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Hydrogen–vacancy interaction in molybdenum

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Abstract. Vacancy–hydrogen interaction in molybdenum was investigated by means of the perturbed angular correlation technique, using the isotope ^{111}In as a probe. The complex InV_2 turned out to trap up to two hydrogen atoms: trapping of a single hydrogen atom gives rise to a decrease of the quadrupole frequency by 3 Mrad s^{-1} , whereas trapping of an additional hydrogen atom causes the frequency to increase by 5 Mrad s^{-1} . Assuming a hydrogen migration energy of 0.35 eV , we found the binding energies of the first and second hydrogen atoms to be $1.07(3) \text{ eV}$ and $0.44(3) \text{ eV}$, respectively, while the binding energy of the next hydrogen atom is $< 0.25 \text{ eV}$. The sign of the frequency shift due to the second hydrogen atom trapped at InV_2 is opposite to that recently observed in tungsten, and the dissociation energy is much smaller. The lattice positions of the second hydrogen atom in molybdenum and tungsten are, therefore, completely different. Two more hydrogen decorated complexes were observed, with a binding energy of $1.07(3) \text{ eV}$. In the high-dose regime, a bubble-like feature was observed, the hydrogen binding energy being $0.72(3) \text{ eV}$.

1. Introduction

Hydrogen decoration of monovacancies in molybdenum has been studied experimentally by using the positron-lifetime technique (Hansen *et al* 1985, Linderoth *et al* 1987). The samples had been electrolytically doped with hydrogen. It was concluded that vacancies may trap up to four hydrogen atoms with a binding energy of $E_b = 1.4(1) \text{ eV}$. A comparison of doped and undoped samples, both annealed at 600 K , gave indications that hydrogen-occupied vacancies act as nucleation centres for further vacancy trapping. It was concluded that each cluster may contain 10–30 vacancies.

The deuterium–vacancy binding energy in molybdenum was derived from deuterium depth profiles measured after subsequent annealing treatments (Myers and Besenbacher 1986). The analysis of the data yielded a value of 1.03 eV for the binding energy of a deuterium atom at a vacancy, and a value of 0.80 eV for the binding energy at a deuterium-decorated vacancy.

Hydrogen–vacancy binding energies in a number of transition metals have been calculated by applying effective-medium theory (Nordlander *et al* 1986, 1989). The results obtained for molybdenum are given in table 1.

Recently, we applied the perturbed angular correlation (PAC) technique to monitor the number of hydrogen atoms trapped at a vacancy in tungsten (Fransens *et al* 1991).

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Table 1. Theoretical and experimental values of the binding energy, E_b^i , for the i th hydrogen or deuterium atom trapped at a lattice vacancy in molybdenum. All values in eV.

Isotope	E_b^1	E_b^2	E_b^3	Reference
H	0.92			Nordlander <i>et al</i> 1986
D	0.96	0.95	0.80	Nordlander <i>et al</i> 1989
H	1.4(1)			Hansen <i>et al</i> 1985; Linderoth <i>et al</i> 1987
D	1.03	0.80		Myers and Besenbacher 1986
H	1.07(3)	0.44(3)	< 0.25	This work ^a

^a Assuming a hydrogen migration energy of 0.35 eV.

In this paper we report on a similar experiment on hydrogen-doped ^{111}In -implanted molybdenum. As will be shown, we are able to set up a unique and reproducible trap, whereas in ion-beam experiments the exact nature of the trap is unknown. We can determine the implanted hydrogen dose very accurately by injecting hydrogen atoms with the aid of a low-energy ion gun, in contrast to cases in which the samples are electrochemically loaded. Finally, the PAC technique makes it possible to discriminate between complexes with different hydrogen occupancies.

2. Experimental procedure

For all experiments we used polycrystalline molybdenum foils with a purity of 99.95%. After the surface had been etched, each sample was annealed in vacuum ($p \approx 1 \times 10^{-6}$ mbar) at 1270 K for 30 min in order to remove the surface oxide layer, and implanted with 50 keV ^{111}In ions to a dose of less than 1×10^{12} cm^{-2} . Details of the PAC technique and the applied data reduction method have been described elsewhere (Fransens *et al* 1991).

