# Dislocation mechanism of deuterium trapping and transport in tungsten under sub-threshold plasma implantation

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# Дислокационный механизм захвата и транспорта дейтерия в вольфраме при подпороговой плазменной имплантации

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Построена модель удержания дейтерия в сплавах вольфрама, основанная на захвате дейтерия дислокациями и диффузии к поверхности по дислокационной сетке с параметрами вычисленными методом ab initio. Модель объясняет наблюдаемые закономерности удержания дейтерия при подпороговой имплантации, не создающей стабильных дефектов, которые обычно рассматриваются как ловушки дейтерия. Насыщение содержания дейтерия с дозой имплантации и эффекты, связанные с легированием вольфрама танталом, описаны в сравнении с экспериментальными данными по плазменной имплантации высокой и низкой интенсивности.

Ключевые слова: сплавы вольфрама, удержание дейтерия, дислокации.

We develop a model for D retention in W alloys based on deuterium trapping at dislocations and transport to the surface via the dislocation network with parameters evaluated by ab initio calculations. The model can explain experimentally observed trends of D retention in W under sub-threshold implantation, which does not produce stable defects that act as D traps in conventional models. Saturation of D retention with implantation dose and effects due to alloying W with Ta are evaluated and compared with experimental observations under low and high flux plasma implantation conditions.

Keywords: tungsten alloys, deuterium retention, dislocations.

## 1. Introduction

The current choice of materials to be used in ITER plasma-facing components includes tungsten and beryllium [1]. The sputtering yield of tungsten is much lower than the one of beryllium, while its melting point is significantly higher. However, the practical use of tungsten is hindered by its high ductile-to-brittle transition temperature and therefore high brittleness at the temperatures of operation. In order to improve the mechanical properties, tungsten alloys are con-

sidered. One of the issues still to be clarified is the retention of hydrogen isotopes (including deuterium and radioactive tritium) in tungsten alloys.

In current models dealing with deuterium (D) retention in tungsten [2], it is argued that nucleation of D-complexes is determined crucially by the concentration of radiation-produced vacancies, which act as traps for fast migrating D atoms. One vacancy has been argued to trap up to six hydrogen atoms [3, 4]. At sufficiently low temperatures

considered in ref. [2] vacancies are immobile while SIAs diffuse and become trapped at impurity atoms (mainly carbon, C) or are absorbed by dislocations. So the result strongly depends on the dislocation density and C-SIA trapping energy, which have to be high enough to trap SIA's so that the remaining vacancies could trap D atoms and act as nucleation cites for D-clusters. This model was developed to describe the ion implantation with energy of 5-30 keV, and it cannot be applied (even qualitatively) to the nucleation of D-clusters at *sub-threshold* implantation conditions, i.e. when the ion energy is too low to produce stable vacancy-SIA pairs in the crystal bulk. While the sub-threshold implantation conditions are important, since they reflect the plasma-wall interaction expected to occur in the ITER and experiments involving high-flux high temperature deuterium plasmas with ion energies of ~ 50 eV [5, 6]. Experimental investigations of trapping and release of D in pure tungsten (W) and tungsten-tantalum (W-Ta) alloys show that there is a considerable amount of trapped D in the bulk up to several microns depth, where no vacancies can be expected since their thermal concentration at the implantation temperature (<500 K) is negligible. Hence, the description of the trapping of D at these irradiation conditions requires alternative mechanisms as compared to those considered in the current models.

## 2. Homogeneous self-trapping of deuterium in the bulk

Ab initio calculations [4] show that two hydrogen atoms trap each other weakly with a binding energy $E_b$ ~0.01 eV, (as compared e.g. with helium forming strong pairs with a binding energy of $E_b$ ~1 eV).
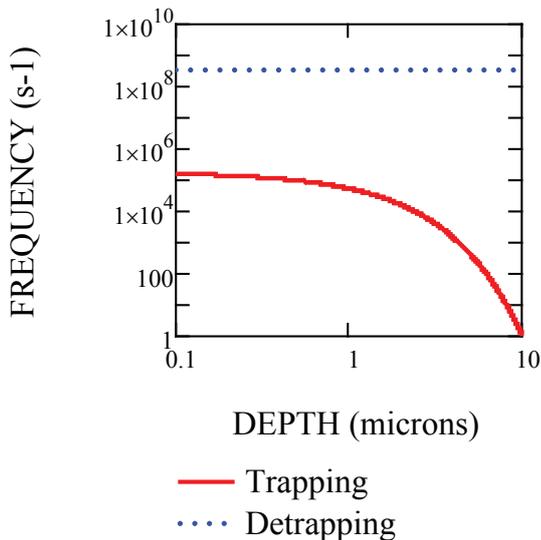


**Fig.1.** Trapping vs. detrapping frequencies for D-D pairs in the bulk under typical implantation conditions (see Fig. 2).

