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Deuterium retention in tungsten and molybdenum

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Abstract

Trapping of D atoms implanted in W and Mo single crystals was investigated in connection with the implantation-induced defects by using ion beam analysis techniques. The amount of the retained D atoms near the surface layer of the W crystal was higher than of the Mo crystal at a temperature range between 300 and 650 K. Depth profile studies of the retained D atoms and defects indicated that trapping of D atoms implanted in the W and the Mo crystal was associated with lattice distortion due to implantation-induced extended defects such as interstitial loops. The D atoms implanted in the W crystal were found to be located near the tetrahedral interstitial site, both in the implant surface layer and in the greater depth where few displacements were expected to be created by collisions. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Due to their favorable physical properties under high-flux particle exposure, W, Mo and their alloys are candidates for plasma facing components in fusion devices. Although the flux of hydrogen with energy of ~1 keV is expected to be much less than that of the low-energy (< 100 eV) ions, they can cause significant damage in the surface of the plasma facing materials. Thus, interaction between the irradiation-induced defects and hydrogen isotopes embedded in Mo and W is important in estimating the fuel recycling and tritium inventory.

There have been many studies on the retention and release of hydrogen isotopes implanted in W and Mo. All results generally indicated that radiation-induced damage plays an important role for trapping hydrogen; however, the mechanism of trapping hydrogen in W and Mo is still not clearly understood [1]. Furthermore, the retention, release and migration of hydrogen depend on the microstructure of the specimens prepared by different methods [2,3], and the impurities contained in the specimens [4,5]. Knowledge of fundamental aspects from a systematic investigation is necessary to improve our understanding about hydrogen behavior in W and Mo.

In the present work, D retention and damage accumulation near the surface of W and Mo single crystals were systematically investigated by varying the implantation temperature, incident D ion energy, and incident ion flux density. Depth profile analysis was carried out for both retained D atoms and irradiation-induced disorder to clarify the interaction between the defects and the implanted D atoms. Also, the lattice location of the D implanted in W crystals was examined by ion channeling experiments.

2. Experiments

The specimens used were W and Mo single crystals with $\langle 1\,0\,0\rangle$ and $\langle 1\,1\,1\rangle$ orientation. Ion implantation and ion beam analysis were performed in a scattering chamber connected to a 1.7 MV tandem accelerator. Details of the experimental setup and the preparation procedure for the specimens are described elsewhere [6]. The incident D energy was varied from 1 to 10 keV and the implantation temperature was in a range 300–650 K. The flux density was controlled within a range between 3×10^{17} and 4×10^{18} D/m^2 s. Concentration depth profiles of D atoms retained near the surface of the W and the Mo crystals were measured by the elastic recoil

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detection (ERD) technique using 2.8 MeV $^4He^{++}$ beam during and after the implantation. To study the lattice disorder produced by the D implantation, ion channeling experiments along the major axis were performed using the backscattering of ^4He ions with an incident energy varied from 0.5 to 4.0 MeV. The lattice location of D atoms implanted in the W crystal was studied at room temperature by using D(^{3}He,p) ^{4}He nuclear reaction with an incident $^3He^+$ energy of 750 keV.

3. Results and discussion

Fig. 1 shows the amount of D atoms retained near the surface of the W and the Mo crystals plotted against the implant D dose. The retention was determined from the ERD spectra by integrating the number of retained D atoms from the surface to the depth of 100 nm. It is in this range that irradiation-induced defects should be accumulated with a high density during the D ion implantation. The D retention near the surface of the W crystal was considerably higher than in the Mo crystal, especially at room temperature. The ERD profiles showed that the D atoms are uniformly distributed in a depth region between 100 and 300 nm for both Mo and W crystals above 390 K. The D concentration at the flat distribution in the W crystal at 500 K is estimated to be less than 0.1 at.%, which is comparable to the value obtained by Haasz et al. [7] for polycrystalline W foils implanted with 500 eV D ions.