The effect of subsequent annealing is demonstrated in figure 1, where the Fourier transform of the perturbation factor is shown as obtained after the ^{111}In implantation at room temperature and after subsequent annealing for 15 min at different temperatures. InV_2 , InV_3 and InV_4 complexes† have been associated (Weidinger *et al* 1979, 1981) with the observed hyperfine interaction parameters: $\omega_0 = 117$ Mrad s^{-1} with $\eta = 0$, $\omega_0 = 256$ Mrad s^{-1} with $\eta = 1$ and $\omega_0 = 92$ Mrad s^{-1} with $\eta = 0$, respectively. The corresponding defect fractions are plotted in figure 2 as a function of the annealing temperature. The proposed (Weidinger *et al* 1979, 1981) structures of these ^{111}In -vacancy configurations are displayed in figure 3.

From figure 1 it is clear that, unlike in the case of tungsten (Fransens *et al* 1991), it is not possible to choose an annealing temperature at which only the InV_2 cluster is stable. We pre-annealed the molybdenum foils, therefore, at 485 K at which temperature the fractions of InV_2 , InV_3 and InV_4 take their maximum values: 14%, 5%, and 6%, respectively. Of the remaining In atoms, about 20% are at substitutional lattice sites in an unperturbed environment, while the others are probably located in small vacancy clusters.

† We write InV_n for a lattice defect that consists of an In atom and n vacant lattice sites. In this notation, InV denotes a substitutional In atom, InV_2 a monovacancy trapped at a substitutional In atom, etc.

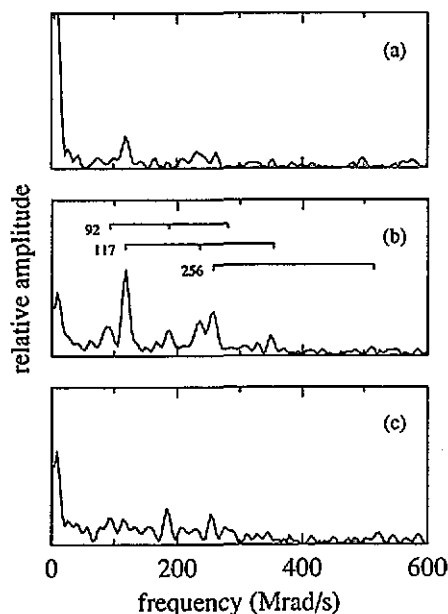


Figure 1. Fourier transform of the perturbation factor measured (a) after 50 keV ^{111}In implantation at 300 K, and after subsequent annealing at (b) 485 K and (c) 565 K. All measurements were conducted at 300 K.

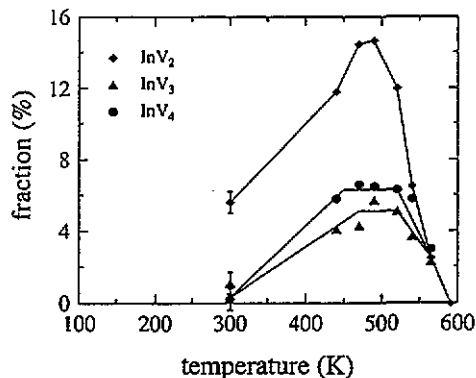


Figure 2. Derived fractions of the different ^{111}In -vacancy clusters, as a function of annealing temperature. All measurements were conducted at 300 K.

