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Deuterium Accumulation in Tungsten under Low-Energy High-Flux Plasma Exposure

P. Yu. Grigorev[a, b], V. I. Dubinko[c], D. A. Terentyev[b], A. V. Bakaev[a, b], and E. E. Zhurkin[a]

[a] *St. Petersburg State Polytechnical University, St. Petersburg, 195251 Russia*
e-mail: ezhurkin@phmf.spbstu.ru
[b] *Belgian Nuclear Research Center (SCK-CEN), Mol, Belgium*
[c] *Kharkiv Physical–Technical Institute (National Scientific Center), Kharkiv, Ukraine*

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Abstract—The accumulation of deuterium implanted in tungsten is simulated within the framework of kinetic diffusion theory. The influence of the tungsten microstructure (dislocation density and impurity concentration) on the process of deuterium capture and accumulation is considered. It is established that, under the chosen irradiation conditions, deuterium accumulation in the near-surface region is determined by capture at defects formed during implantation. The deuterium concentration gradient, together with the material microstructure, determines its accumulation in tungsten. Variation in the dislocation density and impurity concentration does not affect the simulation results, which is, first, related to the fact that the model used does not contain alternative mechanisms for the formation and growth of vacancy clusters under the subthreshold irradiation mode. The simulation results are compared with experimental data, and ways of improving the model are discussed in order to explain the deuterium-saturation effect for high fluences (more than 10^{23} m^{-2}).

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INTRODUCTION

The choice of materials for components interacting with plasma is a very important stage on the way to the construction of future thermonuclear devices, such as the International Thermonuclear Experimental Reactor (ITER). Such a material must satisfy a series of requirements, in particular, it must have good stability to radiation damage, sputtering, and high-temperature effects. In the ITER reactor, hydrogen isotope fluxes reach 10^{22}–10^{24} m^{-2} s^{-1}, the particle energy ranges from several electronvolts to kiloelectronvolts, radiation damage doses reach 0.6–0.7 displacements per atom (dpa), and the temperature in the divertor can be up to 1300 K [1]. Tungsten has a low sputtering coefficient, a high melting temperature (3695 K), a high threshold displacement energy (38–100 keV) [2–5], and high heat conductivity. In view of these features, tungsten was chosen as the material interacting with plasma in order to coat the ITER divertor plates [6]. The ability of the material to capture, accumulate, and retain hydrogen isotopes during reactor operation (and afterwards) is another important criterion applied in the choice of the material interacting with the plasma for the ITER. The accumulation of tritium is the most critical process, because it is a radioactive, toxic, and expensive material. At present, from safety considerations, a restriction is imposed on the amount of retained tritium in the ITER chamber (700 g) [7]. Thus, the study, understanding, and description of mechanisms for the capture, accumulation, and retention of hydrogen isotopes in tungsten is of practical interest from the point of view of the development, planning, and operation of future thermonuclear devices.

The mechanisms for deuterium capture and accumulation in tungsten were studied experimentally and by means of numerical simulation. The authors of [2] experimentally estimated the threshold displacement energy (E_d) in tungsten, which was ~50 eV. The published estimates of E_d range from 38 to 100 eV [4, 5], whence it follows that the minimum deuterium energy required to create a stable Frenkel pair is on the order of 1 keV. Thus, typical irradiation conditions for W in thermonuclear devices (for a D^+ energy on the order of kiloelectronvolts) corresponds, in fact, to the subthreshold irradiation mode (with a low effectiveness of primary defect formation).

The authors of [8, 9] experimentally studied deuterium accumulation after the irradiation of W with beams of D^+ ions with subthreshold energies. It was shown that, at room temperature, for an energy of 1 keV per deuterium atom, the amount of deuterium retained in the material reaches saturation at a level of ~6×10^{20} m^{-2} for fluences of $\geq 10^{23}$ m^{-2} or more. At the same time, the authors of [10] observed the formation of blisters and bubbles after irradiation with a subthreshold energy of ~100 eV, starting from a fluence of 10^{23} m^{-2} or more. The standard procedure before the experiments is tungsten annealing at temperatures of about 1300 K, which is considerably higher than the temperature at which vacancies become mobile (~600–700 K in accordance with [11]); i.e., they can diffuse to the free surface and to the region near the interface between polycrystalline grains. Thus, it can be stated that the material barely has vacancies before irradiation. However, typical spectra obtained using thermodesorption spectroscopy have a characteristic peak of the deuterium yield in the temperature range of ~500 K [12], which corresponds to deuterium escape from the bound state with "light" traps in the material, such as dislocations, vacancies, and vacancy clusters [13]. In addition, quantum-mechanical calculations in the approximation of the electron-density functional showed that the binding energy of two hydrogen atoms in tungsten is less than 0.1 eV [14]. This means that, unlike helium with a high He–He binding energy, hydrogen must have nucleation centers in the material to form bubbles and blisters. Thus, summarizing the foregoing, we can point out the following: although irradiation in the subthreshold mode barely produces defects in W, existing experimental data showed that deuterium is retained by light traps with a low energy of binding with it (on the order of 1 eV) in this case. The physical mechanism of such a process, as well as the mechanism of the formation of bubbles and blisters containing D, is unclear at present and calls for further investigations.