Ion channeling experiments were carried out on the ion-implanted specimens to characterize the nature of the implantation-induced defects and to obtain the depth profile. The dechanneling yields of a backscattering spectrum for the D-implanted crystal can be relate to the number of defects in the path of the incident ions as follows [8]:

$$-\ln\left(\frac{1-\chi_D(z)}{1-\chi_V(z)}\right) = \lambda \int_0^z n(z')\,\mathrm{d}z', \qquad (1)$$

where, $\chi_D(z)$ and $\chi_V(z)$ are dechanneling yields normalized with random yields corresponding to the depth of z obtained from a damaged and an unimplanted crystal, respectively, λ is the dechanneling cross-section for the defects and $n(z)$ is the density of defects. The LHS of Eq. (1) is defined as the dechanneling parameter which can be determined in channeling experiments. The dechanneling cross-section λ for dislocation lines and loops accompanying extensive lattice distortion are known to be proportional to the square root of the incident energy of the analyzing beam [9].

In Fig. 2, the dechanneling parameter for ⟨1 1 1⟩ axis channeling is plotted as a function of the incident energy of ^{4}He for the Mo and the W crystals irradiated by 5 keV D ions to a dose of 1×10^{22} D/m^2. For comparison, results obtained for 200 keV C^+ implantation with 3×10^{19} C/m^2 at room temperature are also shown in the figure. The dechanneling parameter was estimated at 200 nm for the D-implanted crystals and at 400 nm for the C-implanted crystals. In the W crystal, the dechanneling parameter increased linearly with an increase of the square root of the ^{4}He energy, especially for the D ion implantation. The dechanneling parameter for the Mo crystal also showed an $E^{1/2}$ energy dependence, although the slope of the fitted straight line was much smaller than that for the W crystal. The results indicate that lattice distortions, probably due to extended defects such as dislocation loops, were created near the surface

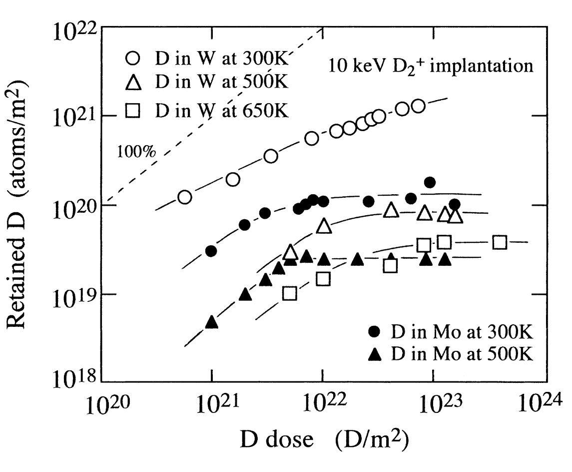

Fig. 1. D retention near the surface layer of W and Mo crystals as a function of the D implantation dose at a temperature range between 300 and 650 K.

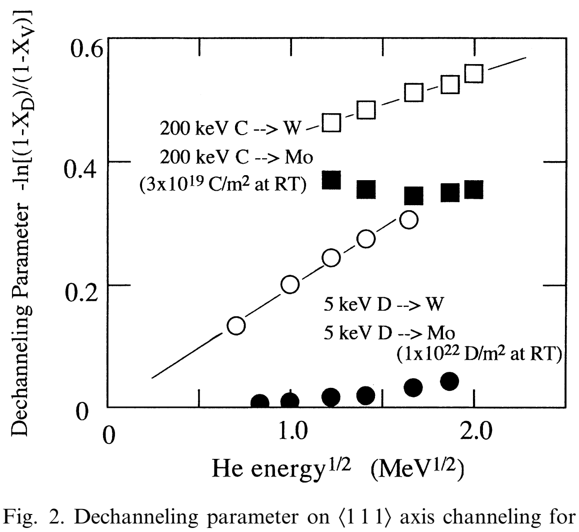

Fig. 2. Dechanneling parameter on ⟨1 1 1⟩ axis channeling for Mo and W crystals irradiated by 10 keV D_{2+} and 200 keV C^+ plotted as a function of the square root of the incident ^{4}He energy.

of both W and Mo crystals. This agrees with the results of transmission electron microscopy observation of W [10] and Mo [11] single crystals irradiated by H^+.

Heavier ion irradiation seemed to introduce more complex features as shown in Fig 2. For the C^+-implanted W crystal, dechanneling might be more effectively caused by the stacking faults and/or voids for which the dechanneling cross-section is known to be constant against the ^{4}He energy. On the other hand, the dechanneling parameter in the Mo crystal irradiated by C^+ decreased slightly with increasing ^{4}He energy. This energy dependence of the dechanneling parameter for the Mo crystal can be explained by the existence of the large number of isolated interstitial Mo atoms created by C^+ irradiation.