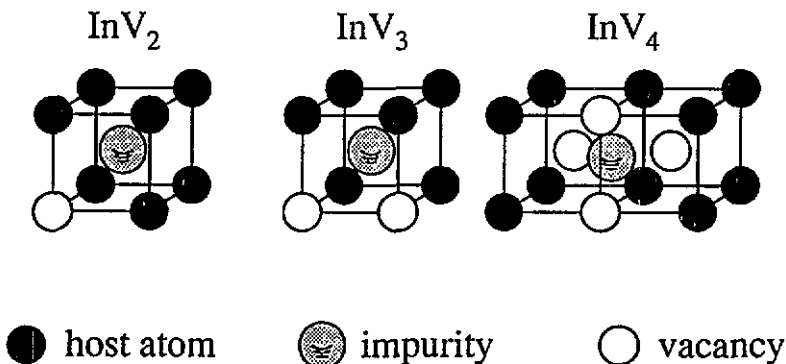


Figure 3. Proposed configurations of InV_2 , InV_3 and InV_4 complexes (Weidinger *et al* 1981).

The situation is even more complicated because the quadrupole frequency corresponding to InV_4 turned out to strongly depend on the sample temperature (figure 4). At the lowest temperatures, the Fourier peaks due to InV_2 and InV_4 nearly coincide. On the other hand, exploratory experiments indicated that hydrogen trapped at InV_2 may detrapp at a temperature as low as about 200 K. Therefore, the samples were doped with 1 keV hydrogen molecules corresponding to 500 eV H^+

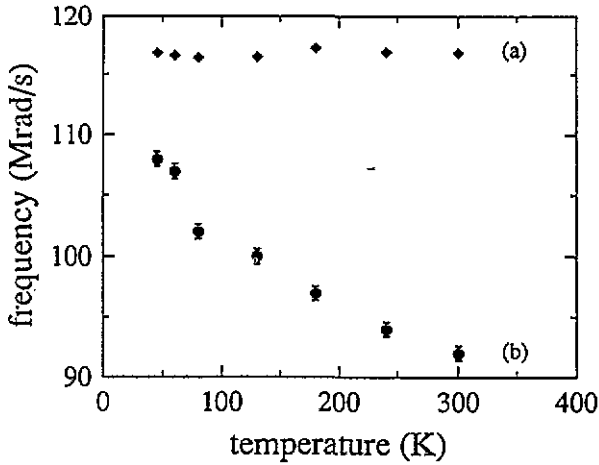


Figure 4. Quadrupole frequencies corresponding to (a) InV₂ and (b) InV₄, as a function of the sample temperature.

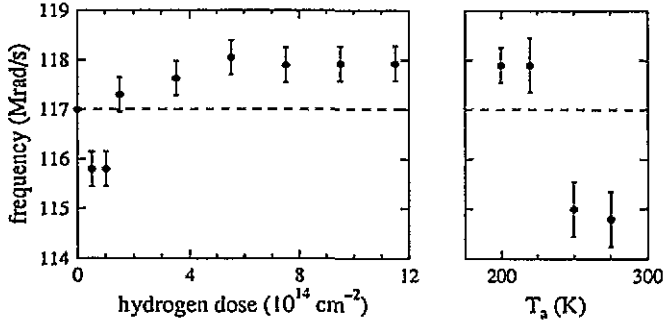


Figure 5. The average value of the quadrupole frequency corresponding to the (decorated) InV₂ defect, as a function of hydrogen dose (left) and annealing temperature (right). All measurements were conducted at 160 K.

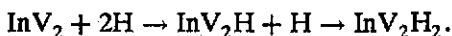
ions, at 170 K, at which temperature the contributions from InV₂ and InV₄ in the frequency spectrum can be well distinguished. The maximum energy transferred by the hydrogen ions to the lattice amounts to 22 eV, which is well below the minimum displacement energy. Therefore, no further damage is introduced in the samples by these hydrogen implantations.

After this preparative treatment, we performed PAC experiments to study (i) the dose dependence of the hydrogen–vacancy interaction by varying the H⁺ dose from $5 \times 10^{13} \text{ cm}^{-2}$ to $2 \times 10^{16} \text{ cm}^{-2}$, and (ii) the annealing behaviour of the decorated vacancy clusters in the temperature range from 200 K up to 475 K. The annealing time was 15 min. The PAC measurements were carried out at a fixed sample temperature of 160 K, except when the samples had been annealed above room temperature, in which case the measurements were carried out at 300 K.

