Range Profiles of 300- and 475-eV $^4He^+$ Ions and the Diffusivity of ^4He in Tungsten

Alfred Wagner[(a)] and David N. Seidman
Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853
(Received 23 October 1978)

Range profiles for 300- and 475-eV $^4He^+$ ions implanted *in situ* in tungsten at 60, 61, 80, 90 K were measured, directly and absolutely, employing an atom-probe field-ion microscope. A mean range ($\bar{x}$) of 40±4 Å and a parent standard deviation (σ) of 20 to 36 Å was obtained for 300-eV $^4He^+$; values of $\bar{x}$ and σ of 56±6 Å and 37 to 42 Å, respectively, were determined for 475-eV $^4He^+$. The existence of an isolated and immobile interstitial ^4He atom was established and an enthalpy change of migration of 0.24 and 0.32 eV was determined.

Current interest in the fundamental properties of helium in metals has been generated by the materials problems associated with the development of the liquid-metal fast-breeder reactor[1] and the controlled thermonuclear reactor.[2] However, because of a lack of appropriate experimental techniques the investigations of the range of low-energy (<1 keV) implanted He ions and the diffusivity of He in metals have been largely theoretical.[3-5] Measurement of the range profiles of implanted He ions have been confined to energies[6] >1 keV; furthermore, the measurement of both the range profiles of implanted He and the diffusivity of He in metals have relied exclusively on the trapping of He at lattice defects introduced as a result of heavy-ion irradiation.[7]

The accomplishments of our work on tungsten (W) reported here are (1) the establishment of the ability of the atom-probe field-ion microscope (FIM)[8,9] to detect implanted ^4He atoms retained in a perfect (i.e., totally defect-free) lattice; (2) the detection of the presence of an isolated and immobile interstitial ^4He atom; (3) the measurement of the range profile of low-energy (<1 keV) implanted ^4He ions in a perfect lattice; and (4) the determination of the temperature at which interstitial ^4He atoms become mobile in a perfect lattice. The above accomplishments represent the first successful study of some very fundamental properties of ^4He under conditions where the ^4He does not interact with other lattice defects; at present the atom-probe technique is the only one available to measure these properties.

The basic physical ideas involved in the experimental procedures are illustrated sequentially in Fig. 1. A single-crystal W FIM specimen, at an irradiation temperature (T_i), was irradiated *in situ* with 300- or 475-eV $^4He^+$ ions parallel to the [110] direction as shown in Fig. 1(a); the corresponding values of the reduced energy parameter (ϵ) in the Lindhard, Scharff, and Schiøtt (LSS) theory[10] are 1.47×10^{-2} and 2.33×10^{-2} for 300- and 475-eV $^4He^+$ ions, respectively, on W. A 300-eV ^4He atom can transfer a maximum energy of ~25 eV to a W atom in a head-on two-body elastic collision. Since the minimum displacement energy for the production of a stable Frenkel pair in W is ≈42 eV,[11] no self-interstitial atoms (SIA's) or vacancies are created at an implanatation energy of 300 or 475 eV. With no SIA's or vacancies present to act as trapping centers, implanted ^4He atoms can remain in the specimen only if ^4He is immobile at T_i. Thus, the state of the W specimen after an irradiation consisted of immobile interstitial ^4He atoms implanted in a perfect W lattice with a depth $^4He^+$ distribution that is determined solely by the range profile of the low-energy ions. Next, the specimen was analyzed chemically, by the atom-probe technique, at a standard reference temperature (T_r), where $T_r \le T_i$, and a ^4He integral profile was plotted as shown in Fig. 1(b); this is an integral profile since it measures the cumulative number of ^4He atoms as a function of the cumulative number of W atoms (depth) from the irradiated surface. The depth scale is converted from cumulative number of W atoms to angstroms from the measured number of W atoms per (110) plane contained within the cylindrical element sampled; see Fig. 1(a). Finally the ^4He range profile, Fig. 1(c), may be constructed by taking the first derivative of the integral profile shown in Fig. 1(b); or alternatively by plotting a frequency distribution diagram.

