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Helium and hydrogen trapping in W and Mo single-crystals irradiated by He ions

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Abstract

Retention of He and accumulation of H in the near surface layer of W and Mo single-crystals were studied during and after the implantation of He ions with 2–10 keV at 295 and 820 K. The He retention was saturated at a concentration of a He/metal ratio of about 0.25, depending on the implantation temperature. Subsequent He implantation caused H accumulation in the He saturated layer, up to a maximum concentration about equal to that of He. The initial H uptake rate just after the He irradiation was comparable to the impingement rate of the H_2 or H_2O molecule at the crystal surface from the residual gas. For the He irradiation at 820 K, blisters and exfoliation with large sizes were observed on the crystal surface, where impurities other than H and He were also enriched.
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1. Introduction

The understanding of the He behavior and He irradiation effects on the transport of hydrogen isotopes is important for plasma facing materials, which will be exposed by He with low energies during the period of burning and He discharge cleaning. Early experiments showed that the He pre-irradiation of metals efficiently enhances the retention of hydrogen isotopes in the He irradiated region [1]. To explain relatively strong hydrogen trapping by He irradiation, trapping mechanisms related to He bubbles were suggested, including an adsorption on the He bubble wall and a stress/strain field around bubbles [2,3]. Besides, the He ion irradiation effect on the metal surface was intensively studied, concerning with microstructural changes such as, blister and bubble super lattice [4,5]. Although a defect accumulation during He irradiation on W was reported [6], the interaction between hydrogen and helium in heavily He irradiated surface has not been investigated in detail.

In our previous study, it was observed that He pre-implantation with a small dose created dense interstitial loops in W crystals [7], which significantly affected the trapping efficiency of post-implanted hydrogen. The present work examines the influence of He irradiation at higher doses, focusing on H accumulation in the He saturated layer of W and Mo single-crystals. Changes of morphology and composition in the surface layer by He irradiation were also investigated to consider the H uptake in the heavily implanted surface layer.

2. Experiments

Specimens used for the present study were W and Mo single-crystal disks of 8 mm diameter and 0.5 mm thickness, cut from single-crystal rods made by the floating zone melting method. Details of the preparation procedure were described elsewhere [8]. The He ion implantation and the ion beam analysis were performed in a vacuum system with a base pressure of 2×10^{-6} Pa, at the Laboratory for Developmental Research of Advance Materials, Institute for Materials Research, Tohoku University. The He ion implantation was carried out with energies of 2, 5 and 10 keV in the temperature range between 295 and 860 K. A typical current density of He was about 1×10^{18} He/m^2 s. During and after He implantation, concentration depth profiles of He and H

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atoms retained in the surface layer of the W crystal were measured by elastic recoil detection analysis (ERDA). A beam of 4.0 MeV O^{3+} was directed on the specimen at an angle of 20° with respect to the surface, and recoiled particles were detected at 35° of recoil angle. An Al foil of 4 mm thickness was placed in front of the detector to absorb scattered and recoiled particles heavier than He. The H concentration was estimated using a standard specimen of a known hydrogen content, and was also checked by a beam of 2.8 MeV $^4He^{++}$. Rutherford backscattering spectroscopy (RBS) measurements were performed to examine impurities and their content in the implanted layer and to compare these results with these of ERDA. Changes of the surface morphology were studied by scanning electron microscope (SEM) observation.

3. Results and discussion

Fig. 1 shows the areal density of He retained in the near surface of W single-crystals during 2, 5 and 10 keV He implantation at 295 and 830 K. The number of retained He atoms were evaluated from the recoiled He yield, calibrated at a small dose where 100% of the incident He ions are assumed to be trapped except for a backscattering fraction. The retention of He increased with an increase of the incident He energy, corresponding to a depth of the projected range of the incident He ions. The total amount of retained 5 keV He, 1.5×10^{21} He/m^2, was slightly larger than the value obtained by desorption measurements [9], in which they implanted both H and He simultaneously and might reduce the He retention. The maximum concentration of He did not change very much with incident He energies between 2 and 10 keV; the atomic ratio of He-to-metal atoms, He/W was roughly estimated to be about 0.25 ± 0.05. A maximum appeared in the 10 keV He retention curve, followed by a gradual decrease with an increase of the incident He dose. The reduction of retained He can be attributed to disruption of the surface layer by the onset of the blistering. This is consistent with the results of SEM observation [10], in which the blisters and exfoliation were found on the surface of W crystals irradiated by 10 keV He at above 1×10^{22} He/m^2 at 820 K.