3. Experimental results and discussion

We studied the hydrogen-vacancy interaction by carefully monitoring the position of the Fourier peak that corresponds with InV_2 , as a function of hydrogen dose and annealing temperature (figure 5). We noticed that, unlike in the case of tungsten (Fransens *et al* 1991), the average frequency first decreases from the initial value of 117 Mrad s^{-1} to $115.5 \text{ Mrad s}^{-1}$ and then, at higher hydrogen doses, increases to about 118 Mrad s^{-1} . The asymmetry parameter is not affected and remains zero. Upon annealing at 250 K, the frequency has dropped suddenly to 114 Mrad s^{-1} .

The interpretation of these observations is obvious. With increasing hydrogen dose, InV_2 is successively decorated with one and two hydrogen atoms, according to the following reactions:



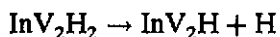
Apparently at 250 K the reverse reaction occurs. It should be noted that the contributions of InV_2H_n ($n = 0, 1, 2$) in the Fourier spectrum cannot be resolved and that the frequencies mentioned before are weighted averages of two or three frequency values.

The thermal stability of the hydrogen-decorated defects was investigated in more detail by performing a thermal annealing sequence. In figure 6 some typical PAC spectra and their Fourier transforms, obtained before hydrogen implantation and after hydrogen implantation to a dose of $3 \times 10^{15} \text{ cm}^{-2}$ and subsequent annealing at different temperatures, are shown. At the end of the annealing sequence, the original undecorated defects reappeared.

Since the frequency shifts induced by trapping of successive hydrogen atoms are too small to be resolved, we had to make the following *a priori* assumptions: (i) the number of occupancies, n , for the cluster InV_2H_n is limited, and (ii) each occupation number gives rise to a well defined and observable shift of the quadrupole frequency. Because the frequency was found to change twice, there are two hydrogen-decorated defects besides the bare vacancy cluster InV_2 .

The quadrupole frequencies and fractions corresponding to the triplet InV_2 , InV_2H and InV_2H_2 were determined from fits to the PAC time spectra. The frequency corresponding to the undecorated vacancy, 117 Mrad s^{-1} , was kept fixed at the value measured on the undoped samples. Next, the frequency corresponding to InV_2H , 114 Mrad s^{-1} , was obtained from a two-component analysis of the summed spectra taken at annealing temperatures above 250 K. The frequency corresponding to InV_2H_2 was found to be 119 Mrad s^{-1} from a similar three-component analysis of the summed spectra taken in the region of large hydrogen doses. Finally, the defect fractions were determined by fitting each individual spectrum assuming three components, the frequencies being fixed at the previously obtained values. The results were normalized to the sum of the fractions of the three defects, which amounted to 12% and, within limits of errors, stayed constant as a function of the annealing temperature. The final results are shown in figure 7.

Two recovery stages are easily recognized. At 230 K, the 119 Mrad s^{-1} and 117 Mrad s^{-1} fractions decrease, while the 114 Mrad s^{-1} fraction increases. The interpretation of this behaviour is as follows: one of the two hydrogen atoms is released from the InV_2H_2 complex according to the reaction



