



Carbon effect on retention and release of deuterium implanted in Mo

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Abstract

Retention and release behavior of deuterium in carbon deposited Mo single crystals were studied during and after 10 keV D₂⁺ implantation. Concentration profile of implanted D atoms and chemical composition in the near surface layer of Mo were measured by ion beam analysis techniques. The amount of retained deuterium in Mo at room temperature increased with carbon content in the surface layer of Mo. For the layer containing high concentration of carbon as 0.5 C/Mo, the saturation concentration of the implanted deuterium was found to be about 0.3 D/host atoms, and the total amount of deuterium in the surface layer reached 2×10^{21} D/m² which was 20 times larger than that in a clean surface of Mo. In comparison with the clean surface of Mo, thermal release of deuterium from the carbon contained Mo surface occurred mainly at lower temperature, and no significant release was observed above 450 K. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years, high *Z* metals such as Mo and W became candidates for plasma facing materials because of low erosion rate and good thermal properties. In a fusion device, carbon is suspected to be one of the major impurities which deposit on the plasma facing materials [1]. Actually, formation of the carbide layers or carbon enriched layers on surface of the plasma facing materials was reported [2].

The hydrogen trapping and release characteristics of materials are important factors which affect fuel recycling and tritium inventory in the first wall and divertors in fusion devices. Hydrogen trapping in Mo and re-emission from it during implantation of energetic hydrogen have been studied by several workers [3–7]. However, the retention and release behavior of hydrogen in molybdenum carbide and carbon-containing molybdenum has not been reported so far, and the effect of carbon on the transport behavior of hydrogen is not understood. In the present work, the retention and release behavior of deuterium in carbon contaminated Mo

crystal was studied during D ion implantation. The depth distributions of deuterium implanted in Mo were measured by elastic recoil detection (ERD) analysis. By heat treatment inside a scattering chamber, a carbon containing layer was formed on the surface of the Mo crystals. The concentration of carbon in the layer and its thickness were determined by ion backscattering methods combined with a channeling technique.

2. Experimental

Most measurements were carried out on $\langle 111 \rangle$ oriented single crystals of Mo, although in a few cases polycrystalline membranes (99.95%) of 5 μm thickness were used. Single crystals were prepared by floating zone methods and were cut to 0.5 mm thickness, followed by electropolishing in a 1:3 mixture of sulfuric acid and methanol. The membranes were annealed at about 1500 K for 2 h in a 10^{-8} Pa vacuum prior to the experiments. During the heat treatment between 500 and 870 K for 1–10 ks in a 10^{-6} Pa vacuum, a thin carbon enriched layer was formed on the surface of Mo crystal, while oxygen atoms on the surface were removed after a heat treatment. The specimen was placed on a sample holder with a heater in a scattering chamber connected to a 1.7 MV

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tandem accelerator. The implantation of D ions was carried out using a 10 kV ion gun with a velocity filter placed at an angle of 40° to the analyzing beam. The D ions bombarded the specimen at an angle of 20° to the surface normal with a flux density of about 1×10^{18} D ions/m².

Concentration profiles of D atoms in the near surface region of the specimen were measured by ERD technique during and after the D implantation at RT, followed by linear ramp annealing at 2 K/min. A ⁴He ion beam of 2 MeV was incident on the specimen at an angle of 75° to the surface normal and the recoiled D atoms were detected at an angle of 25° with respect to the analyzing beam. An Al foil of 6 μ m thickness was placed in front of the detector to absorb the scattered ⁴He ions from the specimen. The depth resolution of the present ERD experiments was estimated to be about 20 nm at the surface of Mo.

Carbon and Oxygen atoms in the surface layer of the Mo crystal were measured using the nuclear elastic scattering method; a large enhancement of the cross section for the ¹²C(⁴He, ⁴He)¹²C [8] and ¹⁶O(⁴He, ⁴He)¹⁶O [9] reactions is utilized for quantitatively analyzing these light elements in a heavier element such as Mo. In comparison with the conventional RBS method using 2 MeV ⁴He beam, the nuclear elastic scattering method with incident energies of 4.265 and 3.034 MeV ⁴He gives 100 and 20 times higher sensitivity for detecting C and O at the surface of a target, respectively. In order to obtain profiles of the displaced Mo atoms in the C enriched layer of the Mo single crystal, RBS experiments combined with a channeling technique were carried out.

