Deuterium Implantation into Tungsten Nitride:
Negligible Diffusion at 300 K

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Abstract:

Magnetron-sputtered tungsten nitride (WN_x) films deposited on bulk tungsten (W) were used as model system to study the interaction of deuterium (D) plasmas with W walls in nuclear fusion devices during or after N-seeded discharges. D plasma implantation was performed at 300 K with ion energies below 215 eV. WN_x composition and thickness was determined by Rutherford backscattering. The deuterium amount in the sample was analyzed by nuclear reaction analysis (NRA). The resolution for D depth profiling was improved compared to standard NRA by consecutive low-energy argon plasma sputtering of the D containing 100-nm-WN_x film. It is shown that D is implanted only within the ion penetration range and does not diffuse into deeper layers at 300 K.

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Introduction

As an important issue for ITER and DEMO, fuel retention and diffusion in first-wall materials presents a safety (tritium < 700 g in ITER [1]) and cost concern. Tungsten (W) is presently the plasma-facing material foreseen for the ITER divertor [2-4]. For fusion devices with a full-W divertor, such as ASDEX Upgrade and JET, impurity seeding is necessary for radiative power dissipation. Recent experiments in both ASDEX Upgrade [5-7] and JET [8, 9] have shown that nitrogen seeding can not only efficiently cool the edge plasma but also improve the overall plasma performance. However, N_2 seeding will add a further plasma species which can lead to surface material sputtering, co-deposition and chemical reactions [10,11] thus causing a more complicated plasma-surface interaction. Co-deposited tungsten nitride (WN_x) layers were observed in TEXTOR after N_2-seeded discharges [12]. For a reliable assessment of the hydrogen isotope inventory it is mandatory to achieve a better understanding of fuel retention and diffusion in such co-deposited layers and in N-implanted W and of the possible influence of such layers on fuel retention in the tungsten bulk material. In general, hydrogen retention in W is low [2,13] but diffusion at elevated temperatures (>400 K) is relatively fast [2].

In the present work, WN_x films sputter-deposited onto bulk W substrates were applied as a model system for re-deposited WN_x layers in fusion devices after discharges with N_2 seeding. D retention in these layers was measured after exposure to a low-temperature laboratory D plasma. The D depth profiles were investigated by $D(^3He,\alpha)p$ nuclear reaction analysis (NRA). Recent experiments [14] have indicated that a thin N-containing layer present during plasma loading at 500 K could reduce the loss of D through the surface thus increasing D retention. Furthermore, NRA depth profiling of D-implanted WN_x films [15] has indicated that D is retained only in a

thin surface layer. It was hypothesized that D is retained only in the ion penetration range of the impinging D ions and does not, as in bulk W, diffuse to greater depth. Unfortunately the depth resolution of NRA is insufficient to finally resolve this issue [16]. For this reason we apply low-energy argon sputtering to determine the D depth profile. In this communication we will show that the depth resolution of argon sputter depth profiling is sufficient to resolve the near-surface D implantation profile of D implanted into WN_x layers.

Experimental details

WN_x films were deposited on mirror polished and degassed (at 1200 K) polycrystalline tungsten specimens ($12 \times 15 \times 0.8$ mm^3). The deposition was carried out in a commercial magnetron sputtering device (Discovery$^®$18, Denton) with a base pressure of 5×10^{-5} Pa. Prior to deposition the bulk W samples were sputter-cleaned with argon plasma. In the following WN_x films were deposited (using a 50 % Ar and 50 % N_2 mixture at 0.6 Pa 300 W RF cathode power, and 420 V cathode voltage) onto the bulk W samples for 15 min without substrate biasing. The temperature during W:N film deposition is slightly higher than room temperature, but not higher than 320 K. A Si wafer partially covered by adhesive kapton tape was put in the chamber together with the W samples. After removal of the adhesive tape the thickness of the WN_x layer was measured by a tactile profilometer. The deposited WN_x film was about 100 nm thick. After deposition, the samples were annealed in vacuum at 600 K for 2 hours to prepare them for experiments at elevated temperature (see [14]).