Fig. 1 shows detrapping frequency, $w_{de}$, for D-D pairs based on these estimates, vs. trapping frequency, $w_{DD}$, i.e. the frequency of collisions of one D atom with others having a concentration of $C_D^b$ in the crystal bulk, which are given by the following expressions:

$$w_{DD} = \alpha_{DD} C_D^b, \quad \alpha_{DD} = \frac{4\pi}{\omega}\left(\frac{3\omega}{4\pi}\right)^{1/3} D_D^b, \quad (1)$$

$$D_D^b \approx b^2 w_0 \exp\left(-\frac{E_m^b}{k_B T}\right) \quad (2)$$

$$w_{de} = w_0 \exp\left(-\frac{E_b + E_m^b}{k_B T}\right), \quad w_0 = 10^{13} s^{-1}, \quad (3)$$

where $\omega \approx 0.5 b^3$ is the atomic volume, b is the atomic spacing, $D_D^b$ is the bulk diffusion of D atoms, $w_0$ is the frequency factor, $E_m^b$ is the bulk migration energy and $k_B T$ has the usual meaning.

One can see that the trapping frequency decreases with distance (depth) from the surface due to decreasing $C_D^b$ (see the next section) and it is several orders of magnitude lower than that of detrapping. So a homogeneous nucleation of D (or H) clusters is indeed very questionable in that case, and one needs an alternative trapping mechanism for D atoms at some intrinsic defects to provide the nucleation cites for gas clusters. In the following section we consider a model of D trapping by dislocations, which does not require vacancies as the nucleation cites.

## 3. Trapping of deuterium by dislocations

Density functional theory (DFT) calculations by the present authors [7] shows that there are at least three positions inside of the screw dislocation core in which D is trapped with the binding energy $E_b^1 = 0.6$ eV. In addition, there are six positions adjacent to the dislocation core in which D is trapped with the binding energy of 0.55 eV. D atoms can migrate along the dislocation core with an activation energy $E_m^d = 0.1$ eV as compared to the bulk migration energy $E_m^b = 0.4$ eV. A free path of the D atom along a dislocation before detrapping is given by [8]:

$$\lambda_d^0 = b \exp\left(\frac{E_m^b - E_m^d + E_b^1}{2 k_B T}\right), \quad (4)$$

and one has $\lambda_d^0 > 10$ micron at T<460 K, which means that D atoms practically don't leave the dislocation core while being trapped and so they can form n-D clusters sitting (or migrating) at the dislocation. The rate of trapping of a subsequent atom by a n-D cluster $w_n^+(x)$ placed at the depth $x$ is given by the product of the D flux from the bulk to the unite length of the dislocation $J_d^D$, and the length along the dislocation from which each cluster is fed up with migrating D-atoms, $\lambda_d$:

$$w_n^+(x) = J_d^D \lambda_d, \quad J_d^D = \frac{Z_d}{\omega} D_D^b C_D^b(x), \quad (5)$$

where $Z_d$ ~1 is the dislocation capture efficiency for D-atoms migrating from the bulk [9]. $w_n^+(x)$ depends on the depth $x$ via the bulk D-concentration, $C_D^b(x)$. At a steady-state (i.e. for times larger than the time of D bulk diffusion to the depth $x$) $C_D^b(x)$ is given by

$$C_D^b(x) = \frac{\omega F_D x_D}{D_D^b} \exp(-x k_D), \quad k_D \approx (Z_d \rho_d)^{0.5}, \quad (6)$$

