The ciné film obtained in the above manner was then examined for the SIA contrast effect, i.e., extra bright-spot which we have denoted a defect.

c. Experimental Results

c.1 Control Experiments

Prior to each irradiation a control experiment was performed. The experimental conditions, i.e., T_i , δ , background pressure and the time the specimen was exposed to the ion source were identical to the experimental conditions for an isochronal warming experiment, except that the ion beam was stopped before it hit the specimen. An average of three artifact SIA contrast effects per control isochronal warming experiment were detected. Since the average number of SIA contrast effects (defects) detected in the isochronal warming experiments was about 30, the background artifact concentration was about 10% of the total number of defects in the irradiated specimens.

c.2 Isochronal Warming Experiments of Pt_3Co Alloy

The presence of a defect in the FIM images was detected by an extra bright-spot contrast effect, ⁽³⁷⁾ which went from no-contrast to full-contrast within one frame of ciné film. Two examples of the appearance of extra bright-spot contrast effects are shown in fig. 36. Each pair of micrographs, recorded before and after the appearance of the defect (see arrows), was taken 1.5 sec apart; the latter corresponded to a temperature interval of 0.05 K. The experimental conditions, the number and the concentration of the defects observed in each isochronal warming experiment are summarized in Table 1. The atomic concentration of defects (f) listed in the last column of Table XVIII was calculated from the equation ⁽⁴⁰⁾

$$f = \frac{N\Omega_a}{V} = \frac{3N\Omega_a}{2\pi R^3(1-\cos\psi)} \quad , \quad (2)$$

where N was the number of defects observed in each isochronal warming experiment and V was the volume element from which the defects originated. The quantity V was calculated for a cone cut out of a sphere of radius R , where the cone's apex coincided with the center of the sphere and its half-angle ψ was 54.7° . The quantity Ω_a was equal to $a_o^3/4$ where a_o was the lattice parameter of ordered Pt_3Co .

The composite isochronal warming spectrum for the three experiments is shown in fig. 37; the ordinate of the spectrum is the fraction of the total number of defects per 5 K interval and the abscissa is the tip temperature. An emergence plot, i.e., the points of emergence of the defects on the surface of the specimen is shown in fig. 38. The five concentric circles shown in this figure divided the area of the hemispherical tip into five equal areas. The angular dependence as a function of θ and ϕ (see inserted drawing in fig. 39) for the emergence distribution presented in fig. 38 is shown in fig. 39. The θ dependence was measured from the [001] direction out to 54.7° and the ϕ dependence was measured from the [011] direction toward the [101] direction. Visually, figs. 39a and 39b demonstrated that the emergence distribution had no angular dependence.

c.3 Isochronal Warming Experiments of Ni_4Mo Alloy

The contrast effect associated with the arrival of an SIA at the surface was identical to that in Pt_3Co , i.e., no-contrast to full-contrast within one frame of ciné film. Two examples of the appearance of extra bright-spot contrast effects are shown in fig. 40. The experimental conditions, the number and the concentration of the defects observed in each isochronal warming experiment are summarized in Table 2. The value of f was calculated using eqn. (2) with $\psi=46.6^\circ$ and Ω_a was equal to $a_o^2 c_o / 10$ where a_o and c_o were the lattice parameters of the ordered bcc Ni_4Mo .

The composite isochronal warming spectrum for the experiments is shown in fig. 41. An emergence plot is shown in fig. 42, and the angular dependence of the emergence distribution as a function of θ and ϕ is shown in fig. 43. The observed emergence distribution showed no angular dependence.

d. Discussion

In the analysis of annealing behavior it is important to pay attention to the state of damage in the irradiated specimen. In a pure metal irradiated with 30 or 60 keV Kr^+ or Xe^+ ions, it has been shown ⁽²³⁾ that depleted zones (DZs) were produced at a depth $\overset{o}{5}$ to 100 Å below the irradiated surface. These DZs

Figure 36: Two examples of SIAs arriving at the surface of an FIM specimen during the isochronal recovery experiment. In (A) the extra bright-spot appeared on the (111) plane at 35 K. In (B) the extra bright-spot appeared on the (224) plane at 45 K. Micrographs (1) and (2) were taken 1.5 sec apart, in both A and B, which corresponded to a temperature interval of 0.05 K.

Table 1. Data for the isochronal recovery experiments of irradiated Pt_3Co .

Specimen Number	Irradiation dose (10^{12} ion cm^{-2})	Xe^+ Ion Energy E_0 (keV)	Tip Radius r_0 (Å)	Number of Defects (N)	Concentration of Defects (f) (10^{-6} at. fr.)
1	7	30	300	20	9.8
2	4	60	310	23	11.3
3	9	60	320	29	14.3

Figure 37: A composite isochronal recovery spectrum for Pt_3Co irradiated at 6 K with 30 or 60 keV Xe^+ ions and warmed to 70 K employing a 2 K min^{-1} warming rate.

Figure 38: An emergence plot representing the positions of the appearance of the extra bright-spots at the surface of an FIM specimen during the isochronal recovery experiments. The five concentric circles in this figure divided the area of the hemispherical tip into five equal areas.

Figure 39: The θ and ϕ dependence for the emergence distribution of defects shown in Fig. 68. In (a) the θ angles $23^\circ 50'$, $33^\circ 54'$, $41^\circ 43'$, $48^\circ 33'$ and $54^\circ 42'$ divided the area observed on the specimens' surfaces into five regions of 0.53 sr each. In (b) the observed area was also divided into five equal regions.

Figure 40: Two examples of SIAs arriving at the surface of an FIM specimen during the isochronal recovery experiment. In (A) the extra bright-spot appeared on the (110) plane at 35 K. In (B) the extra bright-spot appeared on the (150) plane at 50 K. Micrographs (1) and (2) were taken 1.5 sec apart, in both A and B, which corresponded to a temperature interval of 0.05 K.

Table 2: Data for the isochronal recovery experiment of irradiated Ni₃Mo.