Deuterium implantation and argon sputtering were performed in the low-pressure steady-state ECR plasma chamber 'PlaQ' described in [17]. In the present experiments, -200 V DC target bias was applied for D implantation. At the used pressure of 1.0 Pa the D ion flux impinging on the samples consists predominantly of D_3^+ ions (97 % of the deuterons) with minor contributions of D_2^+ (2 %) and D^+ (1 %) [17]. With a plasma potential of 15 eV the maximum ion energy is 215 eV. Although most deuterons, exactly speaking 97 %, will impinge on the surface with an energy of 72 eV per deuteron the maximum D penetration range will be defined by the small fraction of D^+ ions which impinge with the full energy of 215 eV.

D plasma exposure was performed with a constant sample temperature of 300 K for 167 min. The sample temperature was controlled using an ethanol cooling circuit and a thermocouple integrated in the substrate holder just underneath the sample. The surface temperature of the samples was monitored using an infrared camera as described in [17]. At the applied bias voltage this corresponds to an accumulated D fluence of 1.0×10^{24} D/m^2 [17]. Ar plasma (0.5 Pa) sputtering was performed after D implantation also at -200 V DC bias. To reduce the possible D loss by heating during sputtering, an ethanol cooling circuit was used to keep the sample temperature at about 230 K. Six different sputter depths were produced on the very same sample by partially covering an area of the sample with a 300 μm thick tungsten foil while keeping the other parts exposed to Ar plasma. In between the erosion steps the chamber was vented and the position of the covering tungsten foil was changed. For example, we first covered one half of the sample with the tungsten foil and exposed the uncovered half to Ar plasma for 30 min. In the next step we produced the 10-min- and 40-min-sputtering areas by exposing one third of the sample surface containing equal areas of the previously covered area and the 30-min-sputtered

area for additional 10 min to Ar plasma. Finally the 23-min and 53-min areas were produced the same way by exposing another third of the sample surface containing equal fractions of the 0-min and 30-min areas. In total, 6 areas with different Ar plasma exposure time were produced, namely 0 min, 10 min, 23 min, 30 min, 40 min and 53 min.

To determine the amount of WN_x sputtered by the Ar plasma in the different areas Rutherford backscattering (RBS) with 1.5 MeV $^4He^+$ was applied. The backscattered particles were measured using a detector at a scattering angle of 165° with a solid angle of 1.15 msr. The D amount was measured by nuclear reaction analysis (NRA) using the $D(^3He,\alpha)p$ nuclear reaction. The high energy protons were counted using a thick, large angle solid state detector at a scattering angle of 135° equipped with a curved slit reducing the solid angle to 29.9 msr. The emitted alpha particles are detected with a surface barrier detector at the laboratory scattering angle of 102° equipped with a rectangular slit reducing the solid angle to 9.16 msr. Only one ^3He ion energy, namely 500 keV, is used to determine the near surface D amount in the present measurements. For the 500 keV $^3He^+$ projectiles the generated α particles have an energy of about 3100 keV while the protons have a much higher energy of about 13.5 MeV. Based on this, we calculated the information depth, i.e., the maximum depth from which a generated particle still can leave the sample and reach the detector, for each type of reaction products applying SIMNRA [18] using Ziegler/Biersack stopping power data. The NRA information depth in WN_x for the chosen experimental conditions is ~150 nm for the alpha particles and ~400 nm for the high energy protons. For the given geometries, the corresponding depth resolutions at the surface are 18 and 110 nm according to RESOLNRA [18], respectively. The D amount in the sample was quantified using the cross section published by Alimov [19]. For comparison and reference an about

15 nm thick plasma-deposited amorphous deuterated carbon film (a-C:D) layer on a Si wafer with a D amount of 6.7×10^{20} D atoms/m^2 was also measured by the same ^{3}He ion beam. The NRA information depth in a-C:D is larger than the above stated values for W so that the full a-C:D layer contributes to the NRA signals. Combining the results of the sputtered WN$_x$ amount and D amount in the corresponding area, the depth distribution of D in the sample can be reconstructed.

