Hydrogen interaction with point defects in tungsten

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First-principles calculations were used in determining the binding and trapping properties of hydrogen to point defects in tungsten. Hydrogen zero-point vibrations were taken into account. It was concluded that the monovacancy can hold up to five hydrogen atoms at room temperature. The hydrogen was found to distort the self-interstitial atom configuration geometry. The interaction of hydrogen with the transmutation reaction impurities Re and Os were studied. It was found that the substitutional Re and Os have a negligible effect on the hydrogen trapping whereas the interstitial Os may increase the hydrogen inventory in tungsten.

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I. INTRODUCTION

Tungsten (W) has been chosen to be used as the divertor plate material in the next step fusion device ITER.[1,2] The divertor region must withstand high heat and bombardment by particles escaping the plasma. The benefits of W are its low sputtering yield and low tritium retention. Hydrogen has high mobility in W (Ref. 3) but easily congregates in spacious defects with large surface areas, such as grain boundaries, dislocations, and voids. Point defects such as monovacancies (V_1), self-interstitial atoms (SIA) and other impurity atoms can also act as hydrogen trapping defects.

In this work, the hydrogen trapping properties to W monovacancy and SIA are studied using the first-principles calculations based on density-functional theory (DFT). Since the hydrogen atom is a light-mass particle and therefore has a high vibrational energy compared to the relatively slowly moving heavy metal atoms, the quantum-mechanical vibration effects cannot be neglected. Therefore, the hydrogen binding and trapping energies were obtained by taking into account the zero-point energies (ZPEs). In the fusion device conditions impurities such as rhenium (Re) and osmium (Os) are formed in bulk W due to the high flux of fusion reaction neutrons leading to the transmutation of a W atom into Re and further into Os. Results for the trapping energies of hydrogen to a Re and Os impurity atom in W are presented.

Extensive reviews on hydrogen trapping mechanisms in metals can be found in the literature.[4–6] Experimental work has shown that several trapping sites for H with unequal energies are either present in W naturally or initiated with implantations. Various thermodesorption spectrometry (TDS) studies above room temperature (RT) have revealed hydrogen trapping in W defects with release temperatures ranging from 400 to 1000 K.[7–14] Trapped hydrogen concentrations in W have been intensively measured by ion-beam analysis methods.[12,13,15–19] The perturbed angular correlation (PAC) technique has been used to determine the number and energetics of trapped H in a W vacancy.[20] Results on He trapping in W vacancy obtained by PAC and TDS are in good agreement with each other.[21]

II. COMPUTATIONAL DETAILS

The DFT calculations were performed with the Vienna *ab initio* simulation package (VASP).[22–24] The electronic ground state of the studied system was calculated using the projector-augmented wave[25,26] potentials as provided in VASP. For the volumetric and ionic relaxation, the conjugate gradient algorithm was used and the energy cutoff was 450 eV. The electron exchange correlation was described with generalized gradient approximation using Perdew-Burke-Ernzerhof functionals.[27,28] Six outermost electrons of the W atom were used as valence electrons with $\sigma=0.15$ eV and the partial occupancies were integrated with the Methfessel and Paxton method[29] of the first order. The charge density was represented on a real-space grid of 0.035 Å. A $3\times3\times3$ k-point mesh was sampled with Monkhorst and Pack scheme.[30] A supercell with 128 ± 1 W atoms was used for describing the properties of the point defect. The ZPE calculations were performed allowing harmonic vibrations only for the H atom.

III. THEORY

The binding energy of the Nth H atom to a point defect was calculated with

$$E_b(N) = [E(N-1) + E_{\mathrm{sol}}] - [E(N) + E_0], \qquad (1)$$

where $E(N)$ refers to the total energy of a point defect system with N hydrogen atoms. E_{sol} is the total energy with a H atom on the solute site and E_0 is the reference energy of bulk W. If the binding energy calculated with Eq. (1) is positive, the H-point defect system is more stable than the system with H separated from it. To obtain reliable binding energy results, the H atom should not be located in the vicinity of the defect after detrapping. Equation (1) takes into account this condition by providing a possibility to consider detrapped H by placing it to a solute site.

