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Energetics of small helium clusters near tungsten surface by *ab initio* calculations

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HIGHLIGHTS

- Investigating the stability and interactions among small helium clusters in W surface.
- Trapping of multiple He atoms in tungsten surface can induce the formation of vacancy and He_n-V (n=2 and 3) complexes.
- The hybridization and interaction between He and neighbour W atoms grow weaker as the increase of He atom in clusters.

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ABSTRACT

Density functional theory calculations have been performed to study the stability and the interactions of/between small helium clusters at the W(001) surface. Among the studied He clusters, all the He atoms prefer to stay under the second atomic layer from the surface, instead of surface and subsurface. Trapping of multiple He in tungsten surface can induce formation of a new vacancy at nearby lattice site, and the He_n-V (n = 2 and 3) complexes are formed concurrently. The electronic densities of states (DOS) and charge-density distribution are presented for di-helium and tri-helium clusters. Calculated He formation energies and He-vacancy binding energies improve understanding of He trapping behavior and diffusion mechanisms in tungsten surface.

1. Introduction

The fusion energy is considered as one of the key ways to successfully solve the energy problem [1], while the development of fusion materials is one of the keys to the fusion power system. Hydrogen and helium are major transmutation products in structural material of fusion reactor [2], which can influence the microstructure and mechanical properties of the plasma facing materials (PFMs) [3]. Tungsten (W) has been considered as an excellent candidate of PFMs in fusion reactor because of its high melting temperature, high thermal conductivity, low tritium inventory and low erosion rate against sputtering [4–8]. Hence, understanding the fundamental behavior of helium in W, especially W surface, is a critical issue in the research and development of nuclear materials. Theoretical and experimental results indicate that helium is mobile and insoluble in metals even below room temperature [9], but the helium are easily trapped near the vacancies [10,11].

During the past several decades, many of experimental studies and theoretical simulations have been performed to reveal the mechanism of trapping helium in metals. The experimental results [12,13] indicate that helium is deeply trapped in small vacancy clusters and the stabilized bubbles have been forming in the metal. In spite of many efforts on the He effects in metals [10,14], it is very hard to obtain the details about the energetics and stability of He clusters directly from experimental means. Alternatively, theoretical simulations are performed to study the atomistic properties of helium in metals. The relative stabilities of He interstitial sites in bcc and fcc metals are calculated using ab initio calculations based on density functional theory [15], tetrahedral interstitial site is more favorable than the octahedral site in bcc metals (Fe, Cr, Mo and W), and for the fcc metals (Ni, Cu, Ag and Pd) the relative stability of He interstitials varies. For bcc metals (V, Nb, Ta, Mo and W), the formation energy of He substitutional defect is nearly constant; and the formation energy of He interstitial depends on the electronic structure of the host [16]. Becquart and Domain calculated migration energy of He in bulk W, around 0.06 eV [9], which is much lower than that of 0.28 eV obtained from

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experimental [17]. The discrepancy between the experimental and calculated results can be explained by the large binding energy between He atoms. Molecular dynamics (MD) simulations are carried out to investigate the lowest energy structure and lowest energy migration pathway for interstitial He clusters [18]. Hu and et al. [19] studied the dynamics of He clusters near W surfaces using MD, and found that the most important reactions is trap mutation which can significantly effect on the W surface morphology, structure and the He_m-V complexes formation. Wang and et al. [20] investigated the helium dissolution and clustering at W(110) surface by first principles calculations, and reported that the formation energy of He fluctuates around 6.1 eV and He is easier to be self-trapped to form He clusters at the near surface.

As we know, the most theoretical work focus on the migration and diffusion of He on bulk W, very limited studies investigate on the behaviors of He at the W surface using *Ab Initio* Calculations. Because of the highly important role of He in metals, we have studied some properties related to the stability and diffusion of He at the W(001) surface. More precisely, we have determined: the most favored configuration of He clusters in each layer, the binding energies between He atoms in different clusters, and the electronic structure of the various He defects and W atoms.

2. Methodology

Our calculations are performed using the Vienna ab initio Simulation Package VASP [21–23]. The W-6s, W-5d and He-1s electrons are treated as atomic valence electrons. The solution of Kohn–Sham equations [24] is self-consistently obtained with a plane-wave basis set using projector augmented wave pseudopotentials [25,26]. Exchange and correlation functions are obtained in a form proposed by Perdew, Burke and Ernzerhof (PBE) within the generalized gradient approximation. The plane-wave cutoff energy is set as 350 eV. Ion relaxations are performed using standard conjugated-gradient algorithms as implemented in the VASP code. The first-order Methfessel-Paxton method is used for the Fermi surface smearing, with a width of 0.2 eV. Dipole corrections in the z direction are used in all calculations. Geometry optimization is performed until the residual force is within 10^{-2} eV/Å, and the electron self-consistent total energy converged to within 1.0×10^{-5} eV/atom.

