



## Regular Article

# High hydrogen retention in the sub-surfaces of tungsten plasma facing materials: A theoretical insight



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## ABSTRACT

A high hydrogen concentration at the sub-surface layers of tungsten plasma facing materials has been previously observed by experiments. We have performed the first-principles calculations to understand this experimental phenomenon. The layer-dependent hydrogen dissolution energies, vacancy formation energies and hydrogen trapping energies are calculated for the W(110) surface. Our results show that hydrogen dissolving into the vacancy-free sub-surfaces is energetically unfavorable. A surface tungsten vacancy is easier to form than in the bulk and has a large trapping effect on hydrogen dissolving. The present work demonstrates the important role of surface vacancies on the hydrogen retention in the tungsten sub-surfaces.

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Tungsten (W), with the high melting point, high thermal conductivity, and high sputtering threshold for light elements, is an important metal material for plasma facing materials (PFMs) in future nuclear fusion devices [1,2]. During the operation of devices, the PFM surfaces will be directly exposed to hydrogen (H) isotope plasma with low energy and high fluxes [3], which can cause surface sputtering and undesired surface blistering [4–6], and degrade the property and performance of W as PFMs, or even threaten the stable operation of the whole device [4,5].

The depth profile of H isotope in W was measured experimentally [7–10]. A high concentration of H isotope ( $\sim 10^2$  higher than the bulk H retention) was observed in the sub-surface regions [8–10]. Such a high H concentration in the sub-surfaces was believed to contribute to the surface blistering in W, which can cause a severe issue for the application of W as PFMs [9,10]. Therefore, it is crucial to understand why H isotope accumulates in the W sub-surface regions. Although it was speculated such a H depth-profile might correlate with the damage defects created by high hydrogen isotope plasma fluxes [10,11], the defect which is responsible for the high H retention in the W sub-surfaces and the H retention mechanism are still intensively investigated.

The first-principles method has been proved to be one of the most accurate methods for calculating the energetics, the structural and electronic properties of solids, and such calculations can provide very useful insight into the H retention in the W sub-surfaces. Theoretical studies have devoted to investigating the H trapping mechanism by the intrinsic vacancy and H bubble formation in the bulk W [12–19]. Ohsawa et al.

[13,14] found a monovacancy in the bulk W can trap at most 12H atoms and also indicated that the V-H<sub>6</sub> complex is the dominant kind of V-H<sub>n</sub> clusters in W. Liu et al. [15] revealed a vacancy trapping mechanism for the H bubble formation in W by providing an isosurface of optimal charge density for H. Zhou et al. [16] found that an anisotropic strain could enhance H solubility, causing the subsequent H bubble formation and growth. Liu et al. [17] proposed a hydrogen-induced vacancy formation mechanism by helping a certain self-interstitial cluster formation in W. The H adsorption behaviors on the W surface were also examined, and the authors predicted that H could be easily adsorbed at the top-surface [20–23]. Johnson et al. [19] and Heinola et al. [24] provided further insight into H dissolution at the first sub-surface layer of the vacancy-free W surface. However, as shown below in this paper, the experimentally measured high H concentration in W sub-surfaces cannot be understood without invoking surface vacancies.

In this Letter, we make a theoretical attempt to understand the high H retention in W sub-surfaces by performing state-of-the-art first-principles calculations in the framework of density-functional theory (DFT) employing the generalized gradient approximation (GGA). The W(110) surface is chosen in the present work because this surface has the lowest surface energy among various surface orientations [25] and it does not reconstruct as the W(100) and W(111) surfaces do. The H dissolution energy is found to be layer-dependent and is a function of H distribution depth for the vacancy-free W(110). Our results show that the H dissolution energies at the vacancy-free W sub-surfaces are positive and higher than that in the bulk. This suggests that it is energetically unfavorable for H to dissolve into the vacancy-free W sub-surfaces. Therefore, without invoking surface defects possibly caused by high H fluxes we fail to explain the observed H depth-profile. The

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formation energies for W vacancies at the surface layers are calculated and the results indicate that a W vacancy is much easier to form at the surface layers than in the bulk. With the presence of surface vacancies, we find that the H dissolution energy at the vacancy-containing W sub-surfaces is significantly reduced. Consequently, by taking into account the trapping effect of surface vacancies, we are able to rationalize why H isotopes are retained in W sub-surfaces.

