

Helium accumulation in tungsten layers deposited in Ar-He magnetron discharge

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Abstract. W-He co-deposition was studied by means of in-vacuo thermal desorption spectroscopy. W-He co-deposited layers were produced at substrate temperatures varied from 400 K to 800 K with a 50 K temperature step. It was found that the He content decreases from ~1.7 at. % at 400 K to ~0.17 at. % at 750 K. At 800 K, an increase in the He content was observed, that should be caused by significant changes in the film structure. Helium TDS spectra had two main peaks with maxima in the 500-600 K range and at ~960 K; the peaks observed are similar to those previously seen for He ion implantation in W. Several scaling expressions are proposed for He/W vs. T.

1. Introduction

The deuterium-tritium (DT) mixture will be the fuel in future fusion devices. Fuel accumulation in plasma-facing and structural materials of fusion devices is highly important both for radiation safety and for the assessment of the impact of gas recycling on plasma operation. One of the main channels for this accumulation is co-deposition of fuel particles together with the material previously eroded from plasma-facing components [1–4]. In ITER, tungsten is going to be used as the divertor surface material [5], and hydrogen isotope co-deposition with tungsten is under investigation [6–8].

Helium (He) is a product of DT-reaction and will be a natural impurity in burning fusion plasma. Therefore, He accumulation in co-deposited layers and influence on layer properties, such as its structure, and H isotope retention is also important to investigate.

2. Experimental

Co-deposition studies were performed using the MD-2 experimental device [9]. Mixed W-He layers were obtained by means of sputtering of the 99.998% pure W target with Ar (99.998% purity) – He
(99.999% purity) plasma at different temperatures. Ar was used in order to enhance W sputtering rate, as pure He plasmas resulted in impractically low film deposition rates.

The background pressure was $3 \times 10^{-5}$ Pa, determined mostly by protium, water vapor and some deuterium due to the deposition chamber’s previous experimental history, which consists of a number of co-deposition studies where the working gas was deuterium [8–10]. The working pressure of Ar+He gas with the ratio Ar:He = 1:1 was 5.8 Pa, as measured by a capacitance pressure gauge. The deposition rate was $\sim 0.2$ nm/s as measured by a quartz microbalance (QMB) monitor. The total film thickness was $\sim 100$ nm as measured with QMB.

The substrate used for deposition was 0.2 mm thick $10 \times 10$mm Mo plate that had been annealed at $\sim 1400$ K for 7 hours in high vacuum prior to deposition. The same sample was used for several depositions, and it was annealed for 5 minutes after each TDS analysis. In order to minimize the substrate experimental history role, ie the effect of the previous depositions on new ones, the deposition temperature was changed randomly from experiment to experiment, similar to [8], where no history effects were observed. The substrate temperature during deposition was monitored using a K-type thermocouple spot-welded to the backside of the sample. In order to achieve elevated substrate temperatures during deposition, a radiative heater (a 300W lamp in a quartz casing) was positioned behind the experimental sample. The temperature was varied from 400 K to 800 K, with 50 K steps.

After deposition the samples were cooled in 2.9 Pa of He down to $\sim 300$ K, then the deposition chamber was pumped down to the background pressure and the sample was transferred in-vacuo into the thermal desorption spectroscopy (TDS) analysis chamber.

TDS measurements were performed up to the temperature of 1350 K, with the ramp up rate of 2 K/s. The desorption flux of various gases was monitored by two quadrupole mass spectrometers (QMS) Extorr 100M. The energy of ionizing electrons in the first QMS was set to 19 eV. This energy is below the threshold for He ionization and pure $D_2$ signal was measured by the first QMS. The electron energy in the second QMS was set to 31 eV. In this case, both He and $D_2$ were measured. Both spectrometers were calibrated using the standard for MD-2 procedure [11] using leak valves, a calibrated volume, a capacitance pressure gauge, and bottles of pure helium and deuterium.