The D retention and dechanneling parameter in the W and the Mo crystals implanted with 5 keV D ion to a dose of 1.0×10^{22} D/m^2 is plotted in Fig. 3 as a function of the implant temperature. The dechanneling parameter is evaluated at a depth of 100 nm in the spectrum obtained by 1 MeV $^4He^+$. Assuming that the dislocation loops dominate, and neglecting the difference of the dechanneling cross-sections of W and Mo, the plotted dechanneling parameter roughly corresponds to the density of defects. The correlation of the lattice distortion with D retention in W and Mo crystals is clearly seen in the figure. The D retention in the W crystal decreased with an increase in temperature, so that it would be smaller than that in the Mo crystal above 700 K.

Fig. 4 shows the concentration depth distribution of retained D atoms, interstitial atoms and lattice distortion in the W and Mo crystals implanted by 5 keV D at a dose of about 1×10^{22} D/m^2 at 300 K. The depth profile of the interstitial atoms is determined from the high-energy peak of the backscattering spectrum using an iterative procedure [12]. To obtain the depth distribution of the defects accompanying the lattice distortion, Eq. (1) was differentiated [13], and was applied to the backscattering spectra. The interstitial Mo atoms concentrated or the crystal was heavily damaged at the implant surface within 20 nm, while the depth profile of the retained D atoms and the lattice distortion extended to the greater depth in comparison with a vacancy distribution calculated by TRIM-code [14]. The depth distribution of the retained D atoms and disorder in the W crystal showed similar profiles in the Mo crystal, although the concentration of the retained D atoms and disorder in the W crystal was considerably higher than that in the Mo crystal. It is known that hydrogen trapping at an interstitial site locally relaxes the lattice around the hydrogen. As a consequence of the local relaxation of the lattice by ‘self-trapped’ deuterium, the lattice distortion may become stable, and the D atoms and defects simultaneously accumulate in the W crystal during the D implantation. It is consistent with our previous results [6] in which the thermal release behavior of D atoms retained in a heavily damaged layer was identical with that of D atoms retained in the greater depth. The results do not insist that trapping of D atoms at point defects such as vacancies, is ruled out. A part ($\sim$20%) of the total amount of retained D atoms is released above 500 K [6], and it might be trapped in vacancies or voids. On the other hand, at room temperature, vacancies in W and Mo are believed to be thermally immobile due to high migration energy [15]

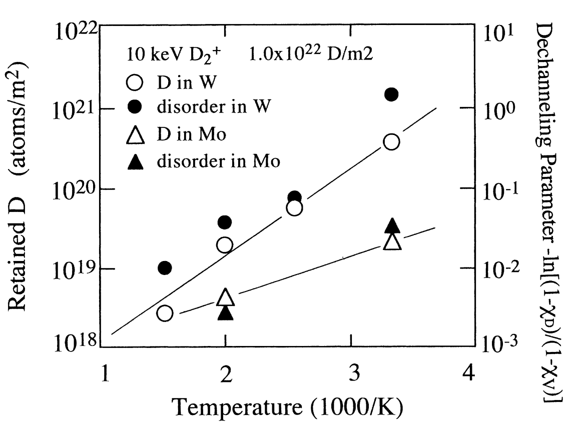

Fig. 3. D retention and the dechanneling parameter near the surface of W and Mo crystal implanted by 10 keV D_{2^+} at the implantation dose of 1.0×10^{22} D/m^2 plotted as a function of the implant temperature.

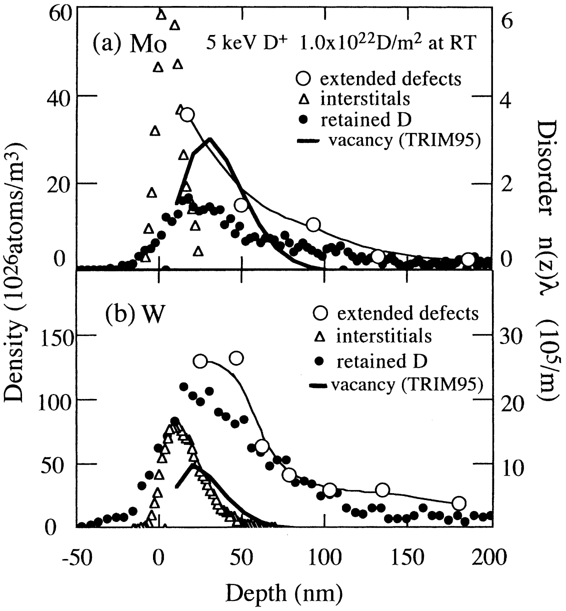

Fig. 4. Concentration depth profiles of implanted D atoms, isolated interstitial atoms, and lattice distortion obtained in (a) Mo and (b) W after 10 keV D_{2^+} ion implantation at about 1×10^{22} D/m^2 at room temperature.