The authors of [15] calculated the accumulation of implanted deuterium in tungsten at room temperature using kinetic transport theory. They considered implantation at energies of 5, 15, and 30 keV per deuterium atom and a fluence of 5.8×10^{20} m^{-2}. The results of this calculation agree well with the experimental data; in this case, it was established that the material microstructure affects the distribution of deuterium retained by tungsten. The authors of [16] presented the results of experiments on the implantation of deuterium with an energy of 1 keV and a fluence of up to 9×10^{23} m^{-2} into tungsten and those of the analysis of the distribution of captured deuterium using methods of nuclear reaction (NRA) and thermodesorption spectroscopy.

In this paper, within the framework of the model in [15], we simulate the subthreshold implantation of D into W; we compare the results with the corresponding experimental data [16]. The aim of this paper is to verify the adequacy of the model, which realistically reproduces the accumulation of deuterium in the case of implantation for an abovethreshold energy, under subthreshold implantation conditions and to study the influence of the impurity concentration and the dislocation density in W on the distribution of retained deuterium.

SIMULATION PROCEDURE

To simulate the diffusion processes in W, we used kinetic diffusion theory based on the solution of standard diffusion equations (describing the Fick's law) including additional terms that take into account sinks and reactions between atoms of different types. The simulation procedure was described in detail in [15]; therefore, we here restrict ourselves to description of the main physical processes taken into account within the framework of this model. All calculations were carried out for room temperature (300 K). In our model, we initially considered deuterium, impurities, vacancies, vacancy clusters, interstitial sites, and interstitial clusters as mobile objects. However, because of the high migration energies of vacancies and carbon (the most widespread impurity in W), which are 1.8 [17] and 1.5 eV [18], respectively, only deuterium, interstitial sites, and interstitial clusters remain mobile at room temperature. The migration energy for deuterium is 0.26 eV [11], and the pre-exponential factor of the diffusion coefficient was recalculated for the hydrogen isotope as $D_0^{\mathrm{D}} = D_0^{\mathrm{H}}/\sqrt{2}$, where D_0^{H} is the hydrogen diffusion coefficient. Diffusing deuterium can interact with vacancies and vacancy clusters, forming stable complexes; in this case, one vacancy can retain a maximum of six deuterium atoms in accordance with [11]. Deuterium can also interact with grain boundaries and dislocations, which are nonsaturated sinks for it within the framework of the considered model. Interstitial atoms can annihilate with vacancies, form clusters, and move to the grain boundaries and dislocations like deuterium.

The spatial distributions of implanted deuterium and primary defects formed during implantation were important initial parameters. To calculate them, the authors of [15] first calculated the energy spectrum of primarily knock-on atoms (PKAs) using the well-known SRIM program [3, 19] and then simulated the formation of defects in the PKA cascade using the method of classical molecular dynamics in order to take defect recombinations into account and to obtain their distributions. In the case under consideration, because of the low irradiation energy, at which the PKA energy does not exceed $2E_{\mathrm{d}}$ and, consequently, the mode of "direct atom ejection" occurs, the number of generated defects in the system is mainly determined by the threshold displacement energy E_{d}. Calculation of the primary defect profiles was carried out using the SRIM code [19]. To verify the influence of the defect concentration profile, we chose the most "optimistic" case with a minimum threshold energy of $E_{\mathrm{d}} = 40$ eV and then considered several versions of inclusion of the effectiveness of Frenkel-pair recombination: its absence and 50 and 90% of the recombination.

To study the influence of the tungsten microstructure (the impurity concentration and the dislocation density) on the process of deuterium capture and accumulation, we varied the dislocation density from

