Argon trapping in the depositing metal coating

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Abstract. The paper has investigated conditions and parameters of argon trapping in molybdenum, tantalum and tungsten layers during their deposition on tungsten substrate by the atoms sputtered from the respective targets in argon plasma. The substrate temperature during deposition was 1273 K. The rate of deposition was 1 µm/h. It was shown that electron irradiation of the deposited layer with the beam intensity of 4 mA/cm² initiated argon trapping in tungsten and tantalum coating with approx. 2 x 10²⁷ at/m³ and 8 x 10²⁶ at/cm³, respectively, but did not stimulate argon trapping in the molybdenum layers. Features of argon trapping in the tungsten coating and its release are investigated in detail.

1. Introduction
Argon trapping in solids during ion and plasma irradiation, as well as in surface films deposited in plasma, has been mentioned in a number of articles [1-4]. The authors of paper [1] have reported argon trapping in tungsten during its irradiation by argon ion beam. Argon trapping and retention in tungsten irradiated by argon plasma ions was observed in [3]. Trapping of argon during coating deposition in plasma, which included tungsten and molybdenum layers, has been found in paper [2], while argon has been detected in carbon layers, irradiated by argon plasma after its formation.

It should be also noted that argon seeding into the divertor plasma is proposed as an option to reduce flux density of divertor irradiation for future ITER and DEMO thermonuclear facilities. Trapping of argon in the plasma-facing materials and deposited layers with its uncontrolled release is still a problem that has not been solved yet.

The development of surface properties modification by argon ion and argon plasma irradiation, as well as the solution of argon trapping in the plasma-facing nuclear fusion facility elements, is hindered by a lack of knowledge in the field of trapping and retention of argon and other noble gases in materials. The research of these processes is the problem presented in this work.

2. The choice of research subject and experiment conditions
In all papers listed above, argon trapping in metals [1–3] and carbon [4] occurred when the surface irradiation by argon atoms at thermal velocities was accompanied by the irradiation with accelerated argon ions (or ion beam as in [3]) or accelerated argon plasma ions and, consecutively, fast recharge atoms [1, 2, 4]. It can be assumed then that argon trapping is stimulated both by processes originating from kinetic energy of fast irradiating particles and by excitation of electron sub-system of surface layers by ion bombardment of the surface. At this stage, it was decided to limit the research to thermal velocity argon trapping in the metallic layer during deposition under fast electron irradiation. In this
case, electron sub-system excitation occurs, and argon atom implantation into the surface due to kinetic energy is excluded.

Tungsten, tantalum and molybdenum layers of equal thickness were deposited on tungsten substrate in argon plasma. Argon trapping in these materials during deposition was studied. This choice of materials for deposition allowed comparing the trapping for different metals with high melting points, the same type of crystal lattice (BCC) and the same lattice parameter \( a = 0.3 \text{ nm} \), but with a number of distinct characteristics. Atomic numbers of tantalum and tungsten are similar, but tantalum has a remarkable oxide layer on the surface. Oxidation properties of tungsten and molybdenum are close, however, the atomic number of molybdenum is half of that of tungsten. The deposition process of aforementioned surface films was conducted with and without electron irradiation of the coating during deposition. The research on argon trapping by the deposited film for different electron flux intensity, deposition rate, substrate temperature and oxygen presence in plasma was then conducted for tungsten films.

3. Experimental
The coatings were deposited on the “COating Deposition and MAterial Testing” (CODMAT) rig. The CODMAT rig allows irradiating materials with high-density ion or electron fluxes and depositing coatings (Airapetov et al. [5]). The experiments were conducted with 15×7×1 mm tungsten substrates rinsed in an ultrasonic ethanol bath and then irradiated by argon ions before the deposition to provide proper coating adhesion.

The deposited layer was formed by atoms sputtered by ions of argon plasma from corresponding targets (tungsten, molybdenum and tantalum). The construction of the experimental setup allows irradiating the deposited film with electrons emitting from ion irradiated targets and accelerating towards the substrate. The use of anti-dynatron electrode allows varying or fully suppressing the electron flux from the target due to ion-electron emission.

