



The influence of nitrogen co-deposition in mixed layers on deuterium retention and thermal desorption



Anže Založnik ^{a,*}, Sabina Markelj ^a, Iztok Čadež ^a, Primož Pelicon ^a, Primož Vavpetič ^a, Corneliu Porosnicu ^b, Cristian P. Lungu ^b

^a Jožef Stefan Institute, Jamova Cesta 39, 1000 Ljubljana, Slovenia

^b National Institute for Laser, Radiation and Plasma Physics, Atomistilor 409, 077125 Magurele, Romania

ARTICLE INFO

Article history:

Received 17 February 2015

Received in revised form

21 September 2015

Accepted 23 September 2015

Available online 28 September 2015

Keywords:

ITER

Mixed materials

Nitrogen

Deuterium retention

ABSTRACT

The influence of nitrogen co-deposition in ITER relevant mixed layers on retention and release dynamics of deuterium was studied *in situ* by Nuclear Reaction Analysis (NRA) and thermodesorption spectroscopy. W:Al and W:Be mixed layers deposited by thermionic vacuum arc (TVA) method were used in order to verify the possibility of Al being used as proxy material for Be in experiments regarding D uptake. Samples were exposed to neutral deuterium atom beam with fluence of 3.24×10^{19} D/cm² (flux 4.5×10^{14} D/cm²s) at 390 K and NRA with ³He ions was used for depth profile analysis of deuterium content after the exposure. For the investigation of deuterium release dynamics the samples were linearly heated to around 1000 K and during this process NRA spectra at single energy were collected every minute. Complementary to NRA a quadrupole mass spectrometer was used, following masses 2, 3 and 4 in the background vacuum. The numeric simulation of deuterium thermal desorption was performed and desorption energies of desorption sites were calculated. Same experiments were performed with mixed material samples produced by TVA in the presence of nitrogen atmosphere. Nitrogen co-deposition in the mixed layers was found to have an important influence on deuterium retention. The concentration of deuterium in the sample increased by a factor of 4.8 in the presence of nitrogen in the W:Al and by a factor of 1.8 in the W:Be layer compared to the nitrogen-free sample.

© 2015 EURATOM. Published by Elsevier B.V. All rights reserved.

1. Introduction

Materials chosen for the plasma facing components in the fusion device ITER are beryllium for the wall of the main chamber and tungsten in the divertor. Erosion and re-deposition of these two materials take place during tokamak operation due to the plasma–wall interaction [1]. This leads to formation of mixed material deposits on various surfaces inside the vessel. Recent results with same wall material composition (Be/W) from JET–ILW experiments are reviewed in Ref. [1]. These deposits can contain also intrinsic impurities (e.g. carbon) and seeding impurities used for plasma control such as nitrogen or noble gas [1–3]. Retention of hydrogen isotopes in mixed material deposits is important for estimation of the overall fuel retention and plasma fueling. It is important to

understand in detail the hydrogen uptake and release dynamics for such mixed layers. The release behavior was well studied in W-containing mixed layers [4] and in Be-containing mixed layers such as Be–W and Be–C exposed to D ion beam [5] at room temperature and at elevated temperatures [6]. However, ion exposure induce additional modification of the layer, increasing the number and changing the characteristics of trapping sites. An alternative way for studying release and absorption kinetics is to expose samples to neutral atom beam with energy below eV, what offers better insight into the physics of the processes. Moreover, there have been few studies on the influence of nitrogen inclusion on D retention in W [7] and Be [8,9] materials, however there have been to our knowledge no studies on how inclusion of nitrogen affects D retention in such deposited mixed layers.

In this work we have studied incorporation and release dynamics of neutral atomic deuterium for W:Al and W:Be mixed layers. We studied the influence of nitrogen inclusion in these mixed layers on deuterium retention. For this purpose some

* Corresponding author.

E-mail address: anze.zaloznik@ijs.si (A. Založnik).

samples were prepared in nitrogen atmosphere thus incorporating N in the mixed layers. The properties of mixed layers, e.g. whether the N inclusion acts as a diffusion barrier [7] also in mixed layers, and the possible difference between atom and ion/plasma exposure, are obtained by exposing these layers to neutral atoms. The applied experimental conditions with exposure to neutral atoms would correspond to the studies of retention in remote areas of the fusion device, however with orders of magnitude lower fluxes. After the exposure of initially deuterium-free samples to low energy (0.2 eV) deuterium atom beam, samples were heated in order to observe the release of the absorbed deuterium. Ion Beam Analysis (IBA) and mass spectroscopy of the background/desorbed gas were used in order to follow deuterium retention and release dynamics from the sample *in situ*. Al was used as a Be substitute, in order to compare the D uptake into Al-based mixed layers and thus verify the possibility of Al being used as a possible proxy material for Be in laboratory experiments. The novelty of this work is that the D atom exposure and ion beam analyses after the exposure were performed promptly in the same chamber without exposing samples to the air and that IBA and mass spectroscopy were used simultaneously during the sample linear heating.

2. Experiment

Samples were prepared using thermionic vacuum arc (TVA) method [10] at National Institute for Laser, Plasma and Radiation Physics, Bucharest. The TVA set-up is equipped with two independent deposition sources, allowing simultaneous deposition of W and Be or Al [11]. Thermo-electrons emitted from the tungsten filaments are accelerated towards the respective W, Be/Al anodes. High evaporation rate of the anode material leads to high vapor density formation in front of the anode. The space density of these particles is high enough to lower the ionization mean free path. As a result, metallic vapor plasma is ignited in that region while the surrounding space was evacuated below 10^{-5} mbar. Pure or N containing compact mixed films of the anode materials were deposited on silicon substrates. The non-gaseous containing layers deposition took place at sample temperature of 550 K while for the ones containing N it was kept below 420 K in order to prevent N outgassing. The target sample composition was W/Al(Be) ratio of 50:50 and with 20 atomic % of N in nitrogen containing samples. However, as will be shown later in the text, the inclusion of N in the mixed layer substantially changes the ratio between W and Al/Be.

