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Journal of Alloys and Compounds 356–357 (2003) 326–329

Journal of ALLOYS AND COMPOUNDS

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Hydrogen accumulation in the helium implanted surface of Mo single crystals

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Received 10 June 2002; accepted 25 October 2002

Abstract

The up-take behavior of hydrogen and deuterium was studied for the surface layer of Mo single crystals irradiated by 10 keV He ions with a high dose, at which the blisters and exfoliation were formed on the surface. Hydrogen accumulation was found in the H saturated layer up to a maximum concentration of about 0.2 H/Mo at room temperature. Although the up-taken H concentration profiles and the morphological changes of the irradiated surface depended on irradiation temperatures, thermal release behavior of up-taken H were similar for both specimens irradiated at 295 and 820 K. The higher pressure of H_2 and/or H_2O caused the quicker accumulation of H, and the hydrogen dissociation seemed to be sensitive to the surface contamination. The up-take rate for H was an order of magnitude larger than that for D, even by letting mainly D_2 and/or D_2O into the vacuum chamber.

Keywords: Metals; Surfaces; Ion impact

1. Introduction

It is well known that the ion irradiation of metals efficiently enhances the retention of hydrogen isotopes in the ion implanted region [1]. Especially, He ion implantation can provide strong hydrogen trapping sites, which are related to hydrogen adsorption on the He bubble walls [2] and a stress/strain field around bubbles [3]. For hydride forming metals, defects induced by He irradiation and hydride precipitates were attributed to the enrichment of H atoms in the He implanted layer, and the association of hydrogen and radiation induced defects were in thermal equilibrium [4,5]. For endothermic hydrogen occluders such as Mo, having low solubility of hydrogen, the hydrogen atoms merely enter the crystal lattice, while dissociative adsorption can easily take place at the crystal surface. The transport of hydrogen in Mo can be significantly influenced by the He ion irradiation-induced defects, but the hydrogen atoms must be forced to dope into the crystals. On the other hand, the porous bubble structure of the He ion irradiated metal surface also may allow the impurity atoms to change the surface properties [6]. Recently, we found the remarkable hydrogen accumulation by absorbing from the surrounding atmosphere into the He saturated surface of Mo crystals [7]. In the present work, we examined hydrogen up-take and release behavior and isotope effects on the phenomena for the He implanted layer of Mo single crystals.

2. Experimental procedure

Specimens used were Mo single crystalline disks of 8 mm diameter and 0.5 mm thickness, cut from a single crystal rod, followed by electropolishing in a 1:3 mixture of sulfuric acid and methanol. The single crystal rod was made by the floating zone melting method from a commercial powder fabricated rod (99.95 wt.%). The ion implantation and the ion beam analysis were performed in a vacuum system with a base pressure of 2×10^{-6} Pa, connected to a 1.7 MV tandem accelerator, at Laboratory for Advanced Materials, Institute for Materials Research, Tohoku University. The He ion implantation was carried out with incident energies of 10 keV at a temperature in the range between 295 and 820 K up to a dose of about 2×10^{22} He/m^2, with a typical current density of about

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0925-8388/02/$ – see front matter
doi:10.1016/S0925-8388(02)01276-8

1×10^{18} He/m^{2}s. During the He ion implantation, the residual gas pressure was kept at about 4×10^{-5} Pa. Concentration depth profiles of hydrogen isotopes and He retained in the surface layer of the specimen were measured at room temperature by elastic recoil detection analysis (ERDA) using 2.8 MeV He^{2+} and 4.0 MeV O^{3+} beams. The experimental setup for the ERD measurements was described elsewhere [8]. Prior to the hydrogen uptake measurements, the specimen was heated up at 850 K for 600 s to remove the hydrogen accumulated at room temperature. The equipments such as ionization gauge, which can create atomic hydrogen, were switched off during the uptake experiments to prevent the effects of atomic hydrogen. H and D up-take measurements were made by letting H_2 and D_2 gas into the analyzing chamber while monitoring the concentration depth profile of H and D by the ERD. The LqN_2 traps situated behind the variable leak valve reduced the water vapor simultaneously coming with H_2 and D_2 gas. The surface morphology of the He irradiated layer was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM) observation in contact mode.