The pressure of residual gas in the stand did not exceed \( 10^{-5} \text{ Pa} \), pressure of plasma-generated gas (argon) was equal to \( 4 \times 10^{-2} \text{ Pa} \). The energy of target sputtering ions was 7 keV for most experiments. The deposition rate was 1 \( \mu \text{m/h} \), and the thickness of the deposited film was 2.5 \( \mu \text{m} \). The temperature of substrate should be taken as 1200 K unless specified.

The amount of argon trapped in the films was measured by the method of Thermal Desorption Spectroscopy (TDS) on the Multifunctional Investigation Complex for Mass Analysis (MICMA) (Begrambekov et al. [6]). The TDS analysis was conducted at the temperatures of up to 1550 K with the heating rate of 5 K/s. The sample was heated by the radiation from tungsten spiral directly below it.

The amount of gas trapped was also determined by Energy-Dispersive X-ray Spectrometry (EDS) via Oxford X-ray console installed on the Tescan Vega 3 Scanning Electron Microscope. The thickness of the deposited films was 2.5 \( \mu \text{m} \), which significantly exceeded the maximum depth of the EDS analysis. FEI Scios dual-beam device was used for making a cross-section of the film and studying its structure.

4. Results and discussion
Deposition of tungsten, tantalum and molybdenum coatings on tungsten substrate with the absence of electron radiation was conducted during the first set of experiments. In this case, the surface of the sample was irradiated by the flux of argon atoms with thermal velocities as well as fast recharge atoms. The rate of deposition of the layers was equal to 1 \( \mu \text{m/h} \), and the deposition process lasted for 2.5 hours. The EDS analysis has shown the absence of trapped argon in all three samples.

In the next set of experiments, the rate of layer deposition and experiment duration were unchanged, but the coating deposition was accompanied by electron radiation. The flux density of electrons during the deposition was 4 mA/cm², the electron energy was 7 keV. The EDS analysis of the deposited layer has shown approx. \( 2 \times 10^{27} \text{ at/m}^3 \) and \( 8 \times 10^{26} \text{ at/m}^3 \) of argon in the near-surface area for tungsten and tantalum, respectively. There was no argon in molybdenum. It can be asserted then
that the electron radiation stimulated the trapping of argon in the tungsten and tantalum layers during
deposition, but not in molybdenum.

The explanation of varying ability of molybdenum, tantalum and tungsten to trap argon requires
additional analysis. We shall only note that the obtained result correlates with the ratio of substrate
temperature during the deposition to melting points of metals, equal to 0.41 for molybdenum, 0.36 for
tantalum and 0.31 for tungsten. The argon atom mobility and, consequently, re-emission flux from
the coatings could increase with the ratio getting higher.

The dependence of argon trapping in the coating during deposition from the experimental
conditions was ascertained on tungsten coatings.

To reveal argon distribution throughout the substrate and determine the presence of argon in the
substrate, a cross-section was cut in the sample down to the near-surface layer of the substrate. The
cutting was conducted on the FEI Scios dual-beam setup with a gallium ion beam. To improve the
quality of the cross-section, an additional layer of platinum was deposited on the cavity about
0.5×0.5×0.8 µm in size (Figure 1). The electron beam was scanning the depth of the deposited coating
and the near-surface layer of the substrate. The analysis has shown a uniform distribution of argon
throughout the deposited coating and its absence in the substrate.

![Figure 1. Cross-section of the deposited film.](image)

The EDS analysis of the tungsten layer surface deposited in the same conditions, but irradiated with
electron flux of halved intensity (approx. 2 mA/cm²), has shown the decrease of argon content in the
analysis zone to nearly halved amount versus the first experiment (approx. 1×10²⁷ at/m³). This
experiment has confirmed the suggestion on the dependence of argon trapping on electron radiation
accompanying the coating deposition.

The use of ion-electron emission from the target for electron irradiation of the deposited film
enabled us to measure argon trapping with differing deposition rates, but constant ratio of flux of
tungsten atoms for deposition to electrons. This was accomplished by varying the flux of ions
sputtering the target, while keeping their energy constant. The deposition rate was changed in the
range of 0.5 to 2.5 µm/h, which was in accordance to the change of electron flux of 2-10 mA/hr.