3. Results and discussion

The concentration profiles of deuterium implanted at 5 keV energy in the Mo single crystals with various amounts of carbon atoms in the surface layer are shown in Fig. 1. These profiles were obtained at an implantation dose of 8×10^{21} D/m² at which the amount of deuterium retained in the surface layer was saturated. Large enhancements in the concentration of deuterium in the near surface region are observed with an increase of the C content in the surface layer. For specimens with a small number of C atoms in the surface layer, the implanted D atoms are trapped mainly at depths shallower than the projected range profile calculated by the TRIM-code [10], and no significant difference in the profile is found among those specimens. Therefore, the small amount of carbon in the surface layer dose not strongly affect the trapping of deuterium, but defects created by the D implantation are responsible for trapping the deuterium. For specimens with a large amount of C atoms in the surface layer, however, the

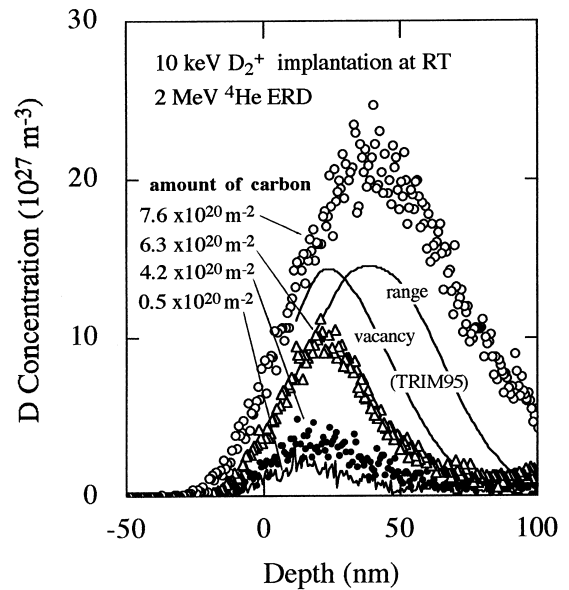


Fig. 1. Concentration profiles of deuterium implanted in Mo single crystals with various amounts of carbon atoms on the surface. The profiles were obtained at an implantation dose of 8×10^{21} D/m² at room temperature.

depth profile extends to the depth beyond the projected ranges, and accumulation of deuterium increases drastically with increase of the C content in the surface layer. The highest concentration of deuterium relative to the host atoms was about 0.3 D/host atoms, which was about 10 times greater than the saturation concentration of D atoms in the clean surface of Mo, where the number of C atoms in the surface layer was below 0.5×10^{20} C/m².

The amount of D atoms retained in the surface layer of Mo with various carbon content is shown as a function of the D implantation dose in Fig. 2, where the areal density of retained D atoms was estimated from the area of the D depth profile from the surface to 80 nm depth in the ERD spectrum. The number of retained D atoms increases with increasing C content in the surface layer of Mo. A remarkable enhancement in the D retention is found especially for the specimens containing C atoms of 7.6×10^{20} C/m²; a rapid increase of the D retention is seen up to a dose of 1×10^{22} D/m². The areal density of retained D atoms reached 2×10^{21} D/m², which was 20 times larger than the retention in the clean surface of Mo. No large difference of the D retention was observed between the single crystal and the polycrystalline membrane containing a small amount of C atoms. However, the D retention in the membrane was slightly higher than that in the single crystal due to the broadening of the D concentration profile towards interior of the membrane.

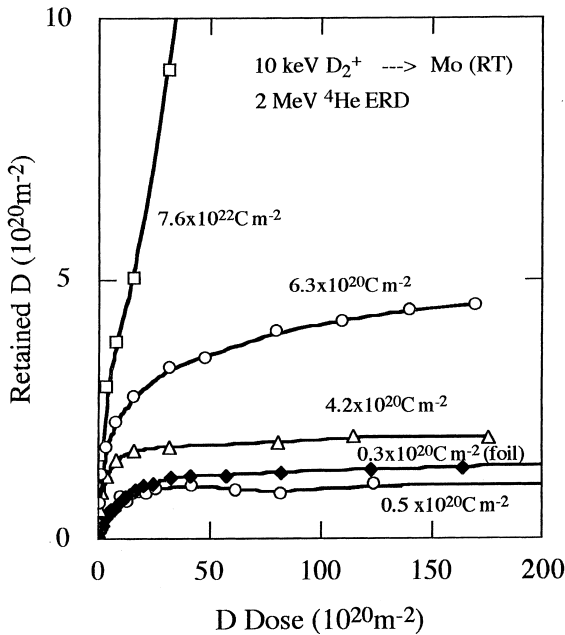


Fig. 2. Amounts of D atoms retained in the surface of specimens with various carbon content in the surface layer of Mo as a function of the D implantation dose during 10 keV D_2^+ implantation at room temperature.