3. Results and discussion

Without post implantation of H ions, an accumulation of H atoms was found in the He irradiated layer of the Mo crystal, when the specimen was kept in high vacuum just after the He irradiation. Concentration depth profiles of up-taken hydrogen are shown in Fig. 1, for a Mo crystal irradiated by 10 keV ^{4}He ions to a dose of 1.5×10^{22} He/m^2 at 295 and 820 K, obtained by the ERD measurements at room temperature. A high concentration of H as a sharp peak appeared for the specimen irradiated at 295 K, while relatively flat distribution of the H atoms was observed in the implanted depth of the specimen irradiated at 820 K. The up-taken H depth profiles in He irradiated Mo crystals were fairly consistent with the retained He profiles calculate by TRIM95, indicating hydrogen trapping around retained He. It should be noted that the depletion was larger than that expected by the increasing of the stopping power owing to the existence of He and H atoms in the Mo crystals [7], suggesting build up of light impurities such as carbon and oxygen.

Changes of the retained amount during the heat treatment of the specimen with isochronal annealing for 600 s are shown in Fig. 2. Total amount of retained hydrogen atoms was measured after each stage of the isochronal annealing, and was estimated by integrating the retained hydrogen up to the depth of 200 nm. The release curves of up-taken H were nearly the same for both specimens irradiated at 295 and 820 K. In comparison with the release behavior of D implanted with 5 keV, however, the thermal release of the up-taken H occurred at the higher temperature from the He irradiated layer. The result indicated that the He-related defects such as H–He complexes and He bubbles are attributed to the trapping of up-taken H atoms. Though there is possibility to form oxides or carbides at the irradiated surface as described above, the release from the oxide and carbide layer occurred at considerably lower temperatures [9].

AFM images of the W crystal surface are shown in Fig.

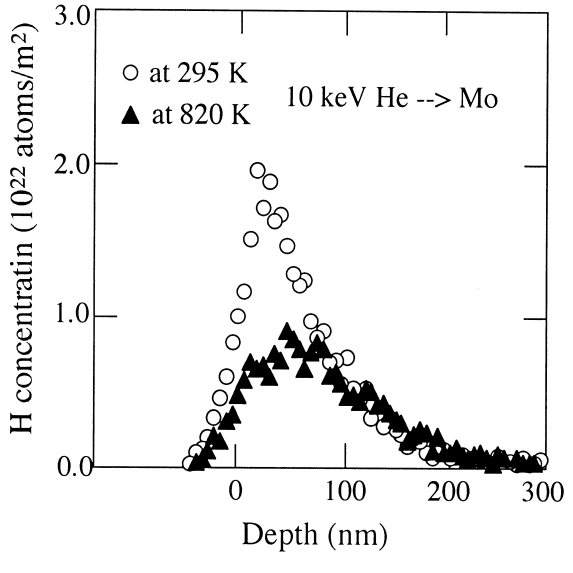

Fig. 1. Concentration depth profiles of up-taken hydrogen in the He saturated layer of Mo single crystals irradiated by ^{4}He ions to a dose of 1.5×10^{22} He/m^2 at 295 (○) and 820 K (▲). The profiles were measured by the ERD using 2.8 MeV $^4He^{2+}$ at room temperature just after the He irradiation.

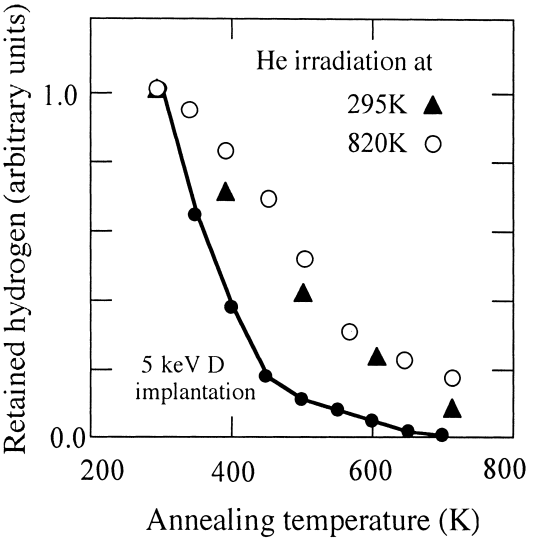

Fig. 2. Integrated amounts of H in the near surface layer of Mo crystals implanted with 10 keV $^4He^+$ to a dose of about 1×10^{22} He/m^2 at 295 K (▲) and 820 K (○) plotted as a function of the annealing temperature. The solid line with solid circles refers to the result for the crystal irradiated 5 keV D ions to a dose of 1.0×10^{22} D/m^2 without the He implantation. The ERD measurements were done after each stage of isochronal annealing for 600 s.