The experiment was performed at the *in situ* IBA chamber on Tandatron accelerator at Jožef Stefan Institute, Ljubljana. Rutherford Backscattering Spectroscopy (RBS) and Nuclear Reaction Analysis (NRA) were used for sample characterization and deuterium depth profiling. The ^3He ion beam was impacting perpendicularly to the sample surface, inducing the nuclear reaction $D(^3\text{He},p)\alpha$ for NRA. A set of different ion beam energies (4300, 3400, 2580, 1550 and 770 keV) were used for determination of accurate deuterium depth profile [12], starting the measurement from the highest energy. The deuterium depth profile was obtained by analyzing the energy distribution of protons, created by this nuclear reaction. Protons were detected by a 1500 μm thick partially depleted Passivated Implanted Planar Silicon (PIPS) detector, mounted at 135° angle with respect to the probing ion beam. A 24 μm thick Al foil was placed in front of the detector in order to stop the backscattered ^3He ions and to reduce the energy of the protons. Second, 300 μm thick detector was mounted at the 170° angle for the RBS. The energy distribution of the backscattered ^3He ions gives the information about the species in the sample that are heavier than the probing ions, thus providing the composition of the sample. A 0.8 μm thick Al foil

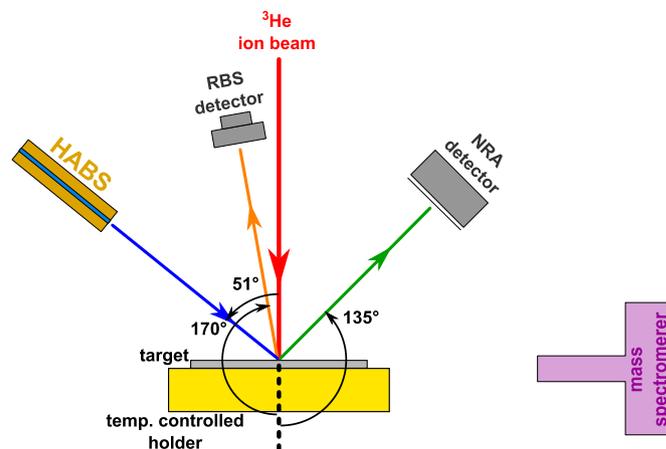


Fig. 1. The scheme of the experimental setup. Incident ^3He beam is perpendicular to the sample surface.

was placed in front of the RBS detector in order to avoid the noise due to the radiation from the hydrogen atom beam source. The configuration of the experiment is shown in Fig. 1. Measured NRA and RBS spectra were analyzed by SIMNRA software [13] in order to get absolute concentrations.

The studied sample was mounted on the temperature controlled holder perpendicular to the incident analyzing ion beam. Its composition was determined by RBS and NRA at the beginning of the experiments. The samples were after that exposed to deuterium atom beam with 4.5×10^{14} D/cm 2 s deuterium flux for 20 h what provided total fluence of 3.24×10^{19} D/cm 2 . During the exposure samples were held at constant temperature of 390 K. The atom beam is created by thermal dissociation of deuterium gas flowing through a hot W capillary of a commercial hydrogen atom beam source (HABS) [14]. The angle between sample surface normal and HABS axis was 51° and the distance between tungsten capillary exit and sample surface was 80 mm. More details on exposure can be found in Ref. [15]. Base vacuum pressure was 1×10^{-7} mbar.

The NRA was performed *in situ* after the sample exposure to D atoms for determination of the deuterium concentration in the sample. In the case of Al containing samples the sample temperature was kept constant at 390 K during the NRA analysis, whereas in the case of Be containing samples the samples were cooled down to room temperature immediately after the end of D atom exposure.

After exposure to D atoms and NRA analysis the sample was heated with a constant heating rate using a computer controlled heater (Boralectric heating element). Sample temperature was monitored by a thermocouple, attached to the sample surface. NRA and RBS spectra were constantly accumulated during the heating using single ^3He ion beam energy of 2.5 MeV, collecting 0.8 μC (5×10^{12} ^3He ions) ion dose on the sample in the case of W:Al and using 1.5 MeV, collecting 1.7 μC (1×10^{13} ^3He ions) ion dose in the case of W:Be. These two energies were chosen as they assure sufficiently deep penetration of the beam and because the RBS signal at these energies is well resolved thus providing information on the layer structure. After the linear heating and subsequent cooling of the sample another NRA measurement was performed using only the two lowest ^3He ion beam energies. Quadrupole mass spectrometer (PRIZMA Plus QME 220, Pfeiffer, 1–100 m/q) was used throughout the heating, following several masses including 2, 3 and 4 which correspond to H_2^+/D^+ , HD^+ and D_2^+ ions, respectively. The vacuum chamber used for this experiment is dedicated for ion beam analyses and not for the thermodesorption studies, so the data obtained with the mass spectrometer are only qualitative and complementary to the NRA results.

3. Results

3.1. W:Al layer

First analyzed and exposed sample was 1 μm thick mixed W:Al layer on Si substrate. Al is often used as Be substitute in experiments due to its chemical similarity to Be on one side and the toxic nature of Be on another. As determined by RBS the layer consisted of approximately 30 atomic % of W and 65 atomic % of Al, homogeneously distributed over the layer depth. We have observed some C contamination on the surface of the sample by NRA measurement before the exposure to D atoms, being 2 atomic %. Some O contamination is also expected to be found on the sample, but due to the low mass, low cross-section and no nuclear reaction with ^3He , producing high energy protons, it could not be detected directly neither with RBS nor with NRA technique. Therefore we attributed the residue in the overall concentration to O contamination, giving the value of 5 atomic %. The W:Al ratio for this layer was 32:68.

The sample was exposed to D atoms to a fluence of 3.24×10^{19} D/cm² at sample temperature of 390 K. After the end of the exposure the sample temperature was kept at the same value as during the exposure. The NRA analysis was performed using the set of ion energies approximately 1 h after the end of exposure. The depth profile analysis was performed at five ^3He energies, starting from the highest, in order to obtain better information about depth profile, possible contamination by C and change of sample structure as could be observed by RBS at higher energies. However, during the analysis it was observed that the NRA signal was dropping during consecutive measurements at individual energy what prevented us to deduce the D depth profile. Thus, the total D concentration in the layer was deduced from measurement with each single energy, since each of them was sufficient to probe the entire layer depth. By this we could only determine the total amount of D from the proton peak integral, assuming a homogeneous distribution throughout the layer. The measurement with five ion beam energies lasted for around 1 h and during that time we have observed an exponential drop of D concentration for 60%, see Fig. 2. The D concentration in the layer after the first measurement was $D/(W + \text{Al}) = 0.004$ and decreased to almost constant value of $D/(W + \text{Al}) = 0.0016$ at the last one of this initial set. Deuterium was found to extend throughout the entire mixed layer.