The quantum-mechanical approximation of the transition state theory[31,32] for reaction rates yields to an activation energy, which depends on the difference in the particle's potential energy on the ground state and on the activated state and on the difference of the corresponding ZPEs.[33] In Eq. (1), the energy of trapped H is compared to the energy of the detrapped H on the solute site, i.e., the corresponding ZPE-corrected binding energy yields $E_b' = E_b + \Delta\mathrm{ZPE}$.

The trapping energy is usually approximated as the binding energy summed with the migration energy of the fastest

TABLE I. Comparison of the results of DFT calculations with experiments: atomic volume Ω (Å^3), vacancy (v), and interstitial (i) formation energy $E_f^{v,i}$ (eV), migration energy $E_m^{v,i}$ (eV), formation volume $\Omega_f^{v,i}$ in units of atomic volume, binding energy E_b (eV), ZPE-corrected binding energy E_b' (eV), trapping energy E_{trap} (eV), and ZPE-corrected trapping energy E_{trap}' (eV) of the Nth H atom.

		DFT	
	Expt.	Other	Present work
bcc W			
Ω	15.87		15.96
E_f^v	3.68 ± 0.2 [a]	3.56[b]	3.34
E_m^v	1.78 ± 0.1 [a]	1.78[b]	1.71
Ω_f^v		0.62[c]	0.62
$E_f^i \langle 111 \rangle$	9.06 ± 0.63 [d]	9.55,[b] 9.82[e]	9.86
$E_m^i \langle 111 \rangle$			0.005
Ω_f^i			0.6

Vacancy

			Present work			
N	E_{trap} [f]	E_b [g]	E_b	E_b'	E_{trap}	E_{trap}'
1	1.55	1.22	1.28	1.43	1.48	1.60
2	1.38	1.17	1.25	1.41	1.45	1.57
3	<1.1	1.04	1.11	1.22	1.32	1.39
4		1.01	1.00	1.11	1.21	1.28
5		0.92	0.91	1.00	1.12	1.17
6		0.27	0.32	0.47	0.53	0.64

[a]Reference 34.
[b]Reference 35.
[c]Reference 44.
[d]Reference 45, E_f^i determined from the SIAs emerging on the sample surface.
[e]Reference 46.
[f]Reference 20, experiments done on $\text{In}V_2\text{H}_N$ systems.
[g]Reference 36.

particle, i.e., $E_{\text{trap}}=E_b+E_m$. The ZPE-corrected trapping energy yields

$$E_{\text{trap}}' = E_b + E_m + \Delta\text{ZPE}, \tag{2}$$

where ΔZPE is the ZPE difference between the trapped H and the detrapped H on the migration barrier.

For vacancy-H detrapping, the E_m for H was taken from the authors' previous work on hydrogen diffusion in W. Also the ZPE of H on the solute site (0.265 eV) and on the migration barrier (0.225 eV), needed for calculating the E_b' and E_{trap}', respectively, were obtained from the corresponding H vibrational frequencies.[3]

IV. RESULTS AND DISCUSSION

A. Hydrogen-monovacancy dissociation

To obtain accurate trapping energetics, the properties of the W point defects, i.e., the formation and migration energies, were first validated. The calculated DFT results compared with experiments and other DFT calculations are presented in Table I. The calculated bcc lattice constant of 3.172 Å agrees well with the experimental value of 3.165 Å. Our results for the vacancy formation and migration energies agree with the experimental results[34] and with other DFT calculations.[35]

According to our calculations the lowest energy site for H in a W monovacancy is the distorted octahedral site (O) (Fig. 1). There the H atom is bound to its nearest W atom, which is located outside the monovacancy. Secondary bondings are with the W atoms at the boundaries of the monovacancy. Due to the strong H-nearest-neighbor W atom bonding, two H atoms do not form a H_2 molecule in the monovacancy but stay separated from each other at the opposing distorted O sites (Fig. 1). This arrangement corresponds to the ground states of H. The energetically most favorable positions for additional H atoms were found to be at the O sites forming triangle, tetrahedron, square pyramid, and square bipyramid for 3, 4, 5, and 6 H atoms, respectively (Fig. 2). The obtained ZPEs in the vacancy were 0.112, 0.106, 0.151, 0.161, 0.172, and 0.117 eV per H atom for $N=1-6$, respectively.

