HYDROGEN CO-DEPOSITION WITH METALS IN PLASMA DISCHARGE

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Deposition of a single element film is always accompanied by co-deposition of a certain amount of other elements. This can be done properly to improve properties of the coating or due to contamination by impurities. In the field of thermonuclear fusion research, where hydrogen isotopes are used as a fuel, co-deposition with sputtered material from the wall is one of major mechanisms of hydrogen isotopes accumulation in the installation. Since D-T fuel will be used in ITER and future fusion reactors, accumulation of radioactive tritium will limit the lifespan of the installations due to safety concerns. For example, tritium accumulation in ITER is limited by 1 kg. This is why carbon materials were not accepted for the use in ITER. Basing on experiments, it was predicted that the safety limit could be reached after 100 of shots with tritium. Recent experiments in JET [1] demonstrated in the case of "ITER-like" wall (first wall – Be, divertor area - tungsten) accumulation of deuterium fuel in the co-deposits was 20 times lower than in the full-carbon wall campaign. This is both due to smaller amount of co-deposits and smaller concentration of deuterium in them.

In parallel to the "ITER-like materials", investigations of hydrogen isotopes co-deposition with some other materials is also actively investigated due to some other alternative reactor concepts. One of them is based on the use of liquid metals, such as lithium and tin, as plasma facing materials [2]. The most perspective among these materials is, probably, lithium, which can efficiently absorb hydrogen isotopes. Therefore, tritium retention in lithium co-deposits is considered also as a potentially serious problem.

All this necessitates development of a unified approach to study of hydrogen co-deposition with materials. At the moment, there is no a detailed analysis of co-deposition mechanisms. Several empirical formulae exist for specific metals, such as tungsten [3] and beryllium [4], but they were developed using regressive analysis of experimental result databases in a limited range of deposition parameters, and cannot be easily extrapolated to other metals. From the experimental data, however, one can conclude that the hydrogen content in co-deposited layers depends on the temperature of the substrate, rate of deposition relative to the flux of hydrogen to the surface, average energy of hydrogen particles impinging on the surface, and the material hydrogen is being co-deposited with.

In order to develop an understanding of co-deposition, series of experiments on deuterium co-deposition with metals, specifically with tungsten and lithium, in various conditions were carried out. The theoretical model describing mechanisms of co-deposition was also proposed and compared with experiments.

The experimental installation MD-2 consists of two separately pumped vacuum chambers, one for deposition and one for analysis (see [5] for details). The ultimate pressure in the deposition chamber is about 10^{-4} Pa, and the ultimate pressure in the analysis chamber is below 10^{-7} Pa. The deposition chamber is equipped with a DC planar magnetron used to deposit films on an experimental sample. The rate of film deposition, and the total thickness of the film are monitored using quartz microbalance deposition monitor placed near the sample. The temperature of the sample during deposition is monitored using a thermocouple. The sample can be heated up to about 530 °C to study co-deposition on heated substrates using a radiative heater. Deuterium (99.98 at.% purity) is used as a working gas to sputter the target and deposit the film, which results in co-deposition. For sputtering of heavy elements, such as tungsten, argon is added to the working gas mixture. The working pressure is about 1 – 4 Pa. After the deposition, the sample is held in deuterium for several minutes until it cools down to room temperature. The sample can be transported into analysis chamber without exposing it to air, which is important for study of chemically reactive elements, such as lithium.

Deuterium content in co-deposited films is analyzed using thermal desorption spectroscopy (TDS). Both total quantity of the deuterium in the film, and the characteristic temperatures of the deuterium desorption are obtained. Spectra of D_2 (4 a.m.u.), HD (3 a.m.u), and H_2 (2 a.m.u.) release are monitored with quadrupole mass spectrometer during a linear heat up. Quadrupole sensitivity is regularly calibrated so absolute quantities of released gases in terms of particle fluxes can be measured. The maximum temperatures achieved during TDS are about 1400 K, which is enough to release deuterium from most co-deposited layers.

Dependence of deuterium content on the temperature of the substrate during the deposition was studied in detail. In all studied co-deposition conditions, deuterium content in the co-deposited layers decreased with increase of substrate temperature during deposition. However, the nature of this decrease varied depending on deposition parameters.