After the initial NRA measurement the sample was heated with

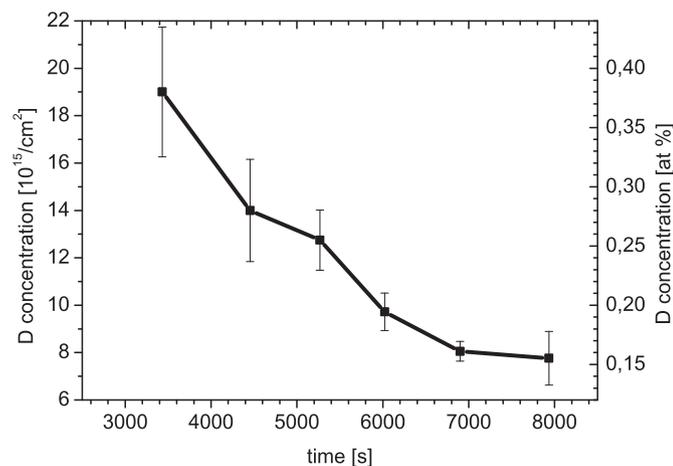


Fig. 2. Time evolution of D concentration in W:Al sample. The origin of t-axis is at the end of D exposure. Each point corresponds to a measurement with another ion beam energy, starting with the highest and at the end repeating with the 2.5 MeV.

linear heating rate of 15.6 K/min up to the sample temperature of 1200 K. During the heating consecutive NRA measurements were performed every minute at 2.5 MeV ion beam energy. The integral of the proton peak from the nuclear reaction gives the information about the total content of the deuterium in the mixed layer. Continuous mass analysis of the background gas was also performed and intensity of several peaks in the mass spectrum including $m/q = 2, 3$ and 4 were followed. The highest drop in the NRA signal, coinciding with the desorption peak in mass 4, took place at 690 K, as can be seen in Fig. 3, where the deuterium concentration is shown as a function of time, for all NRA measurements, during the depth profile analysis at constant temperature and during the linear heating. At higher temperatures the signal of mass spectrometer exhibits high desorption peak for all three relevant masses (2, 3 and 4) at the highest point of the temperature ramp (1200 K) which were mainly due to the outgassing of the sample holder and surrounding material which were also exposed to background D atoms from the HABS. The NRA signal dropped to zero during the heating, so that deuterium was desorbed from the sample below the detection limit. This was verified by the NRA spectrum recorded at the lowest ion energy where the sensitivity for D is the highest for thin layers due to the nuclear reaction cross-section.

Each time the NRA spectrum was collected, the spectrum of backscattered ^3He ions (RBS) was also recorded. This was providing prompt information on the structure of the sample during its heating. Severe modifications of the sample were observed during the heating starting at around 880 K and were progressing to the sample temperature around 930 K. After this temperature the sample did not change any more. The RBS spectrum of the sample before the experiment is shown in Fig. 4a and the RBS spectrum after the layer modification is shown in Fig. 4b. Both RBS spectra were analyzed by SIMNRA and corresponding component spectra are also shown in Fig. 4a and 4b. Our explanation for the modified RBS signal is that the layer decomposed in some regions leading to Si substrate becoming exposed directly to ^3He beam, resulting in the displacement of the Si edge in the RBS signal to higher energy. Since this deterioration of the layer took place after most of D was already released, one could say that the D release is not due to the observed modification. The explanation for layer deterioration could be due to the low melting temperature of Al, being 930 K, which closely corresponds to the temperature, at which the modification of the RBS spectra were observed.

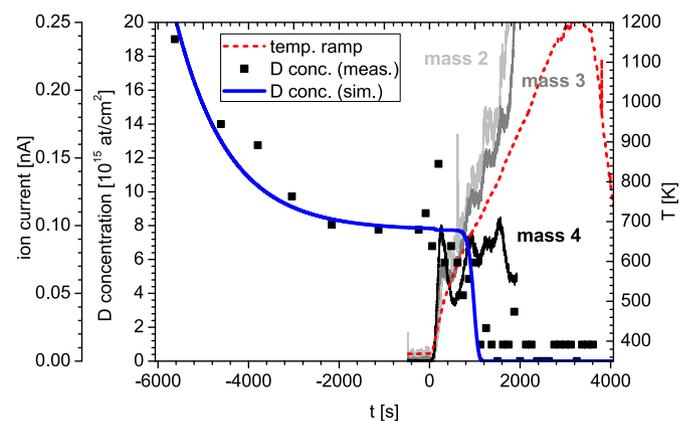


Fig. 3. Time variation of measured deuterium concentration (black dots) and fitted solution of Eq. (3) (blue line) for W:Al layer. Mass spectrometer signal for masses 2, 3 and 4 (light gray, dark gray and black line) and the sample temperature (red dashed line) are also shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

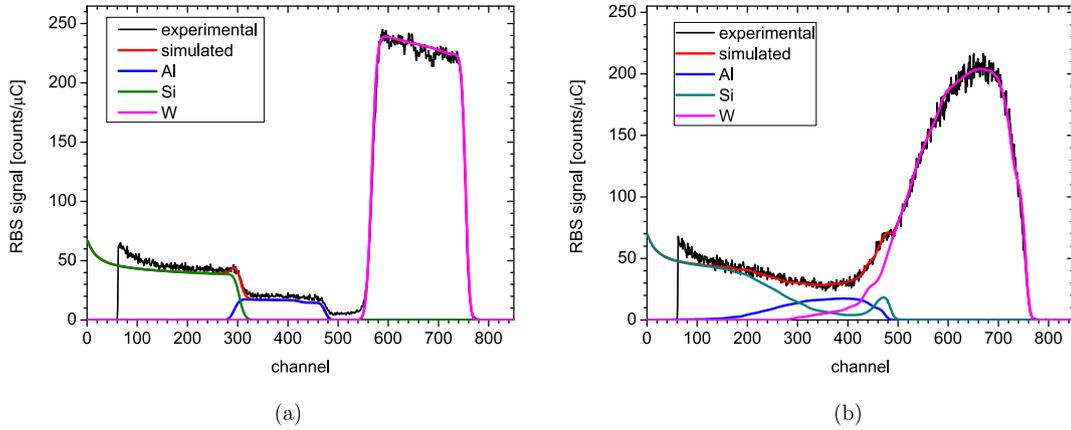


Fig. 4. RBS spectra of W:Al layer on Si substrate. (a) RBS spectrum and simulated signal of the pristine sample. (b) RBS spectrum of the sample and simulated signal after the layer modification.

