Deuterium diffusion and retention in tungsten coated with barrier layer during ion irradiation

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Abstract. The results of the comparative analysis of low-temperature desorption of deuterium from tungsten coated with aluminum and yttrium films under the irradiation by hydrogen plasma with oxygen impurity are presented. The irradiation of aluminum or yttrium coating by H$_2$+1%O$_2$ plasma leads to the desorption of implanted deuterium from the samples. It was shown that the number of atoms desorbed depends on the sign of enthalpy of hydrogen solution in the metal film.

1. Introduction

Beryllium and tungsten are chosen as the materials for the first wall and the diverter of the ITER tokamak, respectively. Beryllium and tungsten have oxide layers formed on their surfaces. It is known that the oxide layers function as barriers for hydrogen diffusion. The surface of tungsten and beryllium will be coated by oxides if the ITER plasma would have an oxygen impurity. Sputtered beryllium atoms will be deposited on the surfaces of tungsten tiles and form oxide layers under these conditions. The research on the influence of beryllium films on hydrogen isotope trapping and desorption from tungsten is of interest from the safety perspective as the limit for the accumulation of tritium in the walls cannot be exceeded.

The authors of paper [1] have discovered the effect of low-temperature hydrogen isotope desorption from stainless steel at $T \approx 320$ K under the irradiation by hydrogen ions in hydrogen atmosphere with oxygen impurity, as well as hydrogen plasma with oxygen impurity. This effect is explained by the processes initiated by inelastic collisions of deuterium and oxygen atoms/ions with the chromium oxide layer on the surface of stainless steel [2]. Trapping and retention of hydrogen in stainless steel and tungsten with oxide layers were studied in several works [3-5]. However, the influence of surface oxide layers on hydrogen trapping and desorption from metal during ion irradiation has not been properly investigated as of today.

In this work, a comparative research on the effect of low temperature desorption of hydrogen isotopes from tungsten samples with surface barrier coatings like aluminum, which is considered as a proxy for beryllium in laboratory experiments, and yttrium with oxidized surfaces. The task was to identify the characteristics of the process in cases when the metal (tungsten) and the barrier layer (aluminum) are metals with positive enthalpy of hydrogen solution (+1.1 eV/at [6] and +0.7 eV/at [6], respectively), and in case when the enthalpy of hydrogen solution in the barrier layer (yttrium) is negative (-0.85 eV/at [6]).
2. Experimental facility and experimental method

Aluminum and yttrium films 200±10 nm thick were deposited on one side of the 7×7×1 mm³ tungsten samples. The Plansee-grade tungsten (99.96% wt. of W) samples were mechanically polished, cleaned with acetone and alcohol ultrasonic baths and then annealed in vacuum with the residual pressure of ≤ 5x10⁻⁶ Pa at a relatively low temperature (1600 K) to remove the “technological” hydrogen. The coating was formed by aluminum/yttrium atoms sputtered from the aluminum/yttrium target with argon plasma ions. The residual gas pressure during the deposition did not exceed 5x10⁻⁴ Pa. The temperature of the samples during the deposition was 450-500 K, the duration of the deposition was 1 hour.

The X-ray Energy Dispersion Spectroscopy (EDS) and the Thermal Desorption Spectroscopy (TDS) analysis has shown that a significant number of hydrogen and oxygen atoms were trapped in aluminum and yttrium films during their respective depositions. In particular, concentrations of hydrogen and oxygen in the films were 30 at.% and 13 at.% for aluminum and 33at.% and 17 at.% for yttrium, respectively. Additionally, Al₂O₃ and Y₂O₃ oxide layers were formed on the surface of the films after being exposed to atmosphere.

The experiments were conducted in the “MIKMA” facility [7]. The pumping system allows for the residual pressure in both radiation chambers to not exceed 1×10⁻⁴ Pa, as well as pump the TDS chamber down to 1×10⁻⁵ Pa.

