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Retention, permeation and re-emission of deuterium implanted in Mo

S. Nagata *, T. Hasunuma, K. Takahiro, S. Yamaguchi

Institute for Materials Research, Tohoku University, Sendai 980-77, Japan

Abstract

Retention, permeation and re-emission of deuterium implanted in Mo have been studied by measuring concentration profiles of D atoms all over the thickness of Mo membranes. The D transport behavior in the Mo membrane was different below and above 400 K. Concentration profiles of the implanted D were clearly observed from the implanted surface to the interior of the membrane below 400 K, while permeation flux of D atom was very little. At steady state, the permeation flux was less than 1% of the incident flux at RT, but it increased up to 6% at 600 K. Additionally, trapping and thermal release behaviors of D atoms at the implant surface layer of the polycrystalline membranes were examined in comparison with those in single crystals. © 1997 Elsevier Science B.V.

1. Introduction

The interaction of implanted hydrogen isotopes with metals is of significant interest in many technological applications, especially in fusion devices. An understanding of hydrogen behavior such as retention, permeation and re-emission is important for controlling fuel recycling between plasma and wall materials. In recent years, because of its low erosion rate and good thermal properties, high Z materials such as Mo and W became candidates for plasma facing materials [1].

The hydrogen trapping in Mo and re-emission from it during implantation of energetic hydrogen have so far been studied by several workers [2–9]. According to gas-release measurements by McCracken and Erents [2], the defects created by the implantation play a dominant role in trapping the hydrogen implanted in Mo. The hydrogen is trapped at an interstitial site associated with a vacancy [4,5], and the trapping binding energy is as high as 1 eV [7,8]. However, these previous investigations have concentrated on the retention and re-emission of hydrogen with higher implantation energy as well as at a lower irradiation dose than those expected in the fusion environment. Furthermore, permeation behavior, which is closely related to the diffusivity of hydrogen in Mo, has not yet been understood well since the diffusion of hydrogen is thought to be very influenced by the trapping effect [2,6].

Our previous study [10] showed that the ERD analysis technique with transmission geometry was an unique and quite useful tool to obtain hydrogen concentration profiles all over the metal membrane. Moreover, it allows us to measure simultaneously trapping, permeation, and re-emission flux of deuterium implanted in the membrane. In the present work, by using this technique, the total depth profile of deuterium implanted in Mo membranes has been measured during D implantation, and permeation and re-emission fluxes have been evaluated to examine the process which controls hydrogen transport. Additionally, the detailed depth profile of deuterium in the near surface region was measured at room temperature as well as at elevated temperatures in comparison with those profiles in single crystalline Mo. Furthermore, channeling measurements were carried out to study the correlation between defect and deuterium trapping.

2. Experimental

Specimens used were polycrystalline Mo (99.95%) membranes with a thickness of 5 μm. The membrane was annealed at 1500 K for 2 h in an ultrahigh vacuum system. On one side of the membrane, a Zr film of 0.2–0.8 μm thickness was evaporated to collect permeating D atoms. Single crystalline disks of 0.5 mm thick prepared by

* Corresponding author. Tel.: +81-22 215 2058; fax: +81-22 215 2061; e-mail: nagata@wani.imr.tohoku.ac.jp.

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floating zone melted methods were partly used to investigate the lattice location and the thermal release of D atoms as well as the damage of Mo lattice by D implantation. The specimen was placed on a sample holder in contact with a ceramic heater in a scattering chamber, which was connected to a 1.7 MV tandem accelerator. Implantation of D ions was carried out using an ion gun with a velocity filter situated at 40° to the analyzing beam. The implantation beam of 10 keV D_2^+ ions was incident on the specimen at an angle 0–20° to the surface normal with a flux density of about 1×10^{18} D ions/m^2 s typically. The base pressure was 2×10^{-6} Pa and the pressure during implantation was kept to be less than 3×10^{-5} Pa.

During D implantation, concentration profiles of D atoms in the membrane were measured by elastic recoil detection (ERD) with a transmission geometry using 4–5 MeV $^4He^{2+}$ ion beams. Details of the experimental arrangement of this technique are described elsewhere [11]. The relatively high energy of the ^{4}He ion as well as the transmission geometry allows us to measure the whole depth profile of D atoms in the membrane during the D implantation. As mentioned above, the permeating D atoms were collected in the Zr layer on the downstream-side surface of the membrane, therefore both retaining and permeating fluxes were simultaneously measured as a function of the incident D dose at temperatures between RT and 600 K.

