First-principles investigation of diffusion behaviours of H isotopes: From W(110) surface into bulk and in bulk W*

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The diffusion behaviours of hydrogen (H), deuterium (D), and tritium (T) from W(110) surface into bulk and in bulk W are investigated using first-principles calculations combined with simplified models. The diffusion energy barrier is shown to be 1.87 eV from W(110) surface to the subsurface, along with a much reduced barrier of 0.06 eV for the reverse diffusion process. After H enters into the bulk, its diffusion energy barrier with quantum correction is 0.19 eV. In terms of the diffusion theory presented by Wert and Zener, the diffusion pre-exponential factor of H is calculated to be 1.57×10^{-7} $m^2\cdot s^{-1}$, and it is quantitatively in agreement with the experimental value of 4.1×10^{-7} $m^2\cdot s^{-1}$. Subsequently, according to mass dependence ($\sqrt{1/m}$) of H isotope effect, the diffusion pre-exponential factors of D and T are estimated to be 1.11×10^{-7} $m^2\cdot s^{-1}$ and 0.91×10^{-7} $m^2\cdot s^{-1}$, respectively.

Keywords: tungsten (W), hydrogen isotopes, diffusion

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1. Introduction

The interaction between hydrogen (H) and metal is of great scientific and technological interest, especially in the energy-related areas like H storage[1,2] and the nuclear fusion reaction.[3–6] At present, energy shortage is considered to be the most important problem that mankind is facing, and great efforts have been made to develop new kinds of energy resources. Nuclear fusion energy, as a clean and unexhausted energy for future generations, is being developed internationally by the ITER (International Thermonuclear Experimental Reactor) Project, which aims to demonstrate the extended burn of deuterium–tritium (D–T) plasma in fusion reaction. In the ITER project, a large magnetic-constrained thermonuclear fusion device, Tokamak, is being constructed. Meanwhile, metal is being used as an important candidate for plasma facing material (PFM) in the fusion reactor. The PFM has to be exposed to extremely high fluxes of H isotope ions.[7–9] The retention control of H isotopes D and T is a major subject for the PFM in the fusion reactor. Accordingly, understanding the interaction between H isotopes and a metal PFM is helpful for designing and preparing the PFM in the fusion reactor.

Among the most promising PFMs, tungsten (W) and W-alloys[10–12] are considered because of their low sputtering erosion and good thermal properties such as high thermal conductivity and high melting temperature. Interstitial H diffusion in W is an important issue because H atoms via diffusion can be trapped by some extended defects such as vacancy and grain boundary that are responsible for H accumulation, bubble formation, and blistering. This is a common cause for degrading mechanical properties of the PFM.[7] Many recent efforts have been devoted to understanding the interaction of H isotopes with W.[3–8,13,14] The main migrating process is that the H atom is absorbed first on the W surface, and then it will diffuse into the subsurface layer. The next issue is how H migrates in bulk W. Above room temperature (T), earlier experimental studies on H diffusion in W have been conducted by many researchers such as Moore and Unterwald[15] (1200 K< T <2500 K), Ryabchikov[16] (1900 K< T <2400 K),

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Frauenfelder[17] (1100 K< T < 2400 K), Zakharov *et al.*[18] (900 K< T < 1100 K), and Benamati *et al.*[19] (850 K< T < 900 K). The diffusivity values from these studies mentioned above were indirectly examined by investigating H concentration based on degassing and permeation into W. In the earlier studies, Moore and Unterwald[15] and Ryabchikov[16] respectively gave two deviating diffusion coefficients $D = 7.3 \times 10^{-8} \exp(-1.80\,eV/kT)$ $\mathrm{m^2{\cdot}s^{-1}}$ and $D = 8.1 \times 10^{-6} \exp(-0.86\,eV/kT)$ $\mathrm{m^2{\cdot}s^{-1}}$. This is because there were strong deviations for the H concentrations in their calculations. Recently, the H diffusion coefficient widely used in W is $D = 4.1 \times 10^{-7} \exp(-0.39\,eV/kT)$ $\mathrm{m^2{\cdot}s^{-1}}$ by Frauenfelder. However, the diffusion energy barrier 0.39 eV is not an experimental value, and to our knowledge it is just a tentative (guessed) value. Furthermore, Macrander and Seidman,[20] and Panitz[21] respectively presented H diffusion properties in defect-free W by the direct measurement of H concentration at low room temperature. Here, a question should be raised because H is generally immobile at the interstitial site at lower temperatures. Thus, H must be treated nonclassically in the lower temperature case, i.e., it is necessary for quantum corrections to the diffusion energy barrier to be taken into account for the light element H. This point was not considered in their investigations.