Our calculations were performed using density functional theory as implemented in the VASP code [26]. We employed projector-augmented wave (PAW) potentials for W and H [27,28], and the GGA-PBE (Perdew-Burke-Ernzerhof) exchange-correlation functional [29]. A slab model was used to mimic the W(110) surface which consists of eleven W atomic layers and a vacuum layer thickness of 13 Å. The slab model constructed with a (3 × 2) surface periodic structure at the theoretical equilibrium lattice constant contains totally 132 W atoms and has dimensions of 9.43 Å, 8.93 Å and 35.39 Å along the [001], [110] and [110] directions, respectively. The surface slab model was tested to be large enough for the examination of H dissolution in W given that the variation of H dissolution energy was <0.01 eV when increasing the vacuum thickness and the slab atomic layers. The energy cutoff for the plane wave basis was set to be 400 eV. The Brillouin zone integration was sampled with the 4 × 4 × 1 *k*-points mesh by the Monkhorst-Pack scheme [30]. The *k*-point spacing for the surface supercell was thus <0.026 (2π/Å), in good agreement with other theoretical works [18–20]. During the structure optimization, only H atom and the W atoms at the top six atomic layers of the slab were allowed to relax until the forces on those atoms were less than 0.01 eV/Å, while the bottom five atomic layers were fixed at the bulk lattice with the theoretical lattice constant.

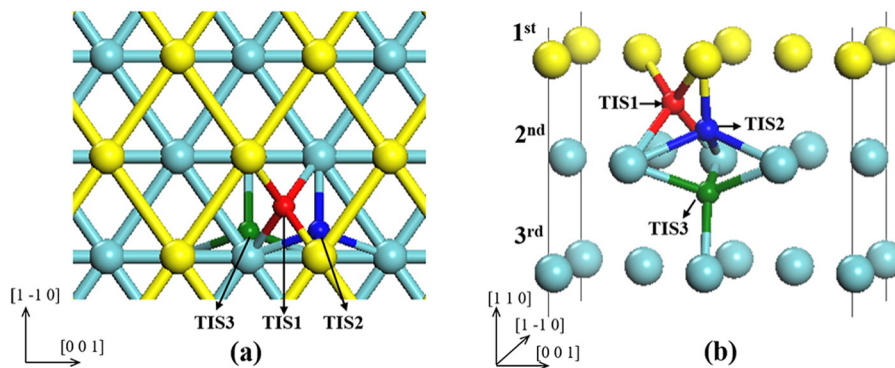
For the convenience of our following discussion, we define a W sub-surface in the present calculations as the region between two adjacent surface layers. For instance, 1sub-surface is the region between the 1st and 2nd layers, and 2sub-surface represents the region between the 2nd and 3rd layers and so on. It is well known that the tetrahedral interstitial site (TIS) is the most stable solution site for H in the bulk W [12–19]. For the sub-surface of W, TIS is also more favorable for H than the octahedral interstitial site (OIS) by ~0.16 eV. Different from the bulk case, there are three kinds of TISs for H to occupy at one W sub-surface, as shown in Fig. 1, named as TIS1 (red sphere), TIS2 (blue sphere) and TIS3 (green sphere), respectively. TIS1 is at the middle of the two layers, at which H respectively bonds with two W atoms of each layer. TIS2 and TIS3 actually corresponds to the two sites at a certain atomic layer with TIS2 located above the atomic layer and TIS3 below the atomic layer. H at TIS2 and TIS3 will bond with three W atoms from this atomic layer and one W from the adjacent atomic layer, as clearly displayed in Fig. 1b.

