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Structure, stability and diffusion of hydrogen in tungsten: A first-principles study

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ABSTRACT

Using a first-principles method, we have investigated structure, stability and diffusion of hydrogen (H) in tungsten (W). We found that single H atom prefers to occupy the tetrahedral interstitial site with the formation energy of ∼−2.45 eV. Two H in the tetrahedral interstitial sites form a pairing cluster along the <1 1 0> directions with the H–H distance of ∼2.22 Å, while the corresponding binding energy is only 0.02 eV, indicating a very weak attractive interaction. This suggests that H itself is not capable of trapping other H atoms to form a H_2 molecule. The kinetics of H in intrinsic W is discussed, and the diffusion barrier of H that jumps between the tetrahedral interstitials is calculated to be 0.20 eV.

1. Introduction

Tungsten (W) and W alloys are the most promising candidates for plasma facing material (PFM) in Tokamak because of their good thermal properties and low sputtering erosion [1]. However, as a PFM, W will be exposed to extremely high fluxes of hydrogen (H) isotope ions. It must not only withstand radiation damage, but also keep intrinsic mechanical properties and structural strength. Previous experimental study shows that H isotope causes blistering at the W surface [2]. So far, however, the physical mechanism of H trapping and blistering in W is not well understood. It is still an open question as to how H blistering nucleates during plasma exposure.

First-principles method is one of widely-used computational methods, and plays more and more important role in investigating and predicting the structure and properties of many material systems [3–6]. A recent first-principles study [7] shows that H prefers to occupy the tetrahedral interstitial site in W, and two H atoms interacts with an equivalent distance of 2.2 Å. In combination with the molecular dynamics and kinetic Monte-Carlo methods [7], it is demonstrated that H cannot be self-trapped in W, which explains the different bubble-formation depth of H from He as observed in the experiment. In order to understand the physical mechanism of H trapping in more detail and investigate the kinetics of H in the intrinsic W, in this paper, we have investigated the structure, stability and diffusion of H in W using the first-principles method. Our calculations will provide a useful reference for further exploration of the blistering mechanism of H in W.

2. Computation method

We employ a total-energy method based on density functional theory [8,9] with generalized gradient approximation developed by Perdew and Wang [10] and the projector-augmented-wave potential. We use a kinetic energy cutoff of 350 eV for all calculations. The uniform grids of k-points are sampled by $5 \times 5 \times 5$ for the 54-atom supercell and $3 \times 3 \times 3$ for the 128-atom supercell. The calculations have been carried out by VASP [11,12]. The calculated equilibrium lattice constant is 3.17 Å for a bcc W, in good agreement with the corresponding experimental value of 3.16 Å. The energy relaxation iterates until the forces on all the atoms are less than 10^{-3} eV/Å

3. Results and discussion

3.1. Single H atom in W

The possible sites for single H atom involve both interstitial and substitutional sites. The results of formation energies in Table 1 show that the tetrahedral interstitial site is energetically more favorable for single H, in good agreement with both computational [7] and experimental results [13–16]. For comparison, we also calculated formation energy of single vacancy, which is 3.14 eV for the 54-atom supercell and 3.11 eV for a 128-atom supercell, consistent with the calculated values from Becquart and Domain [17].

Valence charge density distribution reveals the features of the atomic bonds [3]. Fig. 1 illustrates the charge density distribution map of different configurations for the single H in W. W is a typical transition metal element with d electrons localized around the atom. The charge density between the substitutional H and W is shown to be very low Fig. 1(a), implying their weak interaction

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Table 1
Formation energies (eV) for single H atom in different sites in bcc W for different supercell size in reference with the isolated H.

Configuration	54 atoms (eV)	128 atoms (eV)
Substitutional	0.78	0.76
Octahedral	−2.06	−2.07
Tetrahedral	−2.44	−2.45
Vacancy	3.14	3.11