3. Experimental results

The experimental He/W ratios in at.% vs. the deposition temperature are shown in fig. 1. The He amount was calculated from the integral of the desorption flux during TDS measurements. The W amount was obtained from the QMB data, multiplied by the correction factor due to differing positions of the sample and the QMB detector with respect to the W target [11].
Figure 1. The He content in atomic % in He-W co-deposited layers vs substrate temperatures during deposition. Black dots – experimental data. Lines – scaling equation predictions (see section 4): green – De Temmerman scaling [6,12], red – Krat scaling [8] with two trap types, blue – Krat scaling with three trap types.

One can see that in a temperature range of 400 K to 750 K, the He/W ratio decreases with the substrate temperature from ~1.8 at. % at 400 K to 0.18 at. % at 750 K. The sharpest decrease occurs near 400 K, where the He content decreases about 2 times over the span of 50 K. The signal of D₂ desorption was at the level of the background in all the experiments. At 800 K a significant increase in He concentration and a change in TDS spectra is observed (fig. 2).

Figure 2: TDS spectra of He desorption for different substrate temperatures during deposition. The substrate temperatures are indicated in the figures chronologically from top to bottom in order to showcase possible role of the order in which experiments were performed on the results.

At low substrate temperatures of 400-500 K two broad peaks can be observed in TDS spectra (ref to the Figure 2), one with the maximum in the 500-600 K range and another with the maximum at 960 K.
At higher substrate temperatures (≥600 K) only the high-temperature peak remains. At substrate temperature of 800 K, the high temperature peak shifts to 1040 K, and its amplitude increases significantly. These two regions of He desorption were observed also in TDS analysis of W samples exposed to He ion beams and He plasma [13]. Similar to the current data, the peak at 900-1100 K was usually higher than the low temperature one.

One can also observe an increase in the He release flux at temperatures above 1200 K, indicating that not all He might desorb within the temperature range available. This could be also expected on the base of ion beam experiments [13], where the He desorption during TDS after high fluence exposures was observed in the temperature range from nearly room temperature up to 2500 K.

No chronologically evolving features were observed in the TDS spectra, indicating that the substrate history effect was negligible.

In spite of the same concentration of Ar and He in the plasma, the Ar desorption flux during TDS was very small, close to the background level. The maximum Ar desorption was detected at substrate temperature of 400 K, and it was still below 0.015 at. %. We cannot exclude however, that Ar can release above 1350 K.

4. Discussion

It is interesting to note that the measured absolute amount of He in W co-deposited layer is lower than the amount of deuterium accumulated in similar co-deposition conditions [8]. Assuming that the accumulation is driven by the He trapping in various defects, such as dislocations, vacancies and vacancy clusters, the opposite effect could be expected, as He atoms are bounded stronger than deuterium [14–16]. It is possible that the observed discrepancy is due to relatively low maximum temperature reached during TDS analyses and that a large amount of He still remains in the layers.

Ion beam experiments [13] demonstrated that at low He+ ion fluence, He desorption is observed above 1200 K only. Low temperature peaks in addition to high temperature peaks were observed only after high ion beam or plasma fluence exposure. One can conclude that the He release is incomplete in our experiments.

It is useful nevertheless, to devise or draw a scaling expression for the temperature dependence of the He content in the co-deposited layers. The simplest approach with the fewest number of independent variables is the use of Arrhenius equation, as it was proposed by De Temmerman for D in W [6].

\[
\frac{He}{W} = C_1 \exp \left( - \frac{E_A}{kT} \right)
\]

where \(C_1, E_A\) – scaling parameters.

Another way is to use the model developed in our previous studies [8,9] that is based on hydrogen diffusion and defect trapping:

\[
\frac{He}{W} = \sum_{i=1}^{n} \frac{Z_i}{2\mu_i W D e_i^2 \nu_i^2} + \frac{I_0 h}{2n_i D} + 1
\]
where $D$ – diffusion rate of helium in tungsten, $I_0$ – helium flux to the surface during co-deposition, $h$ - helium implantation depth, $E_b, Z_i$ – binding energies and concentrations of various trapping sites, $n_W = 6.319 \times 10^{28} \text{m}^{-3}$ – tungsten particle density, $\mu \approx 1$.