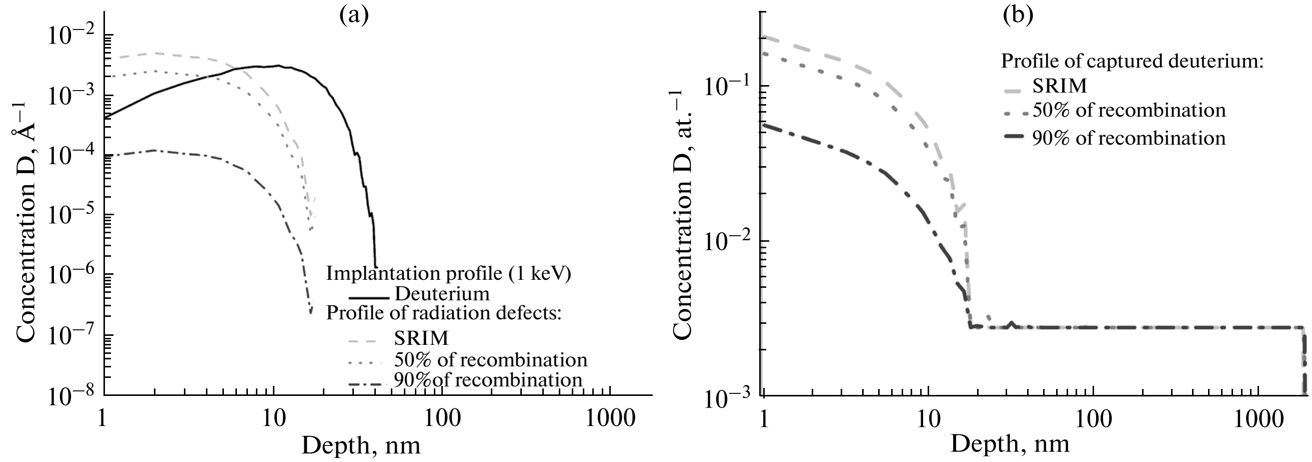

Fig. 1. (a) Profiles of the depth distribution of deuterium with an energy of 1 keV implanted into tungsten and of primary defects for different inclusions of the effectiveness of defect recombination. (b) The dependences of the concentration of captured deuterium on the target depth using the implantation profiles with different inclusions of the effectiveness of defect recombination.

10^{12} to 10^{14} m^{-2} and the relative impurity concentration from 10^{-4} to 10^{-6} at^{-1}.

RESULTS AND DISCUSSION

Influence of the Distribution of Primary Defects

As was mentioned above, in our calculation, we used the profiles of primary defect formation by taking into account the different effectivenesses of Frenkel-pair recombinations. The distribution obtained using the SRIM code (without considering additional recombination) was used for one of the calculation versions. For the two other calculation versions, the initial profile was modified under the assumption that the recombination effectiveness is 50 and 90%, respectively. These profiles are given in Fig. 1a. Figure 1b shows the calculated target-depth distributions of retained deuterium obtained using different initial defect-formation profiles. It can be seen that the differences between the initial defect concentrations only affect deuterium accumulation in the near-surface region of the material with a thickness of up to 10 nm, and D accumulation at a material depth of 10 nm or more is independent of the initial defect concentration. This is related to the fact that the amount and distribution of deuterium retained in the near-surface region is first determined by deuterium capture at vacancies that formed during irradiation. At the same time, D accumulation in the material depth is determined by the D capture at inherent material traps, such as dislocations, impurities, and grain boundaries. The deuterium concentration gradient (from the near-surface layer into the material) is a sort of boundary condition determining its capture inside the material. The process of D penetration into the material can be described as D diffusion in the field of traps.

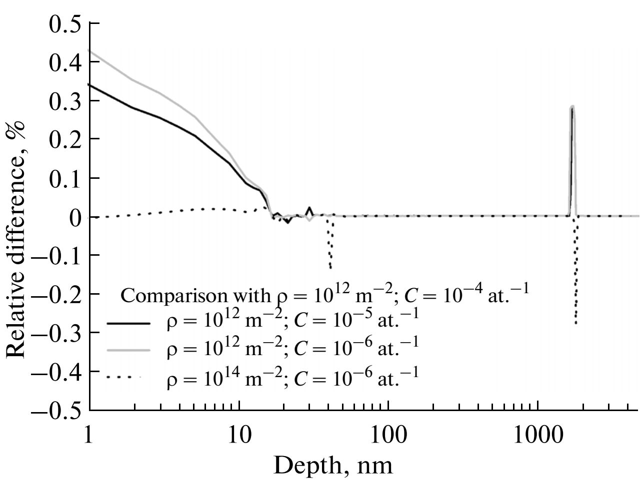

Fig. 2. Comparison of relative differences between the depth distributions of captured deuterium $d(\rho, C)$ for different dislocation densities (ρ) and impurity concentrations (C): $(d(\rho, C) - d_0)/d_0$, where d_0 is the deuterium concentration corresponding to $\rho = 10^{12}$ m^{-2} and $C = 10^{-4}$ at^{-1}.