Specimen Number	Irradiation dose (10^{12} ion cm^{-2})	Kr ⁺ Ion Energy E_0 (keV)	Tip Radius ($\text{\AA}$)	Number of Defects (N)	Concentration of Defects (f) (10^{-6} at. fr.)
1	5	30	390	29	3.6
2	10	30	400	33	4.1
3	10	30	410	33	4.1

Figure 41: A composite isochronal annealing spectrum for Ni₄Mo irradiated at 6 K with 30 keV Kr⁺ ions, and warmed to 100 K at rate of 2 K min⁻¹.

Figure 42: An emergence plot showing the positions of the appearance of the extra bright-spots at the surface of an FIM specimen during the isochronal recovery experiments. The five concentric circles in the figure divided the area of the hemispherical tip into five equal areas.

Figure 43: The θ and ϕ dependence for the emergence distribution of defects shown in Fig. 72. In (a) the θ angles $20^\circ 22'$, $28^\circ 58'$, $35^\circ 41'$, $41^\circ 23'$ and $46^\circ 35'$ divided the area observed on the specimens' surfaces into five regions of 0.39 sr each. In (b) the observed area was also divided into five equal regions.

consisted of a vacancy-rich core (~ 10 at.%) surrounded by a mantle of SIAs (~ 1 at.%), and a number of SIAs which were separated from the DZs by a distance of $50-100 \text{ \AA}$ produced by the focused RCS mechanism. In irradiated ordered Cu_3Au Jenkins et al. ^(47,48) reported on the creation of zones of disorder within the volumes of the displacement cascades. In summary, the state of damage in an ordered alloy has the characteristics of an irradiated pure metal with the addition of the various disordering effects.

The fact that a binary ordered alloy has two different atoms which accommodate two different sublattices (A atoms on α -sites and B atoms on β -sites) causes the nature of the point defects to be more complex than in pure metals. In an ordered alloy both the α -sites and the β -sites can be vacant, and the A and B atoms can both be in interstitial positions. The atomic configuration of each of these defects will determine the mobility of these defects. Also, the atomic size of the different species and the ordering energy can effect the mobility of these defects. All of the above characteristics of the point defects in ordered alloys cause the recovery behavior to be more complex than in pure metals. Nevertheless, to obtain a first order estimate of the physical quantities relevant to the recovery behavior of point defects the results were analyzed under the assumption of a single thermally-activated diffusion model developed by Scanlan et al. ⁽⁴⁰⁾ for the case of an FIM specimen. The results are also compared with the annealing results for the component elements of the ordered alloys.

The diffusion model ⁽⁴⁰⁾ was based on the following assumptions: (1) the FIM tip was approximated by a sphere of radius R; (2) the initial distribution of SIAs was uniform; (3) the specimen's surface was the dominant sink for SIAs; (4) there were no SIA clusters or SIA-impurity atom clusters formed during the recovery; (5) the diffusion of SIAs occurred via a single thermally-activated process; and (6) the concentration gradient had no angular dependence. The expression ⁽⁴⁰⁾ for the flux of SIAs (J_{1i}) crossing the surface of the FIM tip as a

function of the tip temperature (T) was given by

$$J_{li} = \gamma \exp(-1/y) \sum_{n=1}^{\infty} \exp[-n^2 \Gamma y^2 \exp(-1/y)], \quad (3a)$$

where

$$y = kT/\Delta h_{li}^m, \quad (3b)$$

$$\gamma = f_r 8\pi R c_{li}^0 D_{li}^0, \quad (3c)$$

and

$$\Gamma = \pi^2 D_{li}^0 \Delta h_{li}^m / R^2 \delta k, \quad (3d)$$

The quantity D_{li}^0 is the pre-exponential factor of the SIA diffusion coefficient, c_{li}^0 is the initial concentration of SIAs (cm^{-3}), f_r is the fraction of the total area of the sphere which was observed and k is Boltzmann's constant. This model predicted the Δh_{li}^m value to be:

$$\Delta h_{li}^m = kT_{\max}/y_{\max}, \quad (4)$$

where $T_{\max}$ was obtained from the observed isochronal spectrum and $y_{\max}$ was given by: (49)

$$y_{\max} = 1.25 \cdot 10^{-3} + 0.937(\ln \Gamma - 2 \ln \ln \Gamma)^{-1}. \quad (5)$$

The results of this analysis give a Δh_{li}^m value which is probably accurate to $\leq 10\%$, while the value of D_{li}^0 is most likely uncertain by a factor of ~ 10 . (42)

In order to obtain the best values of Δh_{li}^m and D_{li}^0 using this analysis we had to determine which Γ value was the appropriate one to use; this was done employing eqn. (3d). For each case the values of R and δ were known, and were inserted in eqn. (3d). An approximate value of Δh_{li}^m was obtained employing eqn. (3b) where $y_{\max}$ was calculated employing eqn. (5) with different values of Γ ($10^{10} < \Gamma < 10^{17}$); because of the $\ln \ln \Gamma$ dependence the $y_{\max}$ value did not vary much. The D_{li}^0 value was obtained from (50)

$$D_{li}^0 = g a_0^2 v_0 \exp(\Delta s_{li}^m/k)$$

where g is a geometric factor which depends on the configuration of the SIA (~ 0.3), a_0 is the lattice constant, ν_0 is the attempt frequency and Δs_{li}^m is the entropy change of migration. The attempt frequency (ν_0) was estimated employing the expression⁽⁵¹⁾

$$\nu_0 = \left(\frac{2\Delta h_{li}^m}{ma_0^2} \right)^{1/2}$$

where m is the mass of SIA. This ν_0 was defined⁽⁵¹⁾ as the frequency of the small-amplitude oscillations of an atom in the minima of a potential energy profile.

