



# Effects of nitrogen on hydrogen retention in tungsten: First-principles calculations



Sheng Wang<sup>a</sup>, Xiang-Shan Kong<sup>a</sup>, Xuebang Wu<sup>a</sup>, Q.F. Fang<sup>a</sup>, Jun-Ling Chen<sup>b</sup>, G.-N. Luo<sup>b</sup>, C.S. Liu<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, P.O. Box 1129, Hefei 230031, PR China

<sup>b</sup> Institute of Plasma Physics, Chinese Academy of Sciences, Hefei 230031, PR China

## ARTICLE INFO

### Article history:

Received 30 July 2014

Accepted 8 January 2015

Available online 14 January 2015

## ABSTRACT

While the use of nitrogen seeding to reduce the edge plasma temperature has been successfully applied in many tokamak experiments, questions remain as to effects of the nitrogen-enriched layer on hydrogen retention in tungsten. In this paper, we investigate the influence of nitrogen on hydrogen dissolution and diffusion behavior in tungsten using the first-principles. The nitrogen has little effect on the dissolution of hydrogen in the interstitial site but significantly impedes the accumulation of hydrogen in the vacancy, leading to the decrease of hydrogen retention in nitrogen-enriched layer. Meanwhile, both the interstitial nitrogen and the vacancy–nitrogen complex can significantly reduce the hydrogen effective diffusivity. This suggests that the nitrogen-enriched layer forming on the tungsten surface can act as a diffusion barrier for the re-emission of implanted hydrogen, enhancing hydrogen diffusion into the bulk, and consequently, increasing of hydrogen retention in bulk. These results provide a sound explanation for the recent experimental results.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Tungsten has been selected as the plasma-facing materials (PFM) at the divertor baffles in the ITER design and is a leading candidate material for the PFM of the fusion reactor [1–3]. With the transition to a full tungsten coated first wall, the lack of radiation from carbon in the edge plasma has led to an increase in the power flux to the outer target making it necessary to seed impurities into the edge plasma for radiative cooling. Nitrogen has shown favorable properties in cooling the edge plasma and increasing the plasma confinement in ASDEX Upgrade [4]. Recently, nitrogen seeding experiments from the JET ITER-like wall project have shown increased radiative power and improved plasma energy confinement in the high-shape ELMy H-mode [5–7]. While the above results are encouraging, questions remain as to the influences of nitrogen on hydrogen retention in tungsten [8,9], which are important processes due to their impact on both the safety and operation of fusion reactors [10]. Laboratory experiments have shown increased hydrogen retention in the presence of nitrogen [11–15]. The reasons for this increase are unclear, and while the detailed physics by themselves are of considerable interest, a more pressing matter in estimating nitrogen effects on the hydrogen

retention requires information on how hydrogen dissolution and diffusion are influenced by nitrogen.

In previous theoretical studies, impurities have been found to interact strongly with the intrinsic defects and hydrogen in tungsten, which sheds light on the influence mechanism of impurities on the hydrogen retention, especially for carbon [16–20]. However, little theoretical work has been reported about the influences of nitrogen on hydrogen dissolution and diffusion in tungsten. Correspondingly, many fundamental aspects underlying the interaction of nitrogen with hydrogen remain not well understood. Since there are two typical dissolution sites, i.e., the interstitial site and the vacancy, for hydrogen retention in tungsten, we systematically investigate the interaction structures and energetics between hydrogen and nitrogen in interstitial site and the vacancy, respectively, using first-principles calculations. And then, using these energetics parameters, we estimate the influence of nitrogen on hydrogen dissolution and diffusion in tungsten. These results will not only be quite helpful to understand the interaction of nitrogen with hydrogen but can also provide a sound explanation for the experimental phenomenon, i.e., the increase of deuterium retention in the presence of nitrogen.

## 2. Computation method

The present calculations are performed within density functional theory as implemented in the VASP code with Blöchl's

\* Corresponding author. Tel.: +86 551 65591062.

E-mail address: [cslu@issp.ac.cn](mailto:cslu@issp.ac.cn) (C.S. Liu).

projector augmented wave potential method [21]. The generalized gradient approximation and the Perdew–Wang functional are used to describe the electronic exchange and correlation effect [22]. The supercell composed of 128 lattice points ( $4 \times 4 \times 4$ ) is used. The relaxations of atomic position and optimizations of the shape and size of the supercell are performed. The plane wave cutoff of 500 eV and  $k$ -point density of  $3 \times 3 \times 3$ , obtained using the Monkhorst–Pack method [23], are both checked for convergence for each system to be within 0.001 eV per atom. The structural optimization is truncated when the forces converge to less than 0.01 eV/Å.

The binding energy between two point defects ( $A_1$ ,  $A_2$ ) is calculated as follows:

$$E_b^{A_1-A_2} = E_{tot}^{A_1} + E_{tot}^{A_2} - E_{tot}^{A_1-A_2} - E_{tot}^{bulk}, \quad (1)$$

where  $E_{tot}^{A_1}$  and  $E_{tot}^{A_2}$  are the total energies of the supercell with a single defect  $A_1$  and  $A_2$ , respectively, and  $E_{tot}^{A_1-A_2}$  is the total energy of the supercell containing both  $A_1$  and  $A_2$ . All supercells contain 128 lattice sites. With such a scheme, a positive binding energy means attraction between the entities, while a negative binding energy indicates a repulsion.