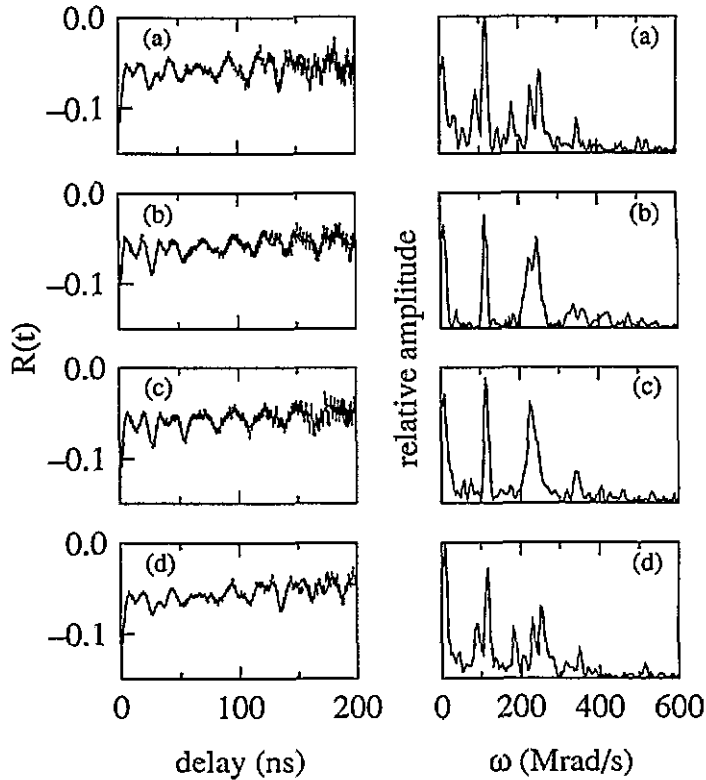
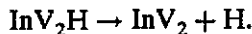


Figure 6. PAC spectra (left) and their Fourier transforms (right) measured (a) before hydrogen implantation, and after hydrogen implantation to a dose of $3 \times 10^{15} \text{ cm}^{-2}$ and subsequent annealing at (b) 325 K, (c) 400 K and (d) 475 K. All measurements were conducted at 300 K.

and either traps at an undecorated InV_2 or another vacancy cluster, or it escapes to the surface. During annealing at 410 K the last hydrogen atom is also released through the reaction



As a result, the 114 Mrad s^{-1} fraction completely disappears and the 117 Mrad s^{-1} fraction is restored to its original value.

We define the dissociation temperature, T_d , as the temperature at which the fraction is reduced by 50%. This temperature is related to the dissociation energy, E_d , by the expression

$$E_d = kT_d \ln(\nu_0 t / \ln 2).$$

Here, $t = 900 \text{ s}$ is the annealing time and $\nu_0 = 2 \times 10^{14} \text{ s}^{-1}$ is the attempt frequency, which is taken to be equal to the value for tungsten (Fransens *et al* 1991). From the observed recovery stages (figure 7) we calculate dissociation energies of $1.42(3) \text{ eV}$ for the first and $0.79(3) \text{ eV}$ for the second hydrogen atom. The corresponding binding

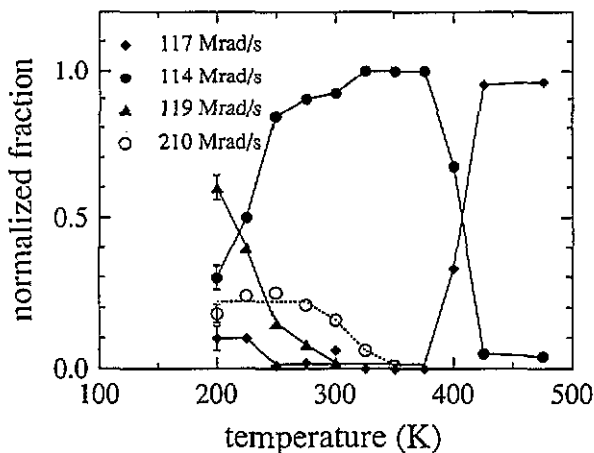


Figure 7. Defect fractions as a function of the annealing temperature. The fractions have been normalized such that the intensity of the '117-114-119 Mrad s^{-1} triplet' amounts to 100%, at each temperature. The error bars in the data points for an annealing temperature of 200 K give an indication of the accuracy of the results. Samples annealed at temperatures less than 300 K were measured at 160 K, otherwise the measurements were conducted at 300 K.