d.1 Annealing Behavior of the Pt₃Co Alloy

The isochronal warming experiments were performed between 6 and 70 K. The annealing spectrum shown in fig. 37 showed a broad peak centered around 37.5 K which extended to ~ 65 K. No long-range migration (extra bright-spot contrast effects) was observed below 29 K. Employing $\Delta h_{li}^m \approx 0.1$ eV and $m = 1.67 \cdot 10^{-24}$ gr we obtained $\nu_0 \approx 10^{12} \text{ sec}^{-1}$ and $D_{li}^0 \approx 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$, with these values eqn. (3d) yielded $\Gamma \approx 10^{14}$. The exact end of the first thermally activated long-range migration peak could not be determined precisely, therefore in order to calculate Δh_{li}^m the experimental data was terminated at 45 K. The calculated peak shown in fig. 44 superimposed best on the experimental spectrum for $\Gamma \approx 10^{14}$. The fit was made such that the areas under the calculated curve and under the experimental spectrum, which was terminated at 45 K, were equal. The calculated spectrum peaked at $T_m = 38.0$ K and the Δh_{li}^m value obtained for $\Gamma \approx 10^{14}$ was 0.084 eV. Table 3 shows the calculated Δh_{li}^m and D_{li}^0 values obtained for different Γ values. These values indicated that the value of D_{li}^0 was quite sensitive to the value of Γ whereas the Δh_{li}^m value was not; a change by a factor of 10 in Γ , i.e., from 10^{14} to 10^{15} , yielded a $\sim 9\%$ increase in the Δh_{li}^m value, whereas D_{li}^0 increased by a factor of ~ 10 .

The isochronal annealing spectrum of the alloy Pt_3Co was compared mainly to the annealing spectrum of pure Pt for the following reasons: (1) no annealing data for Pt_3Co alloy was available in the literature; (2) the majority of the atoms (75%) constituted the Pt_3Co alloy were Pt atoms; (3) both the alloy Pt_3Co and the metal platinum have the same crystal structure, i.e., fcc; and (4) the metal cobalt has an hcp structure. Standard resistivity measurements of the annealing of pure cobalt showed that the long-range migration state occurred around 55 K.⁽⁵²⁾ For pure platinum, standard resistivity measurements determined the activation energy for migration Δu_{1i}^m to be 0.063 eV at $T \approx 25.5$ K.⁽⁵³⁾ An FIM isochronal warming experiment on pure Pt, performed by Pétroff and Seidman⁽⁴²⁾, was characterized by $T_m = 15$ K and $\Delta h_{1i}^m \approx 0.042$ eV. The difference in the values of Δu_{1i}^m and Δh_{1i}^m was attributed⁽⁴²⁾ to the effect of E_i on the mobility of the SIA and enabled these authors to place a limiting value on the quantity Δv_{1i}^m of about $(2-3)10^{-2}\Omega_a$. In comparison with the FIM isochronal warming experiment on pure platinum the annealing spectrum of Pt_3Co alloy was broader and the peak shifted to higher temperatures, and the Δh_{1i}^m value was higher. These observations agreed with the general annealing behavior of point defects in other order-disorder alloy systems.^(54,55)

d.2 Annealing Behavior of the Ni_4Mo Alloy

The annealing spectrum shown in fig. 41 showed two broad peaks, one peak around 37.5 K and one around 77.5 K. No long-range migration was observed below 29 K. The appropriate Γ value was calculated to be $\sim 10^{14}$. Thus, the calculated peaks superimposed on the experimental spectrum shown in fig. 45 were fitted with $\Gamma = 10^{14}$. The fit was made such that the area under the first calculated peak was equal to the area under the experimental spectrum which was terminated at 45 K. The area under the second calculated peak was equal to the area under the experimental spectrum of the second peak. The first calculated spectrum peaked at $T_m = 37$ K with $\Delta h_{1i}^m = 0.083$ eV and $D_{1i}^0 = 4.14 \cdot 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$, the second peaked at

Figure 44: A calculated isochronal annealing spectrum for a single thermally activated process superimposed on the experimental spectrum for Pt_3Co irradiated with Xe^+ ions.

Table 3: The calculated values of Δh_{11}^m and D_{11}^o obtained for different Γ values.

Γ	Δh_{11}^m (eV)	D_{11}^o (cm ² sec ⁻¹)
10^{12}	0.070	$3.2 \cdot 10^{-5}$
10^{13}	0.077	$2.9 \cdot 10^{-4}$
10^{14}	0.084	$2.6 \cdot 10^{-3}$
10^{15}	0.091	$2.4 \cdot 10^{-2}$
10^{16}	0.098	$2.3 \cdot 10^{-1}$

Figure 45: The calculated spectrum for two single activated processes superimposed on the experimental spectrum obtain for Ni_4Mo irradiated with Kr^+ ions.

$T_m = 75.5$ K with $\Delta h_{11}^m = 0.174$ eV and $D_{11}^0 = 2.0 \cdot 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$.

No isochronal recovery data, for irradiated Ni_4Mo , was found in the literature to compare with the present annealing spectrum. An FIM isochronal warming experiment on pure Mo performed in our laboratory ⁽⁵⁶⁾ showed a major peak centered at 32 K and a minor peak at 45 K which extended to 120 K. Neutron ⁽⁵⁷⁾ and electron ⁽⁵⁸⁾ irradiation of pure Ni showed a long-range migration peak at 57 K with activation energy of about 0.15 eV. A comparison between the alloy and the pure metals data is difficult in this case.

e. Summary

Results of the isochronal recovery behavior of ion-irradiated order-disorder Ni_4Ni and Pt_3Co alloys between 6 and ~ 90 K were reported. The FIM specimens were irradiated in situ under ultra-high vacuum conditions at 6 K, with either 30 or 60 keV Kr^+ or Xe^+ ions, to a total fluence of $(2-10) \cdot 10^{12} \text{ ions cm}^{-2}$. The experimental results showed that in both cases there was no long-range migration of SIAs between 6 and 30 K. The isochronal annealing spectrum for Pt_3Co showed a broad peak centered around 37.5 K which extended to ~ 65 K. The experimental results were analyzed on the basis of a single thermally activated diffusion mechanism. The analysis of the experimental spectrum gave an enthalpy change of migration (Δh_{11}^m) of 0.084 eV and a pre-exponential factor of the SIA diffusion coefficient (D_{11}^0) of $\sim 2.6 \cdot 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$. The isochronal annealing spectrum for Ni_4Mo showed two broad peaks, the first one was centered around 37.5 K and the second one around 77.5 K. The analysis of the experimental results on the basis of a single thermally activated diffusion mechanism gave a Δh_{11}^m value of 0.84 eV and D_{11}^0 value of $\sim 4.14 \cdot 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$ for the first peak, and a Δh_{11}^m value of 0.174 eV and D_{11}^0 value of $\sim 2.0 \cdot 10^{-3} \text{ cm}^2 \text{ sec}^{-1}$ for the second peak.