To investigate the detailed concentration depth profile at the near surface region, a conventional ERD method using a 2.0 MeV ^{4}He ion beam was applied in which recoiled deuterons were detected at an angle of 20 or 30° to the incident beam. Changes in the concentration profiles in the implanted surface layer were measured during implantation at RT, followed by linear ramping of 2 K/min. In order to estimate the number of displaced Mo atoms as a function of implantation dose, a Rutherford backscattering/channeling (RBS/C) experiment was carried out with a 1 MeV $^4He^{2+}$ beam. The angular dependence of the channeling yield was measured to study the lattice location of the implanted D atoms in Mo by using the D(^{3}He, p)^{4}He reaction.

3. Results and discussion

3.1. Retention, permeation, and re-emission of the membrane

Fig. 1 shows the concentration profiles of deuterium in the Mo membrane with a Zr layer during 10 keV D_2^+ implantation at 298, 346 and 500 K. These spectra were obtained at an implantation dose of about 1×10^{22} D/m^2, at which the amount of D atoms trapped in the membrane were saturated and the permeation flux of D was constant. At room temperature, a considerably high concentration of D was observed not only at the surface, but also in the

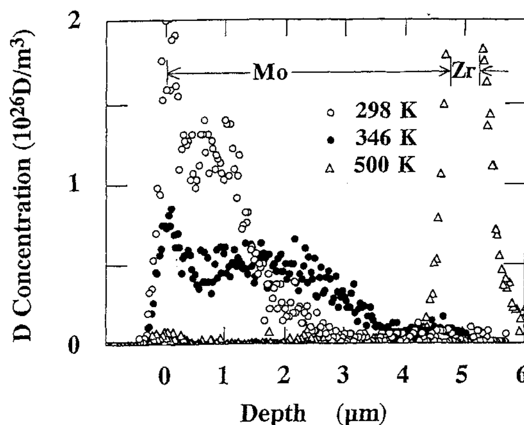

Fig. 1. Concentration profiles of deuterium in the Mo membrane with a Zr layer measured during 10 keV D_2^+ implantation at temperatures of 298, 346 and 500 K. The profiles were obtained at an implantation dose of about 1×10^{22} D/m^2.

interior of the membrane up to 2 μm. Since a predicted projected range of the incident D ion of 5 keV is about 40 nm [12], it was supposed that part of the implanted D diffused toward the downstream side and was trapped by defects, which originally existed in the sample and/or were created by the analyzing beam of ^{4}He ions with high energy. Although the total amount of trapped D atoms exceeded several % of the incident D fluence, few D atoms were collected in the Zr layer; no permeation of D atoms was observed. With increasing temperature, from RT to 350 K, the concentration of trapped D atoms decreased and the depth profile extended to larger depth, but still very little D atoms permeated. An appreciable amount of permeated D was observed at 400 K. When the temperature increased to 500 K, the D atoms were almost uniformly distributed in the interior of the membrane at low concentration, and the permeated D atoms were observed in the Zr layer as a large peak. In recent re-emission experiments [9], it was reported that the re-emission behavior in Mo was similar to those in the hydride forming metals below 500 K, and the re-emission is supposed to be mainly affected by defects created by D implantation. The present results indicated that low diffusivity and trapping effects in the interior of the Mo membrane also play an important role in the D transport behavior around ambient temperature.

Ratios of the permeation flux (J_p) to the re-emission flux (J_r) of D atoms at the steady state are shown in Fig. 2 as a function of temperature, where the re-emission flux was evaluated by subtraction of the permeating flux from the incident flux after saturation of the retained D atoms at steady state. A large deviation from the straight line indicates a shift of the transport regime between 300 and 400 K. In this experiment, the D concentration at the back (downstream) side surface is thought to be zero because of

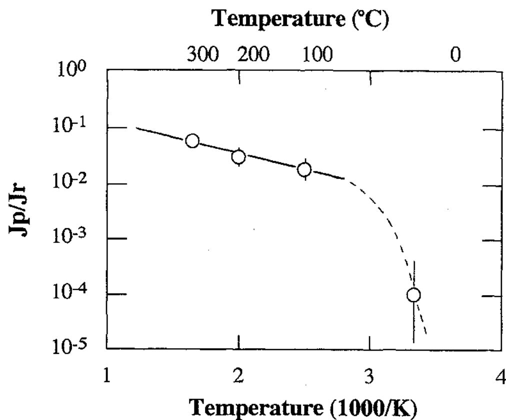

Fig. 2. Temperature dependence of ratios of the permeation flux (J_p) to the re-emission flux (J_r) for Mo membranes at steady state during 10 keV D_2^+ implantation.