The results of the binding and trapping energies for H in the W monovacancy are presented in Table I. The E_b values agree well with the theoretical values recently obtained by

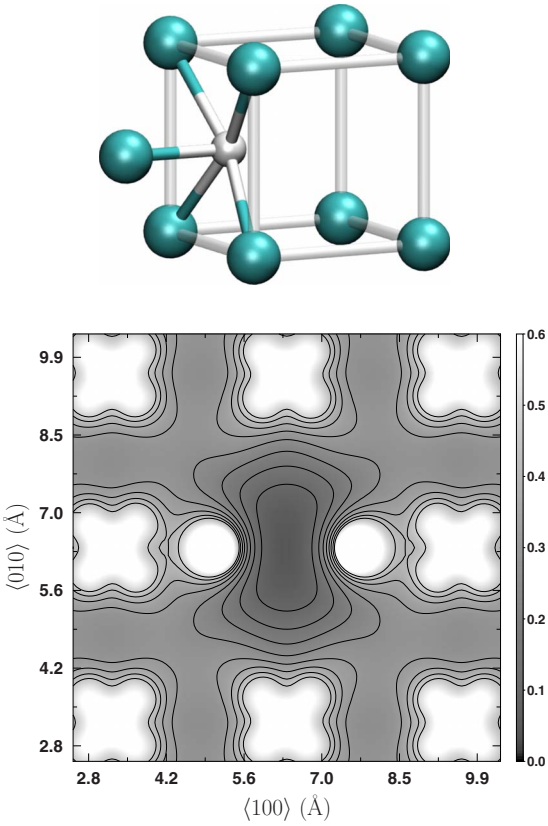

FIG. 1. (Color online) Top: hydrogen atom in its ground state at the distorted octahedral site in a W monovacancy. Hydrogen bonds to its nearest neighbor in the vicinity of the vacancy and to the four second-nearest neighbors surrounding the vacancy. Bottom: The charge densities of two hydrogen atoms at their lowest energy states bonding to their nearest-neighboring W atoms viewed on the (001) plane.

Becquart and Domain.[36] It can be seen from Table I that the binding energies for 1 and 2 H atoms in the monovacancy are almost identical, which can be explained by the H atoms coupling to the surrounding W atoms (Fig. 1). Results with same tendency were obtained in computational studies[37] and experiments performed for hydrogen in a monovacancy in other metallic matrices (fcc: Pd, Cu, Ni and bcc: Mo, Ta, Fe).[38–43] According to the reported data, 1 and 2 H atoms are trapped with identical energies, whereas ensuing H atoms are bound with lower energies.

In the work by Fransens *et al.*,[20] the H population and detrapping in W vacancies were measured by PAC (experimental E_{trap} values in Table I). There is an excellent agreement for the first trapping energy with PAC and our DFT calculated E'_{trap} result. We propose that the discrepancy for the other energies is due to the fact that Fransens's E_{trap} for the first H atom actually comprises the trapping energies for both the first and the second H atoms. This means, that 1 and 2 H in W monovacancy are trapped with equal energies as described above for other metals as well. Consequently, Fransens's second E_{trap} is the trapping energy for the third (and possibly fourth) H atom in the vacancy, which is in agreement with the present DFT result.