During the He implantation into W crystals, H accumulation started when the He concentration completely saturated [10]. A similar H accumulation in the He implanted layer was found for Mo crystals situated in the vacuum with residual gas pressure of about 2×10^{-6} Pa, under the same experimental circumstance for W crystals. Typical energy spectra of recoil particles were shown in Fig. 2, obtained from a Mo single-crystal irradiated with 5 keV He at 295 K. A small surface peak followed by a flat distribution with a low concentration of H atoms was observed in the crystal before He implantation. Retained He in the crystal appeared as broad energy distribution nearly saturated at He doses above 2×10^{21} He/m^2, where no significant increase of the H atoms was detected on the tail of the He distribution. With an increase of the He dose above 5×10^{21} He/m^2, however, the H signal significantly enlarged within the thickness corresponding to the He saturated layer. Because of the low solubility of H in Mo [11], H atoms originally distributed in the crystal were trapped and was not anticipated to move at room temperature. If there exist freely movable H atoms in the Mo crystal at room temperature, the H accumulation may start owing to extensive damage created by He irradiation with a small dose. Therefore, it can be stated that the H uptake

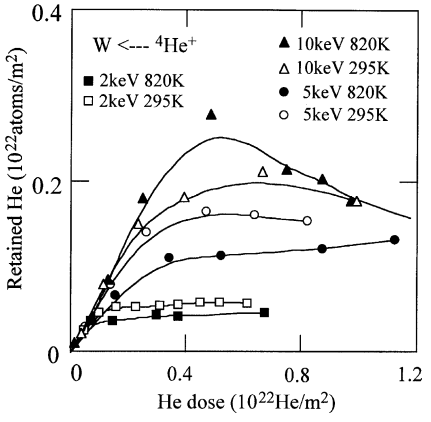

Fig. 1. The areal density of retained He in near surface of W crystals irradiated with 2, 5 and 10 keV $^4He^+$ at 295 and 820 K, plotted against He irradiation doses.

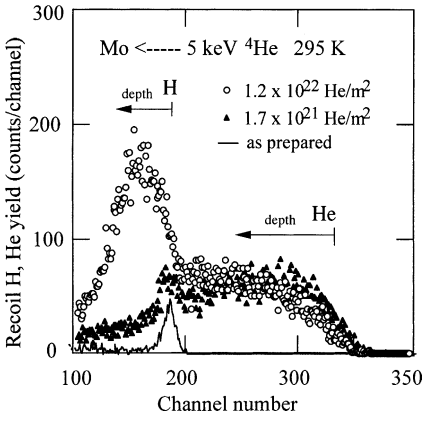

Fig. 2. Energy spectra of He and H recoil particles from a Mo single-crystal before (solid line) and after implanted with 5 keV $^4He^+$ at doses of 1.7×10^{21} He/m^2 (▲) and 1.2×10^{22} He/m^2 (◯) at 295 K.

in the He saturated layer occurred from the residual gas in the vacuum system.