The isochronal annealing spectrum of irradiated Pt_3Co alloy was broader and slightly shifted to higher temperatures when compared to the annealing spectrum of electron irradiated pure Pt. These effects agreed with the general annealing behavior of point defects in other order-disorder alloy systems as described in the literature.

F. An Atom-Probe Field-Ion Microscope Investigation of Tungsten Irradiated with Very-Low Energy (100-500 eV) Hydrogen Ions. (Dr. A. Macrander)

a. Introduction

A study of hydrogen ions implanted in tungsten- at very low energies (100-500 eV)- was undertaken for a number of reasons. First, the successful measurement of projected range profiles of $^4\text{He}^+$ and $^3\text{He}^+$ ions, implanted along the [110] direction in tungsten, made recently in the same apparatus⁽²⁰⁻²²⁾, indicated that such measurements might also be successfully made for hydrogen ion irradiations. Second, recent thermal desorption measurements indicated that channeling may be an important phenomenon even at extremely low energies⁽⁵⁹⁾ and the atom-probe technique affords a means of confirming this, at least in principle. In addition, if range measurements are made at a series of temperatures or after conducting an annealing schedule, the diffusion constant (D) is obtainable, again in principle. Determinations, of D for ^3He ⁽⁶⁰⁾ and of the activation enthalpy for diffusion of ^4He ⁽²⁰⁾ were made recently using this technique. Similar measurements for hydrogen diffusion in W are desirable because of the quantum mechanical nature of the process believed to be responsible for the diffusion of hydrogen in tungsten, namely, tunneling between octahedral interstitial sites of the bcc lattice.

The range of energies available for such studies is limited by the imposition of a perfect lattice. The minimum transferred energy necessary to create a stable Frenkel pair is $\geq 43\text{eV}$ in the center-of-mass frame of reference.⁽⁷⁾ This implied that for laboratory energies $\leq 1,860\text{ eV}$ Frenkel pairs were not created by proton irradiations*. Analyzing an irradiated specimen is time consuming

*Whether or not an H_2^+ ion impinging on the surface can be considered as two protons each with one half the projectile energy - for the purposes of these experiments - is not known. It seemed likely that this was a good assumption⁽⁶¹⁾ and, if one has confidence in the results exhibited in fig. 46, it appeared that the two assumptions differ only slightly below 500 eV. It will be assumed in what follows that the molecular ion does indeed breakup at the surface into two protons, each with one half the total energy. Fluences were thus expressed as protons cm^{-2} .

since careful analyses required three to five minutes per plane. Thus to analyze 100 (110) planes required from five to eight hours. One hundred planes corresponds to a depth of only 22.4° Å. It was thus essential to have a good estimate of the mean projected range to gauge the probing depth required. To this end, TRIM Monte Carlo simulations were performed on our NOVA 1220 mini-computer. The results of the mean projected range versus proton energy calculations are presented in fig. 46. Deuterium (or H_2^+) points are also shown. A full discussion of the TRIM code employed will be presented elsewhere. The lower limit on useful projectile energies was set by the maximum depth of the surface peak, which arose from the background (see Section G). This peak never extended beyond the tenth plane or 22.4° Å. It was thus clear that the most desirable H_2^+ irradiation energies lay in the range 100-500 eV- i.e., proton irradiation energies in the range 50-250 eV- because they provided projectile ranges beyond the surface peak and they required the least probing time. Also, recent unpublished work by Kornelsen and van Gorkum⁽⁵⁹⁾ suggested that the optimum low-energy channeling conditions should prevail in part of this energy range.

b. Null Results at High Temperatures

Meaningful information about the mobility of hydrogen in tungsten was obtained for experiments conducted in the temperature range 29-49 K[†]. The data shown in fig. 47 typify these results. These data were obtained subsequent to a 200 eV H_2^+ irradiation at an angle of $5 \pm 5^{\circ}$ from the normal to tungsten (110) surface and to a fluence of $2.9 \times 10^{15} \text{ cm}^{-2}$ at a temperature of 29 K. The background pressure in the UHV main chamber (gauge pressure)* was 5.8×10^{-10} torr at the start

† Temperatures were measured with a Rosemount platinum resistance thermometer and are believed to be accurate to ± 1 K.

* Approximate H_2 partial pressures can be obtained from gauge pressures by assuming that the entire background is due to H_2 and by correcting for the increased ionization efficiency of H_2 compared to N_2 . This implied that gauge pressures had to be multiplied by 2.0. (62)

Figure 46: TRIM Monte Carlo simulation results for the mean range of protons ($^1\text{H}^+$) and deuterons ($^2\text{H}^+$) in tungsten. The TRIM code is based on a binary collision model and applies to an amorphous solid. It was tailored to apply to low energies by means of modifications which are based on theoretical grounds. General agreement between experimental atom-probe results and TRIM results has been found for low energy helium ion irradiations of tungsten.