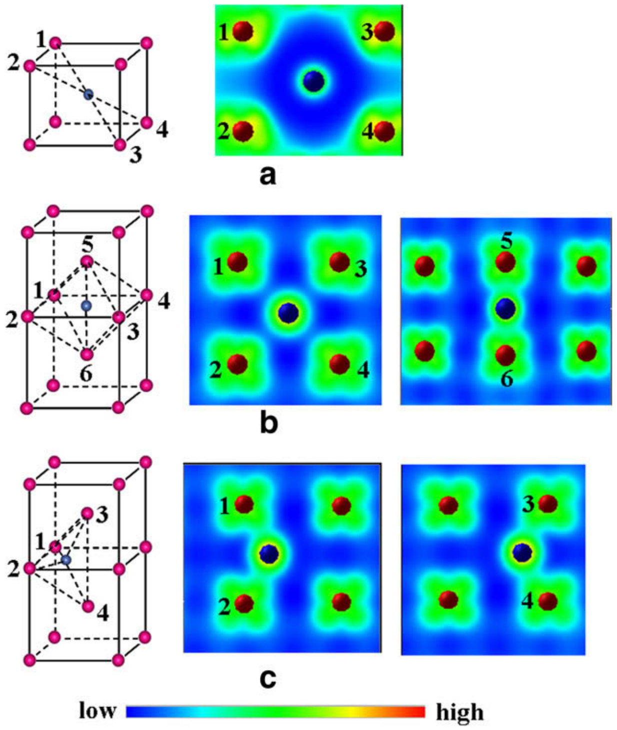

Fig. 1. The valence charge density distribution maps for the cases of (a) substitutional site, (b) octahedral interstitial site, and (c) tetrahedral interstitial site, respectively. The larger red balls represent the W atoms and the smaller grey balls represent H atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and thus the substitution of H in W is unfavorable. This corresponds to the higher formation energy of substitutional H in W. For the octahedral case Fig. 1(b), the charge density is higher between H and W only for two 1NN W atoms with shorter W–H bond length, suggesting the formation of two stronger bonds containing covalent components, but all other four W–H bonds are weak. Two covalent-like W–H bonds gives rise to negative formation energies. The tetrahedral interstitial H is shown to form directional bonds with all of four equivalent 1NN W atoms Fig. 1(c), making the formation energy of the tetrahedral case lowest. Correspondingly, the tetrahedral interstitial H in W is energetically most favorable as compared with the octahedral interstitial and substitutional cases.

3.2. Double H atoms in W

We next investigate the interaction of double H atoms in W, in order to understand if H atom can be self-trapped in W or forms a H_2 molecule directly. As obtained above, the tetrahedral interstitial site is most stable for single H atom. Here, we thus insert two H atoms at different tetrahedral interstitial sites to investigate H–H interaction. Fig. 2 shows ten different sites of the second interstitial H atoms in W. We calculate the energies of W–H system containing 54 W and two H atoms as a function of the H–H atomic distance for the different configurations. The initial and final distance between two H atoms and the corresponding binding energies are given in Table 2.

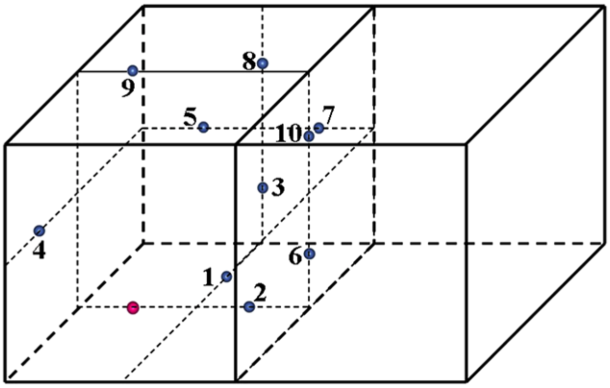

Fig. 2. Different configurations for two tetrahedral interstitial H atoms in W. The red ball (without number) represents the first H atom at a tetrahedral interstitial site, while the grey balls (with number) represent the introduced other H atom, which changes from site 1 to 10 at the different tetrahedral interstitial sites. For clarity, W atoms are not shown in the figure. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The distance between two H atoms increases in the configurations 1–3, suggesting a repulsive interaction when H is close to each other. Configuration 1 is the most typical, the final distance of which increases by ~37% (1.53 Å) as compared the initial distance of 1.12 Å.

The binding energy E_b between H atoms is defined as

$$E_b = 2E_{1H} - E_{2H} - E_{ref} \quad (1)$$

where E_{1H} and E_{2H} are the energy of the supercell with one tetrahedral interstitial H atom only and two H atoms, respectively, while E_{ref} is the energy of the supercell without H atoms. Here, negative binding energy indicates repulsion between H atoms, while positive indicates attraction.

As shown in Fig. 3, it is clear that two H atoms can not bind with each other due to the strongly negative binding energy (~−0.44 eV) with the final distance of 1.53 Å. The binding energy decreases with increasing H–H distance, and moves towards positive at a distance of ~2.22 Å. Further distance increase leads to negative binding energy again. The results suggest that two H atoms in W are basically repulsive, but can be attractive only around a small distance range, i.e. around ~2.22 Å. The two H atoms form a pair cluster along the <1 1 0> directions. However, the binding energy of 0.02 eV implies a very weak attractive interaction between H atoms in W. The optimum distance of 2.22 Å is consistent with previous calculated result [7].

According to the binding energy results, the self-trapping of H in W is almost impossible due to large repulsive energy between

Table 2
The initial and final distance (before and after the relaxation, Å) between two H atoms and the corresponding binding energies (eV).