3.2. W:Al(N₂) layer

The second sample was W:Al film co-deposited with nitrogen in order to study influence of nitrogen on deuterium retention. The thickness of the sample was the same as for the first one, 1 μm, but the composition of the layer was much more inhomogeneous. Depth profile of W and Al was determined from the RBS spectra, but nitrogen could not be directly determined by RBS due to its low mass and low RBS cross-section. However, the determination of N concentration was done indirectly based on the residue in the overall concentration after taking into account also the C contamination, determined from NRA spectra to be around 4 atomic % distributed through the entire layer. Total nitrogen concentration was also verified by integral of the proton peaks from nuclear reaction ¹⁴N(³He,p)¹⁶O in NRA spectra which was in agreement with the concentration determined by RBS. The concentrations of W, Al and N throughout the layer are shown in Fig. 5, W being approximately 25 atomic %, Al 51 atomic % and N 20 atomic %, giving the W:Al:N ratio of 26:53:21.

The procedure of the NRA measurements and exposure to D atom beam was the same as in the case of W:Al sample: D atom exposure at 390 K, NRA depth profile measurement after the exposure and then heating of the sample to perform deuterium thermal desorption. The temperature of the samples after the D

exposure was again kept at 390 K. Similar to the first sample we have also observed D desorption from the sample during the initial NRA depth profile measurement. Again, only total D concentration was deduced from measurement with individual energy, since each energy was sufficient to probe the entire layer. The first NRA measurement was performed around 6000 s after the end of exposure to D atoms. During the depth profile measurements at constant temperature the deuterium concentration dropped for 60% in 1 h and became constant by the end of this time. Deuterium was not present in the entire W:Al(N₂) layer. Its depth range was 4100 × 10¹⁵ at/cm² which is less than the thickness of the layer which is 5900 × 10¹⁵ at/cm². The D concentration as obtained from the first measurement is D/(W + Al + N) = 0.019, taking into account only the thickness of the layer where the D is present. The time evolution of the overall D concentration is shown in Fig. 6.

Heating of the W:Al(N₂) sample was carried out with heating rate of 13.1 K/min. The integrated NRA signal at 2.5 MeV ³He energy dropped between 580 K and 880 K sample temperature. This is shown in Fig. 7 where deuterium concentration before and during thermal desorption is shown. The NRA signal drop was correlated also with the increase of mass 3 and 4 measured by the mass spectrometer, also shown in Fig. 7. The highest drop in the NRA signal, coinciding with the highest peak in the mass 4 in the mass spectrometer signal, took place at 680 K. Looking more closely in

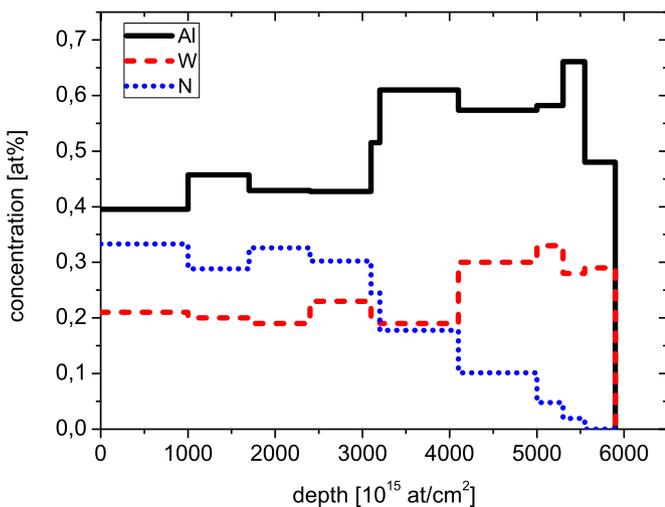


Fig. 5. Depth profile of W, Al and N in W:Al(N₂) sample.

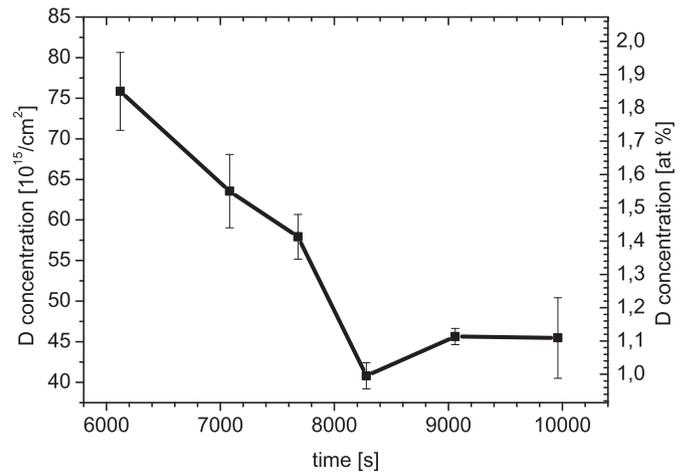


Fig. 6. Time evolution of D concentration in W:Al(N₂) sample. The origin of t-axis is at the end of D exposure. Each point corresponds to a measurement with another ion beam energy, starting with the highest and at the end repeating with the 2.5 MeV.

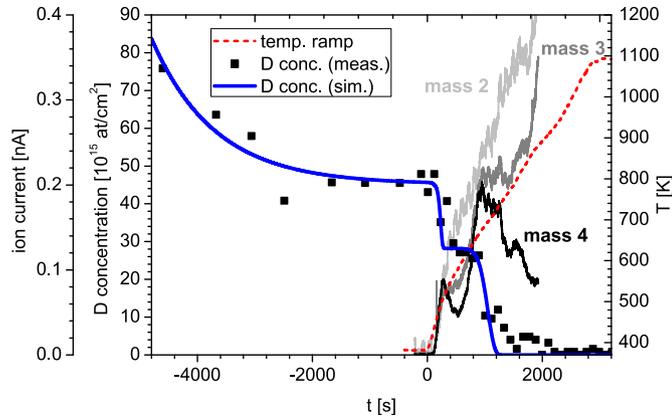


Fig. 7. Time variation of measured deuterium concentration (black dots) and fitted solution of Eq. (3) (blue line) for W:Al(N₂) layer. Mass spectrometer signal for masses 2, 3 and 4 (light gray, dark gray and black line) and the sample temperature (red dashed line) are also shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the decrease of the proton signal with temperature one can observe two drops in deuterium concentration, what could be explained by deuterium being trapped in different sites as will be discussed and analyzed in more detail in Section 3.5. The NRA measurement after the heating again revealed no deuterium left in the sample.

