



# Hydrogen assisted vacancy formation in tungsten: A first-principles investigation



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## ARTICLE INFO

### Article history:

Received 29 March 2015  
Received in revised form  
27 May 2015  
Accepted 30 May 2015  
Available online 3 June 2015

### Keywords:

Hydrogen  
Vacancy  
Tungsten  
First-principles

## ABSTRACT

The effects of hydrogen induced vacancy formation in tungsten have been investigated with a first-principles method based on the density functional theory. Hydrogen is demonstrated to assist the formation of vacancy and such effect is enhanced with increasing of hydrogen concentration. Using the energy of a single tungsten atom for the bulk as the reference energy, a spontaneous vacancy formation in tungsten is observed when more than two hydrogen atoms are introduced. These results provide a good explanation for creation of super-abundant vacancies in tungsten and can contribute to understand the mechanism of hydrogen bubble formation.

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## 1. Introduction

Tungsten (W), with its good properties such as low sputtering erosion, high thermal conductivity and high melting temperature, is considered to satisfy the basic demands of plasma facing materials (PFMs) in future fusion power plants. However, the problem of hydrogen (H) bubble formation and blistering in W under plasma irradiation remains as a challenging issue, which can degrade mechanical properties of W [1], reduce the lifetime of W as PFMs and influence the plasma stability.

Numerous works have been done aiming at revealing the mechanism underneath the blistering phenomena, which has been considered to be attributed to the vacancy clustering as reviewed by Condon and Schober [1]. In several theoretical studies, it was also found that H bubble formation is closely related to the vacancy formation, which has been tentatively reviewed by Lu et al. [2]. Recently, first-principles calculations suggest that the vacancy in W can act as a trapping site for H, which leads to the H segregation to vacancy and thus the H bubble nucleation [3,4]. The trapping process of H by the vacancy is determined by the “optimal charge density” provided by the vacancy [3], which is also applicable for the H bubble formation in the grain boundary [5]. H firstly saturates the internal surface of the vacancy to form a “screening layer”,

which can screen the interaction between the further trapped H and the surrounding metal atoms, leading to the formation of H<sub>2</sub> molecule at the vacancy center as a result [4]. Moreover, H bubble will form and grow in a cascading way as revealed by Zhou et al. that H solution can induce the anisotropic strain to enhance the H solubility and cause subsequent bubble formation and growth [6]. In addition, a critical H concentration and pressure at certain temperature for the H bubble formation in W in the case of monovacancy was proposed in a recent study [7].

The results above are helpful to understanding the H bubble nucleation and growth process in W with high vacancy concentration. However, it is known that the equilibrium vacancy concentration in W is as low as 10<sup>-4</sup> even at the melting point [8]. Different explanations have been proposed to figure out how abundant vacancies are generated in W. In both experimental and theoretical researches, H has been shown to assist the vacancy formation in different metals such as Ni, Cr, Pd, Al, Mo, Nb, which can be also applied to W [9–13]. It is concluded from experiments that vacancies are produced by the deuterium induced plastic deformation [14] and local super-plasticity [15,16]. In recent theoretical study, Liu et al. showed that the mechanism of vacancy formation is closely related to the formation of certain self-interstitial structures, and H assists the creation of vacancies by determining the configuration of self-interstitial atoms based on molecule dynamics simulations [17]. Middleburgh et al. found that H can promote vacancy population by decreasing the vacancy formation energy according to the mass action equation. Moreover,

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the binding of vacancies associated with H is demonstrated to be favorable, in contrast to that without the association of H. This may lead to the coalescence of vacancies in the H-rich environment [18]. On the other hand, impurities in W are also found to assist the vacancy formation via trapping H around the impurities. For example, it is shown by first-principles calculations that the interstitial oxygen or carbon atom can trap multiple H atoms, which induces the instability of the lattice sites nearby and leading to the formation of vacancy [19].

In this paper, we perform a first-principles simulation to investigate the effects of H induced vacancy formation in W. The energy difference of the initial system without vacancy and the final system with a created vacancy has been compared and the dependency of the vacancy formation energy on the number of H in W was derived to determine the energetically effect of H on vacancy formation. It is believed that these results will play a vital role for further understanding of the mechanism of H bubble formation in W as PFM.

## 2. Computational method

The first-principles calculations are performed using the VASP code based on the density functional theory (DFT). The generalized gradient approximation of Perdew and Wang [20] and projector augmented wave potentials [21] with a plane wave energy cutoff of 350 eV are used. It is found to be sufficient to converge the total energy and geometry of W supercell. During geometry optimization, a bcc-W supercell of 128 atoms is used with the side length of 12.64 Å and the Brillouin zones are sampled with  $3 \times 3 \times 3$  k-points grid according to the Monkhorst-Pack scheme [22], which is sufficient to converge the total energy with an energy convergence of 0.01 eV. The calculated equilibrium lattice constant is 3.17 Å, which is in agreement with the corresponding experimental value of 3.16 Å [23]. During the calculation, all the supercell size, shape and atomic positions are relaxed to equilibrium, and the energy minimization is converged until the forces on all the atoms are less than  $10^{-3}$  eV Å.