where $F_D$ is the D ion flux, $x_D$ is the implantation strag-gling, and $k_D$ is the sink strength for migrating D-atoms. Fig. 2 shows that the depth of D penetration is determined mainly by the dislocation density, $\rho_d$, which act as the main sink for migrating atoms.
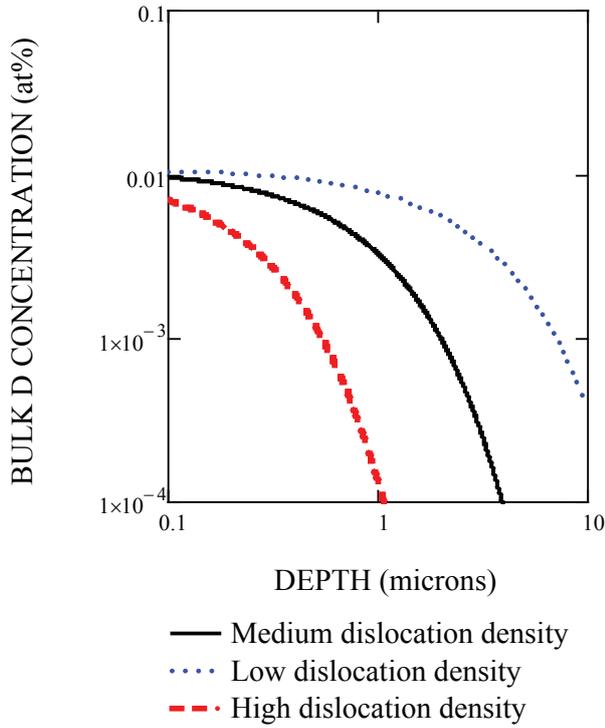


**Fig.2.** Steady-state D-concentration in the bulk, $C_D^b(x)$ at different dislocation densities and the following implantation conditions: Low $\rho_d = 10^{11} \text{m}^{-2}$, Medium $\rho_d = 10^{12}$ m$^{-2}$, High $\rho_d = 10^{13}$ m$^{-2}$, $F_D = 10^{20}$ m$^{-2}$s$^{-1}$, $x_D$ = b, T = 460 K.

Now we can determine a sufficient condition for D clustering at dislocations by comparing the rate of trapping (5) with the rate of detrapping of an atom from n-D cluster, $w_n^-$, which is given by

$$w_n^- = w_0 \exp\left(-\frac{E_b^n + E_m^d}{k_B T}\right), \quad (7)$$

where $E_b^n$ is the binding energy between one D and n-D cluster. DFT calculations [7] give the following values for $n = 2 \div 5$: $E_b^2 = 0.55$ eV, $E_b^3 = 0.6$ eV, $E_b^4 = 0.48$ eV, $E_b^5 = 0.45$ eV.

One can see from Fig. 2 that at high dislocation density, D-concentration falls down sharply below a micron depth, whereas at medium and low dislocation densities it extends to several microns so that the trapping rate of a D-atom by n-D cluster exceeds its detrapping in this region as shown in Fig. 3, which provides sufficient conditions for the D-clustering at dislocations up to a depth of several microns, which agrees with experimental data on high-flux low-energy

plasma implantation [5, 6] that detected D retention in W and W-5%Ta alloy up to 5 micron depth.
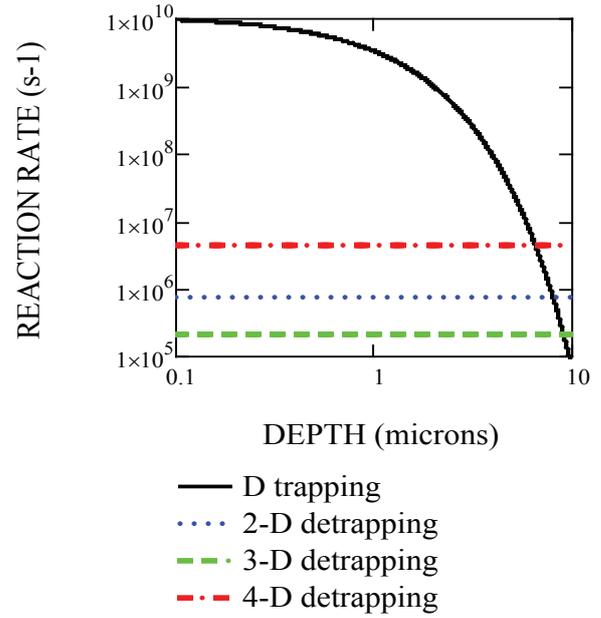