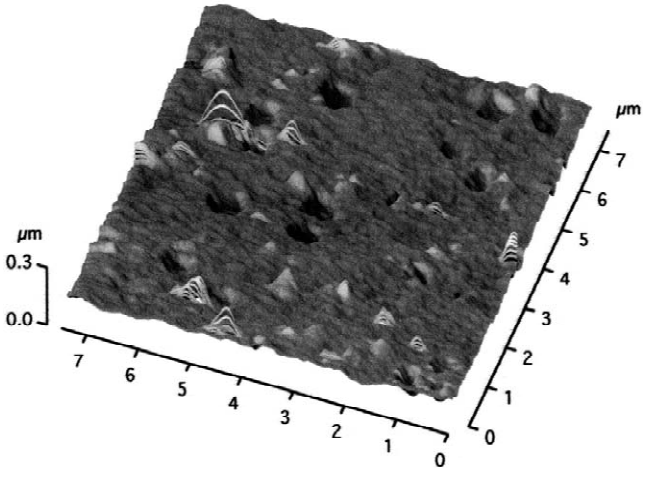

Fig. 3. AFM images of irradiated surface of the Mo crystal irradiated by 10 keV He to a dose of 1.5×10^{22} He/m^2 at 820 K.

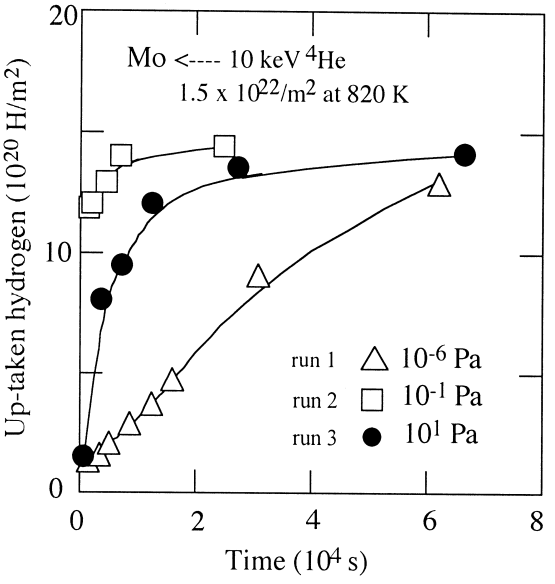

Fig. 4. The H uptake in the He implanted layer plotted against time while introducing H_2 gas, for a Mo crystal irradiated by 10 keV He at 820 K to a dose of about 1.5×10^{22} He/m^2. The specimen was kept at 850 K for 10 min to remove the accumulated H, followed by the ERD measurements after cooling down the specimen below 320 K, repeatedly, at various residual gas pressures.

3, for the He irradiation of about 1.5×10^{22} He/m^2 at 820 K. Etch-pits with sizes of about 1 μm diameter were created probably because of the bursting of the He-containing blisters. No particular morphological changes were observed for the specimen irradiated at 295 K by the present AFM and SEM observation, indicating formation of bubbles with smaller sizes [10]. The amount of the retained He for the specimen irradiated at 295 K was about twice as much as that for 820 K irradiation, and it decreased above 0.5×10^{22} He/m^2 irradiation. Thus, the surface irradiated at 295 K seemed to be covered with smaller bubbles and etch-pits, which were not detected by the present AFM observation, probably due to the poor preparation of the surface of the specimen. In spite of the large differences on the up-taken H concentration profiles, the H up-take and release behavior was similar for both irradiation temperatures. It can be concluded that the hydrogen trapping and thermal release behaviors were influenced by nanostructure of the irradiated layer, which could not be resolved by the present surface observation.

About 90% of accumulated H at room temperature was released by heat treatments for 10 min at 850 K as seen in Fig. 2. When the specimen was cooled down to room temperature, we found the up-take of H atoms in the He irradiated layer again. Although prompt accumulation of H was not observed during the isochronal annealing experiments, the H retention slowly recovered even in the vacuum of 2×10^{-6} Pa. The H uptake in the He implanted layer of a Mo crystal was examined repeatedly after the heat treatment for different H_2 and D_2 pressures as shown in Fig. 4. The specimen was irradiated by 10 keV He at 820 K to a dose of about 1.5×10^{22} He/m^2, followed by the heat treatment up to 850 K for 600 s. After cooling the specimen below 370 K, the up-taken H concentration was measured by the ERD analysis. When we left the specimen in the vacuum chamber with the vacuum of about 2×10^{-6} Pa, the up-take of H occurred slowly, but finally reached the retention comparable to the original up-taken value (run 1). Then, the specimen was heated up to release up-taken H atoms, and was cooled down to room temperature. Subsequently, H_2 gas of about 1×10^{-1} Pa was introduced into the analysis chamber. The H retention immediately went up to the saturation level after the exposure of about 1 h (run 2). The up-take H was released again by the heat treatment, and the specimen was exposed to the H_2 gas of about 10 Pa at room temperature. The lower uptake rate at higher H_2 pressure of 10 Pa might be due to the surface contamination [11], which can be simultaneously brought with H_2 gas and can occupy the sites for dissociation of hydrogen. The H up-take curve suggests that the up-take rate depended on the number of un-occupied trap sites for hydrogen. To compare the up-take behavior, initial up-take rates of hydrogen were plotted against the residual gas pressure as shown in Fig. 5. In general, the higher residual gas pressure resulted in higher values for the initial up-take rates. Above 10^{-2} Pa of residual gas pressure, the up-take rates were nearly constant, probably owing to surface contaminants.