Results and discussion

Fig. 1 shows RBS spectra of different areas of the sample after different Ar sputtering durations and, as a gray dashed line, the RBS spectrum of a W sample without WN$_x$ coating. The shown model spectra were simulated with SIMNRA [18] using Ziegler/Biersack stopping power data and taking dual scattering into account. At very low backscattering energy the simulated spectra do not fit very well to the experimental data. This is due to the large uncertainty of the stopping power data when the energy loss is very large. For the WN$_x$-coated samples the W concentration within the coating – corresponding to the RBS signal from the high energy edge at about 1375 keV to the interface at about 1200 keV – is lower than for the W substrate because of the presence of nitrogen. The width of the W-depleted region in the RBS spectra corresponds to the thickness of the WN$_x$ layer and the height of the RBS signal at a specific energy depends on the local W concentration. The RBS signal corresponding to the N species in the WN$_x$ layer, which should appear in the backscattering energy range of 390-475 keV, cannot be directly seen due to the intense W background at the lower backscattering energies and the low cross section for N. However the N concentration can be derived from a simulation of the RBS spectra by SIMNRA [18]. The N concentration is derived as the balance to the W signal in the W-depleted

layer assuming N is the only species that dilutes W in this layer. As a result a W concentration in the WN_x layer of roughly (50 ± 2) % is deduced. That means the atomic ratio of W:N in our layers is about 1:1. In the area without Ar sputtering the WN_x layer is, of course, the thickest compared with the other areas. The step at about 1200 keV for the unsputtered WN_x layer (black solid squares in Fig. 1) marks the transition from the WN_x layer to the underlying bulk W sample. With increasing sputtering time this edge shifts to higher backscatter energy indicating the decrease of the thickness of the WN_x layer. After 10 min Ar plasma sputtering about 5 % of the WN_x layer was sputtered and after the longest sputtering time of 53 min about 27 % were removed.

The amount of sputtered WN_x was determined by fitting the RBS spectra with SIMNRA based on the assumption that there was no preferential sputtering. The amount of sputtered WN_x is in principle linear with sputtering time. However, the difference between the 23- and 30-min Ar sputtering is much larger than that between any other two adjacent time steps. The reason for this deviation from the linear behavior is unclear. In any case, the following two sputter steps showed the same sputter rates as the first two steps. Although this ambiguity is unsatisfactory it has no influence on the further evaluation of the data.

Fig. 2 shows the proton and alpha spectra from the nuclear reaction of $D(^3He,\alpha)p$ with a 500 keV $^3He^+$ ion beam after different Ar sputtering times. Without Ar sputtering, the D amount in the WN_x layer is, of course, the largest which correspondingly yields the highest proton and alpha peaks. Also plotted are the proton and alpha spectra from an about 15 nm thick a-C:D layer on a silicon substrate (divided by a factor of 2.5 for easy comparison). 30 min Ar plasma sputtering is sufficient to almost completely remove the D-containing layer. From the RBS measurements

which yield areal densities and from the initial thickness measurement of the deposited film we can determine a value for the density of our WN_x layer. Based on this density (9.1×10^{28} WN-molecules/m^3) we can calculate the removed layer thicknesses. After 30 min Ar sputtering about 15 nm WN_x is removed. This means all the D in the sample was retained in this 15 nm thick WN_x layer.

Because the information depth of the alpha and proton signals is much larger than this removed layer thickness this means that both signals show the complete amount of D remaining in the sample after a certain sputtering time. From the peak integrals we can in turn derive the total retained D amounts. These total D amounts determined from the proton signal are shown in Fig. 3 as a function of the removed WN_x layer thickness. The total D amount remaining in the WN_x layers decreases quickly with increasing Ar sputtering time. The non-linear decrease is most probably a consequence of an inhomogeneous D distribution in the WN_x layer.