The RBS spectra, measured during sample heating, again showed drastic modification of the sample structure, what was also visible by the optical microscope, photo shown in Fig. 8. Our explanation for the change of RBS spectra is the same as it was for previous sample, described in Section 3.1. Modification of the layer began at higher temperature than in the case of W:Al layer, starting at around 950 K, and was progressing to the highest point of the temperature ramp, around 1100 K. The modification was also more comprehensive than in the case of W:Al and resulted in grained surface. The layer modification took place again at the temperature above the total D removal.

3.3. W:Be layer

The purpose of the present experimental study was also to evaluate the justifications of the use of Al as a Be substitute in the experiment. For this purpose we repeated the same experimental procedure with the third sample where Be was present instead of Al. The sample was 1.8 μm thick W:Be layer on Si.

Before sample exposure to D atom beam the layer was analyzed by RBS with ³He ions, giving 41 atomic % of W in the layer. The mass and cross-section for Be are too low to be seen by the RBS. However,

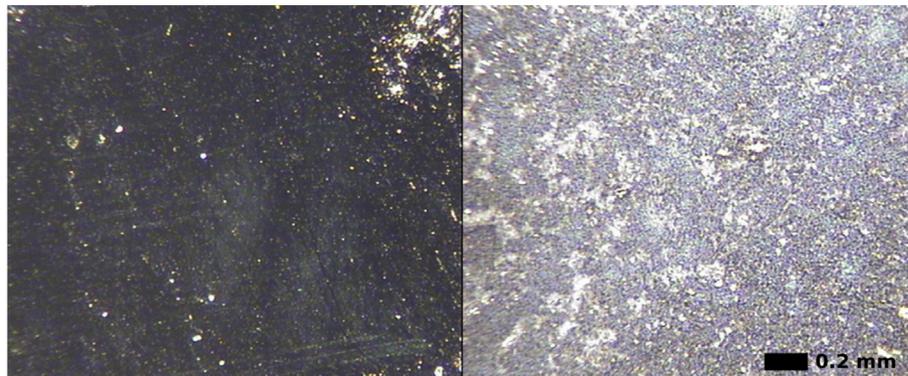


Fig. 8. W:Al(N₂) layer modification, observed by optical microscope.

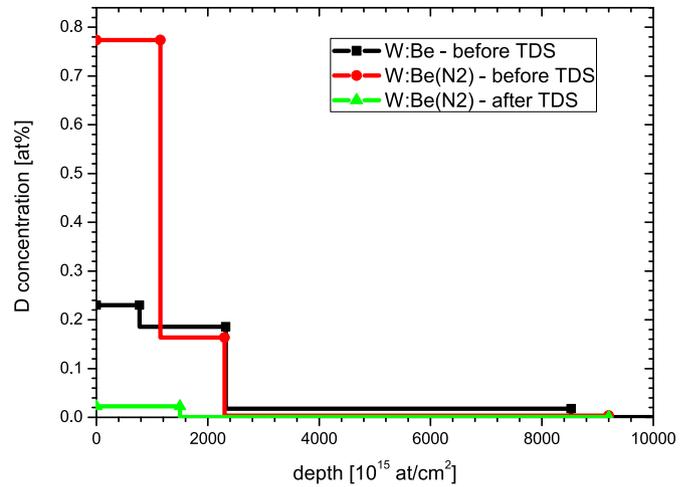


Fig. 9. Deuterium concentration depth profiles for W:Be and W:Be(N₂) layers, measured by NRA.

the proton peaks, induced by reaction ${}^9\text{Be}({}^3\text{He},p){}^{11}\text{B}$ are clearly visible in the NRA spectra [16]. From this the Be concentration was determined to be 47 atomic %. C contamination was estimated to be about 4 atomic % from the proton peak in the NRA spectra and the residue in the overall concentration was attributed to O contamination. The obtained W:Be ratio for this layer was 47:53.

Experimental conditions during D atom exposure were the same as for previous samples. The sample temperature was 390 K and the fluence was 3.24×10^{19} D/cm². In contrast to previous two samples, this sample was after the exposure immediately cooled down to the room temperature for the NRA depth profile measurement in order to avoid the outgassing that we experienced with Al containing samples. The total D amount in the layer was $(5.8 \pm 0.4) \times 10^{15}$ at/cm², giving the concentration D/(W + Be) = 0.0028 in the penetration depth, which was approximately 2300×10^{15} at/cm², corresponding to 0.33 μm. The thickness of the entire layer was 12400×10^{15} at/cm². The deuterium depth profile is shown in Fig. 9.

The sample was heated up to 980 K with the heating rate of 17.2 K/min. In Fig. 10 total D amount in the sample, obtained by NRA measurement with ³He ions at 1.5 MeV is shown together with the sample temperature during the heating. The main desorption occurred between 650 K and 900 K, as observed by both, NRA and mass spectrometer signal. Two step-like concentration drops can be observed, similar to the W:Al sample co-deposited with nitrogen. During the heating the deuterium signal dropped under the detection limit.

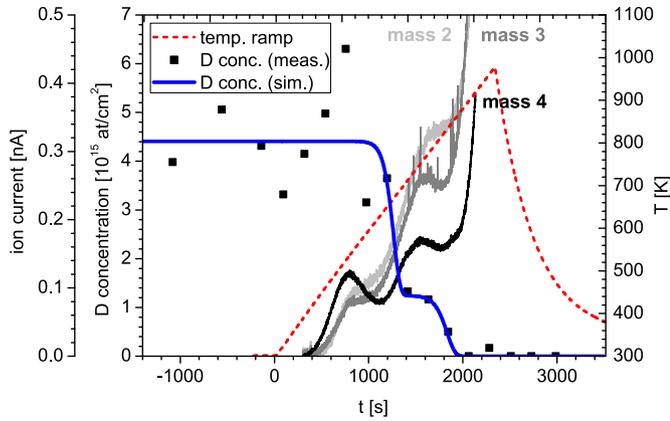


Fig. 10. Time variation of measured deuterium concentration (black dots) and fitted solution of Eq. (3) (blue line) for W:Be layer. Mass spectrometer signal for masses 2, 3 and 4 (light gray, dark gray and black line) and the sample temperature (red dashed line) are also shown.