**Fig.3.** D atom trapping/detrapping reaction rates by/from n-D cluster sitting at a dislocation under implantation conditions shown in Fig. 2, $\rho_d = 10^{12} m^{-2}$ and $\lambda_d = \lambda_d^0 < \rho_d / N_C$.
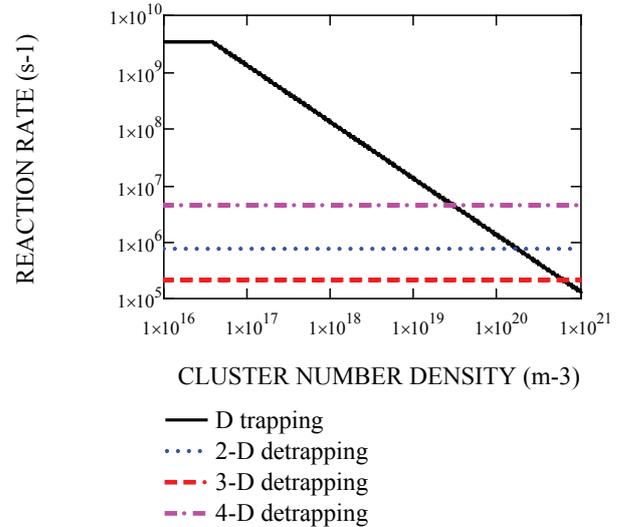


**Fig.4.** D atom trapping/detrapping reaction rates by/from n-D cluster sitting at a dislocation vs. cluster number density $N_c$ at $\lambda_d = \rho_d / N_c < \lambda_d^0$ at the depth of 1 micron.

Naturally, as the clustering process starts, the distance along the dislocation from which each cluster is fed up with migrating D-atoms, $\lambda_d$, becomes determined by the cluster number density $N_c$: $\lambda_d = \rho_d / N_c$ as soon as $N_c$ becomes larger than $\rho_d / \lambda_d^0$. Accordingly, the trapping rate will decrease inversely proportional to $N_c$, as shown in Fig. 4, which will limit the ultimate number density of D clusters nucleated at dislocations at about $N_C^{max} \approx 10^{19} \div 10^{20} m^{-3}$, which would correspond to the mean cluster spacing $\lambda_d \approx 100 \div 10$ nm.

Note that D trapping/detrapping balance from/to the bulk by/from dislocations, which actually determines the deuterium retention in the present model, is not expected to depend strongly on the clustering kinetics. Roughly, the net

trapping rate of D at dislocations is given by the following difference:

$$\left(\frac{dC_D^d(x)}{dt}\right)_b = Z_d \rho_d D_D^b \left[ C_D^b(x) - \exp\left(-\frac{E_b^1}{k_B T}\right) \right] \quad (8)$$

which is positive at depth up to 5 micron depth as can be seen from Fig. 5.
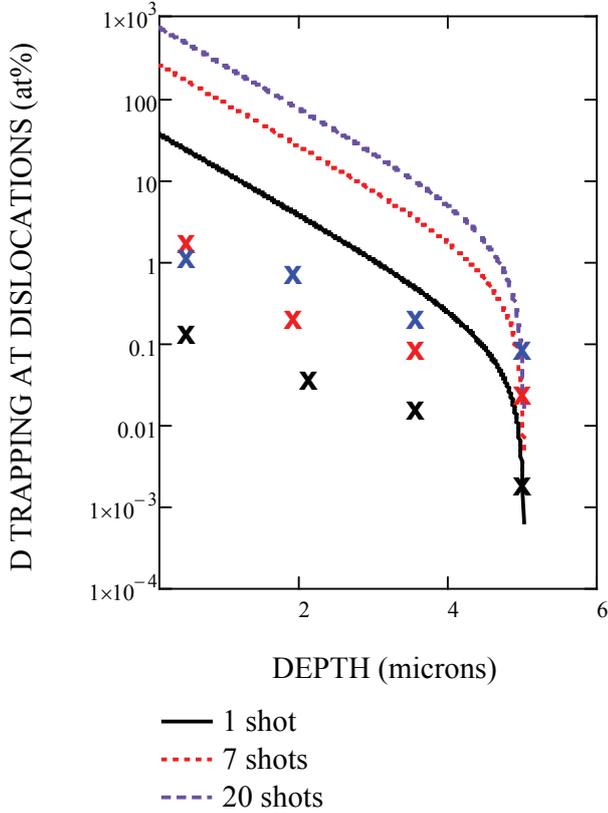


**Fig.5.** Depth profile of D-trapped at dislocation vs. number of implantation shots (1 shot time = 70 s) at implantation conditions shown in Fig. 2, $\rho_d = 10^{12} m^{-2}$ assuming immobile D-clusters. Symbols **x** show data [5, 6] for the corresponding number of shots.