A novel technique for the determination of an absolute depth scale was developed; Fig. 2 schematically illustrates the method. During the atom-probe analysis the specimen was oriented and the magnification adjusted so that only the central portion of the W(110) plane was chemically analyzed. The specimen was then pulsed field evaporated through the repeated application of high-voltage pulses. Three successive stages in

© 1979 The American Physical Society

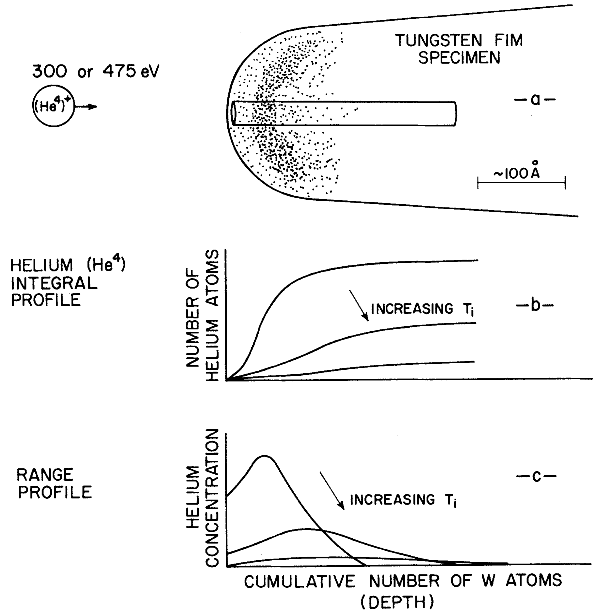

FIG. 1. (a) The *in situ* irradiation of a W FIM specimen with 300-eV $^4He^+$ ions at a T_i where the implanted ^4He atoms are immobile. The density of spots corresponds to the approximate range profile of ^4He in W. The cylindrical volume element represents the volume chemically analyzed by the atom probe. (b) The number of ^4He atoms versus depth as a function of T_i. Note that the ^4He integral profile tends to flatten out as a T_i is increased. (c) The range profiles of ^4He in W as a function of T_i.

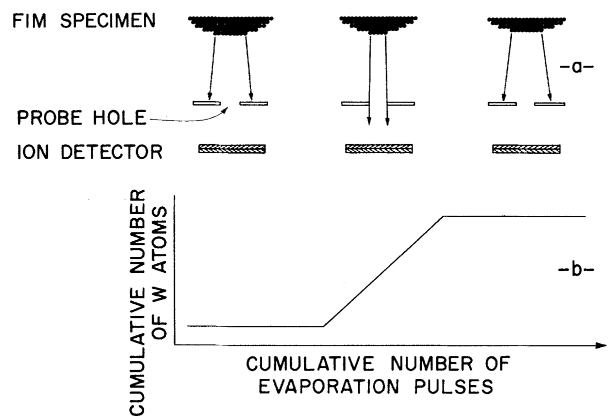

FIG. 2. A schematic diagram illustrating the method employed to determine an absolute depth scale. Three states in the field evaporation of one (110) plane of W are shown in (a). The field-evaporation behavior of this plane is indicated in (b) by the steplike increase in the rate at which tungsten atoms are detected.

the pulsed field evaporation of one (110) plane are indicated in Fig. 2(a). As the plane was pulsed, field-evaporated atoms were detected as indicated by the positive slope in Fig. 2(b). When a plane was completely evaporated the slope of the curve in Fig. 2(b) returned to zero. Therefore the removal of one (110) plane resulted in a single-step increase in the plot of the number of W atoms detected versus the number of field-evaporation pulses applied to the specimen. Since the W lattice was employed as a depth marker, the absolute depth of each implanted ^4He atom from the initial irradiated surface was measured to within one (110) interplanar spacing (≈ 2.2 Å) independent of the total depth of analysis. Thus the spatial depth resolution of the atom-probe technique is limited solely by the interplanar spacing of the region being analyzed.

Figure 3(a) shows a composite of two ^4He integral profiles for a W specimen which has been irradiated at $T_r = 60 \pm 2$ K with 300-eV $^4He^+$ ions to a fluence of 4×10^{15} cm^{-2}, at a flux of 3×10^{12} cm^{-2} sec^{-1}, along the [110] direction (±5°) and analyzed at $T_r = 60 \pm 2$ K. Figure 3(b) exhibits the 300-eV ^4He range profile, which was constructed from four integral profiles for $T_i = 60$, 61, 80, and 90 K and $T_r = 60 \pm 2$ K; the fluence, flux, and irradiation direction were identical for all four irradiations; at these four T_i's ^4He is *immobile* in W. The uncorrected values of the mean range ($\bar{x}$) and the parent standard deviation (σ) are given in Table I. The ^4He integral profiles include a contribution due to the random arrival of ^4He atoms from the gas phase, as detected in the control runs; an upper limit to this effect is 20% of the total number of events collected from the irradiated specimens; in the case of the 475-eV $^4He^+$ irradiation at $T_i = 60$ the random arrival contribution was $< 5\%$. The magnitude of this contribution was determined experimentally in a series of control runs and thus the *actual* $\bar{x}$ and σ at 300 eV were estimated to be 40 ± 4 and 23 to 36 Å, respectively, for the composite integral profile ($T_i = 60$, 61, 80, and 90 K); while at 475 eV they were 56 ± 6 and 35 to 43 Å, respectively. The ± values for $\bar{x}$ represent 1 standard deviation in the mean (s_m). The quantity s_m is given by the experimental standard deviation s divided by the square root of the number of measurements n in a single set; therefore even for n as small as 25 and an s of ≈ 37 Å the quantity s_m is only ±7 Å. Thus the fractional standard deviation in the mean, or fractional standard error ($s_m/\bar{x}$), of the composite (all 4 T_i's) 300-eV inte-