To compare the DFT trapping energies with the actual temperatures needed for H to detrap, the equation $E'_{\mathrm{trap}}/kT_m^2 = \nu/\beta \exp(-E'_{\mathrm{trap}}/kT_m)$ can be used.[47] ν is the particle's attempt frequency to detrap, β is the linear heating rate of the sample, and T_m is the temperature with the maximum detrapping rate. The ν value for H in various V_1H_N systems was approximated as a mean value of the DFT calculated H vibrational modes. The obtained values varied from 17 to 38 THz for V_1H_{1-6}, respectively. According to the E'_{trap} data presented in Table I and the corresponding values of ν, a heating rate of 10 K/min results in the maximum release of the sixth hydrogen atom at 225 K (for comparison, a heating rate of 10 K/s yields to 252 K). For the fifth hydrogen atom the corresponding E'_{trap} and ν yield T_m=406 K for β =10 K/min. This leads to the conclusion that the W monovacancy can be occupied with maximum of five hydrogen atoms at RT. Using the same β, the remaining H detrap from W monovacancy at 443 K, 482 K, 549 K, and 560 K, respectively. At higher temperatures, the empty W monovacancies start to diffuse with E_m^v=1.7 eV. This is consistent with positron annihilation studies, whereby the W monovacancies diffuse at 600–750 K forming clusters with four to ten vacancies.[7,8]

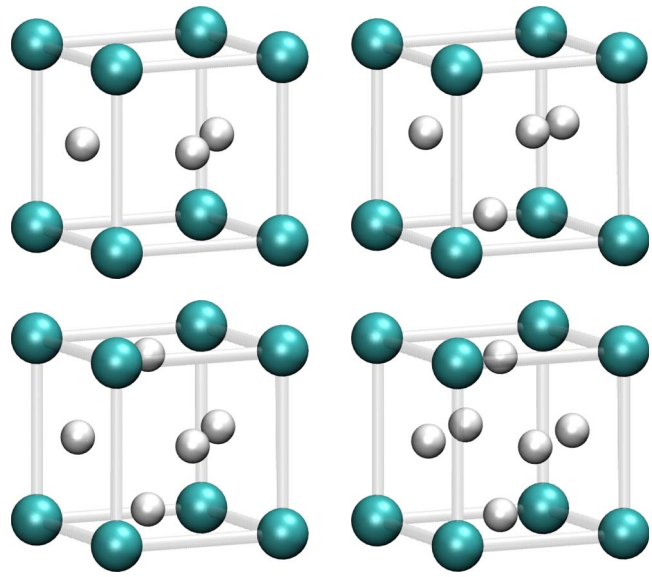

FIG. 2. (Color online) Geometries for the lowest-energy sites of three to six hydrogen atoms in a W monovacancy.

B. Hydrogen bonding to W self-interstitial and Re and Os impurity

The ⟨111⟩ SIA geometry has been deduced to give the lowest energy for the SIA configuration in the nonmagnetic transition-metal group 6B.[35] Our ⟨111⟩ SIA crowdion formation energy for W agrees with the other DFT calculations[35,46] and with recent experiments.[45] Since the ⟨111⟩ SIA is a quasiparticle extending over at least three displaced W atoms in the forward and backward directions, the ⟨111⟩ SIA migration barrier was calculated with a larger 250+1 W atom supercell. Large number of experimental results on SIA-related recovery in bulk W can be found in the literature.[48–55] Various results for activation energies, i.e., temperatures for W SIA migration have been reported, what indicate the com-

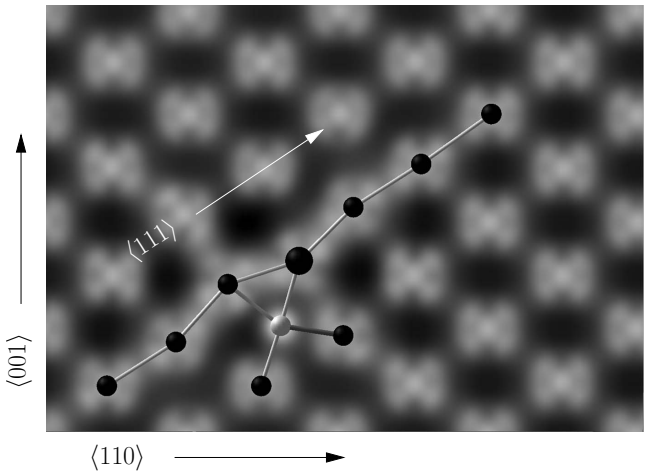

FIG. 3. The distortion of the ⟨111⟩ SIA produced by the H atom (light colored sphere) in the presence of the W adatom (larger dark sphere). The charge densities are visualized on the background.