If all trapped deuterium was retained at dislocations in the form of immobile clusters, then its retention would increase with time as $C_D^d(x,t) = \left(dC_D^d(x)/dt\right)t$, and it would have been unrealistically high as shown in Fig. 5 in comparison with experimental data [5, 6].

Implantation was performed in a number of shots each having duration of 70 s at the following conditions: surface temperature 460-510 K, ion energy 50 eV, ion flux ~8x10²³-10²⁴ m⁻²s⁻¹ corresponding to the total ion fluence of 5x1025 m⁻² in one shot. The number of shots varied from 1 to 20 resulting in D retention saturated at levels ranging from 0.01 to 0.1 % at a micron depth and reaching several % near the surface.

In contrast to these observations, the model of immobile D clusters trapped at dislocations predicts no saturation in D retention by tungsten, and it will be modified in the next section to account for release of D to the surface via diffusion along dislocation network.

## 4. Trapping and release of deuterium by dislocations

Let's take into account mobility of small D-clusters along dislocations, which should provide deuterium release to the surface via the dislocation network as illustrated in Fig.6.
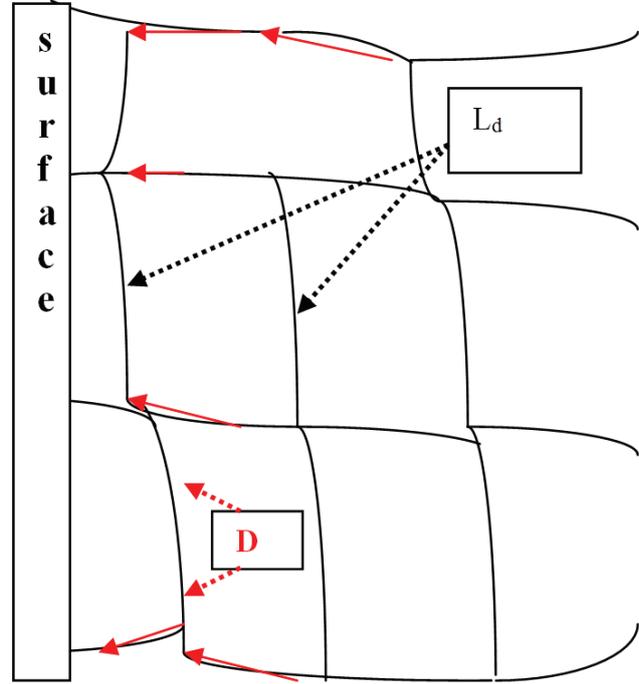


**Fig.6.** Illustration of D-transport via the dislocation network with dislocation segments $L_d$.

In this case, the retention rate of deuterium at dislocation would be given by the balance between the *net trapping rate* of D by dislocations from the bulk and its *transport to the surface* via the dislocation network:

$$\frac{dC_D^d(x)}{dt} = \left(\frac{dC_D^d(x)}{dt}\right)_b - \sum_{n=1}^{N} \frac{C_n^d(x)}{\tau_n}, \quad (9)$$

where $C_n^d(x)$ is the concentration of n-D clusters and $\tau_n$ is the time it takes for them to reach the surface via the dislocation network, which is given by

$$\tau_n(x) = \frac{x^2 + L_d^2}{D_n^d}, \quad (10)$$

where $D_n^d$ is the n-D cluster mobility along a dislocation and $L_d$ is the mean length of dislocation segments (see Fig.6) that determines diffusion length and time near the surface: $x << L_d$. Substituting (10) into (9) the retention rate takes the following form:

$$\frac{dC_D^d(x)}{dt} = \left(\frac{dC_D^d(x)}{dt}\right)_b - \frac{D_{eff}}{x^2 + L_d^2} C_D^d(x), \quad (11)$$

$$D_{eff} = \frac{\sum_{n=1}^{N} D_n^d C_n^d}{C_D^d}, \quad C_D^d = \sum_{n=1}^{N} C_n^d, \quad (12)$$

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