A Monkhorst-Pack k-points grid of $4 \times 4 \times 1$ is chosen for relaxation and $8 \times 8 \times 1$ for property calculations. As shown in Fig. 1, the dimensions of our surface slab model of the W (001) surface is $9.50 \times 9.50 \times 29.24$ Å^3, which contain 10 atomic layers and 15 Å vacuum. The bottom three layers are fixed to the bulk structure to simulate a semi-infinite crystal. For easy recognition, all the inserted He atoms are labelled as "A to U". In the beginning structures, we attempt to place He atom and clusters in the 6th-9th layers. The initial configuration are also listed in Table 1. Because of the weak interaction between He and W, He is easy to escape from the W surface (the 10th layer). All the calculations were done at constant volume fully relaxing the atomic positions in the supercells.

The following definitions are used throughout the paper. The relaxation energy of a crystal is determined as a difference between the total energy of a crystal before and after relaxation. The relaxation volume is similarly determined. The formation energies of the He interstitial is calculated as follows:

$$E_n^f = E_{W,nHe} - E_W - nE_{He} \quad (1)$$

where $E_{W,nHe}$ and E_W are the total energy of an optimized supercell with and without nHe atoms, and E_{He} is the energy of an isolated He atom.

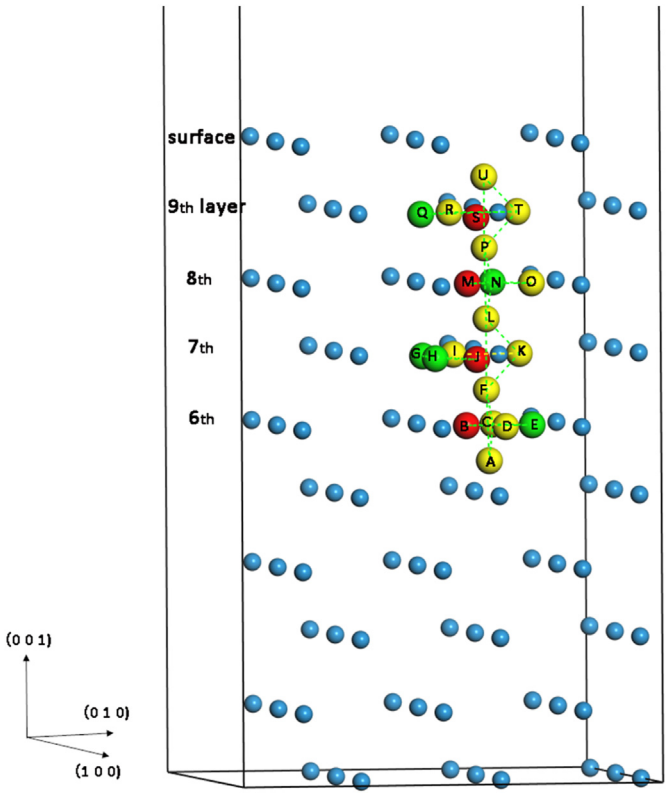

Fig. 1. Slab model of the W(0 0 1) surface.

The binding energy E^b between two He atoms in clusters is determined as

$$E_2^b = 2E_{W,He} - E_{W,2He} - E_W \quad (2)$$

For the multiple He atoms, the average solution energy is determined by

$$E_n^s = (E_{W,nHe} - E_W - nE_{He})/n \quad (3)$$

In such a scheme, a positive, binding energy means attraction between entities, whereas a negative binding energy indicates repulsion.

3. Results and discussion

We are interested in four primary aspects of single He and He clusters at tungsten surface: dissolution of single He atom, interaction and stability of the small clusters, and electronic structure of He_n-V complexes. All these mechanisms have significant impact on the microstructural of tungsten surface. Each will be discussed in turn in the following sections.

3.1. Dissolution of single He atom

In order to investigate the dissolution behavior of He atom on the W(0 0 1) surface, the possible interstitial sites are considered for a He atom, including tetrahedral (T) and octahedral (O) sites (not shown in this paper). Based on our previous and other's work [9,16,18–20], the T interstitial site is more favorable than O site for He atom(s). The O site is considered to be a diffusion saddle point during migration [9]. Hence, in this paper only the T sites are taken into account for the dissolution of a single He atom.