3.4. W:Be(N₂) layer

The last studied sample was a 1.2 μm thick W:Be layer with co-deposited nitrogen on Si. Before D exposure the sample composition was analyzed by RBS and NRA, giving 54 atomic % of W and 23 atomic % of Be. C contamination was determined to be 6 atomic % throughout the entire mixed layer. The nitrogen concentration was determined as a residue in the overall concentration, since the proton peaks, induced by reaction $^{14}\text{N}(^3\text{He},p)^{16}\text{O}$ were not visible in the NRA spectrum due to the overlap with the strong Be signal. N concentration was determined to be approximately 17 atomic %, giving the W:Be:N ratio of 57:25:18.

The sample was again exposed to D atoms at 390 K to a fluence of 3.24×10^{19} D/cm². After the exposure the sample was immediately cooled down to the room temperature for the NRA depth profile measurement. The depth range of the deuterium was found to be 2300×10^{15} at/cm², what is approximately one quarter (0.3 μm) of the entire mixed layer, whose thickness was 9400×10^{15} at/cm². The penetration depth is similar to the one obtained in W:Be layer. The deuterium depth profile is shown in Fig. 9. The total D amount in the sample was $(11.0 \pm 0.4) \times 10^{15}$ at/cm², giving the D concentration of $\text{D}/(\text{W} + \text{Be} + \text{N}) = 0.005$ in the penetrated layer. However, as can be observed in Fig. 9, there is a gradient of concentration, having four times more D near the surface.

The heating of W:Be(N₂) sample was performed at 17.4 K/min heating rate, starting at sample temperature of 300 K and heating up to 920 K. Total D amount in the layer obtained by NRA measurement is shown in Fig. 11, together with the sample temperature during the heating. From comparison of the NRA signal and ion current for masses 2, 3 and 4 measured by the mass spectrometer, also shown in Fig. 11, the main desorption from the sample occurred between 600 K and 850 K. Again, two step-like concentration drops can be observed. Final depth profile analysis was performed after the sample was cooled down to a room temperature. The total D amount of $(0.39 \pm 0.06) \times 10^{15}$ at/cm² was found to remain in the sample after the thermodesorption study. The depth profile is shown in Fig. 9.

3.5. Simulation

For the simulation of deuterium mass spectra and concentration decrease during thermal desorption Polanyi–Wigner equation is usually used [17]:

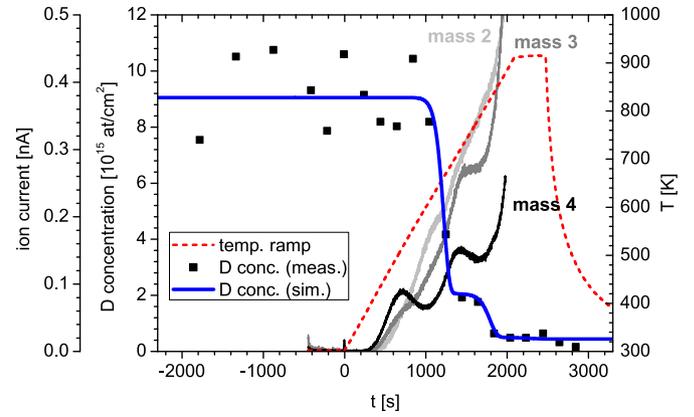


Fig. 11. Time variation of measured deuterium concentration (black dots) and fitted solution of Eq. (3) (blue line) for W:Be(N₂) layer. Mass spectrometer signal for masses 2, 3 and 4 (light gray, dark gray and black line) and the sample temperature (red dashed line) are also shown.

$$\frac{dc}{dt} = \nu^{(n)} c^n e^{-E_d/kT(t)}, \quad (1)$$

where c is deuterium concentration in the layer, $\nu^{(n)}$ is desorption rate, E_d is deuterium atom desorption energy and n is the kinetic order. Generally first and second order kinetics are expected for thermal desorption. In case where deuterium atom surface recombination is the rate limiting process the thermal desorption can be described by the second order kinetics ($n = 2$). In case where de-trapping of deuterium atoms from subsurface and bulk is the rate limiting process the desorption can be described by the first order kinetics ($n = 1$). Naturally this is a very simplistic way of simulation, not including any diffusion etc., and more complex models exist (e.g. TMAP [18]).

As will be shown below our data can be well described by first order kinetics, being typical for bulk desorption. Moreover, it was also observed that concentration is decreasing in steps at different temperatures. This can be explained by several different trapping sites in the sample, each having different desorption energy and concentration. Therefore to simulate the thermal desorption of deuterium out of the thin layer we used differential equation for each trapping site, described by first-order kinetics:

$$\frac{dc_i}{dt} = \nu^{(1)} c_i e^{-E_{di}/kT(t)}, \quad (2)$$

where c_i is deuterium concentration of the i -th desorption site in the layer, $\nu^{(1)}$ is desorption attempt frequency and E_{di} is deuterium atom desorption energy for i -th desorption site. The overall deuterium concentration is

$$c = \sum_i c_i. \quad (3)$$

The solution of Eq. (3) was fitted to measured deuterium concentrations for each film separately, shown in Figs. 3, 7, 10 and 11, with E_{di} and initial concentration c_{0i} being the fitting parameters. For the attempt frequency $\nu^{(1)}$ a fixed value of 10^{13} s^{-1} was used [19]. The sample temperature used in simulation was obtained by interpolation of the experimental data.

For W:Al layer two desorption sites were needed to describe experimental data, as shown in Fig. 3. Deuterium was desorbing from the first desorption site already before the heating of the sample, when the temperature was kept at 390 K. The calculated initial population of this desorption site is $c_{01} = (2.4 \pm 0.2) \times 10^{17}$ at/

cm^2 and the desorption energy is $E_{d1} = (1.175 \pm 0.001)$ eV. The initial population of the second desorption site is $c_{02} = (7.73 \pm 0.03) \times 10^{15}$ at/cm 2 and the desorption energy is $E_{d2} = (2.033 \pm 0.007)$ eV. The initial total deuterium concentration calculated from simulation is $c = (2.5 \pm 0.2) \times 10^{17}$ at/cm 2 .