In the case of W-D co-deposition this model gave a very good description of stepwise shapes of experimental curves matched well to trap binding energies known for tungsten [8]. The disadvantage of the mentioned scaling is a rather large number of fitting parameters, some of which can be difficult to quantify. For example, different studies [17–20] report helium diffusion activation energy ranging from 0.06 eV, as obtained by ab initio calculations [17] to 0.24–0.32 eV as measured experimentally [19,20] and obtained via molecular dynamics simulations [18]. For the purposes of the modeling in this paper, He diffusion rate was taken as $D = 4.7 \times 10^{-7} \exp \left(\frac{-0.28 \text{[eV]}}{kT} \right) \text{m}^2 \text{s}^{-1}$ [14, 16], The $I_0 h$ parameter was taken as $2.5 \times 10^{12}$ particles/(m×s) identical to that used in [8], as the experimental conditions were similar.

The fitting parameters used to plot Fig.1 are given in table 1. Data for D-W co-deposition are also given for comparison. The scalings describe experimental results reasonably well up to 750 K. From the Krat’s approach one can estimate the energies of trapping site, responsible for He accumulation. Additional trapping sites with higher detrapping energy can be expected as discussed above, but to get an information about them one should perform experiments in a wider deposition temperature range and with TDS measurements up to higher temperatures.

**Table 1.** Fitting parameters for scaling equations predicting He content in W co-deposited layers He/W depending on the substrate temperature during deposition

| Parameter | De Temmerman-like scaling | De Temmerman-like scaling D/W | Krat scaling 2 traps | Krat scaling 3 traps | Krat scaling 3 traps D/W |
|-----------|---------------------------|-------------------------------|---------------------|---------------------|--------------------------|
| $C_1$     | 8.93±0.03                 | --/--                         | --/--               | --/--               | --/--                     |
| $E_A$     | 1680±230                  | 736±228                       | --/--               | --/--               | --/--                     |
| $Z_{1, \text{at}\%}$ | --/--                   | 0.9                           | 1.3                 | 2.3                 |                          |
| $E_{b_1} + E_D$ | --/--               | 1.04±0.06                     | 0.90±0.06           | 0.74±0.08           |                          |
| $Z_{2, \text{at}\%}$ | --/--                  | --/--                         | 0.3                 | 1.8                 |                          |
| $E_{b_2} + E_D$ | --/--               | 1.21±0.12                     | 1.18±0.12           |                    |                          |
| $Z_{3, \text{at}\%}$ | --/--                  | 0.36                          | 0.3                 | 1.0                 |                          |
| $E_{b_3} + E_D$ | --/--               | 1.61±0.07                     | 1.64±0.08           | 1.56±0.16           |                          |

At the highest deposition temperature (800 K), the experimental point deviates from continuously decreasing scalings. The integral He retention is clearly higher than in the case of 750 K deposition. This can be due to significant changes in the structure of the film at this temperature, which is not
considered in the models. Most probable explanation for this effect is higher mobility of point defects and He-V clusters and their agglomeration into larger He bubbles. However, more investigations are need to understand the details of this process.

Significant changes in the W near-surface layer under ion or plasma irradiation are usually observed at slightly higher temperatures, above 1000 K. Under low flux ion irradiation [21], increase of the bubbles and formation of sponge-like surface was observed. Under high flux plasma irradiation above 1000 K, formation of so-called fuzz-like structure is observed [22], that is also an evidence of higher mobility lattice atoms in the material. In the case of growing film, some changes are likely possible at slightly lower temperatures.

5. Conclusions

Helium accumulation in W layers deposited in Ar-He magnetron discharge was studied by means of thermal desorption spectroscopy. TDS measurements were limited by 1350 K. The total He amount varied from He/W=1.8 at. % at the substrate temperature of 400 K to 0.18 at. % at 750 K. Two main desorption peaks at 500-600 K and at ~960 K were observed in the TDS spectra of He. Release of He is supposed to be incomplete in these experiments, and additional He release is expected at higher temperatures.

The Ar desorption flux from the films was about two orders of magnitude lower than that of He.

At 800 K, the increase in the He retention was observed, and this effect needs more experiments to be described. Significant changes in the structure of the film and He bubbles formation can be expected at these temperature.

Several scaling expressions were proposed to describe the temperature dependence of the He amount in defects active in the range of 400-750 K in W films.

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