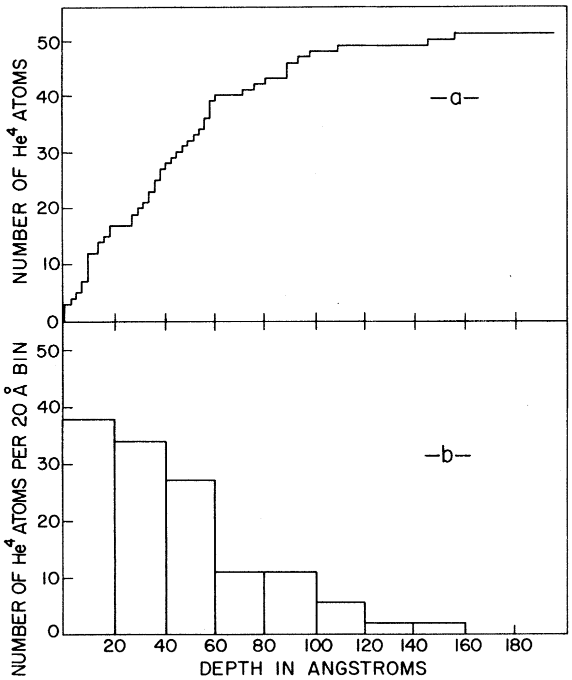

FIG. 3. (a) The composite integral profile for 300-eV ^4He implanted in W at 60 and 61 K. (b) The composite helium range profile for 300-eV ^4He implanted in W at 60, 61, 80, and 90 K.

gral profile is ~0.10, while for the 475-eV profile $s_m/\bar{x}$ is ~0.11. The results presented for the 475-eV $^4He^+$ irradiation demonstrate that both $\bar{x}$ and σ increase with increasing ion energy; $\bar{x}$ increased by 40% for a 58% increase in the ion energy. This energy-dependent increase in $\bar{x}$ is additional proof that we are dealing with a true implantation effect. Thus, in conclusion, we believe that data ($\bar{x}$ and σ) for the five range measurements reported in Table I are statistically significant. The composite range profile [Fig. 3(b)] represents the only experimentally determined one for ^4He, in any metal, for an implantation energy of <1 keV; experiments are currently in progress to determine its exact shape more quantitatively. It is interesting to note parenthetically that Biersack,[12] employing his latest version of the TRIM program, has calculated $\bar{x} = 40$ Å and $\sigma = 34$ Å for 300-eV $^4He^+$ ions impinging on an amorphous W target. Biersack[12] has also calculated the lateral width of the distribution and it is small compared to the radii of curvature of the specimens we employed.

In order to establish that the ^4He detected in the previous experiment was *not* trapped at structural defects in the W lattice, the following isochronal recovery experiment was performed. A W specimen was irradiated along the [110] direction with 300-eV $^4He^+$ ions at ~30 K. After the irradiation ≈2 (110) planes, corresponding to ≈4.4 Å of material, were pulsed field evaporated from the specimen. This procedure removed the sputtered surface and restored the surface to a nearly perfect state. The specimen was then warmed isochronally from ≈30 to 90 K at a rate of 1.5 K min^{-1}, while the FIM image was photographed at a rate of two 35-mm ciné frames sec^{-1}. *No* SIA contrast effects were observed during this experiment indicating that *no* SIA's crossed the surface of the FIM specimen. Our previous work[13] demonstrated that if SIA's were present they would have appeared throughout the entire range of 38 to 90 K. The specimen was then dissected by the pulsed field-evaporation technique and was examined for point defects. The density of point defects was determined to be $<8\times10^{-4}$ (atomic fraction); their depth distribution was not related to the ^4He integral profiles. These results constitute conclusive evidence that the ^4He was *not* trapped at SIA's or vacancies. This indicates that the ^4He atoms were located in

TABLE I. A summary of the range measurements for 300- and 475-eV $^4He^+$ ions implanted in W.