In spite of many years of research, many fundamental properties of H diffusion behaviors in W remain poorly understood. For instance the diffusion and permeation of the H isotope into a fusion reactor are great concerns of safety, especially for the diffusion of T in the W system. Furthermore, the diffusion coefficients for H, D, and, T in W as well as other metals are different due to their mass differences,[22] leading to different diffusivities. In order to understand these behaviours of H, D, and T in W, in this paper we first examine how H diffuses into the bulk W, then investigate the diffusion properties of H, D, and T in bulk W using a first-principles method. The diffusion coefficients of H, D, and T are obtained according to the first-principles calculations combined with simplified models.

2. Computational method

Our first-principles calculation is performed using the Vienna *ab-initio* Simulation Package (VASP) code[23,24] based on the density functional theory. We use the generalized gradient approximation of Perdew and Wang[25] and projector augmented wave (PAW) potentials.[26] Experimental research data are easily obtained for W. Two different lattice structures exist for W, i.e., bcc structure which is ground state, and fcc structure which is metastable and transforms back to the lowest energy bcc ground state structure at a transformation temperature higher than 600 K.[27] Thus, we choose bcc W as the present research object. A plane wave energy cutoff of 350 eV is found to be sufficient to converge the total energy and geometry of the bcc W supercell. The Brillouin zone is sampled in terms of the Monkhorst–Pack scheme[28] during the geometry optimization for bcc W supercell. The calculated equilibrium lattice constant is 3.17 Å (1 Å=0.1 nm), which is in good agreement with a corresponding experimental value of 3.16 Å.[29] This demonstrates the accuracy of the current PAW method. For the study of H diffusion from W(110) surface into the subsurface, we use a periodic supercell containing a seven-layer slab of W and a 13-Å thick vacuum presenting a corresponding surface system. A k-point sampling of 6×6×2 is chosen by the Monkhorst–Pack scheme. As to the H diffusion in bulk W, we find that the 128 atom bulk supercells and 3×3×3 k-points are very well converged in the range of error. During the calculations, the super-cell size, shape, and atomic position are relaxed to equilibrium states, and energy minimization is converged until the forces on all the atoms are less than 10^{-3} $\mathrm{eV{\cdot}\AA^{-1}}$.

In all the calculations, we choose the H chemical potential μ_{H} as the reference energy which ishalf the energy of an H_2 molecule with a value of −3.36 eV according to the present calculation. Further, the zero-point energy (ZPE) of H should not be negligible to study the H-metal system. The ZPE of H can be obtained by summing up the zero-point vibrational energies of H'normal modes, i.e., ZEP = $\sum_\nu h\nu/2$, where ν is a real normal mode frequency. For the H_2 molecule, the ZPE of H is calculated to be ∼ 0.135 eV with a vibrational frequency of 4315 $\mathrm{cm^{-1}}$, which accords reasonably well with the experimental value of 4395 $\mathrm{cm^{-1}}$.[30]

For H migrating from the W(110) surface into the subsurface and further into bulk W, the corresponding diffusion barriers are calculated using the nudged elastic band (NEB) method.[31] In the calculations, the parameters and convergence criteria are kept the same as those in the ground state calculations.

3. Results and discussion

3.1. Diffusing energy landscape of H entering into bulk W

We first examine the energetic stability of H adsorbed on the W(110) surface in all the possible positions. Here, we choose the W(110) surface as a model system, which is partly because it is considered as the lowest-energy surface which is easily obtainable in bcc W as well as in most bcc metals. The energy minimization shows that the H atom prefers to be adsorbed at the quasi-three fold hollow site, which is in good agreement with experimental[32] and theoretical results.[33] As to the stability of H in bulk W, we find that H is more favourable to occupy the tetrahedral interstitial site (T-site) than the octahedral interstitial site (O-site) in previous studies.[3−5] The ZPE of H has an effect only on the absolute values of the solution energy of H at the two interstitial sites in bulk W, but the relative stability of H at the T-site and the O-site remains unchanged.[5]