The maximal penetration depths in the WN_x layer for the different ion species from our D plasma were calculated using TRIDYN [20]. For the target material a W:N ratio of 1:1 and an ion energy of 215 eV for the impinging ions were used. As shown in the experimental section the D plasma produces D^+, D_2^+ and D_3^+ ions. In the simulation, the molecular ions are treated as individual particles impinging with the same velocity. That means a D_2^+ ion is treated as two deuterons with half the ion energy and correspondingly a D_3^+ ion as three deuterons with 1/3 of the full energy. The penetration depths of D atoms with the energy of 215 eV, 108 eV and 72 eV from these TRIDYN simulations are 17.2, 9.9, and 9.5 nm, respectively. The values are also shown in Fig. 3. Obviously, D^+ ions with the highest energy per deuteron lead to the largest penetration depth. The penetration depth corresponding to the D^+ ions is in good agreement with the experimentally

determined thickness of the D-containing layer. The comparison between the penetration depths and the experimentally measured thickness of the D-containing layer shows that D is retained only within the ion penetration range and that implanted D atoms do not diffuse into deeper WN_x layers under the present conditions. The total fluence of D^+ ions impinging on the sample (1 % of the total D fluence of 1×10^{24} D/m^2) would be sufficient to account for the total retained D amount of about 2×10^{20} D/m^2.

Conclusion

D retention in WN_x layers deposited on bulk W was studied as a model system for some aspects of plasma-surface interaction in N-seeded discharges in fusion devices with a W first wall. Results show that D is retained in the topmost surface only and does not diffuse into deeper layers of the WN_x film at the temperature of 300 K. This is in contrast to the behavior of pure W films [21] and bulk W samples [2] which clearly show diffusion to larger depth at this temperature. Our findings indicate that WN_x films might be applicable as D diffusion barriers in future fusion applications. The presented novel analysis method of low-energy Ar plasma sputter depth profiling combined with NRA analysis of D retention has proven to be capable of resolving the D depth profile with a depth resolution in the nm range which is superior to the standard NRA depth resolution.

interpretation of experimental results is highly appreciated. Thanks are further due to G. Meisl for the TRIDYN simulations. This project has received funding from the EURATOM research and training program 2014-2018.

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__Note:__ Unfortunately, the information given in the last paragraph of this article is not correct, but the information in figures 5 and 6 is correct. The contribution of the molecular ions to the total ion flux for standard conditions is: D_3^+ = 94%, D_2^+ = 3% and D^+ = 3%. Correspondingly, the contributions to the total deuteron flux in form of ions are: 97%, 2%, and 1%.

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Figure Captions:

Figure 1: RBS spectra of magnetron-sputtered WN_x on a bulk W sample after D plasma exposure in areas with different Ar sputtering fluences. The insert shows an enlarged view of the region of the WN_x layer. The shift of the step at about 1200 keV is due to partial sputter removal of the WN_x layer. The experimentally measured data are plotted as solid symbols, the simulation results as solid lines.

Figure 2: NRA spectra of D plasma implanted WN_x on W after different Ar sputtering fluences: (a) proton spectra, (b) alpha spectra. Measured at a ^{3}He energy of 500 keV from the $D(^3He,\alpha)p$ nuclear reaction.