plex nature of the SIA energetics. Dausinger and Schultz[52] annealed irradiated W samples at temperatures $T_a > 4.5$ K and reported W recovery at 24 K with corresponding SIA long-range migration energy of 0.054 eV. Recovery temperatures 10, 14, 30, and 53 K, corresponding to activation energies of 0.016 eV, 0.021 eV, 0.057 eV, and 0.130 eV, respectively, have been reported by Townsend *et al.*[53] for T_a above 4.2 K. Okuda and Mizubayashi[50] have observed W relaxation peaks at 8 and 27 K ($T_a > 4$ K). Our DFT result for the SIA barrier height was $E_m^i \approx 0.005$ eV, which is well below the majority of the experimental results, except the experimental results by Tanimoto *et al.*[55] where mobile SIAs below 1.5 K were observed.

Hydrogen trapping to the ⟨111⟩ SIA was obtained by placing the hydrogen in the ⟨111⟩ plane in the vicinity of the W adatom. The cell size was 128+1 W atoms. After relaxation, the H ground state was found with nearly equal distances of 2.01 Å and 2.02 Å to the SIA and its first nearest neighbor (1NN), respectively. The SIA 1NN was displaced perpendicularly from the ⟨111⟩ direction by 0.42 Å. The H atom's nearest neighbors were found on the adjacent ⟨111⟩ row at distances of 1.89 and 1.91 Å. The distorted SIA geometry is presented in Fig. 3.

It is important to note, that the SIA-H detrapping is dominated by the migration barrier of the SIA since E_m^i is much lower compared to the H migration barrier. Moreover, since E_m^i is vanishing low, it follows that $E_{\text{trap}} \sim E_b$ and $E'_{\text{trap}} \sim E'_b$. For SIA-H the obtained $E'_{\text{trap}} \sim E'_b$ of 0.43 eV (Table II) results in $T_m = 152$ K ($\beta = 10$ K/min), which implies that a SIA does not act as an effective H trapping site near RT. However, the distortion caused by the presence of hydrogen might possibly increase the formation of other defect types, e.g., SIA clusters and SIA loops, that trap hydrogen efficiently. Detrapping of hydrogen from W dislocations at ~450 K has been observed experimentally.[17]

TABLE II. DFT results for H binding and trapping energies (eV) including ZPE corrections. For the Interstitial-H dissociation $E_{\text{trap}} \sim E_b$ and $E'_{\text{trap}} \sim E'_b$ (see text for details).

Substitutional	E_b	E'_b	E_{trap}	E'_{trap}
Re	−0.09	0.01	0.12	0.17
Os	0.02	0.12	0.23	0.32
Interstitial ⟨111⟩	E_b	E'_b	E_{trap}	E'_{trap}
SIA	0.33	0.43	≳0.33	≳0.43
Re	0.42	0.52	≳0.42	≳0.52
Os	0.75	0.85	≳0.75	≳0.85

The mechanical properties of W-Re and W-Re-Os alloys have been recently studied experimentally.[56,57] It has been shown that the enrichment of W by Re and Os can lead to ductilization of the W samples. According to our calculations the effect of the substitutional Re and Os on the hydrogen trapping in W cannot be determined straight forward (Table II). The same issue was demonstrated by the recent experimental studies on deuterium trapping in Re-doped W, which have indicated that the Re atoms do not act as an active trapping site for hydrogen.[58] However, the results in Table II show that interstitial metallic impurities can play a role in the H retention in W. In the presented trapping energies it is presupposed, that the E_m of interstitial Re and Os in W equals with E_m^i for W SIA. As a result, the H trapping energy to interstitial Os (0.85 eV) corresponds to a release temperature of ~300 K as $\beta \sim 10$ K/min.

To summarize, hydrogen trapping properties to W point defects have been investigated using DFT calculations. The trapping energies were calculated taking into account zero-point vibrations of the H atom. As a result, the W monovacancy can act as an H reserve, with no more than five H atoms at RT. The W SIA geometry gets distorted by the presence of H. The interstitial Os was found as a possible H trapping site.

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