Figure 47: Atom-probe FIM depth profile of a W(110) specimen irradiated with 200 eV molecular hydrogen ions ($^1\text{H}_2^+$) to a fluence of $2.9 \times 10^{15} \text{ atoms cm}^{-2}$. The temperature during both the irradiation and the analysis was 29 K, and the background gauge pressure was $5.8 \times 10^{-10} \text{ Torr}$.

of probing and decreased to 2.8×10^{-10} torr by the end of the experiment. The dramatic surface peak shown was consistently observed in such experiments and arose from the background (see Section G). The major point of these data was that no implanted profile was found; the TRIM results would have placed the mean projected range at $\sim 38 \text{ \AA}$. Other runs were continued to greater depths; for example, a null result was also obtained for a specimen irradiated at 500 eV ions to a fluence of $12.9 \times 10^{15} \text{ cm}^{-2}$, held at 38 K, and probed to a depth of 157 planes or $352 \text{ \AA}$. Two interpretations were possible based on these data alone: (1) hydrogen was mobile in tungsten at temperatures as low as 29 K; or (2) the reflection coefficient for the irradiations was so large that no implanted hydrogen could be measured. The second possibility was supported, somewhat, by the TRIM results which indicated that the reflection coefficient could be as high as 80% (see also ref. 63). However, even with a reflection coefficient of 80%, a fluence of $12.9 \times 10^{15} \text{ cm}^{-2}$ implied that roughly 500 implanted hydrogen ion events should have been detected in a profiling experiment, in the cylinder of tungsten analyzed. Qualitative observations presented in section F.d suggested that the first possibility is probably correct.

c. Profiles Obtained at Temperatures Near 25 K

The data discussed in section F.b suggested that the temperature had to be reduced in experiments hoping to measure a range profile of implanted hydrogen atoms. Data for a 200 eV H_2^+ irradiation to a fluence of $3.0 \times 10^{15} \text{ cm}^{-2}$ are shown in fig. 48. During this run the temperature oscillated from 20 to 23 K, and the gauge pressure oscillated from 3.0×10^{-10} to 3.6×10^{-10} Torr at the start of probing and decreased to 2.0×10^{-10} to 2.2×10^{-10} Torr by the end of the experiment. Such oscillations were apparently unavoidable below 24 K due to the design of the atom-probe specimen stage. The specimen stage was not attached directly to the cold finger but was heat linked via a gold braid. This arrangement was necessary because of the need to have the specimen mounted on a goniometer and limited very stable

Figure 4B: Atom-probe FIM depth profile of a W(110) specimen irradiated with 200 eV molecular hydrogen ions ($^1\text{H}^+$) to a fluence of $3.0 \times 10^{15} \text{ atoms cm}^{-2}$. The temperature during both the irradiation and the analysis ranged from 20 to 23 K, and the background gauge pressure ranged from 2.0×10^{-10} to 3.6×10^{-10} Torr.

temperatures to the approximate range of 24 K and above. A stable temperature of 24 K was achieved but could not be reproduced at will. Positioning of the transfer tube was crucial and could not be controlled well enough. Evident in fig. 48 are the occurrence of H^+ ionization events in an apparently random fashion and to much greater depths than predicted by the Monte Carlo simulation program. The data suggested that a high background count rate interfered with the range measurement. Expressed as the average number of $^1H^+$ ionization events per plane and reduced by the average number of tungsten atoms per plane this irradiation profile (beyond the surface peak) corresponded to 4.4×10^{-3} . The control run shown in fig. 49 bears this out. These data were obtained for a 200 eV irradiation on the ion gun flag for conditions very closely resembling those present when the data in fig. 48 were obtained. The results implied a value of $9 \times 10^{-3} H^+$ ionization events per tungsten ionization event. Evidently, the high background H^+ ionization rate was a serious limitation.

Perhaps the most likely reason for this high background was suggested by our observation that the pressure in the FIM oscillated when the temperature oscillated. These oscillations followed each other closely and were undoubtedly due to the condensation and subsequent evaporation of the background hydrogen in the FIM. During almost all the experiments a significant fraction of the background gas in the atom probe was hydrogen. It seemed likely, therefore, that an enhanced hydrogen vapor phase density in the vicinity of the critical region for ionization caused the high background count rate at and below 25 K. At higher temperatures this effect was apparently not significant. These observations suggested that an hydrogen partial pressure at least a decade lower (10^{-11} Torr) would probably be required to successfully measure profiles of hydrogen implanted into tungsten using the atom-probe FIM technique.

d. Qualitative Observations

Three distinct qualitative observations were made during the course of the H_2^+ irradiation studies. All three suggested that hydrogen is immobile in tungsten

Figure 49: Atom-probe FIM depth profile of a W(110) specimen obtained subsequent to a control irradiation with 200 eV molecular hydrogen ions (H_2^+ on the ion gun flag, i.e., the ion beam was blocked off from the specimen). Experimental conditions resembled quite closely those present when the data in Figure 48 were obtained.

at 25 K.

Specimens that were irradiated to high fluences and at temperatures ≤ 25 K were mechanically very weak. Two specimens irradiated to fluences of $9.8 \times 10^{15} \text{ cm}^{-2}$ and $7.4 \times 10^{15} \text{ cm}^{-2}$ —both with 100 eV H_2^+ ions—failed mechanically at the very onset of vacuum field evaporation, for example. Specimens irradiated to a fluence of $\leq 3 \times 10^{15} \text{ cm}^{-2}$ were generally more successfully probed. If the implanted hydrogen atoms had diffused to the surface (the dominant sink) it would be difficult to explain such a mechanical weakening. On the other hand, it is much easier to understand how a specimen might be weakened if it remained supersaturated with hydrogen subsequent to an irradiation.

The second observation concerned the altered surface peak in profiles obtained for specimens irradiated to high fluences at high temperatures. This is typified by the data shown in fig. 50. These data were obtained for a specimen irradiated at 205 eV to a fluence of $6.8 \times 10^{15} \text{ cm}^{-2}$ at 40 K. The background pressure was 6.7×10^{-10} Torr. The altered nature of the surface peak compared to fig. 47-49 (see also Section G) suggested that the outward flux, through the surface, of a large quantity of implanted hydrogen somehow altered the hydrogen concentration near the surface. Other runs which had similarly distorted surface peaks were observed at 38 K and involved irradiations at 500 eV to fluences of $7.1 \times 10^{15} \text{ cm}^{-2}$ and $12.9 \times 10^{15} \text{ cm}^{-2}$. Such surface peak distortion was not observed for 100 eV irradiations made at 25 K, 26 K, and 25 K and irradiated to fluences of 6.1×10^{15} , 7.4×10^{15} and $9.6 \times 10^{15} \text{ cm}^{-2}$, respectively, suggesting that in these cases the hydrogen was immobile. In runs at high temperatures involving irradiations to lower fluences ($\leq 4 \times 10^{15} \text{ cm}^{-2}$) such distorted surface peaks were not observed (see, for example, fig. 47).