For the W:Al(N $_2$) sample the solution of Eq. (3) was again fitted to measured concentrations, Fig. 7, using three different desorption sites. Again, deuterium was desorbing from the first site already before the heating of the sample. The initial population of this site is $c_{01} = (9.15 \pm 0.09) \times 10^{18}$ at/cm 2 and the desorption energy $E_{d1} = (1.218 \pm 0.001)$ eV. To the second desorption site the deuterium atoms are bound with energy $E_{d2} = (1.41 \pm 0.02)$ eV and initial deuterium concentration is $c_{02} = (1.74 \pm 0.03) \times 10^{16}$ at/cm 2 . The third site is populated with initial concentration $c_{03} = (2.82 \pm 0.02) \times 10^{16}$ at/cm 2 and the desorption energy is $E_{d3} = (2.075 \pm 0.006)$ eV. The initial total simulated deuterium concentration is $c = (9.20 \pm 0.09) \times 10^{18}$ at/cm 2 .

Two step-like decreases of total D amount were observed for W:Be layer. The fitting of the solution of Eq. (3) to measured concentrations, Fig. 10, yielded the value of (2.00 ± 0.03) eV for the desorption energy for the first desorption site, with the initial population of $(3.1 \pm 0.2) \times 10^{15}$ at/cm 2 . For the second desorption site, the initial population is $(1.3 \pm 0.2) \times 10^{15}$ at/cm 2 and the desorption energy is (2.5 ± 0.1) eV. The initial total D amount in the layer is $(4.4 \pm 0.3) \times 10^{15}$ at/cm 2 .

Three different desorption sites were also used for W:Be(N $_2$) layer when fitting the solution of Eq. (3) to measured concentrations, Fig. 11. The initial population of the first site is $c_{01} = (7.00 \pm 0.06) \times 10^{15}$ at/cm 2 and the desorption energy $E_{d1} = (1.95 \pm 0.02)$ eV. The second desorption site has the desorption energy $E_{d2} = (2.44 \pm 0.07)$ eV and initial deuterium concentration is $c_{02} = (1.56 \pm 0.05) \times 10^{15}$ at/cm 2 . After the heating there was still some deuterium retained in the layer, giving the initial population of the third site $c_{03} = (0.503 \pm 0.003) \times 10^{15}$ at/cm 2 . Since we did not observe the desorption from this desorption site, only the lower limit of desorption energy could be guessed, $E_{d3} > 2.9$ eV. The initial total deuterium concentration for W:Be(N $_2$) is calculated to be $c = (9.06 \pm 0.08) \times 10^{15}$ at/cm 2 . In Table 1 all the fitting parameters are summarized for all the analyzed samples.

4. Discussion and conclusions

Deuterium uptake and thermodesorption were studied *in situ* by NRA on four mixed material samples prepared on Si support by the TVA technique (W:Al, W:Al(N $_2$), W:Be, W:Be(N $_2$)). Samples were exposed to neutral D atoms at 390 K temperature and fluence 3.24×10^{19} D/cm 2 . It was shown that deuterium atoms were absorbed in the films penetrating into the mixed layer. Contrary to the ions that penetrate directly into the bulk, the deuterium atoms with low energy (<eV) have a barrier between the surface and the bulk for the case of pure W and Al, but not for Be. Namely, Al and W have positive heat of solution: 0.65 eV for Al, 1.1 eV for W [20,21] thus experiencing no subsurface absorption. This could mean that the film is porous and D can diffuse into the bulk through the pores of the film and being trapped at the defects created at the deposition procedure.

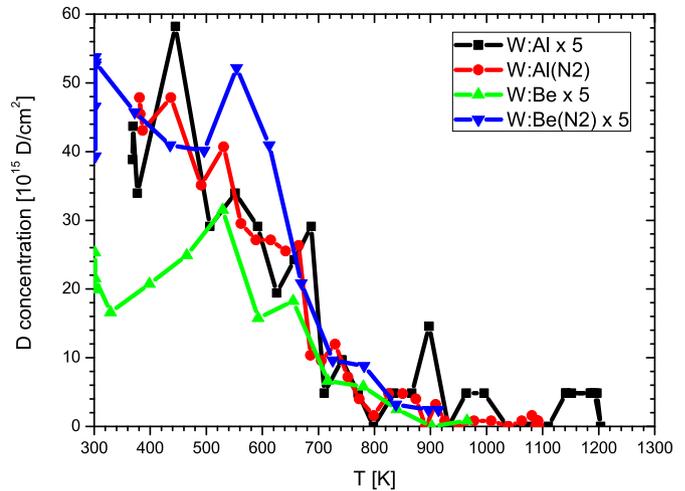


Fig. 12. Total D amount measured by ^3He ions at single energy during the heating for all four samples as a function of sample temperature.

Since, during the D atom exposure and depth profile analyses, W:Al samples were held at 390 K the deuterium desorption took place already during the depth profile analyses before the start of the sample heating. This is consistent with the measurements of thermal desorption on pure Al exposed to D/H atoms [20] exhibiting surface desorption peak at 340 K. The desorption at higher temperatures could be attributed to the traps in W. Namely, during the linear heating the main desorption from all samples occurred in similar temperature range, roughly between 600 K and 900 K, as seen in Fig. 12, where total D amount in the layer during the heating of the sample is shown as a function of sample temperature. The numeric simulation of deuterium thermal desorption yields similar values for the desorption site with the lowest desorption energy for Al containing layers, namely $E_d = (1.175 \pm 0.001)$ eV and (1.218 ± 0.001) eV for W:Al and W:Al(N $_2$), respectively. Desorption of deuterium atoms from this site occurs already when the sample temperature is held constant at 390 K. Another desorption site with similar calculated desorption energy for all layers has energy of $E_d = (2.033 \pm 0.007)$ eV, (2.075 ± 0.006) eV, (2.00 ± 0.03) eV and (1.95 ± 0.02) eV for W:Al, W:Al(N $_2$), W:Be and W:Be(N $_2$), respectively. Moreover, both W:Be and W:Be(N $_2$) layers have one additional common desorption site with desorption energy $E_d = 2.5 \pm 0.2$ eV for W:Be and $E_d = 2.44 \pm 0.07$ eV for W:Be(N $_2$) layer. The simulation yields one additional desorption site for W:Al(N $_2$) with $E_d = (1.41 \pm 0.02)$ eV and one for W:Be(N $_2$) with $E_d > 2.9$ eV. Further studies and comparison to theory are needed to exactly pin down which desorption energy corresponds to individual trapping site in these mixed layers.