To examine the isotope effects, D_2 gas was let into the vacuum chamber instead of the H_2 gas. The D-up-take rates were an order of magnitude less than H-up-take rates for a wide range of the residual gas pressure. According to the quadruple mass analysis for the pressure better than 10^{-2} Pa, the D containing gas such as D_2 and D_2O were dominant components, while H containing molecules such as H_2, H_2O, HDO still existed. Thus the H atoms were preferentially taken up, even though the partial pressure of

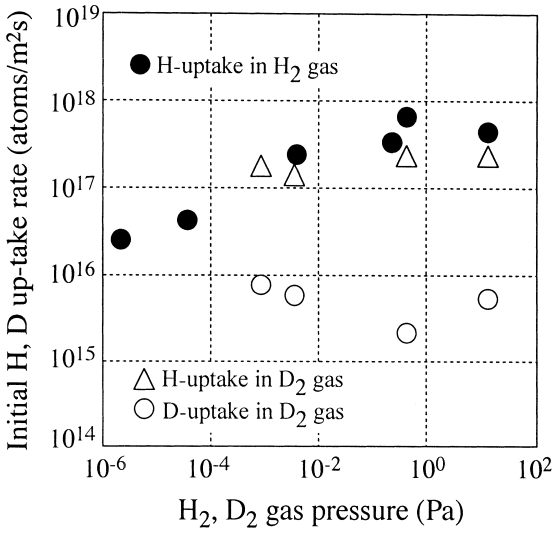

Fig. 5. Initial up-take rate for H and D in He irradiated layer of Mo crystals exposed to H_2 and D_2 gas, plotted against the residual gas pressure. The Mo crystals were irradiated by 10 keV He at 820 K to a dose of 1.5×10^{22} He/m^2.

D_2 and/or D_2O was higher than the hydrogen containing gas. Considering very high rate of up-take from residual gas and evidence of unexpected large depletion observed in RBS spectrum [7], a build up of oxygen was also plausible in the He implanted layer; there might be formed Mo trioxide hydrate (MoO_3 $2H_2O$ [12]), which is known to be proton conductive materials. The isotopic difference between the H and D uptake can be attributed to proton conductive oxides which can shows remarkable isotope effects in H and D exchange [13]. Detailed surface analysis is needed for the surface layers heavily irradiated by He ions, to determine the elemental composition and to confirm formation of the oxide materials.

4. Conclusions

He implanted Mo crystal surface showed the capability for hydrogen up-take from the surrounding gas atmosphere. The up-taken H concentration at room temperature reached 10–20 at.% at room temperature depending on the irradiation temperature. The release and accumulation of hydrogen repeatedly occurred by heating and cooling the specimen, respectively. Although the concentration depth profile of up-taken hydrogen and surface morphology depended on the irradiation temperature of He ions, the thermal release behavior was similar. The hydrogen up-take rate varied with the hydrogen containing gas pressure, and seemed to be very sensitive to the surface contamination, while the up-taken concentration reached the same level as that retained before the heat treatment. The results indicated that H dissociation and the H trapping are closely related with nanostructure around He bubbles. Preferential up-take of H atoms was found in the He saturated layer, when the specimen was exposed to the atmosphere mainly containing D_2 and D_2O gas; the up-take rate for H was an order of magnitude higher than that for D during D_2 gas exposure. The observed isotope effects on the up-take behavior might be due to the proton conductive oxides formed on the He irradiated surface of the Mo crystal.

Acknowledgements

A part of this work was performed under the inter-university cooperative research program of Research Institute for Applied Mechanics, Kyushu University.

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