The third observation was made during an aborted run. A specimen which had been implanted with hydrogen, at 26 K, using 100 eV H_2^+ ions to a fluence of $5.8 \times 10^{15} \text{ cm}^{-2}$ was abruptly warmed to room temperature. Subsequently, the micrograph shown in fig. 51 was made. Apparently, the rapid diffusion of hydrogen to

Figure 50: Atom-probe FIM depth profile of a W(110) specimen irradiated with 205 eV molecular hydrogen ions ($^1\text{H}^+$) to a fluence of 6.8×10^{15} atoms cm^{-2} . The temperature during both the irradiation and the analysis was 40 K, and the background gauge pressure was 6.7×10^{-10} Torr. The altered nature of the surface peak compared to previous figures is believed to be significant.

Figure 51: Two FIM micrographs of a single W(110) specimen. The top one shows the specimen before performing the irradiation. The lower one shows this same specimen subsequent to an irradiation with 100 eV molecular hydrogen ($^1\text{H}_2^+$) to a fluence of 5.8×10^{15} atoms cm^{-2} at 23-25 K. After implanting the specimen with hydrogen it was warmed to room temperature. Three days later the specimen was again cooled to ~ 24 K and imaged. The lower photograph was then made after field evaporating several W(110) layers to improve the quality of the image. Note the presence of the large black hole.

the surface during the rapid warming resulted in a violent explosion of a small part of the field-ion tip. An unusually large concentration of carbon, 8.7 at.%, was detected near the ruptured region, whereas none was detected in a run completed on the specimen prior to the development of the rupture. Also the concentration of oxygen found near the rupture was only 1.2% eliminating the possibility that the carbon resulted from dissociation of CO_2 . We hypothesize that a hydrogen bubble was nucleated at the carbon atoms and formed a blister, which subsequently burst; see the black hole in fig. 51.

e. Conclusions

The three qualitative observations taken separately may not provide very strong evidence for the mobility of hydrogen. However, considered together and in conjunction with results of section F.b it seems plausible that interstitial hydrogen was immobile in tungsten at 25 K and became mobile in the temperature range 25 - 29 K. This temperature range when converted to an activation energy for SIA diffusion ⁽⁶⁴⁾ yielded Δh_{1H}^m approximately equal to 0.07 eV.

G. An Atom-Probe Field-Ion Microscope Study of Hydrogen Adsorption on the (110) Plane of Tungsten (Dr. A. Macrander)

a. Introduction

In experiments attempting to measure projected range profiles of low-energy hydrogen implanted normal to the (110) plane of tungsten a large surface peak was generally observed (see Section F). The data presented below demonstrated that this surface peak arose from the partial pressure of hydrogen in the background of the atom-probe FIM. Results that have, so far, been obtained from the adsorption studies presented here and that were critically contrasted to other results in the literature are: (1) the saturation coverage at 30 K; and (2) sticking coefficients of hydrogen on the (110) plane of tungsten. As demonstrated in Section F, specimens pulse field evaporated subsequent to an extended exposure to the atom-probe background gases exhibited a hydrogen profile during the field evaporation of

approximately the first five to ten (110) layers of tungsten. The data in Section G were obtained subsequent to irradiations, during which the partial pressure of hydrogen in the main chamber of the atom-probe was $\sim 1 \times 10^{-7}$ Torr. Irradiations lasted typically from one-half to one hour. The results presented in this section demonstrated that these conditions were sufficient to saturate the surface with hydrogen. After an irradiation, the main chamber was pumped to the 10^{-10} Torr range before the field evaporation experiments were conducted. To increase our understanding of the surface profile a sequence of experiments - in which clean* specimens were exposed to the background for controlled exposures - were conducted.

b. Standing Voltage Dependence

It is clear from the data presented in Section F that for temperatures ≥ 29 K, hydrogen was not field desorbed once one had removed, by pulse-field evaporation, about ten (110) layers of tungsten. In this state a specimen was designated as clean. The procedure for the experiments discussed here was to rapidly decrease to zero both the pulse and standing voltages applied to a clean tip - wait for a specific length of time - then rapidly increase the voltages to the field desorption values and probe through the new hydrogen surface profile. Preliminary to these experiments, however, the data shown in fig. 52 were obtained. These data were obtained by turning off the pulse voltage and decreasing the standing voltage to a given value - then waiting five minutes - and finally probing to determine how much hydrogen had been adsorbed. The abscissa indicates the standing voltages present during the waiting time and the ordinate indicates the total number of hydrogen atoms in the entire surface peak, $N_H^V(5 \text{ min})$ divided by the average number of tungsten atoms per plane, $\bar{N}_w$. As will be demonstrated in Section G.c the fact that at zero volts DC, $\theta = N_H^V(5 \text{ min})/\bar{N}_w$ equaled one is significant; the saturation

* The significance of the word clean will be apparent in this section.

Figure 52: The surface coverage of hydrogen on W(110) after five minute exposures to the background gases at various standing voltages. The ordinate gives the total number of hydrogen counts ($^1\text{H}^+$) obtained in an entire surface peak normalized by the average number of tungsten atoms in a single plane.

coverage was such that there was one hydrogen atom in the surface peak per tungsten atom on the top plane. It will be seen that the deviation from unity for $N_H^V(5 \text{ min})/\bar{N}_W$ for the datum at 2 kV is not significant given the resolution of our experimental technique.