After establishing the stability of H on the W(110) surface and in bulk W, we examine the preferable site for H at the subsurface. We know that the positions of the nearest-neighbour W atoms around H in the subsurface are basically the same as those for H in bulk W. Thus, just as in bulk W, H should also prefer to occupy the T-site or the O-site in the subsurface. Two kinds of T-sites exist between the surface layer and subsurface layer W atoms for the W(110) surface. For the first kind of T-site, there are three W atoms from the surface layer and one W atom from the subsurface layer, respectively. The H atom can be found to spontaneously relax to the surface quasi-three fold hollow site if it is imbedded into the first kind of T-site. This suggests that this site is not the local energy minimum for H binding. The second kind of T-site consists of one W atom from the surface layer and three W atoms from the subsurface layer, respectively and we find that the second kind of T-site is indeed a local energy minimum for H binding. The possible reason might be that the second kind is away from the surface in comparison with the first kind. Further, we find that there exists only one kind of O-site in the subsurface, and the energy of H at this site is higher than that at the T-site. Apparently, the H atom will occupy the T-site consisting of one surface W atom and three subsurface W atoms.

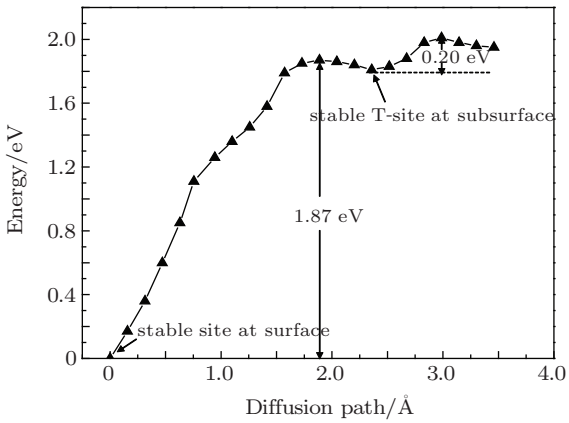


Fig. 1. Variation of diffusion energy with diffusion path for H entering into the subsurface and further bulk W from the W(110) surface.

Now, we address the diffusion process of H from the W(110) surface to the subsurface. Figure 1 shows how H can diffuse into the W(110) subsurface. It is important to note that H atom will overcome an energy barrier of 1.87 eV from the W(110) surface to the subsurface. Apparently, H has to encounter a significant endothermic process, indicating that it is not easy for H to go into the subsurface of the W(110) surface. For further penetration of H into W, the energy barrier becomes 0.20 eV. We believe that this is close to bulk diffusion behaviour of H, which will be addressed in the following section. However, we can see that only a much reduced barrier of 0.06 eV needs to be overcome for the reverse process, i.e., coming back from the subsurface, and further a down-hill "drift" diffusion of H towards the W(110) surface. This indicates that it is very easy for H to escape from the subsurface to surface.

3.2. Diffusion behaviours of H isotopes in bulk W

We now concentrate on the diffusion properties of H isotopes in bulk W. The diffusion properties are quite important for us to understand the behaviour of H in bulk W. On the one hand, the diffusion coefficient, as one of the most fundamental properties in metal, will affect the migration and the retention of H in bulk W. On the other hand, the diffusion coefficient is also an important index to determine the diffusion velocity of H in bulk W, which can help us to quantitatively understand the diffusion properties.

In our previous studies,[3] we only investigated the diffusion activation energy with a value of 0.20 eV us-

ing the drag method.[34] However, the detailed diffusion behaviours such as the diffusion coefficient and ZPE-correction of H were not given. Here we will further account for these questions step by step. As shown in Fig. 2, the preferred diffusion path for H in a bcc metal is jumping from one T-site to the first nearest neighbour (1NN) T-site (T→T path) directly via a mediate transition state between two T-sites in bulk W. We can obtain a diffusion energy barrier (E_a) of 0.22 eV using the NEB method. This value is lower than the value of 0.39 eV obtained by Frauenfelder in a temperature range of 1100 K–2400 K[17] employing mass spectroscopic and ultrahigh vacuum techniques to investigate H diffusion in W. It can be seen that this value is basically consistent with 0.20 eV calculated using the drag method in our previous study. Additionally, we also investigate another possible H diffusion path in which it migrates from one T-site to the 2NN T-site via a mediate transition state O-site (T→O→T path). The corresponding diffusion activation energy for this path is 0.38 eV, which is just the energy difference between the O-site and T-site. Such a T→O→T path should be possible only for the migration of H at the higher temperature because of the high activation energy in comparison with the T→T path.