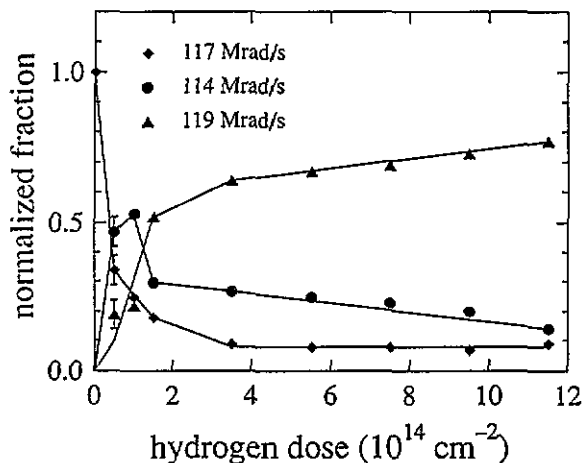


Figure 8. Defect fractions as a function of the hydrogen dose, measured at 160 K. The fractions have been normalized such that the intensity of the '117-114-119 Mrad s^{-1} triplet' amounts to 100% at each dose. Samples annealed at temperatures less than 300 K were measured at 160 K, otherwise the measurements were conducted at 300 K.

energy, E_b , follows from the relation $E_d = E_b + E_m$. Assuming† the hydrogen migration energy to be $E_m = 0.35$ eV, we obtain the binding energies 1.07(3) eV

† The assumption is based on the energy range $E_m = 0.3-0.4$ eV (Hansen *et al* 1985). We think our assumed value of E_m is realistic, considering the migration energy of 0.39 eV reported for tungsten (Frauenfelder 1969) and the difference between the melting temperatures of tungsten and molybdenum. A different value of the migration energy merely leads to a common shift of all derived binding energies.

and 0.44(3) eV. Since trapping of a third hydrogen atom was not observed, we conclude that the dissociation energy for any further hydrogen atom is less than 0.6 eV, corresponding to a binding energy of less than 0.25 eV.

Additional support for the previously given interpretation was obtained by varying the H^+ dose from $5 \times 10^{13} \text{ cm}^{-2}$ to $2 \times 10^{16} \text{ cm}^{-2}$. The measurements were carried out at 160 K. The different defect fractions, calculated in the same way as in the case of the annealing experiment, are plotted in figure 8. As expected, the 114 Mrad s^{-1} fraction increases at low hydrogen doses and decreases at higher doses in favour of the 119 Mrad s^{-1} defect.

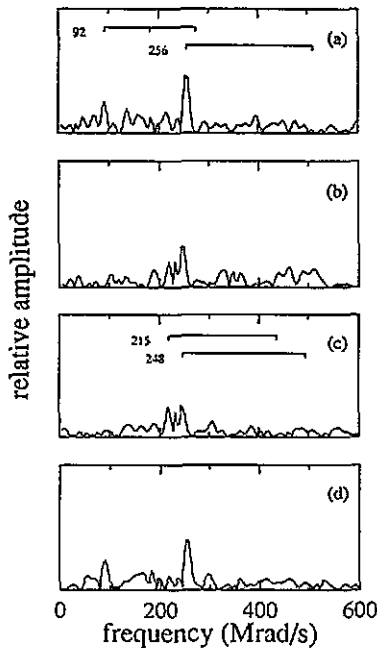


Figure 9. Fourier transform of the PAC spectra shown in figure 6, after subtraction of the least-squares fitted '117–114–119 Mrad s^{-1} triplet'.

The effective trapping cross-section at small hydrogen doses amounts to $\mu_{\text{eff}} \cong 2 \times 10^{-14} \text{ cm}^2$, which is approximately equal to the value observed for tungsten (Fransens *et al* 1991). However, the effective cross-section rapidly decreases by almost two orders of magnitude in the high-dose region, indicating the formation of new trapping centres.

Up to this point we have only discussed the fate of InV_2 . However, a close inspection of the Fourier spectra shown in figure 6 reveals two more peaks at 215 Mrad s^{-1} and 248 Mrad s^{-1} . This is most easily demonstrated by subtracting the least-squares fitted '117–114–119 Mrad s^{-1} triplet' from the experimental data (figure 9). The two peaks most likely belong to two different defect clusters, the corresponding asymmetry parameters being 1.0. From the intensity balance we conclude that the clusters are related neither to InV nor to InV_2 , but may very well be formed by decoration of InV_3 and/or InV_4 . The stability of these decorated clusters is the same as that of InV_2H .