For each sub-surface, there exist such three sub-TIS sites for H to occupy. We then put H at those TISs in different sub-surfaces one by one, i.e., 1sub-TIS1, 1sub-TIS2, 2sub-TIS3, etc., and calculate the H dissolution energy ( $E_{\text{H}}^{\text{sol}}$ ) using the following equation

$$E_{\text{H}}^{\text{sol}} = E_{\text{Wsurf,H}} + E_{\text{surf-H}}^{\text{zpe}} - E_{\text{Wsurf}} - \frac{1}{2}E_{\text{H}_2} - E_{\text{H}}^{\text{zpe}}, \quad (1)$$

where  $E_{\text{Wsurf}}$  is the total energy of the vacancy-free W surface supercell,  $E_{\text{Wsurf,H}}$  is the total energy of the vacancy-free W surface with a sub-TIS H.  $\frac{1}{2}E_{\text{H}_2}$  is one-half the total energy of a H<sub>2</sub> molecule which is calculated to be -3.37 eV by placing the molecule in a cubic box with sides of length 10 Å. This reference energy is consistent with the value of -3.38 eV reported by Zhou et al. [31]. It should be noted that the energy of the reference atom has been subtracted from the total energy in VASP calculations. Since H is a light element, the quantum-mechanical vibration effects of H when dissolving in metals cannot be neglected. That is to say, the zero point energy (ZPE) of H should be taken into account for the calculation of H dissolution energies at W sub-surfaces. H ZPEs in W were calculated from the Hessian matrix of H atom with finite displacements of ±0.015 Å applied on H and each direction. Only the harmonic vibration of H was allowed, while all the W atoms were kept fixed. The vibrational frequency of H<sub>2</sub> is thus calculated to be 4328 cm<sup>-1</sup>, and corresponds to the ZPE of H of 0.134 eV, in good agreement with previous studies [13,14,18,19]. Thus  $E_{\text{H,Wsurf}}^{\text{zpe}}$  and  $E_{\text{H}_2}^{\text{zpe}}$  in Eq. (1) represent the ZPE corrections for H dissolved in W sub-surfaces and H in H<sub>2</sub> molecule, respectively.

Using Eq. (1), we obtain H dissolution energies at those sub-TISs in W(110) sub-surfaces. For the first sub-surface, as an example, H resided at 1subTIS1 and 1subTIS2 has a dissolution energy of 1.12 eV and 1.30 eV, in reasonable agreement with the values of 1.05 eV and 1.24 eV reported by Johnson et al. [19]. We choose to set the zero point at the 1st atomic layer, then the vertical distance of each sub-TIS from the 1st layer is just the distribution depth of H, which has a negative value. Therefore, H dissolution energies are plotted as a function of distribution depth in the range of the 1sub-surface to the 5sub-surface in Fig. 2. In general, when the H distribution depth increases (i.e. more negative for the distribution depth), the H dissolution energy decreases and becomes steady starting from the 3sub-surface, where the energy is already close to that at TIS in the bulk W. We obtain the H dissolution energy in the bulk W as 1.07 eV with H ZPE. This ZPE-corrected result is in agreement with the previously reported values of 1.09 eV [19], 1.04 eV [32], and 1.00 eV [31] by various research groups. Note that H dissolution energies at W sub-surfaces are all positive, and the values are larger than the H solution energy in the bulk W, especially for the 1sub-surface and 2sub-surface cases with the energy range of 1.12–



**Fig. 1.** Dissolution sites for H at the vacancy-free W(110) sub-surfaces. (a) Top view. (b) Tri-dimensional view. Large dark cyan spheres represent surface W atoms (the top-layer atoms are specially marked with yellow). Small red, blue and green spheres represent H at TIS1, TIS2 and TIS3, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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