(1.3 eV for Mo, 1.7 eV for W). If the vacancy type defects are responsible for trapping at room temperature, an alternative mechanism for vacancy formation is required to explain D trapping at a large depth where few displacements can be created by collisions.

According to a TRIM calculation, the number of displacements created by the D ion implantation is estimated to be somewhat larger in Mo than in W for 5 keV D implantation, assuming the same displacement threshold energy for both metals. The observed difference in the rate of defect accumulation between Mo and W was not simply explained by the rate of displacement generation by collisions. Formation of bubbles can introduce dislocation and grain cracking at high implantation dose [16], although they are not supposed to be formed in W at a low dose ($< 1 \times 10^{22}$ D/m^2) where the accumulation rate of D atoms and distortion is quite large. Formation of hydrogen clusters in W [10] and Mo [11] crystals irradiated by H^+ was identified by electron diffraction. If D atoms are retained as molecules in crystals, a higher pressure would be expected in W than in Mo because of higher free energy of solution of hydrogen in W [17]. Thus, the observed difference of the D retention between W and Mo might be attributed to the formation of bubbles and/or clusters.

Fig. 5 shows the D retention and the dechanneling parameter near the surface of W crystals plotted against the incident D energy. Typical depth profiles of retained D atoms for 1 and 4 keV implantation are inserted in the figure. The implantation was performed at room temperature to a dose about 1×10^{22} D/m^2 and the D distribution profiles were obtained about 50 hours after the implantation. The solid line indicates the total number of displacements in arbitrary units, calculated by TRIM-code. It is conjectured that collisional displacements are responsible for creating the trapping sites for D atoms for higher energy implantation. For 1 keV D implantation, instead of a peak, a flat distribution of D atoms with a concentration about 0.3 at.% was observed up to a depth of 200 nm, where no large displacements was supposed to be created. This suggests that the D atoms were trapped in the W crystal without knock-no process. Depth profiles of D atoms with a long tail extending beyond 500 nm were observed by Nuclear Reaction Analysis for 1 keV D implanted W foils [7]. Defect clusters were found to be formed in W by 3 keV H^+ irradiation [11], and in Mo by 0.5 keV H^+ irradiation [10], although they grew up very slowly. In the present experiments using 1 keV D implantation, locally concentrated D atoms may help to create fine defect clusters and/or bubbles, while the D atoms were likely trapped by impurities at the beginning of the irradiation.

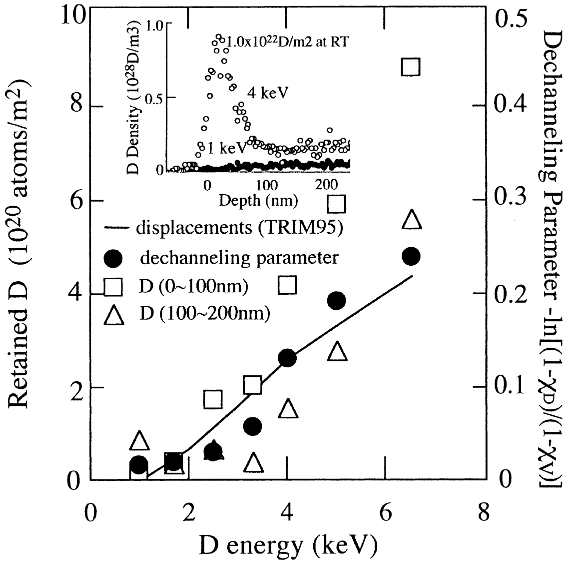

Fig. 5. D retention near the surface layer,(0–100 nm: □), in the deeper depth (100–200 nm: △) and dechanneling parameter (●) of the W crystals plotted against the incident D energy, incorporated with depth profiles of D atoms implanted with 1 and 5 keV. Solid line indicates the total number of displacements calculated by TRIM-code [14].