The results of the EDS analysis have shown that the amount of argon trapped in the deposited layer
is kept constant throughout the entire range of deposition rates. To determine the influence of oxygen
in plasma on argon trapping, a series of experiments was conducted with tungsten deposition on a
substrate and oxygen content in plasma varying from 4% to 10%. The EDS analysis has shown that
the increase of oxygen concentration in plasma led to the increase of oxygen in the deposited layer,
reaching 7 at.% with the concentration of oxygen in plasma equaling to 7 at.%. At the same time, the
amount or trapped argon was kept constant at the level of the coating deposited with no oxygen
present in plasma.

For thermal desorption of argon from the coating, the substrate was heated by the irradiation from
the heated flat tungsten spiral installed under the bottom of the sample. In the first experiment, the
temperature of the sample was raised at the rate of 5 K/s. The thermal desorption spectrum is shown in Figure 2.

Obviously, the peak of desorption is observed at approx. 1370 K. The amount of desorbed argon from the sample was equal to $1.6 \times 10^{20}$ at/m$^2$. After the TDS measurements, exfoliation of the film from the substrate was found. The comparison of the results measured by EDS of argon in exfoliated fragments with argon in the sample before the heating has shown that about 10% of argon was liberated from the sample during the heating. This result can be explained by the temperature of the film reducing quickly after exfoliation to the point not sufficient for argon desorption.

![Figure 2. TDS spectra for tungsten film.](image)

Slow heating (1 K/s) and 1-hour exposure of sample to the temperature of 1473 K was performed in the second experiment. After such heating, the EDS analysis has shown the absence of argon in the deposited coating. The cross-section of the heated sample (Figure 3) has shown exfoliation of the film from the substrate. Such defects can happen as a result of stress appearing in the coating during argon desorption or due to argon accumulation along the boundary between the deposited film and the substrate.

![Figure 3. Cross-section of the heated sample.](image)

A significant amount of argon in the deposited layer allows for making an assumption that most of it is held in microscopic pores formed during the crystallization of the layer. The size of such pores, supposedly, does not exceed 20 nm, which prevents them from being observed using the methods of analysis used in this research. The pressure of argon in such pores should balance out the pressure of
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surface tension. The value of surface energy $\varepsilon = 4 \text{ J/cm}^2$[8] was used to calculate the pressure of surface tension in a pore, equaling to 600 MPa[7] for a pore of 20 nm in diameter and argon being in a supercritical fluid state. With the diameter of the pore $d \leq 1.3 \text{ nm}$, the pressure of surface tension would exceed 6 GPa. In such pores, according to paper [7], solid argon is expected to be formed.

5. Conclusion
The paper has investigated conditions and parameters of argon trapping in molybdenum, tantalum and tungsten layers during their deposition on tungsten by the atoms sputtered from the respective targets in argon plasma. The substrate temperature during deposition was 1200 K. The rate of deposition was equal to 1 $\mu$m/h.

It was shown that electron irradiation of the deposited layer with the intensity of 4 mA/cm$^2$ has stimulated argon trapping in the tungsten and tantalum coating layers with approx. $2 \times 10^{27} \text{ at/m}^3$ and $8 \times 10^{26} \text{ at/m}^3$, respectively, but did not lead to argon trapping in molybdenum. A suggestion was made that the obtained result correlates with the ratios of temperatures of substrates during the deposition process to the melting points of molybdenum, tantalum and tungsten, which are 0.41, 0.36 and 0.31, respectively.

The research on the specifications of argon trapping in the coating layers during deposition has allowed making the following conclusions. Argon is uniformly distributed throughout the entire depth of coating and does not penetrate tungsten substrate. The amount of trapped argon is approximately proportional to the intensity of electron radiation. The concentration of argon in the deposited film was kept constant with constant ratio of deposited tungsten atom flux to electron flux, respectively, in the range of 0.5 to 2.5 $\mu$m/h and 2-10 mA/hr. The amount of trapped argon did not change with the addition of oxygen into plasma of up to 10 at.%. The argon desorbed from the deposited film during heating for 1 hour at 1473 K. It is assumed that most of argon is held in microscopic pores formed during crystallization of the deposited coating. The size of the pores does not exceed 20 nm, with argon inside being in a state of supercritical fluid.

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