the presence of Zr sink; transport in the back side surface is limited by the diffusion process. According to a simplified transport model [13], a ratio of the permeation flux to the re-emission flux is written as

$$\frac{J_p}{J_r} = \frac{D_2}{D_1} \frac{R}{T-R} \frac{C_R}{C_R - C_0},$$

where D_1 and D_2 are diffusion coefficients in the upstream-side and in the downstream-side, respectively. R is the mean projected range of the incident deuterium ions, T is the thickness of the membrane, C_0 is the deuterium concentration at the implant surface, and C_R is the deuterium concentration at depth R. If the same diffusivity in the front (implant) side and the back side are assumed, the minimum ratio of permeation flux to re-emission flux is calculated to be 0.8%, where R and T are taken as 40 nm and 5 μm, respectively. However, a much smaller value of J_p/J_r was observed as 0.01% at 300 K, so that the diffusivity at the front surface is considered to be larger than that in the back side at this temperature. Diffusion in the downstream-side might be suppressed by trapping because of the relatively low concentration of D compared to that of the trapping site at 300 K, as seen in Fig. 1. On the contrary, the trapping process at the front surface is supposed to be less important at 300 K than at higher temperatures, because most of the trapping sites are occupied. Thus, the change of D transport behavior at ambient temperature might be explained by the diffusion in both (front and back) side surfaces.

The trapping of D in the membrane and the permeation flux of D at lower temperatures were affected by thermal treatment of the membrane prior to implantation. There exists very large scattering in the data of the diffusion coefficient for D in Mo [14], and this is believed to be due to the trapping effect; impurities and defects work as trapping sites to suppress the hydrogen migration. On the contrary to the above statement, a higher permeating rate was observed for the membranes annealed at lower temperatures than that for adequately annealed membranes

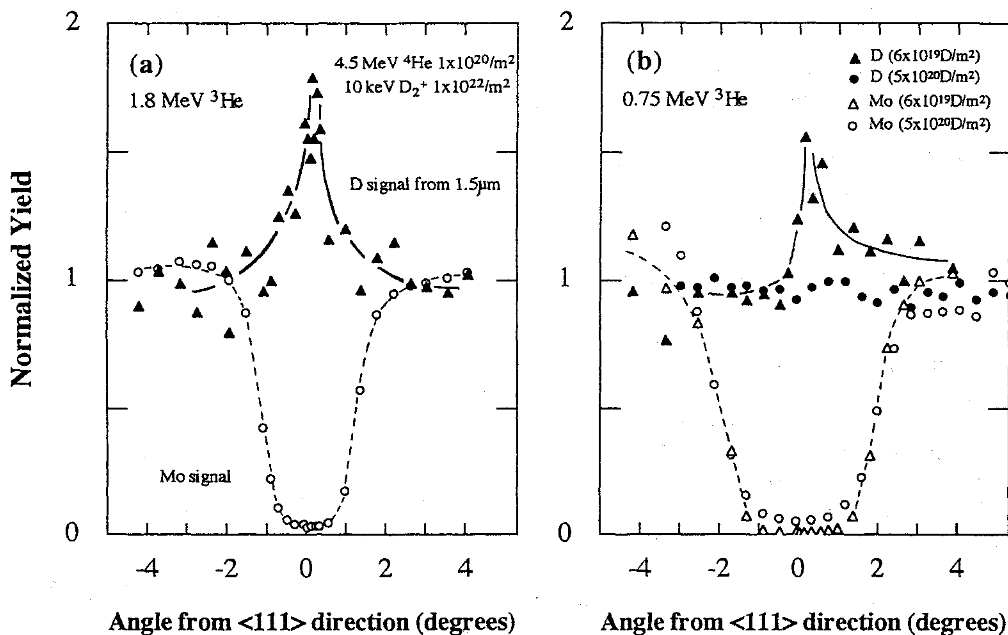

Fig. 3. ⟨111⟩ angular yield curve for D in Mo using a 1.8 MeV (a) and 0.75 MeV (b) ^{3}He beam. To simulate the trapping effect by the ERD analyzing beam during the permeation experiments, sample (a) was pre-bombarded by 4.5 MeV ^{4}He ions up to a dose of 1×10^{20} He/m^2. Each angular curve was obtained at a various D implantation dose as indicated in the figure.