These experiments were conducted to determine what voltages were required to keep hydrogen off of the surface of the specimen, i.e., to keep hydrogen from adsorbing on the tip. Figure 52 demonstrates that below a value of $V_{dc} = 7.4 \text{ kV}$ hydrogen was adsorbed. This voltage was simply the value required to produce an electric field sufficient to ionize the hydrogen gas before it could be adsorbed. The radius of the specimen was $292 \text{ \AA}$ and the tip to screen distance was 1.87 cm . These imply an electric field value of $2.83 \text{ V \AA}^{-1}$ existed at the surface of the tip.⁽⁶⁵⁾ The electric field necessary to produce FIM images with hydrogen as the imaging gas is $2.28 \text{ V \AA}^{-1}$.⁽⁶⁵⁾ The difference between these two values were not considered significant. It was clear from these results that we had some flexibility in decreasing and increasing the voltages during an adsorption experiment conducted as described above; the critical voltage for adsorption was fortunately lower than the field evaporation voltage.

c. Adsorption Experiments

In fig. 53 are shown the results of 28 experiments, i.e., the total number of hydrogen atoms found in the analyses of the surface peak in each of 28 separate exposures. To decrease the applied voltages to zero and to increase them back to the field evaporation voltages required a finite length of time during which some hydrogen was adsorbed. Thus there is some offset for $t=0$ in fig. 53. Three sets of conditions prevailed as indicated; these data were obtained on three separate days. Immediately obvious from these data is the fact that the saturation coverage corresponds to one hydrogen atom in the surface peak per tungsten atom in the top plane. This result was expressed as a saturation coverage of $(1.4 \pm 0.1) \times 10^{15} \text{ cm}^{-2}$ for hydrogen on W(110) at 30 K. Saturation values for the coverage have been published in the literature and they are listed in Table I. It appears

Figure 53: The surface coverage of hydrogen on W(110) after exposures to the background gases at zero applied field for controlled time

Table I: Saturation Coverage and Sticking Coefficients of Hydrogen on W(110)

Year	Authors	Saturation Coverage (θ_{sat}) atom cm ⁻²	Sticking Coefficient (S)
1971	Tamm and Schmidt (67)	1.05×10^{15} (a)	≤ 0.07
1973	Madey (73)	1.42×10^{15} (b)	----
1974	Barford and Rye (69)	1.82×10^{15} (c)	0.22

(a) Based on a ratio of 0.7 ± 0.1 (obtained in a thermal desorption experiment) for W(110) coverage to W(100) coverage and an assumed value of 1.5×10^{15} atoms cm⁻² for the saturation coverage of W(100).

(b) Based on the experimental value of 2.0×10^{15} atoms cm⁻² (obtained by extrapolating to zero sticking coefficient in an electron stimulated desorption experiment) for the saturation coverage of W(100) and using the relative coverage data of ref. 67.

(c) Based on the value of 0.91 (obtained in a flash desorption experiment) for the ratio at the W(110) to W(100) saturation coverages and the absolute coverage result for W(100) cited in ref. 73.

that the present field desorption technique has yielded the most direct measurement of the saturation coverage, a crucial quantity in deciding between models for adsorption sites. Furthermore, none of the authors quoted in Table I gave experimental uncertainties. In the present case the standard deviation of saturation coverages yields our experimental uncertainty.

The present data also allowed a comparison of sticking coefficients (S) with values published in the literature. The coverage after an exposure to a pressure (P) at a temperature (T) lasting for a time (t) in seconds is given by

$$\theta = \frac{2}{\beta} \frac{P}{\sqrt{2\pi m k T}} \int_0^t S(t') dt'$$

where S is the sticking coefficients, $\beta = 1.4 \times 10^{15} \text{ cm}^{-2}$ is the surface density of W atoms in the (110) plane and m is the mass of a hydrogen molecule. It is clear from the data in fig. 53 that in two cases S behaved almost singularly. In the third case, the coverage increased almost linearly with time, implying a value of 0.15 for S . In Table I are listed two values for S which were found in the literature. These were obtained using oriented single crystals cut to expose the W(110) face, with an attendant uncertainty about the microstructure of the surface. In the present technique, the field evaporation end form of the field-ion specimens had perfect W(110) planes, a fact which was checked visually by field-ion microscopy.

It is hoped that the detailed behavior in fig. 53 will yield information about the surface diffusion and adsorption processes. These experiments are very sensitive to ambient conditions as illustrated by the data in fig. 54. Further experiments to determine the pressure and temperature dependence of these adsorption data are planned.

d. Conclusions

In order to obtain agreement with published values for the saturation coverage it appeared that the entire surface peak of hydrogen that was observed in

Figure 5b: The surface coverage of hydrogen on W(110) after exposures to the background gases at zero applied voltage for controlled time periods.

the field evaporation experiments of W(110) must be considered as lying on the surface of the specimen. It may, however, be the case that the solubility of hydrogen near the (110) top surface of our specimens was high enough to allow some penetration (which could also have been the case in the published studies). Bulk solubilities are believed to be extremely small.⁽⁷²⁾ The details of the field desorption process must be examined before such a conclusion can be made based on present results.

H. Atom-Probe Field-Ion Microscope System Improvements

(Drs. A. Macrander and M. Yamamoto)

a. Peripherals to the NOVA 1220 Minicomputer

A DEC writer II was installed to replace the ASR 33 teletype. Because of the expense involved in making photographic hard copies of the Tektronix 4010 CRT display, a good hard copy capability was needed. The new terminal prints at 30 cps (characters per second) on ordinary paper and has a maximum column width of 132 characters. Whereas the teletype printed at 10 cps with a maximum column width of 80 characters. The DEC writer is also far quieter at 48 db, and with a 20 mA interface we were able to attach it to the same connector that had been used for the teletype.

Data shortage had been on cassette magnetic tapes. Presently, each cassette costs ~ \$6 and can store up to 50 K 16 bit words. A Data General model 6030 dual disk drive unit (with interface board in the NOVA 1220 main chassis) was installed not only to upgrade the data storage capability but also to facilitate programming. A single eight inch floppy disk can store up to 150 K 16 bit words and presently costs ~ \$3. The NOVA 1220 with cassettes had been (and still can be) operated under SOS (Stand-alone Operating System). Tapes do not have directories and must repeatedly be rewound, and there was no capability to edit parts of BASIC programming lines. FORTRAN programs under SOS required mounting new tapes for each of the steps: editing, compiling,

assembling and loading. The disk unit is now operated using DOS (Disk Operating System). Under DOS disks have directories - a fact which greatly facilitates bookkeeping; BASIC programming lines can be edited in whole and in part; and FORTRAN programs can be edited, compiled, assembled and loaded using a single floppy disk. Furthermore, DOS allows overlaying portions of memory on disks to extend memory and allows configuration of a multi-user system (although in the present hardware configuration this would require additional interfaces).