Fig. 3 shows the total amount of retained He and H in the surface layer of Mo crystals during 10 keV $^4He^+$ implantation at 295 and 820 K. A rapid increase of H in the surface layer was observed when the reduction of the retained He started at 295 K. The accumulation of H in the He saturated layer was also found for the crystal implanted at 820 K, just after stopping He implantation and cooling the crystal down below 400 K. Assuming that the source of the accumulated H is residual gas in the vacuum chamber, the H uptake rate was estimated to be about 3×10^{17} H/m^2 s, which was comparable to the impingement rate of H_2 or H_2O from the residual gas of about 10^{-6} Pa. The H uptake in the He implanted layer was examined repeatedly, for a specimen irradiated by 10 keV He at 820 K to a dose about 1.5×10^{22} He/m^2. To remove the accumulated H from the He implanted layer before this experiment, the specimen was kept at 820 K for 10 min. Though the final amount of accumulated H did not change for residual gas pressure, the initial H uptake rate depended on it. The uptake rate can be related not only with the impingement rate of H_2 and H_2O molecules, but also with the surface contamination such as oxygen [12].

If the large H uptake rate was accomplished by the enhancement of dissociative adsorption of gas molecules impinging the irradiated surface from the residual gas, other impurities such as carbon and oxygen can also be adsorbed. In an RBS spectrum, the deficiency in the heavy element signal can be caused by the presence of light elements in the surface [13]. Fig. 4 shows RBS spectra for 2 MeV $^4He^{++}$ beam incident along random direction in Mo (a) and W (b) crystals after implantation with 10 keV $^4He^+$ at a dose about 1.5×10^{22} He/m^2 at 295 and 820 K. A remarkable reduction of the scattering yield was detected in the depth corresponding to the He implanted layer of the Mo crystal implanted at room temperature. Qualitatively, it is consistent with the retained amount of He in the Mo crystal obtained by the ERD measurements, as seen in Fig. 3; the He retention at 295 K was about twice of that for 820 K. By using the deficiency method [13], the ratio of retained He-to-Mo atoms, He/Mo in the crystal implanted at 820 K, was estimated to be about 0.8, which is considerably higher than the value obtained form the ERDA measurements. This large discrepancy may not be reasonably explained by taking account of an enlargement of the stopping power which depends on the physical state of implanted He atoms in the crystals. The results suggest a possibility of the presence of impurities other than He and H in the irradiated surface of Mo crystals. Heavier impurities were not detected by characteristic X-ray analysis. By RBS measurement using resonant scattering for oxygen [14], oxygen atoms of about 5×10^{20} O/m^2 were found in the He implanted surface, although it is not sufficient to explain the large deficiency. No large blister and

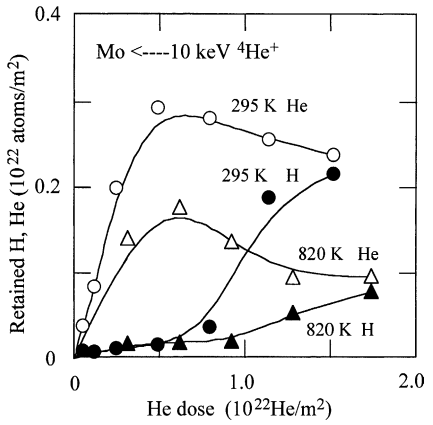

Fig. 3. Total amounts of retained He and H in the surface layer of Mo crystals irradiated by $^4He^+$ with 10 keV at 295 and 820 K. For 820 K implantation, the ERDA measurements were made at temperatures below 400 K, after stopping $^4He^+$ implantation.