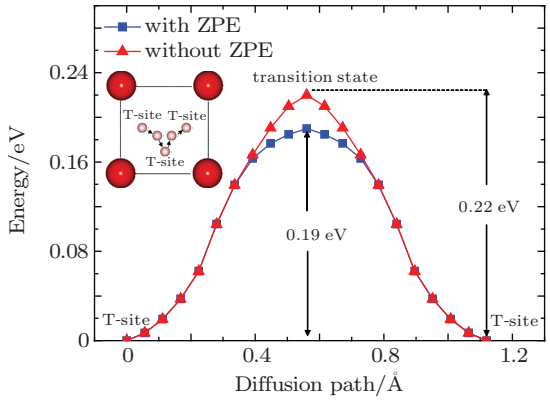


Fig. 2. (colour online) Variations of diffusion energy barrier with diffusion path for H diffusing along the T→T path in bulk W with and without ZPE-corrections.

The diffusion coefficient of an interstitial impurity atom in metal can generally be written as

$$D = D_0 \exp(-E_a/kT), \tag{1}$$

where D_0 and E_a are, respectively, the temperature-independent pre-exponential factor and the diffusion energy barrier of H atom, and T and k are the absolute temperature and the Boltzmann constant, respectively. In terms of the diffusion theory from Wert and Zener,[22] D_0 can be written as $(n/6)(\sqrt{2}a/4)^2\nu$ and $(n/6)(a/4)^2\nu$ respectively, for T→T path and T→O→T path due to bcc structure metal, where n, a, and ν are a geometrical factor for the number of equivalent jump paths ($n = 4$ and 2, respectively, for H jumping along T→T path and T→O→T path), the lattice constant, and the vibration frequency, respectively. The ν can be approximately expressed as $\nu = \sqrt{2E_a/ma^2}$, where m is the mass of the H atom. Using the calculated H activation energy barriers of 0.22 eV and 0.38 eV, we can thus obtain the vibration frequencies $\nu = 2.01\times10^{13}$ Hz and $\nu = 2.64\times10^{13}$ Hz, respectively. Further substituting the two values into the diffusion coefficient equation, the diffusion coefficients of H in bulk W are $D = 1.69\times10^{-7}\exp(-0.22\ eV/kT)$ and $D = 0.55\times10^{-7}\exp(-0.38\ eV/kT)$ for T→T path and T→O→T path, respectively.

Quantum corrections for the diffusion energy barrier are necessarily taken into account for the light element H, i.e., the ZPE of H should be not neglected for the H–W system. Correspondingly, the diffusion coefficient is written as

$$D = D_0' \exp[-(E_a + \Delta\mathrm{ZPE})/kT], \tag{2}$$

where D_0' will also become

$$\frac{n}{6}\left(\frac{\sqrt{2}}{4}a\right)^2\sqrt{2(E_a + \Delta\mathrm{ZPE})/ma^2}$$

for T→T path (here we only analyse the T→T path because H prefers to migrate along this path). The ΔZPE is the difference between the transition state configuration and T-site in ZPE, and its value is −0.03 eV. The exponential term E_a + ΔZPE can be treated as a ZPE-corrected diffusion activation energy barrier with a value of 0.19 eV. This demonstrates that the ZPE-correction can reduce the H activation energy barrier. Our calculation predicts that the diffusion coefficient of H in bulk W with ZPE-correction is $D = 1.57\times10^{-7}\exp(-0.19\ eV/kT)$ $m^2{\cdot}s^{-1}$. In previous experimental studies, Frauenfelder employed mass spectroscopy and ultrahigh vacuum techniques to investigate H diffusion in W in a temperature range of 1100 K–2400 K.[17] The diffusion pre-exponential factor was obtained to be 4.1×10^{-7} $m^2{\cdot}s^{-1}$. Our result (1.57×10^{-7} $m^2{\cdot}s^{-1}$) is quantitatively in agreement with experimental results. Figure 3 shows the diffusion coefficients of H isotopes versus reciprocal temperature with ZPE-correction.