Three tungsten samples with aluminum and yttrium films were used to measure the average number of “technological” hydrogen atoms in the samples using TDS. Then deuterium was implanted into the coating-free side of the rest of the samples by irradiating them with 650 eV/at. energy deuterium plasma ions. The plasma consisted mostly of D₂⁺ (82-85%) ions, with the rest being D⁺ and D₀ ions. For this reason, the experimental results were analyzed assuming that the samples were irradiated by D₂⁺ ions only. The parameters of implantation were as follows: ion flux density \( j = 3.7\times10^{19} \text{ at/m}^2\text{s} \), fluence \( F = 1.3\times10^{23} \text{ at/m}^2\), the temperature of the samples during the irradiation \( T = 500 \text{ K} \).

The first sample with implanted deuterium was used to measure the number of deuterium and hydrogen atoms after the irradiation by deuterium plasma. The second sample was kept in vacuum for 1 hour after the implantation at 500 K i.e. for the same duration at the same temperature as the one irradiated by H₂+1% O₂ plasma. It was made to see whether the exposure of the sample to vacuum would lead to the desorption of the implanted deuterium. The measurement of the number of deuterium atoms was then conducted using TDS. The third sample was irradiated by the ions with energy of 50 eV/at. (mostly H₂⁺) of H₂+1% O₂ plasma. The parameters of irradiation were the following: ion flux density \( j = 3.7\times10^{19} \text{ at/m}^2\text{s} \), fluence \( F = 1.3\times10^{23} \text{ at/m}^2\), the temperature of the samples during the irradiation \( T = 500 \text{ K} \).

The heating rate of the samples during TDS was 5 K/s. The temperature of the samples during plasma irradiation and the TDS analysis was measured using W-Re thermocouple welded to the samples. Desorption signals of H₂, HD, D₂, H₂O, HDO and D₂O molecules were measured during TDS. Desorption of another hydrogen isotopes-containing molecules was negligible.

3. Results and Discussion

The results of the experiments with tungsten samples coated withaluminum filmare shown in Table 1. It can be seen (Table 1.1) that during the coating deposition trapping of a large number of hydrogen molecules from the residual gas occurs. During the deuterium implantation about 14% of hydrogen is desorbed from the sample (Table 1.1, 1.2). The exposition to vacuum does not lead to the change in hydrogen or deuterium content in the sample (Table 1.2, 1.3). After the irradiation of the aluminum film by H₂+1% O₂ plasma ions at the energy of 50 eV/at., the concentration of deuterium in the sample decreased significantly. At least 48% of the implanted deuterium has passed through the bulk of the tungsten and aluminum oxide and was removed during the irradiation in hydrogen plasma with the
oxygen impurity. At the same time, the number of hydrogen atoms in the sample was practically unchanged.

Table 1. The number of trapped hydrogen and deuterium atoms in tungsten samples with aluminium coating after deuterium implantation, exposition to vacuum and irradiation in H₂+1% O₂ plasma.

| №  | Experiment                        | Deuterium trapping, \(\times10^{20}\) at/m² | Hydrogen trapping, \(\times10^{21}\) at/m² | \(D_{before}/D_{after}\) | \(H_{before}/H_{after}\) |
|----|-----------------------------------|------------------------------------------|------------------------------------------|--------------------------|--------------------------|
| 1  | Before implantation in D₂ plasma  | -                                        | 3.6                                      | -                        | -                        |
| 2  | After implantation in D₂ plasma   | 2.9                                      | 3.1                                      | -                        | ≈ 0.86                   |
| 3  | After exposition to vacuum        | 3.1                                      | 3.3                                      | ≈ 1.07                   | ≈ 0.92                   |
| 4  | After irradiation by H₂+1 at.% O₂ plasma | 1.5                                      | 3.2                                      | ≈ 0.52                   | ≈ 0.89                   |

Thermal desorption spectra of D₂ and HD molecules, by which approx. 90% of deuterium is desorbed, from tungsten samples with aluminum coating shows two thermal desorption peaks at \(T \approx 830\) K and 1450 K (Figure 1). Figure 1 also includes D₂ and HD molecules’ spectra from a tungsten sample not coated with aluminum. It has only one peak at \(T \approx 830\) K. The comparison of D₂ and HD molecules’ spectra from both samples leads to the conclusion that the peak at 1450 K shows the desorption of deuterium from aluminum film. Deuterium implanted at \(T = 500\) K diffuses through tungsten and enters aluminum layer from the coating-free side of the sample. Deuterium can diffuse through tungsten for large distances (≈ 0.1 mm) at \(T = 500\) K [8]. TDS analysis of the spectra in Figure 1, we can conclude that approx. 25% of deuterium implanted into tungsten passes into the aluminum film.