Figure 3: Total D amount in different areas of the WN_x sample after 1×10^{24} D/m^2 implantation and different Ar plasma exposure durations. The lower scale shows the removed WN_x layer thickness in units of molecules/m^2; the initial film thickness is about 1.2×10^{22} WN-molecules/m^2. The upper scale is a thickness scale in nanometers calculated using a WN density of 9.1×10^{28} WN-molecules/m^3. The penetration depths for D_3^+, D_2^+, and D^+ ions are indicated.
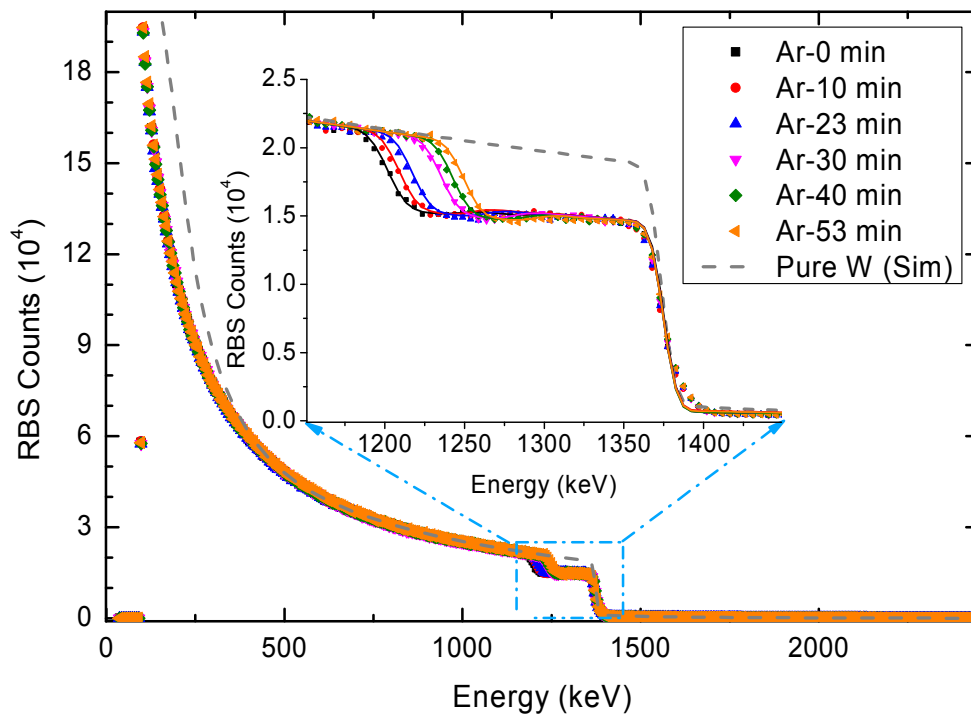
Figure 1: RBS spectra of magnetron-sputtered WN_x on a bulk W sample after D plasma exposure in areas with different Ar sputtering fluences. The insert shows an enlarged view of the region of the WN_x layer. The shift of the step at about 1200 keV