Influence of the Dislocation Density and the Impurity Concentration

Figure 2 shows comparison of the results of calculating the D accumulation in W obtained for different impurity concentrations (varied from 10^{-6} to 10^{-4} of the relative atom concentration) and the dislocation densities (varied from 10^{12} to 10^{14} m^{-2}). It can be seen from this figure that the relative difference between the deuterium distributions in the material does not exceed 0.5%. Thus, we can state that, under the considered irradiation conditions, the impurity concentration and the dislocation density have no significant influence on the deuterium capture and accumulation in tungsten. The D accumulation at depths of 20 nm or

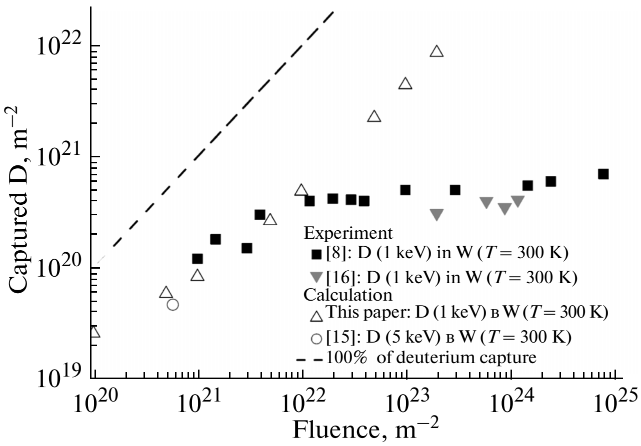

Fig. 3. Comparison between the results of calculating the concentration of deuterium retained in tungsten for different fluences and the published experimental data.

more is mainly due to the capture of D at material grain boundaries.

Comparison of the Calculated Results with the Experimental Data

Figure 3 shows the comparison of the calculated results with the experimental data [8, 15, 16]. It can be seen that the model shows good agreement with the experimental data for low fluences (10^{22} m^{-2} or less). However, for fluences exceeding 10^{23} m^{-2}, the effect of captured-deuterium saturation was observed in the experiments [8, 9]. Moreover, it can be seen from this figure that the results in [16] (corresponding to implantation in the subthreshold mode) also satisfy this tendency. The saturation effect was not manifested in the performed calculations, and the amount of captured deuterium continued to grow with increasing fluence. This distinction can be related to the absence of the inclusion of mechanisms of additional-trap formation leading to an increase in D under irradiation in the subthreshold mode (at room temperature) within the framework of the considered model. The authors of [10] established that the blister formation begins at a threshold fluence of ~10^{23} m^{-2}, which coincides with the onset of D concentration saturation. This fact can indicate that the bubble formation prevents deuterium from penetrating into the material, decreasing the effectiveness of deuterium capture and accumulation. In addition, the output of such bubbles on the surface and the blister formation decrease the amount of retained deuterium. We can assume that the saturation is related to the establishment of equilibrium between the arrival of "new" deuterium under irradiation and its departure on the surface because of blister formation. Thus, to improve the agreement between the model and the experimental data in the range of high fluences, it is necessary to introduce new mechanisms for deuterium bubble nucleation and growth into the model. The capture of D atoms at dislocations with subsequent deuterium migration along the dislocation lines leading to the formation of immovable clusters can serve as a bubble-formation mechanism. The subsequent growth of such clusters can lead to detachment of the bubble from the dislocation. Then the growth of such clusters (potential blisters) can occur in the subthreshold implantation mode because of the effect of deuterium supersaturation in the near-surface region [20], deuterium capture at stable clusters with the formation of interstitial sites and interstitial dislocation loops [21].

CONCLUSIONS

In this paper, using computer simulation within the framework of kinetic diffusion theory, we have studied the process of deuterium capture and accumulation in tungsten in the mode of subthreshold irradiation (i.e., for a low effectiveness of the processes of primary defect formation). We considered the influence of the dislocation density and the impurity concentration on the process of D accumulation in W. We compared our results with the existing experimental data. We established that (i) the change in the initial concentration of primary defects affects D capture only in the near-surface region, while accumulation in the material depth is independent of the concentration of primary defects; (ii) under the considered irradiation conditions, the change in the dislocation density and the impurity concentration does not affect deuterium accumulation and retention in tungsten; (iii) the calculated results agree well with the experimental data for fluences of 10^{23} m^{-2} or less; and (iv) for fluences of 10^{23} m^{-2} or more, the calculated results predict an increase in the amount of deuterium accumulated in the material, which does not correspond to the experimental data demonstrating the effect of accumulated deuterium saturation.

Analysis of the results indicates that the model used must be supplemented with alternative mechanisms for deuterium bubble formation and growth. The primary interaction of deuterium with dislocations and small-angle polycrystal grain boundaries with subsequent migration along the dislocation lines leading to cluster formation must be regarded as possible mechanisms. A further study of the indicated processes within the framework of atomistic simulation (using methods of ab initio and classical molecular dynamics) is planned in order to perform correct parameterization and improvement of the kinetic model.

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