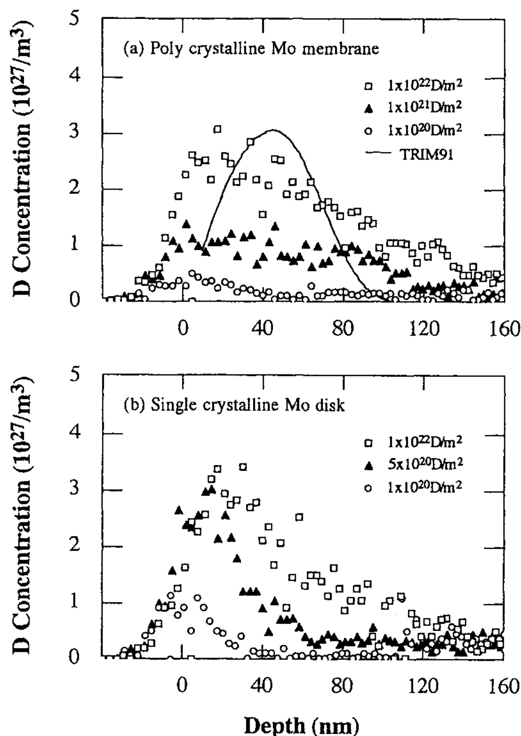

Fig. 4. Concentration profiles of deuterium in the near surface region of a poly crystalline Mo membrane and a single crystalline Mo disk, (a) and (b), respectively. Each profile was obtained at a various implantation dose of 10 keV D_2^+ as indicated in the figure. The distribution of D atoms estimated by TRIM code [12] is also shown in arbitrary units.

which might contain a lower concentration of defects. This indicates that the short-circuit diffusion of D atoms through dislocations and grain boundaries is operative on the imperfectly annealed membrane. Moreover, an unclean surface might reduce recombination at the implanted surface and thus enhance the permeating flux.

When the dose of the analyzing beam was very low, the trapped D concentration was very small in the interior. Therefore the defects created by the irradiation of the high energy analyzing ^{4}He beam contributed mainly for the trapping of D atoms in the interior of the adequately annealed membrane. These trapped D atoms are supposed to occupy interstitial sites of the Mo lattice from the channeling experiment using the D(^{3}He, p)^{4}He reaction on the single crystals of Mo; a peak was observed in the angular yield curve along the ⟨111⟩ axis for the D atoms trapped at about 1.5 μm depth as shown in Fig. 3(a).

3.2. Trapping and release of D atoms at the implant surface layer

Fig. 4(a–b) show the deuterium concentration profiles at the implant surface layer of polycrystalline membranes and single crystals, respectively, for the various D implantation doses at room temperature. At the beginning of implantation, very low concentrations of D atoms were trapped within the surface layer of the membrane. With increasing D implantation dose, the D profile extends to a depth of more than 100 nm, which was much larger than the projected range profile calculated by TRIM-code [12], and then the surface concentration was finally saturated but the depth profiles did not change after the saturation even if the implantation dose became more than 5×10^{22} D/m^2.

In the single crystal, however, different retention behavior was observed. At lower implantation dose, D atoms were trapped mainly at depths shallower than the projected range, so that the D atoms are supposed to be trapped by the surface defects and/or the defects created by the D implantation. The depth profiles extended to larger depth with increasing implantation dose even after the saturation of D concentration at the surface was established. From these results, it is supposed that some of the implanted D atoms migrate from the end of their ranges to interior and are trapped by the intrinsic defects and/or the migrated point defects from the implanted layer. For the single crystals, the defects could not be created in the deep region until the density of defects at the implanted surface layer became very high. Recent TEM study [15] reported the formation of defect complex such as dislocation loops and dislocation networks by 4 or 8 keV H^+ irradiation. Also, a long tail of trapped hydrogen was observed after prebombardment by heavy ions such as Ne and Bi [7].

Fig. 5 shows the areal density of the D atoms and the number of displaced Mo atoms in the implant surface layer of single Mo crystals versus the D implantation dose at RT and 500 K. The areal density of D atoms was estimated

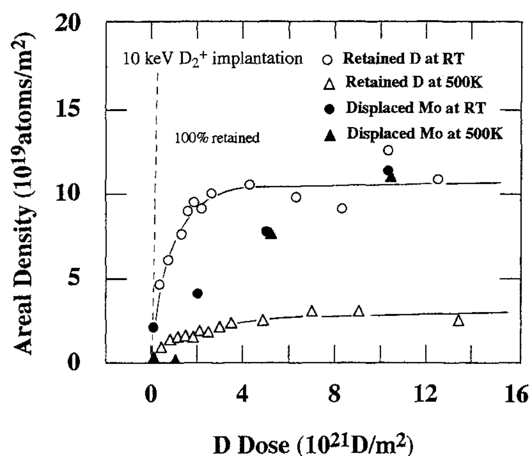

Fig. 5. Total D amount retained in the near surface layer of single crystalline Mo plotted as a function of 10 keV D_2^+ implantation dose at RT and 500 K, together with the number of the displaced Mo atoms estimated by RBS/C experiments.