### 3. Results and discussion

#### 3.1. Interstitial hydrogen and nitrogen in intrinsic tungsten

In a bcc lattice, an interstitial impurity atom can occupy either an octahedral interstitial site (OIS) or a tetrahedral interstitial site (TIS). Each of these sites is investigated for both hydrogen and nitrogen in order to find the ground state energy associated with an isolated hydrogen and nitrogen point defect. The favorable interstitial position for the hydrogen is the TIS, where the solution energy is 0.93 eV less than the value of the OIS, 1.31 eV. The calculated energy difference between the OIS and TIS (0.38 eV) agrees well with previous DFT studies, which reported energy differences of 0.38 eV [18,24–28] and 0.36 eV [29]. The calculated solution energy in the TIS site agrees within the limits of accuracy with the experimental value  $1.04 \pm 0.17$  eV [30]. In contrast, the OIS is the best interstitial position for the nitrogen atom. The solution energy is 1.37 eV in the OIS, which is much lower than the value of TIS, 2.11 eV. The calculated energy difference between the OIS and TIS, 0.74 eV, agrees well with previous DFT studies (0.72 eV [29,31]).

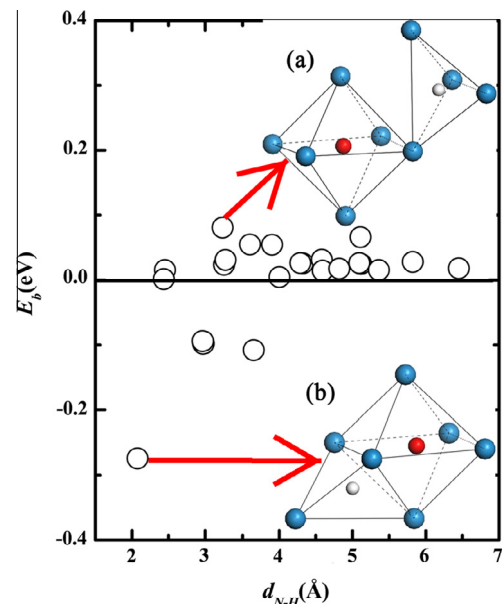
#### 3.2. The influence of nitrogen on hydrogen dissolution in interstitial site

To estimate the influence of nitrogen on hydrogen dissolution in interstitial site, it is a good start point to investigate the interaction between interstitial hydrogen and nitrogen when they form a defect cluster. From the above calculation, we know that the hydrogen prefers the TIS and the nitrogen prefers the OIS. After carefully checking, it has been found that these individual equilibrium sites do not change when interstitial hydrogen and nitrogen form a defect cluster. The possible configurations of the arrangement of OIS nitrogen atoms and TIS hydrogen atoms are so many that it is impossible to take all configurations into account. Here, we only focus on the hydrogen dissolution behavior in the presence of a single OIS nitrogen. We design three kinds of situations for this task: (1) a single TIS hydrogen atom around an OIS nitrogen atom, (2) two TIS hydrogen atoms around an OIS nitrogen atom, (3) multiple TIS hydrogen atoms around an OIS nitrogen atom.

For the first situations, we arrange the OIS nitrogen atom and the TIS hydrogen atom in a number of different configurations, which are as following: a nitrogen atom is first placed on the OIS and then a hydrogen atom is placed on the TIS surrounding the

nitrogen to form a nitrogen–hydrogen ( $N-H$ ) pair. After full relaxation of these configurations, the binding energies between the nitrogen and the hydrogen are calculated using Eq. (1) and represented in Fig. 1. It can be clearly seen that the binding energies depend on the configurations of  $N-H$  pairs, which are mostly positive with a few exceptions. This indicates that the attractive interaction plays a dominant role between the interstitial nitrogen and hydrogen. However, it should be noted that most of absolute values of these binding energies are lower than 0.1 eV, indicating that the interaction between the interstitial nitrogen and hydrogen is very weak. The separation distance of the most stable  $N-H$  pair is  $\sim 3.2$  Å. From the stable separation distance, on the whole, the positive binding energy between interstitial nitrogen and hydrogen decreases with the increase of  $N-H$  separation distance and ultimately decreases to almost zero at a certain distance ( $\sim 4.5$  Å), beyond which the interstitial nitrogen and hydrogen are nearly non-interactive. The interaction radius between TIS hydrogen and OIS nitrogen is  $\sim 4.5$  Å, which is very local.

We next turn to the second situation of two TIS hydrogen atoms around an OIS nitrogen atom. For a given double TIS hydrogen atoms defect ( $H-H$ ), the  $H-H$  defect geometry that contains two separate  $H-W$  tetrahedra is usually energetically favorable over the defect geometry where the hydrogen atoms share a nearest-neighbor tungsten atom. This is also confirmed by our calculations (see Fig. 2) showing that the binding energies of  $H-H$  defect pairs are mostly negative with a single exception, which is so small (0.01 eV) that it can be negligible. On the other hand, the results of the first situation indicate that the attractive interaction plays a dominant role between the interstitial nitrogen and hydrogen. Whether the repulsive interaction of  $H-H$  pair or the attractive interaction of  $N-H$  pair plays a governmental role when two TIS hydrogen atoms and an OIS nitrogen atom form a defect cluster ( $NH-H$ )? To answer this question, we construct a number of plausible geometries for an OIS nitrogen atom binding two TIS hydrogen atoms where all the  $N-H$  separation distances are between 2.4 and 3.6 Å and the  $H-H$  separation distance increases from 1.4 to 5.8 Å.



**Fig. 1.** Variation in the binding energy of an interstitial hydrogen atom and a nitrogen atom as function of the distance between them. The insert two figures (a) and (b) represent the defect complexes with the maximal and minimal binding energies, respectively. The large blue, small red and small white balls indicate the tungsten, nitrogen, and hydrogen atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Download English Version:

<https://daneshyari.com/en/article/7966384>

Download Persian Version:

<https://daneshyari.com/article/7966384>

[Daneshyari.com](https://daneshyari.com)