Fig. 3 shows the RBS/channeling spectra from $\langle 111 \rangle$ oriented Mo single crystals, where the surface layer of the crystals contains various amounts of C atoms. The enhancement of the scattering yield near the high energy edge is due to the lattice distortion near the surface of Mo crystal. More Mo atoms are displaced from the

original site of the bcc lattice in the specimens containing a larger number of C atoms. Similarly, the thickness of the distorted layer is increased by an increase of the carbon content in the surface layer. It is reasonable to suppose that the distorted layer may correspond to the carbon enriched surface layer, although the depth profile of C atoms could not be measured owing to the poor depth resolution of the nuclear elastic scattering. However, an RBS measurement using 1.0 MeV ^4He beam gives the depth profile of C atoms if the concentration of C atoms is very high, because the backscattering yield corresponding to the carbon enriched Mo layer is reduced by an increase of the stopping power due to the dissolution of carbon atoms [11]. As seen in Fig. 3, the width of the dip observed in the random spectra is nearly the same as the width of the peak in channeling spectra. Therefore, the thickness of C enriched layer is considered to coincide with the thickness of distorted layer. For the specimen containing $7.6 \times 10^{20} \text{ C/m}^2$ of carbon, the thickness of distorted layer was found to be 40 nm, and the concentration of C atoms relative to Mo atoms was estimated to be about 0.5 C/Mo, which may indicate the formation of Mo_2C . In earlier work with annealing experiments for carbon doped Mo [12], carbon precipitation in Mo occurred at 520 and 650 K and molybdenum carbides MoC and Mo_2C precipitated at 880 and 940 K, respectively. The detailed mechanism of the enrichment of C or formation of carbides in the surface layer of Mo during the heat treatment are not known at the present.

Fig. 4 shows areal densities of both the retained D atoms and the displaced Mo atoms in the surface layer of Mo as a function of the C content in the layer after the D implantation at $5 \times 10^{21} \text{ D/m}^2$ at room temperature.

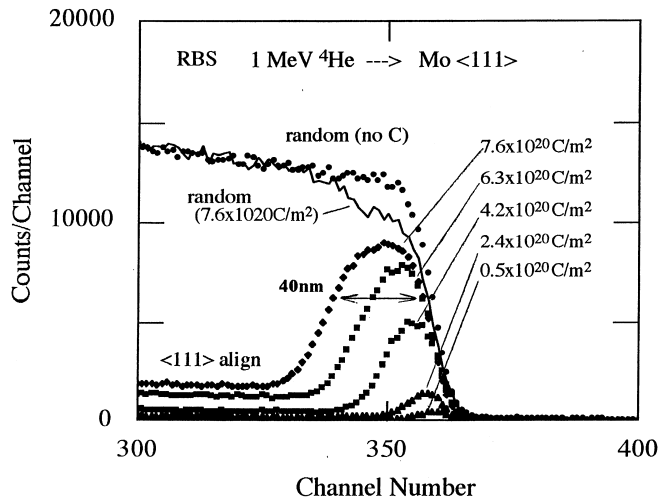


Fig. 3. Backscattering spectra from $\langle 111 \rangle$ oriented Mo single crystals, where the surfaces of the crystals were covered with various amounts of C atoms as indicated in the figure.

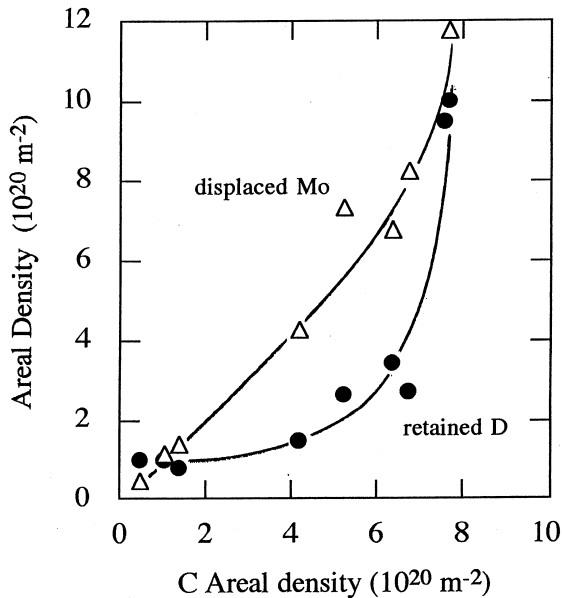


Fig. 4. The areal densities of retained D atoms and of displaced Mo atoms in the surface layer of Mo versus carbon content in the surface layer after a D implantation dose of $5 \times 10^{21} \text{ D/m}^2$ at room temperature.