A converter program has been installed to read programs from cassettes and then write them on disks. This program is operated under RTOS (Real Time Operating System). The atom-probe FIM is operable exactly as it had been using the same BASIC language code (APOS).

b. Additions to the Goniometer

The original design of the goniometer in the atom-probe FIM by Brenner and McKinney (73) has been given two small additions. The tube, rod, collar with pins, bushings, and bellows attachment cap (all pertaining to the horizontal motion driveshaft) were replaced (and a spare set made) owing to wear. In addition, the drive arm was modified to provide better clamping to the rod and two new clamps were added to the drive shaft - one on the bellows side and the other on the specimen side - to prevent slippage and subsequent backlash.

I. Segregation to Voids in Fast-Neutron Irradiated Refractory Metals and Alloys

A large number of wire specimens of tungsten, tungsten (rhenium), molybdenum, molybdenum (titanium), TZM, iron and iron (silicon) were irradiated in EBR-II. The specimens that were irradiated with the generous help of Dr. Martin Grossbeck of the Oak Ridge National Laboratory (ORNL) were removed from their capsules and are in the midst of "cooling off", i.e. there are a

number of radioactive elements in some of the specimens which make them too hot for us to receive at Cornell. It's anticipated that we will be able to accept a significant fraction of the specimens within the next three months. Once we receive the specimens we plan to resume our studies on the segregation of alloying elements to voids. (74)

J. The Recovery Behavior in Stages I, II and III of Proton-Irradiated Tungsten (Dr. R.S. Averback - Argonne National Laboratory)

A cooperative program, with Dr. R.S. Averback of the Argonne National Laboratory, was initiated during the 1977-78 contract year. This work is being done with no direct costs to the present contract. The objective of this work is to study recovery mechanisms in Stages I, II and III of proton-irradiated tungsten to both supplement and complement our work on tungsten ion or electron irradiated tungsten. The spatial arrangement of damage in proton-irradiated tungsten consists of almost a random distribution of vacancies and SIAs; thus the initial state of damage is very similar to that of electron-irradiated tungsten. In addition, because of the high incident energy (up to 450 keV) of the proton beam and the small diameter of the FIM specimens ($<1000 \text{ \AA}$) it is possible to irradiate the specimens in-situ without implanting any hydrogen in them. During the past year the FIM was attached to the 459 keV ion-accelerator. This program will continue as soon as a graduate student or technical assistant can be located to help with the experimental work as Dr. Averback is rather "short of hands" at present.

K. SEMINARS AND MEETINGS

Seminars and talks were presented at the following institutions and meetings:

1. Advances in Instrumentation Symposium, Invited Lecture, University of Connecticut, Storrs, Connecticut, May 1979.
2. Sandia Laboratories, Albuquerque, New Mexico, Surface Physics Group, June 1979.

3. Metropolitan New York Section of the Microbeam Analysis Society, Invited Lecture, Paramus, New Jersey, June 1979.

4. 8th International Conference on Atomic Collisions in Solids, Hamilton, Canada, August 1979. One invited paper plus three poster session papers were presented.

5. 1979 TMS-AIME Fall Meeting, Milwaukee, Wisconsin, September 1979: Three papers were presented at this meeting.

6. Westinghouse Research and Development Laboratory, Pittsburgh, Pennsylvania, Invited Lecture, September 1979.

7. Pennsylvania State University, Joint Materials Science and Solid State Physics Seminar, Invited Lecture, October 1979.

8. Spring Meeting of the AIME, Invited Lecture, Las Vegas, Nevada, February 1980.

9. University of California, Berkley, California, Department of Materials Science, Invited Lecture, February 1979.

III. OTHER FINANCIAL ASSISTANCE

A total of \$23,741 will have been received, by June 30, 1980, from the National Science Foundation through the Cornell University Materials Science Center, for the period July 1, 1979 to June 30, 1980. These research funds were used to support one graduate research assistant on a project involving the study of segregation to stacking faults in the refractory metal alloy $C_0(Nb)$.

IV. LIST OF DOCUMENTS GENERATED DURING THE CONTRACT PERIOD

1. "The Study of Defects and Radiation Damage in Solids by Field-Ion and Atom-Probe Microscopy", D.N. Seidman, COO-3158-78.
2. "Direct Determination of Radiation Damage Profiles in the Order-Disorder Alloy Pt_3Co Irradiated with Low-Energy (500-2500 eV) Ne^+ Ions", J. Aidelberg and D.N. Seidman, COO-3158-79.
3. "Sputtering of Tungsten: A Direct View of the Near Surface-Damage Created by a Single 30 keV $^{63}Cu^+$ Projectile", M.I. Current and D.N. Seidman, COO-3158-80.

4. "The Direct Determination of Radiation Damage Profiles in the Order-Disorder Alloys Ni_3Mo and Pt_3Co Irradiated with 500 to 2500 eV Ne^+ Ions", J. Aidelberg, Ph.D. Thesis, Cornell, January 1980, C00-3158-81.
5. "Single Atom Sputtering Events: Direct Observation of Near-Surface Depleted Zones in Ion-Irradiated Tungsten", M.I. Current, C.-Y. Wei and D.N. Seidman, C00-3158-32.
6. "On the Low-Temperature Mobility of Hydrogen Implanted in Single-Crystal Tungsten", A.T. Macrander and D.N. Seidman, C00-3158-83.
7. "A Field-Desorption Study of Hydrogen Adsorbed on the (110) Plane of Tungsten at 25 to 40 K", A.T. Macrander and D.N. Seidman, C00-3158-84.
8. "Modifications to the TRIM Monte Carlo Simulation Program", A.T. Macrander, C00-3158-85.
9. "On the Spatial Resolution of Field-Evaporation from (110) Planes of Tungsten", A.T. Macrander, M. Yamamoto and D.N. Seidman, C00-3158-86.
10. "Defects in Metal Crystals", Annual Progress Report, D.N. Seidman, C00-3158-87.

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