The NRA depth analyses after the thermodesorption revealed no deuterium left in W:Al, W:Al(N $_2$) and W:Be but still 0.004 atomic % of D in W:Be(N $_2$). The highest temperature of W:Be(N $_2$) sample was lower compared to the other samples what might be the explanation of the observed difference. The first two samples, both containing Al, experienced severe layer modification during the

Table 1
The values of fitting parameters for all analyzed samples.

	E_{d1} [eV]	c_{01} [10^{15} at/cm 2]	E_{d2} [eV]	c_{02} [10^{15} at/cm 2]	E_{d3} [eV]	c_{03} [10^{15} at/cm 2]
W:Al	1.175 ± 0.001	240 ± 20	2.033 ± 0.007	7.73 ± 0.03	/	/
W:Al(N $_2$)	1.218 ± 0.001	9150 ± 90	1.41 ± 0.02	17.4 ± 0.3	2.075 ± 0.006	28.2 ± 0.2
W:Be	2.00 ± 0.03	3.1 ± 0.2	2.5 ± 0.1	1.3 ± 0.2	/	/
W:Be(N $_2$)	1.95 ± 0.02	7.00 ± 0.06	2.44 ± 0.07	1.56 ± 0.05	>2.9	0.503 ± 0.003

heating, but no modification was observed in the last two samples. This indicates that the Al-based mixed films are less stable for temperature excursions above 800 K, probably due to low melting temperature of Al, being contrary to Be film where such modifications were not observed [5,6].

Comparing the D uptake in the four samples shows that nitrogen has substantial influence on the uptake of deuterium in the studied mixed material layers. The concentration of D increased by a factor of 4.8 in the presence of nitrogen in the sample W:Al(N₂), being $D/(W + Al + N) = 0.019$, as compared to pure W:Al layer, being $D/(W + Al) = 0.004$. In the case of Be containing samples, the concentration of D increased by a factor of 1.8 in the presence of nitrogen in the sample, being $D/(W + Be + N) = 0.005$ in the case of W:Be(N₂) and $D/(W + Be) = 0.0028$ in the case of W:Be. Moreover, as can be observed from the obtained concentrations of W:Be/Al the inclusion of nitrogen gas at the deposition procedure substantially changes the ratio between the heavier elements. There was also a slight difference in D concentration comparing W:Be and W:Al sample, being lower in case of Be. The ratio between W and Al or Be was not exactly the same, however it was similar, being 32:68 for W:Al and 47:53 for W:Be. Compared to the literature we observed much lower deuterium uptake in W:Be. Namely, the deuterium concentration in W:Be layer is around $D/(W + Be) = 0.015$ [6] in case of deuterium ion implantation at sample temperature 400 K. However, one should take notice that in this experiment the stoichiometry of the W:Be layer was not the same as in our case. Namely, the sample used in Ref. [6] contained approximately 6 atomic % of W, whereas we used the sample with 41 atomic % of W. No substantial influence or hindering of deuterium diffusion with nitrogen inclusion was observed in these mixed samples as was observed in the literature with pure W/N_x [7], however the deposition procedure could play some role and further studies are needed.

Acknowledgment

This work was supported by EURATOM – Slovenian Fusion Association and carried out under the framework of the European Fusion Development Agreement. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

References

- [1] S. Brezinec, J. Nucl. Mater. 463 (2015) 11–21. <http://dx.doi.org/10.1016/j.jnucmat.2014.12.007>.
- [2] M. Oberkofler, et al., J. Nucl. Mater. 438 (2013) S258–S261.
- [3] J. Schweinzer, et al., Nucl. Fusion 51 (2011), 113003.1–113003.7.
- [4] S. Markelj, et al., in: Proceedings of 22nd International Conference Nuclear Energy for New Europe, 2013.
- [5] K. Sugiyama, et al., J. Nucl. Mater. 415 (2011) S731–S734.
- [6] K. Sugiyama, et al., J. Nucl. Mater. 438 (2013) S1113–S1116.
- [7] L. Gao, et al., J. Nucl. Mater. 451 (2014) 352–355.
- [8] M. Oberkofler, Ch Linsmeier, Nucl. Fusion 50 (2010), 125001.1–125001.9.
- [9] T. Dittmar, et al., J. Nucl. Mater. 438 (2013) S988–S991.
- [10] C.P. Lungu, et al., Phys. Scr. T. 128 (2007) 157161.
- [11] A. Marcu, et al., Thin Solid Films 519 (2011) 4074–4077.
- [12] M. Mayer, et al., Nucl. Instrum. Methods B 267 (2009) 506–512.
- [13] M. Mayer, SIMNRA User's Guide, Max-Planck-Institut für Plasmaphysik, Garching, 1997. Report IPP 9/113, <http://home.rzg.mpg.de/%7Emam/>.
- [14] K.G. Tschersich, et al., J. Appl. Phys. 104 (2008) 034908. <http://www.mbe-komponenten.de/products/mbe-components/gas-sources/habs.php>.
- [15] S. Markelj, et al., Phys. Scr. T. 159 (2014), 014047.1–014047.5.
- [16] N.P. Barradas, et al., Nucl. Instrum. Methods B 346 (2015) 21–25.
- [17] D.P. Woodruff, T.A. Delchar, Modern Techniques of Surface Science, Cambridge University Press, Cambridge, 1986.
- [18] G.R. Longhurst, TMAP7: Tritium Migration Analysis Program, User Manual, Idaho National Laboratory.
- [19] C.T. Rettner, M.N.R. Ashfold, Dynamics of Gas-Surface Interactions, The Royal Society of Chemistry, Cambridge, 1991.
- [20] J. Boh, et al., Surf. Sci. 359 (1998) 98–100.
- [21] Y. Fukai, The Metal-hydrogen System, Springer, 2005.