The number of displaced Mo atoms is estimated from the area of the displaced Mo peak obtained from the channeling experiment. The areal density of displaced Mo atoms agrees nearly with the areal density of C atoms below $7 \times 10^{20} \text{ C/m}^2$. However, the amount of retained D atoms slowly increases with an increase of the areal density of C atoms up to $7 \times 10^{20} \text{ C/m}^2$, and suddenly enhances at higher C concentration where Mo_2C might be formed in the surface layer of Mo.

Thermal release of trapped D atoms was investigated for the specimens with various carbon content in the surface layer of Mo. Fig. 5 shows the temperature dependence of the implanted D atoms retained in the surface layer during the linear ramping of 2 K/min after the D implantation up to $1 \times 10^{21} \text{ D/m}^2$ at room temperature. For higher concentrations of C atoms in the surface layer, more D atoms are retained at room temperature as shown in Fig. 4. For the specimen with clean surface, the release of deuterium starts above room temperature and continues up to 600 K. On the other hand, with increasing C concentration in the surface layer, the amount of retained deuterium rapidly decreases between 330 and 430 K, and then reaches lower levels than in the clean surface. The result implies that the trapping of D atoms in the carbon enriched layer is not so strong, comparing to the defect trapping in pure Mo [5]. Because hydrogen is released from graphite materials at much higher temperature [13], molybdenum carbide could be formed in the surface layer of Mo and

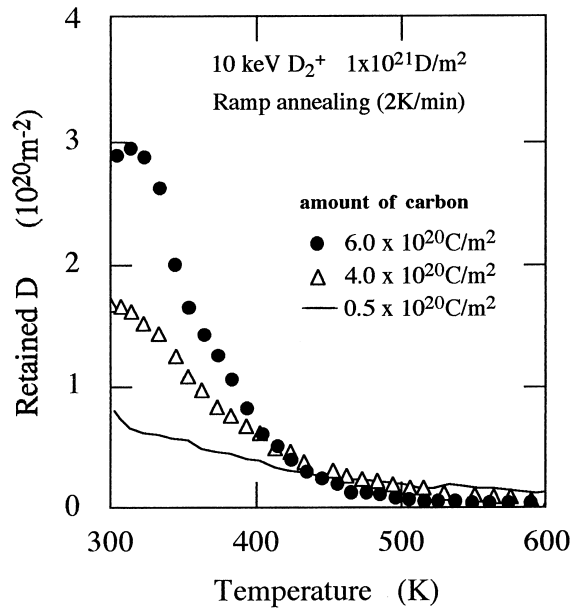


Fig. 5. The temperature dependence of D retention in the surface layer during linear ramping of 2 K/min after the D implantation up to $1 \times 10^{21} \text{ D/m}^2$ at room temperature. The concentration of carbon in the surface layer is indicated in the figure.

the carbide layer would be responsible for hydrogen trapping. Similar thermal release behavior of deuterium affected by carbon impurities is reported for W and WC [14].

4. Conclusions

Retention and thermal release of deuterium implanted in Mo were investigated during and after 10 keV D_2^+ implantation in connection with the carbon impurities in the surface layer of Mo. The concentration profile of implanted D atoms in the surface layer of Mo was measured by an ERD analysis, and the carbon concentration and thickness of the C enriched layer were determined by a backscattering technique combined with ion channeling.

The amount of retained deuterium in Mo at room temperature is enhanced by the existence of the carbon enriched layer on the Mo surface. The trapping of D atoms in the carbon enriched layer was not so strong as that of the defect trapping in pure Mo. For the specimen containing as high concentration of carbon as 0.5 C/Mo, the maximum concentration was 0.3 D/host atoms, and the total amount of D retained in the surface layer reached $2 \times 10^{21} \text{ D/m}^2$; 20 times larger than the retention in carbon-free Mo. Thermal release of deuterium from the carbon enriched surface layer of Mo occurs

mainly at lower temperatures than that from Mo with clean surface. In a sample containing large amounts of carbon in its surface layer, most of the trapped D atoms were released at temperatures between 330 and 430 K, and no significant release was observed at higher temperatures. The results suggest that molybdenum carbide such as Mo₂C formed in the near surface layer is responsible for trapping of deuterium, although it does not work as the strong trap for deuterium.

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