The binding energy of  $n$  H atoms in intrinsic W is defined as

$$E_b = nE_{128W+H} - E_{128W+nH} - (n-1)E_{128W} \quad (1)$$

, where  $E_{128W+H}$ ,  $E_{128W+nH}$  and  $E_{128W}$  is the energy of the supercell with 128 W atoms and one interstitial H, the energy of the supercell with 128 W atoms and  $n$  interstitial H, and the energy of supercell with 128 W atoms, respectively.

The formation energy of vacancy is obtained from the following equation

$$E_V^f = E_{127W+nH+V} + E_{1W} - E_{128W+nH} \quad (2)$$

, where  $E_{127W+nH+V}$ ,  $E_{128W+nH}$  and  $E_{1W}$  is the energy of the supercell with 127 W atoms, a vacancy and  $n$  H, the energy of the supercell with 128 W atoms and  $n$  interstitial H and the energy of a single W atom, respectively. Here, the reference energy of  $E_{1W}$  is considered for three different cases (the energy of a lattice W atom in the bulk, a self-interstitial W atom (SIA) and an isolated W atom in the vacuum).

The zero point energy (ZPE) is the energy of vibration of the molecule at temperature of absolute zero ( $T = 0$  K). As a light element, the ZPE of H cannot be neglected [24]. ZPE of H is calculated from the Hessian matrix by allowing only the harmonic vibration for H [25,26]. Therefore, the ZPE of H is taken into account in all the calculations in this article. Generally, the ZPE will not change the relative energy but change the absolute energy values [4,27].

## 3. Results and discussions

### 3.1. Multiple H in intrinsic W

We first examine the most stable site for single H in W and the tetrahedron interstitial site (TIS) with a solution energy of 0.89 eV is found to be the most stable site for single H in W, which is consistent with the previous studies [5,28]. Next, the favorable configurations of multiple H at different TISs in intrinsic W are studied. In each case, for which the number of H is equal to or larger than two, several possible configurations are considered to determine the most stable one with the lowest total energy. The configurations and the corresponding H–H distances are shown in Fig. 1.

The binding energy of H for different H numbers is calculated according to Eq. (1), and the results are presented in Table 1. The H binding energy increases with the increasing number of H in W. This indicates that the interaction of H becomes stronger with the increasing number of H, which is different from the recent calculations [29]. The difference may result from the different stable configurations of multiple H in W. It is extracted that multiple H show a tendency of H accumulation on slight longer distance as shown in Fig. 1. Two H atoms form a H–H pair along the  $\langle 110 \rangle$  direction with a distance of 2.23 Å (Fig. 1a) and a weak binding energy of 0.02 eV, in good agreement with the previous work [30]. Three H atoms form a triangle configuration, and the lengths of three sides of the triangle are 1.97 Å, 2.49 Å and 2.23 Å respectively as shown in Fig. 1b. In principle the binding energy of 3H should be three times of that of 2H (0.02 eV) but in the present case the energy of 3H is observed 0.08 eV, with an energy gain of 0.02 eV. This energy gain may be due to the attractive interaction between multiple H atoms. Four H atoms form a tetrahedral structure, the six side lengths of which are ranging from 1.97 Å to 3.45 Å (Fig. 1c). The binding energy of 4H is six times higher than that of the 2H case with an energy gain of 0.08 eV. This also suggests a multi-H attractive interaction, which is stronger than the 3H case. For the stable hexahedron configuration of 5H, the distances between every two H still range from 1.97 Å to 3.45 Å (Fig. 1d) and the binding energy is ten times higher than that of 2H with an energy gain of 0.07 eV. It is found that in each multiple H case, the distance between each two H atoms is as close to 2.23 Å as possible, which is the optimal distance of the H–H pair. This suggests that H exhibits attractive interaction with each other when multiple H simultaneously stay in the intrinsic W, leading to energy gains as compared with the 2H case.

To further analyze the interaction between H and W atoms and the bonding character between them, the local density of states (LDOS) of  $s$  orbital of H and  $s$  and  $d$  orbitals of the nearest neighboring W are investigated. Fig. 2 shows the LDOS of  $s$  orbital for H and  $s$  and  $d$  orbitals for the nearest W from the multiple H atoms. The LDOS of  $s$  and  $d$  orbitals of pure W atom without H are presented in Fig. 3 for comparison. When H atoms occupy the TIS, the LDOS of the first nearest neighboring W exhibits an obvious variation as compared with the case for intrinsic W. In each case of  $n$  H atoms in W,  $n$  additional peaks appear at the lower energy part of the LDOS for W and  $n$  corresponding peaks with the same energy appear in the LDOS of  $n$  H atoms. This suggests that during H implantation W–H form covalent bonds.

### 3.2. Dependence of vacancy formation energy on the hydrogen-vacancy (H–V) distance

To investigate the effects of H–V distance on vacancy formation, the formation energy of vacancy with different distances from H is calculated. The vacancy formation energy is determined by Eq. (2),

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