An attempt was made to check the flux dependence by varying the flux of the incident 5 keV D ion between 3×10^{17} and 4×10^{18} D/m^2 s. The retention for the highest flux was about three times larger than that for the lowest flux, although the effect of the incident flux was not evident. As the concentration of D atoms near the surface depends on the diffusivity of D atoms and the molecular recombination rate, the flux dependence would be more pronounced at lower implantation energy. Further investigation is needed to clarify the mechanism of defect accumulation during the low-energy hydrogen implantation.

Typical angular scans for normalized backscattering and nuclear reaction yields from the D ion implanted W crystals are shown in Fig. 6. The D ion implantation was carried out at room temperature, with energies of 1 and 5 keV, up to a dose of about 1×10^{21} and 1×10^{20} D/m^2, respectively. The clear peaks of the nuclear reaction yields for the ⟨1 1 1⟩ axial direction were observed for both 1 and 5 keV D implanted W crystals. This indicates that the D atoms are located at interstitial sites for either 1 keV or 5 keV implantation. The ⟨1 0 0⟩ axis was scanned close to ⟨1 0 0⟩ or ⟨1 1 0⟩ planes, and relatively broad peaks appeared in ⟨1 0 0⟩ axial direction of the W crystal implanted with 5 keV D. It was reported [18] that the D atoms implanted at 15 K appeared to be displaced from tetrahedral and toward the octahedral site in W and Mo. The present angular scan yields on the ⟨1 0 0⟩ axis was similar to the previous results, however, the displacement from the tetrahedral site seemed to be slightly out of the ⟨1 0 0⟩ plane. The discrepancy might be attributed to the relatively large implantation dose

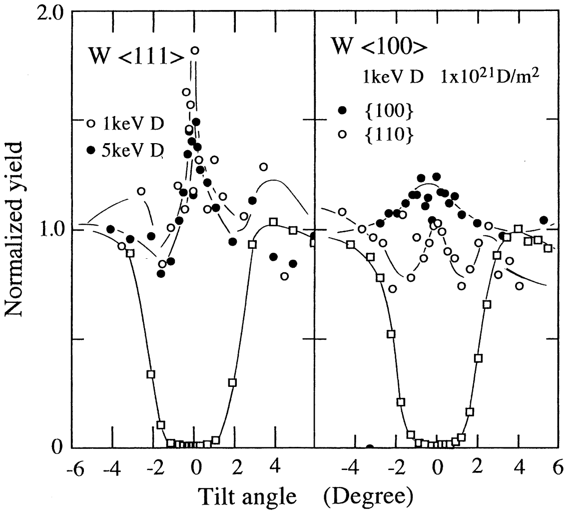

Fig. 6. Angular yield curve for normalized backscattering (□) and nuclear reaction (○, ●) yields from the D ion implanted W crystals for (a) ⟨1 1 1⟩ and (b) ⟨1 0 0⟩ axial directions.

introducing larger distortion in the crystal, or it may be related to the formation of D_2 molecules. The angular scans through ⟨1 0 0⟩ axis indicated no significant difference between 1 and 5 keV implanted W crystals. This suggests that the trapping of the D atoms is the same for the implant layer and for the deeper layer where no collisional displacements are expected.

4. Conclusions

From the depth profile studies of the retained D atoms and the implantation-induced disorder, it may be concluded that the trapping of D atoms in Mo and W crystals is associated with lattice distortion caused by the implantation-induced extended defects such as interstitial loops. The lattice distortion may become stable due to the local relaxation by trapping D atoms, especially in the W crystal at room temperature. This was consistent with results of ion channeling experiments: D atoms implanted in the W crystal were located near the tetrahedral interstitial site, and no significant difference was found among the trapping sites in the implant depth and in the deeper layer where very few displacements were created by implantation.

The D retention near the surface layer of W crystals was higher than that in Mo crystals at temperatures between 300 and 650 K up to an implantation dose of 2×10^{23} D/m^2. On the other hand, the D retention and defect accumulation in W crystals would be smaller than that in Mo crystals above 700 K. The reason of the different retention properties of W and Mo is still not clear, however, it may be attributed to the difference of the strain field around D atoms which can be retained as molecules and/or clusters in these metals.

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