is due to partial sputter removal of the WN_x layer. The experimentally measured data are plotted as solid symbols, the simulation results as solid lines.
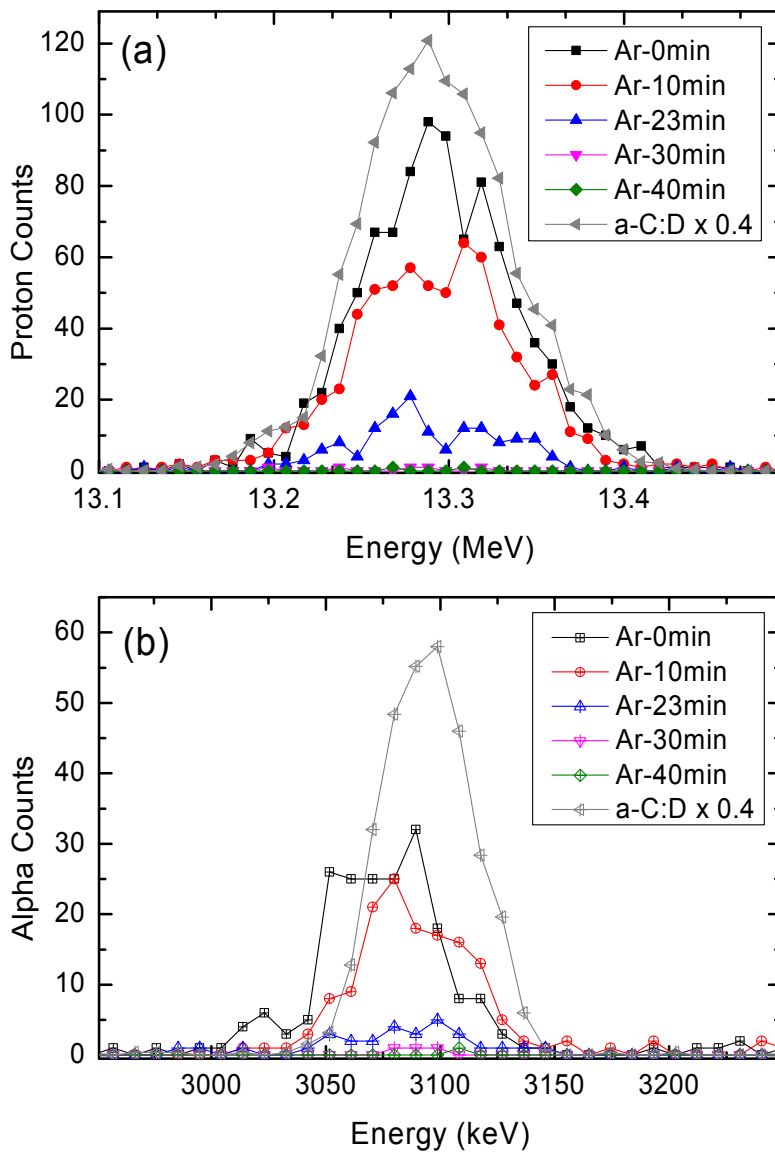
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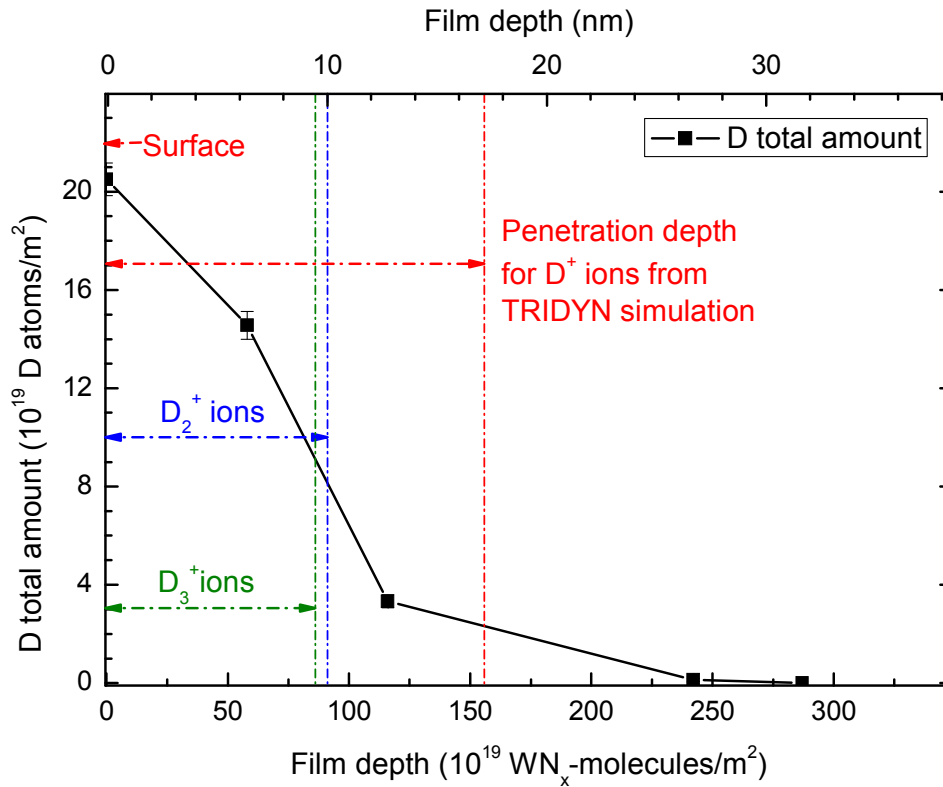**Figure 3:** Total D amount in different areas of the WN_x sample after 1×10^{24} D/m^2 implantation and different Ar plasma exposure durations. The lower scale shows the removed WN_x layer thickness in units of molecules/m^2; the initial film thickness is about 1.2×10^{22} WN-molecules/m^2. The upper scale is a thickness scale in nanometers calculated using a WN density of 9.1×10^{28} WN-molecules/m^3. The penetration depths for D_3^+, D_2^+, and D^+ ions are indicated.