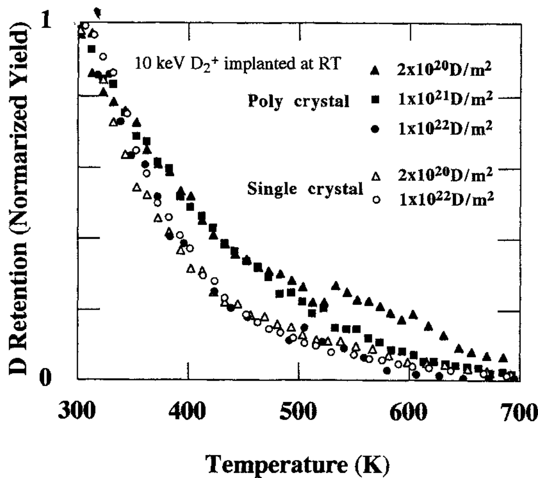

Fig. 6. Normalized D retention within the near surface implanted layer during temperature ramping at 2 K/min for the Mo membrane and the single crystalline Mo disk after 10 keV D_2^+ implantation at room temperature to various doses from 2×10^{20} to 1×10^{22} D/m^2.

from the area of the D depth profile from the surface to 80 nm depth in the ERD spectrum. The areal density of displaced Mo atoms was estimated by RBS/C experiments along the ⟨111⟩ direction. The number of displaced Mo atoms from this experiment may not correspond to the trapping center for deuterium because the channeling technique is insensible to a vacancy type defect and dislocation. In order to study the lattice location of the implanted D atoms in Mo, the angular yield scans were made using a $^3He^+$ beam of 750 keV. As shown in Fig. 3(b), D atoms distributed randomly in the Mo lattice above the implantation dose of 5×10^{20} D/m^2, where the defect concentration estimated from the RBS/C experiment was less than the trapped D concentration. This result indicates that the deuterium trapping is associated with a point defect at low implantation dose, but the trapping by defect clusters and dislocation or multiple D occupancy might occur at higher dose.

Fig. 6 shows the normalized D retention in the implant surface layer during the linear ramping of 2 K/min on the polycrystalline membrane and the single crystalline disk. In this experiment, the implantation dose is varied from 2×10^{20} to 1×10^{22} D/m^2. Three identical curves were obtained for single crystals and the high dose implanted membrane, in which the trapped concentration just after implantation is nearly saturated as seen in Fig. 3. On the other hand, in the lower dose membrane, a larger fraction of D atoms remained at higher temperature. It is reasonable that at high concentration, multiple D atoms are easily bound to a vacancy with lower binding energy in comparison with a single D atom-vacancy pair.

4. Conclusion

Concentration profiles of deuterium all over the thickness of the Mo membrane were measured during D implantation at temperatures between RT and 600 K. The fraction of permeating and re-emitting fluxes at steady state was obtained as a function of temperature. With increasing temperature, the permeation flux increased and the re-emission flux decreased. The D transport behavior in the Mo membrane changed between 300 and 400 K. In order to explain the very low permeation flux at RT, diffusivity in the front surface is considered to be larger than in the back surface, if the molecular recombination at the implant surface does not change drastically at RT. The D release from the implanted surface was limited by surface recombination above 400 K. The trapping process is supposed to play an important role in the deuterium transport at lower temperatures, though the recombination at the front surface can be a rate limiting process.

In order to investigate the mechanism of the D trapping, detailed D depth distribution in the implant surface layer as well as the retention curve against temperature was measured on the polycrystalline membranes and on the single crystals. In the D implanted single crystal specimen, the defect production by the D implantation and the lattice location of the implanted D atoms were examined by means of channeling experiments. Depth profiles of D atoms had a pronounced tail which extended to a large depth where the implantation induced defects are absent. These D atoms located randomly in the Mo lattice except for a very low dose, although the Mo lattice was not heavily damaged. Thermal release behavior varied with the concentration of the originally trapped D atoms and showed a broad retention curve which showed no abrupt release stage. The results described above suggest that the implantation induced defects migrate from the damaged surface layer toward the interior, and the D atoms are trapped there by the defect complex with multiple occupancy at higher implantation dose.

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