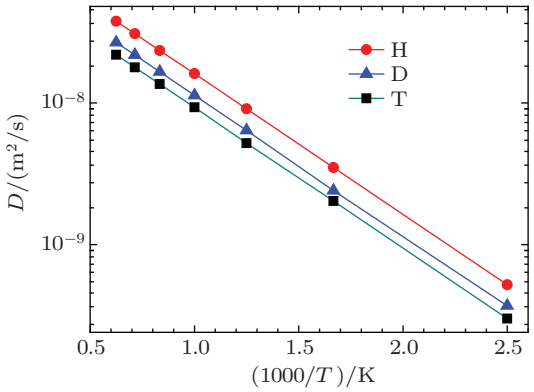


Fig. 3. (colour online) Calculated diffusion coefficients of H, D, and T in bulk W versus reciprocal temperature.

Further, H, D, and T have different masses, which leads to their different diffusion behaviours. According to the relation between diffusion pre-exponential factor and mass, we can see that isotope effect will become $\sqrt{1/m}$ dependent. Based on such a mass dependence, the pre-exponential factors of D and T are calculated to be 111×10^{-7} $\mathrm{m}^2\cdot\mathrm{s}^{-1}$ and 0.91×10^{-7} $\mathrm{m}^2\cdot\mathrm{s}^{-1}$. As plotted in Fig. 3, the diffusion coefficients of D and T are apparently lower than that of H.

Generally, at room temperature, the $h\nu$ is larger than kT (~ 0.026 eV). For the H atom at the T-site in W, $h\nu$ is calculated to be 0.263 eV. This value is much larger than the room-temperature value of 0.026 eV so that the limit of $h\nu \gg kT$ can be applied here. According to Kehr's theory,[35] the diffusion coefficient can be written as

$$D = \frac{n}{6}\left(\frac{\sqrt{2}}{4}a\right)^2 \frac{kT}{h}\exp[-(E_\mathrm{b} + \Delta\mathrm{ZPE})/kT]. \quad (3)$$

The expression of diffusion pre-exponential factor will correspondingly become $(n/6)(\sqrt{2}a/4)^2(kT/h)$, which is independent of H isotope mass but dependent on temperature. In many metals, quantum diffusion can be considered as the main mechanism for H at low temperature.[36,37] Several quantum theories have been developed to investigate interstitial diffusion of light atoms in metals in the past few years. For example, the phonon-assisted tunneling theory[35] and small polaron theory[38,39] were applicable for understanding H diffusion behaviours in metals at low temperatures, such as Ta, Nb, and V. Some results have been obtained[36] at low temperatures such as 1 K $\sim$ 10 K. However, up to now, the relevant diffusion data are not available for H in bcc W. This is attributed mainly to the fact that H has an extremely low solubility in W at low temperature. Thus, we can provide a quite useful reference to quantitatively understand the diffusion behaviours of H isotopes in W.

4. Conclusions

From the W(110) surface into bulk and in bulk W the diffusion properties of hydrogen (H), deuterium (D), and tritium (T) are investigated employing a first-principles calculations in combination with simplified models. We find that the H diffusion energy barrier is 1.87 eV from the W(110) surface to the subsurface, and a very low barrier of 0.06 eV for the reverse diffusion process. This indicates that it is very easy for H to diffuse into the W(110) surface from the subsurface. The H energy barrier in bulk with quantum correction is 0.19 eV which is lower than the value of 0.39 eV measured in a temperature range of 1100 K–2400 K using mass spectroscopy and ultrahigh vacuum techniques. In the light of Wert and Zener's diffusion theory, the diffusion pre-exponential factor of H is calculated to be 1.57×10^{-7} $\mathrm{m}^2\cdot\mathrm{s}^{-1}$, which is quantitatively in agreement with the experimental value of 4.1×10^{-7} $\mathrm{m}^2\cdot\mathrm{s}^{-1}$. Subsequently, we also estimate the diffusion pre-exponential factors of D and T, which are 1.11×10^{-7} $\mathrm{m}^2\cdot\mathrm{s}^{-1}$ and 0.91×10^{-7} $\mathrm{m}^2\cdot\mathrm{s}^{-1}$, respectively. We believe that these results can provide a useful reference to understanding the diffusion behaviours of H isotopes in W.

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