In certain cases, for example in case of slow codeposition with tungsten in a mixed Ar-D atmosphere, a clear correlation between temperature and D content in the film was observed. In fig 1a D/W ratios are shown for several substrate temperatures. Also, the amount

of D remaining in the film by the time it reaches a given temperature during TDS of a film deposited at near room temperature is shown. One can see that the two curves map to each other very precisely, which means that there is no difference between heating up the substrate during or after the codeposition where it comes to D removal.

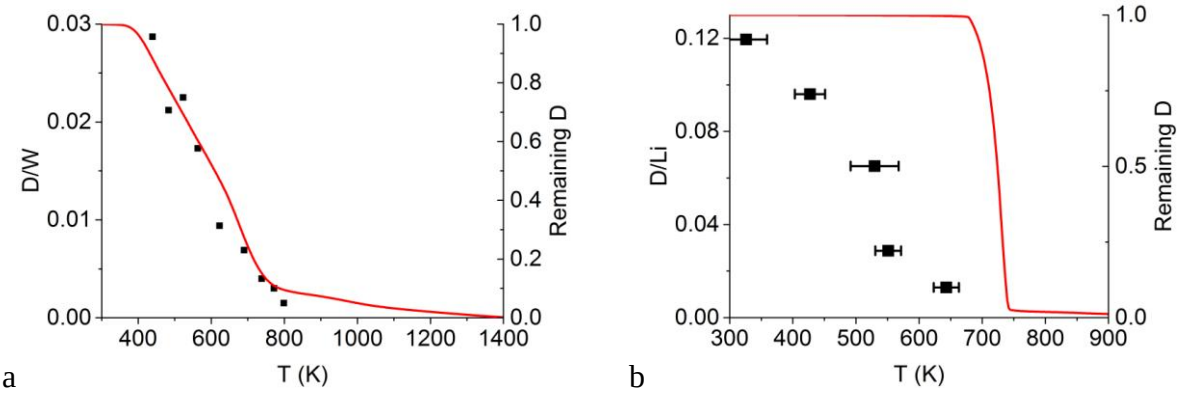

Figure 1. Deuterium content in co-deposited films on surfaces held at different temperatures : a) W-D, b) Li-D. On the right y axis, the portions of D retained in the film deposited at room temperature at the time it was heated to a given temperature is shown.

In different co-deposition conditions, for example in the case of faster Li-D co-deposition in a mixed atmosphere of D and Li vapor, another situation was observed, as can be seen in fig. 1b. D content in the films decreases strongly, by about one order of magnitude at substrate temperatures above about 550 K. However, as was observed earlier [5], most of D trapped in Li-D co-deposits is released in one sharp peak at temperatures close to 700 K. The difference can be explained in several ways. Unlike W, Li readily forms hydrides, and D is likely to be bound in the form of lithium deuteride in the co-deposited layer. It is possible that at higher temperatures, especially past the lithium melting point of 453 K, different chemical processes take place, leading to lower D content. During deposition on the hot substrate, Li could be constantly evaporating. Li evaporation rate increases rapidly with temperature. This means that the actual thickness of the films deposited at higher temperatures might be significantly lower than one measured by water-cooled QMS, which would also result in lower absolute amount of D observed during TDS analysis and perceived lower D content.

An analytical model predicting deuterium content in thick layers deposited in plasma discharge was developed. It incorporated implantation of deuterium ions at the certain depth, gas trapping and detrapping, diffusion of gas in solute form through the co-deposited layer, and implantation of energetic particles, ie gas ions and atoms reflected from the magnetron target, into the film. The constant deposition rate was assumed. It was assumed that no diffusion of gas into the substrate occurred. The thickness of the film was assumed to be

much higher than the energetic particles implantation range, and it was assumed that the deposition proceeded in a quasi-stationary mode, where deuterium concentration in the film depended only on the distance to the film surface, and not on time. Two specific edge cases were analyzed, with different assumptions about the rate of film deposition.

Firstly, the situation of slow deposition, where metal deposition rate was much lower than the flux of hydrogen atoms to the film. This case is characteristic for co-deposition of heavy elements with low sputtering yields. Secondly, a situation of rapid deposition, where metal deposition rate is much higher than the hydrogen flux to the surface, and the number of available trap sites in the co-deposited layer is much higher than the number of filled trap sites, was studied.

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