Energy (eV)	Irradiation temperature (T_i) (K)	Total number of ^4He atoms	Uncorrected mean range ($\bar{x}$) (Å)	Uncorrected parent standard deviation (σ) (Å)
300	60	26	43.9	36.4
300	61	25	44.0	37.3
300	80	27	47.1	35.0
300	90	53	40.7	34.7
475	60	41	55.8	40.3

the interstices of the lattice and that they were immobile in tungsten at 60, 61, 80, and 90 K.

The temperature at which the interstitial ^{4}He atoms became mobile in W was determined by implanting ^{4}He in an FIM specimen at different T_i's and then analyzing at $T_r = 60$ K. The ^{4}He integral profile determined at T_r was independent of T_i only if the ^{4}He was immobile at all values of T_i. However, when T_i was above the temperature at which the ^{4}He interstitials became mobile, the ^{4}He implanted during the irradiation diffused to the surface of the FIM specimen and entered the gas phase. Therefore a sharp decrease in the measured ^{4}He concentration was expected as T_i was increased (see Fig. 1). Since only T_i was varied, significant changes in the integral profile could only be attributed to a sharp increase in the mobility of the interstitial ^{4}He atoms at T_i. A dramatic change in the integral profile was observed upon increasing T_i from 90 to 110 K; thus indicating that interstitial ^{4}He atoms were immobile at 90 K but were highly mobile at 110 K. By employing a diffusion model, a value of the enthalpy change of migration ($\Delta h_{\mathrm{He}}{}^m$) of 0.24 to 0.32 eV was estimated.

We wish to thank Dr. J. Amano, Dr. J. P. Biersack, Dr. R. S. Averback, and Dr. A. Macrander for discussions and Mr. R. Whitmarsh for technical assistance. This research was supported by the U. S. Department of Energy. Additional support was received from the National Science Foundation through the use of the technical facilities of the Materials Science Center at Cornell University.

[a]Present address: Bell Laboratories, 600 Mountain Avenue, Murry Hill, N. J. 17974.

[1]*Radiation-Induced Voids in Metals*, edited by J. W. Corbett and L. C. Ianniello (National Technical Information Service, Springfield, Va., 1972).

[2]See, for example, J. Nucl. Mater. 53 (1974), 76 (1978), and 77 (1978).

[3]W. D. Wilson and C. L. Bisson, Radiat. Effects 22, 63 (1974).

[4]O. S. Oen and M. T. Robinson, Nucl. Instrum. Methods 132, 647 (1976).

[5]D. J. Reed, Radiat. Effects 31, 129 (1977).

[6]B. Terreault, R. G. St-Jacques, G. Veilleaux, J. G. Martel, J. L'Ecuyer, C. Brassard, and C. Cardinal, Can. J. Phys. 56, 235 (1978).

[7]E. V. Kornelsen, Radiat. Effects 13, 227 (1972).

[8]E. W. Müller, J. A. Panitz, and S. B. McLane, Rev. Sci. Instrum. 39, 83 (1968).

[9]T. M. Hall, A. Wagner, and D. N. Seidman, J. Phys. F 10, 884 (1977).

[10]J. Lindhard, M. Scharff, and H. E. Schiøtt, K. Dan. Vidensk. Selsk. Mat.-Fys. Medd. 33, No. 14 (1963).

[11]F. Maury, M. Biget, P. Vajda, A. Lucasson, P. Lucasson, Radiat. Effects 38, 53 (1978).

[12]J. P. Biersack, private communication.

[13]R. M. Scanlan, D. L. Styris, and D. N. Seidman, Philos. Mag. 23, 1439 (1971); K. L. Wilson and D. N. Seidman, Radiat. Effects 27, 67 (1975); D. N. Seidman, K. L. Wilson, and C. H. Nielsen, Phys. Rev. Lett. 35, 1041 (1975).

Site-Bond Correlated-Percolation Problem: A Statistical Mechanical Model of Polymer Gelation

Antonio Coniglio, H. Eugene Stanley, and W. Klein
Physics Department, Boston University, Boston, Massachusetts 02215
(Received 2 October 1978)

A new model for polymer gelation is presented that predicts new effects that can not be derived from the conventional theory of Flory and Stockmayer. An exact solution is obtained for the Bethe lattice, and is related to recent experimental results of Tanaka. Under certain conditions, the gelation curve terminates at the consolute point; at this point, both connectivity and concentration fluctuations are critical, just as in the random magnet at the percolation threshold.

Recently, there has been renewed interest in applications of critical-phenomena concepts to polymers.[1] The gelation transition is particularly intriguing, in part due to superficial resemblances to the bond percolation problem.

In 1941, Flory[2] proposed an elegant model of polymer gelation, which has the virtue of being amenable to closed-form solution for the special case in which one neglects the possibility of intramolecular binding. Flory's original model and

© 1979 The American Physical Society