The results of the experiments with tungsten samples coated with yttrium film are shown in Table 2. It is shown (Table 2.1) that, as with aluminum coating, a significant number of hydrogen atoms is trapped from the residual gas during yttrium film deposition on tungsten. Deuterium implantation did not lead to hydrogen atoms desorption from the sample (Table 2.1, 2.2). Sample exposition to vacuum also did not lead to the change in deuterium and hydrogen content in the sample (Table 2.2, 2.3). After the irradiation of the yttrium coating surface by 50 eV/at H₂+1% O₂ plasma ions, the concentration of deuterium in the sample decreases. At least 21% of implanted hydrogen has passed through tungsten and yttrium coating and was removed by irradiation in H₂+1% O₂ plasma. At the same time, the number of hydrogen molecules has increased by a factor of 3.
Thermal desorption of D\textsubscript{2} and HD molecules from tungsten samples with yttrium coating have a peak at $T \approx 830$ K and two steep peaks at $T \approx 900$ K and 1100 K. It was shown before that the peak at 830 K is the desorption of deuterium from tungsten. It can be concluded, therefore, that the steep peaks at the range of $T = 900$-$1100$K are caused by the desorption of deuterium from the yttrium coating. TDS analysis of the spectra (Figure 2) has shown that approx. 60% of deuterium implanted into tungsten passes into the yttrium film.

Table 2. The number of deuterium and hydrogen atoms in tungsten samples with yttrium coating after deuterium implantation, exposition to vacuum and irradiation in H\textsubscript{2}+1% O\textsubscript{2} plasma.

| № | Experiment                                      | Deuterium trapping, $\times 10^{20}$ at/m$^2$ | Hydrogen trapping, $\times 10^{21}$ at/m$^2$ | D\textsubscript{before} / D\textsubscript{after} | H\textsubscript{before} / H\textsubscript{after} |
|---|-------------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| 1 | Before implantation in D\textsubscript{2} plasma | -                                             | 2.0                                           | -                                             | -                                             |
| 2 | After implantation in D\textsubscript{2} plasma  | 4.7                                           | 2.0                                           | $\approx 0.98$                                | 1.0                                           |
| 3 | After exposition to vacuum                      | 4.6                                           | 2.0                                           | $\approx 0.98$                                | 1.0                                           |
| 4 | After irradiation by H\textsubscript{2}+1 at. % O\textsubscript{2} plasma | 3.7                                           | 5.8                                           | $\approx 0.79$                                | $\approx 2.9$                                |

As shown above, during deuterium implantation into the coating-free side of the sample, 25% and 60% of trapped atoms pass through into aluminum and yttrium layers, respectively. Enthalpy of hydrogen solution in yttrium is lower than that for aluminum; therefore, it is more energetically favorable for deuterium to pass into yttrium than into aluminum.

![Figure 2](image-url)  

Figure 2. TDS spectra of D\textsubscript{2} (a) and HD (b) from tungsten and tungsten with yttrium coating after deuterium implantation, exposition to vacuum and irradiation with H\textsubscript{2}+1% O\textsubscript{2} plasma ions.

The comparison (Table 1.3, 1.4 and 2.3, 2.4, respectively) shows that after the irradiation with H\textsubscript{2}+1% O\textsubscript{2} plasma ions, there is twice as many desorbed deuterium atoms from metal with positive enthalpy of hydrogen solution (aluminum) than from the metal with negative enthalpy of hydrogen solution (yttrium). It can be explained by the fact that the energy levels of hydrogen in yttrium (negative enthalpy) and aluminum (positive enthalpy) are lower and higher than the vacuum level, respectively. Hydrogen needs to pass through the potential barrier in yttrium before it can desorb from its surface, which leads to the desorption of less deuterium atoms compared to the aluminum film.
4. Conclusion
A comparative study of low-temperature desorption of deuterium from tungsten with aluminum and yttrium coatings under the irradiation by H₂+1% O₂ plasma ions has been conducted. A dependence on the number of deuterium atoms desorbed from the value of enthalpy of hydrogen solution under the irradiation of H₂+1% O₂ plasma ions has been established.

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