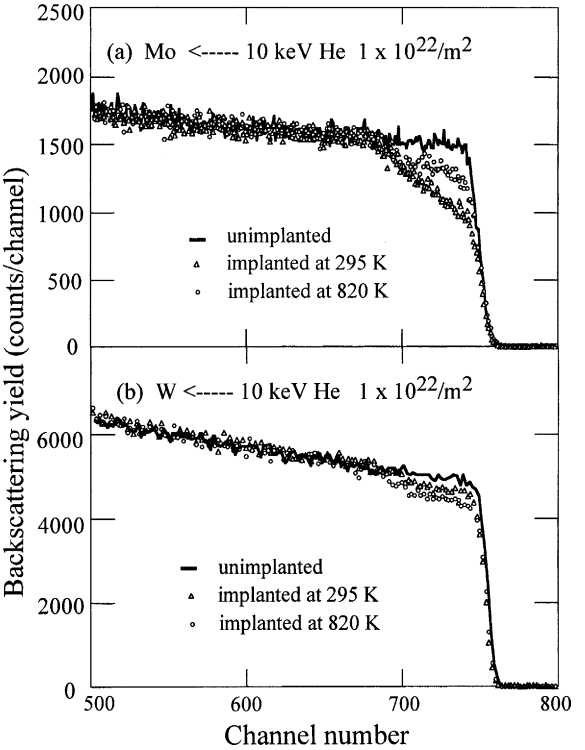

Fig. 4. Backscattering spectra for 2 MeV ^4He ion beam incident along random direction in Mo (a) and W (b) crystals after the implantation with 10 keV $^4He^+$ at a dose of about 1×10^{22} He/m^2 at 295 K (△) and 820 K (◯), the spectra without He implantation (solid line) are also included.

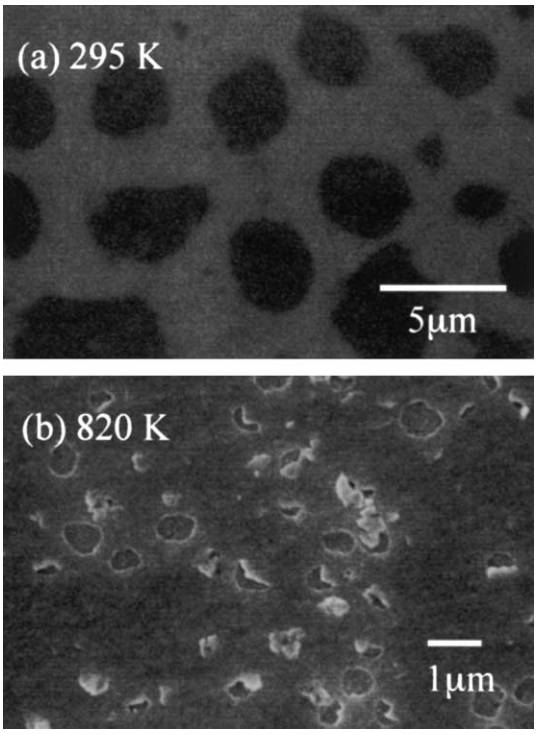

Fig. 5. SEM micrographs of the surface of Mo crystals implanted with 10 keV $^4He^+$ to a dose of about 1.5×10^{22} He/m^2 at 295 and 820 K, for (a) and (b), respectively.

exfoliation was recognized for the Mo crystal irradiated at 295 K, by SEM observation as shown in Fig. 5(a). However, there were contrasted patterns, which may be related to the impurity enriched area. Formation of blisters and exfoliation was confirmed for the Mo crystal irradiated at 820 K as shown in Fig. 5(b), and the similar surface morphology was seen in the W crystal irradiated at 820 K [10]. The evaluated ratio of retained He-to-W was in fair agreement between RBS and ERDA measurements for the W crystals irradiated at room temperature. However, the deficiency of backscattering yield from the W crystal irradiated at 820 K was larger than that for 295 K, indicating an increase of the impurity content at higher temperature irradiation. Further investigation is now progressed to determine the concentration of impurities in the He implanted layer.

4. Conclusions

For W and Mo single-crystals, a significant accumulation of H was observed in the He implanted surface layer with highly concentrated He created blisters and exfoliation. The initial H uptake rate was comparable to the impingement rate of the residual gas, such as H_2 and H_2O, to the crystal surface. Furthermore, a reversible change of the H release/accumulation in the He implanted layer of the Mo crystal was observed by heating/cooling the crystal. The RBS measurements indicated that impurities other than H and He atoms were enriched in the He implanted layer. During the He ion irradiation, carbon and oxygen atoms may also be absorbed and may form oxide and/or carbide in the near surface of W and Mo crystals. Although the mechanisms of the H uptake are not clear, the remarkable H accumulation in the He implanted layer can be attributed to an enhancement of the dissociative adsorption of hydrogen at the modified surface.

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