Site	Initial distance	Final distance	Binding energy
1	1.12	1.53	−0.4456
2	1.58	1.79	−0.0931
3	1.77	1.99	−0.0140
4	1.94	1.98	−0.0305
5	2.24	2.22	0.0201
6	2.51	2.48	0.0141
7	2.75	2.75	−0.0138
8	2.97	2.98	−0.0346
9	3.17	3.21	−0.0347
10	3.36	3.46	−0.0529

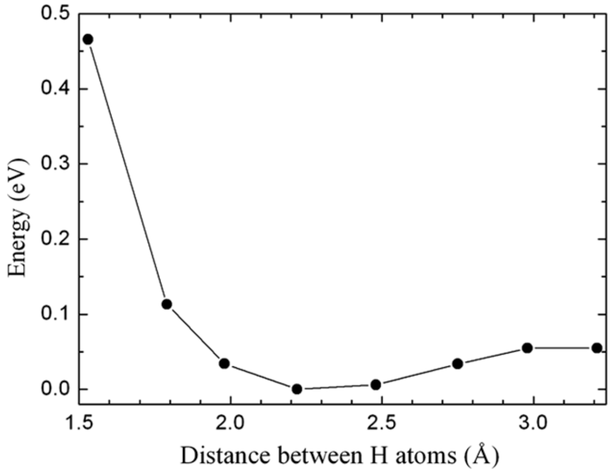

Fig. 3. The energy of W containing two H atoms as a function of the H–H distance.

the H atoms. The equilibrium distance of double H atoms (2.22 Å) is much larger than that in a H_2 molecule (0.75 Å according to the present calculation). Consequently, H_2 molecule can not be formed at an interstitial site in ideal bulk W. This differs much from behavior of helium (He) in W. Two He atoms tend to be close to each other, and the equilibrium distance is about 1.5–1.7 Å, much smaller than that in vacuum (2.97 Å) [18]. Further, the binding energy is as large as ~1 eV [7,19] to form He bubble, much higher that that of two H in W (0.02 eV). Thus, H cannot trap itself, and it is quite difficult to form blister in ideal bulk W. Other defects should be taken into account.

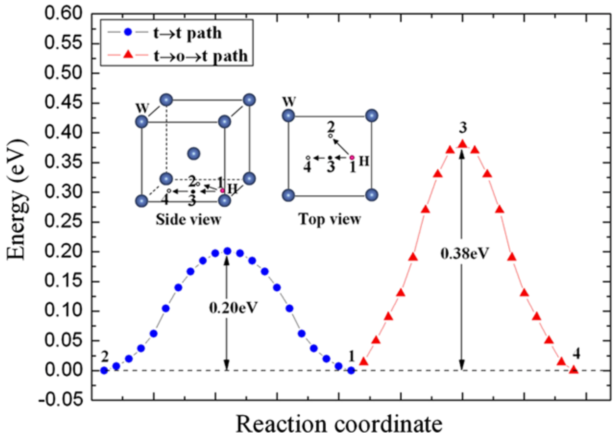

Fig. 4. Diffusion energy profile and the corresponding diffusion paths for H in W. Sites 1, 2 and 4 represent the tetrahedral interstitial sites, respectively. Site 3 is the octahedral interstitial site. The arrows show the corresponding diffusion paths. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3. Diffusion of H in W

Finally, we determine the diffusion energy barrier of H in W. We use a drag method at a fixed volume and constrain the atomic positions to relax in a hyperplane perpendicular to the vector from the initial to finial positions [20]. The diffusion barrier is calculated to be 0.20 eV via the optimal diffusion path between the tetrahedral interstitial sites ($t \rightarrow t$ path), as shown in Fig. 4. If H atom migrates through an octahedral interstitial site ($t \rightarrow o \rightarrow t$ path), a higher diffusion barrier of 0.38 eV is obtained (Fig. 4). Frauenfelder [21] reported the activation energy of 0.39 eV for H diffusion in W, which seems to be close to that of $t \rightarrow o \rightarrow t$ path.

4. Summary

We have studied structure, stability, and diffusion in a W single crystal using a first-principles method. Single H atom prefers to occupy the tetrahedral interstitial site in W with the formation energy of ~−2.45 eV in comparison with the octahedral interstitial and substitutional case. Two H atoms in the tetrahedral interstitial sites form a pairing cluster along the <1 1 0> directions with the H–H equilibrium distance of 2.22 Å, while the corresponding binding energy is only 0.02 eV, indicating a very weak attractive interaction. We suggest that H atom hardly traps each other to form a H_2 molecule in the intrinsic W, and thus the blistering of H cannot occur. Other factors such as defects should be taken into account in order to explore the blistering mechanism.

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