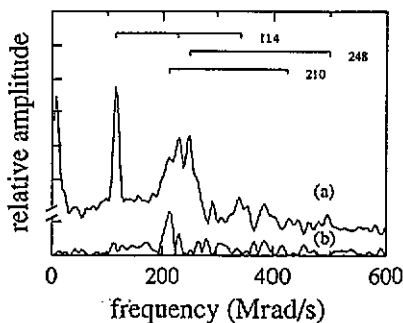


Figure 10. Curve (a), Fourier transform of the summed PAC spectra taken after implantation of 2×10^{16} H cm $^{-2}$ and subsequent annealing at temperatures between 225 K and 275 K. Measurements were conducted at 160 K. Curve (b), residual frequency spectrum after subtraction of the '117–114–119 Mrad s $^{-1}$ triplet' and the 248 Mrad s $^{-1}$ defect.

In the high-dose regime, additional Fourier power is observed at 210 Mrad s $^{-1}$ (see figure 10). In order to investigate the thermal stability of the corresponding defect, we post-implanted a hydrogen dose of 2×10^{16} cm $^{-2}$ and annealed the sample at stepwise increasing temperatures in the range between 200 K and 400 K. First, the quadrupole frequency corresponding to the defect was determined from a five-component analysis of the summed spectra, the frequencies of the '117–114–119 Mrad s $^{-1}$ triplet' and the 248 Mrad s $^{-1}$ defect being fixed at the previously obtained values. Next, the defect fraction was determined by fitting each individual spectrum, with all frequencies kept fixed. The results are plotted in figure 7 and show a recovery stage at 310 K. From this we calculate a dissociation energy of 1.07(3) eV, corresponding to a binding energy of 0.72(3) eV. Since the trapping cross-section dramatically decreases at large hydrogen doses, we tentatively assign the 210 Mrad s $^{-1}$ defect to a bubble-like feature similar to the one that is observed in tungsten (Fransens *et al* 1991).

4. Conclusions

We applied the PAC technique to monitor the number of hydrogen atoms that trap at a vacancy in molybdenum. The very fact that hydrogen traps proves that hydrogen is able to diffuse over a distance of at least 100 Å, being the projected range of the ^{111}In atoms, during the average implantation time of about 30 min at the implantation temperature of 170 K. This is consistent with the reported migration energy, 0.3–0.4 eV, of hydrogen in molybdenum (Hansen *et al* 1985).

The measurements show that InV $_2$ can trap two hydrogen atoms. Trapping of a single hydrogen atom gives rise to a decrease of the quadrupole frequency by 3 Mrad s $^{-1}$, while trapping of an additional hydrogen atom causes the frequency to increase by 5 Mrad s $^{-1}$. From the observed recovery stages we derive binding energies of 1.07(3) eV and 0.44(3) eV for the first and second hydrogen atoms, assuming a migration energy of 0.35 eV. The binding energy for any further hydrogen atom is less than 0.25 eV. The binding energy of the first hydrogen atom is in agreement with the values obtained from depth-profiling experiments (Myers and Besenbacher 1986) and effective-medium theory, but disagrees with the value obtained in positron-lifetime

experiments (Hansen *et al* 1985, Linderoth *et al* 1987) (see table 1). The deduced binding energies of additional hydrogen atoms, however, are considerably smaller than any measured or calculated value that has been reported so far.

Surprisingly, the sign of the frequency shift due to the second hydrogen atom trapped at InV₂ is opposite to that observed in tungsten, and the dissociation energy is much smaller. The lattice positions of the second hydrogen atom in molybdenum and tungsten are, therefore, completely different.

In the low-dose regime, two more quadrupole frequencies are observed. The annealing behaviour indicates a hydrogen binding energy of 1.07(3) eV. In the high-dose regime we observed a bubble-like feature similar to the one in tungsten, the hydrogen binding energy being 0.72(3) eV. No trapping of hydrogen at substitutional In atoms was observed.

Acknowledgments

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