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First-principles study on stability and electronic properties of W(001), W(110) and W(111) surfaces

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ABSTRACT

Based on Density Functional Theory (DFT), using first-principles pseudopotential plane wave method, surface relaxation, surface energy and Density of states (DOS) of metal W on low index surfaces (001), (110) and (111) were calculated. The results showed that: the relaxation and surface energy were $|\Delta_{14}(110)|<|\Delta_{14}(111)|<|\Delta_{14}(001)|$ and $E_{surf}(110)<E_{surf}(111)<E_{surf}(001)$, respectively. The surface relaxation and surface energy of W(110) were both minimum, which proved that W(110) was the most stable surface. This result was in good agreement with experimental XRD pattern. According to Density of states, the essence of the distinct stability of W(001), W(110) and W(111) was discussed further.

1. Introduction

Nowadays, numerous investigations have confirmed that surface science is of key importance both by theoretical calculations and experimental methods, which contains surface morphology [1,2], surface reconstruction [3,4], surface diffusion [5,6] and so on. The driving force for all these phenomena is electronic structure near the surface region of a metal. Therefore, the electronic structure of surface is crucial in researching and understanding the solid surfaces as well as their properties [7].

In the family of metals, the transition metals play a vital role in an increasingly large number of industrial applications. As a significant transition-metal, W possesses many unique physical properties, such as high melting point, high chemical stability and high hardness and so on. Traditional applications of such materials are alloyed with steel to form tough metals that are stable at high temperatures. Tungsten-steel alloys are used to make such things as high speed cutting tools and rocket engine nozzles [8,9].

Interface effects induced by metal films on ceramic substrates have attracted much attention due to their novel physical and chemical properties [10,11]. Recently, we have succeeded in growing W epitaxially on Si, which exhibited promising mechanical properties. X-ray diffraction (XRD) pattern showed that only W(110) peak was found in the structures. In this work, our purpose was to understand why W only displayed (110) surface among a large number of distinct surfaces. For a better understanding of the characteristic of XRD and the appearance of only W(110) surface in the structure, we calculated the electronic structure and surface energy of three W surfaces of (001), (110) and (111) that were sufficient to representative all surfaces due to its cubic structure. This work can also give a help to understand the surface adsorption and initial oxidation of W surface.

With the rapid development of computer simulation technology, based on Density Functional Theory, first-principle has been more advanced calculation software. In recent years, the structure of a large number of crystal surfaces was calculated by different calculation methods [12–14]. Since the mechanical properties of a surface depend sensitively upon the detailed atomic and electronic structure at the junction, understanding of this type of surface would be helpful to optimize the performance of the surface. In this work, we used plane-wave pseudopotential density functional theory to investigate the surface relaxation, surface energy and density of states of W(001), (110) and (111). The simulated results were hoped to be consistent with the experiment.

2. Calculation method and model

The total energy calculations were performed with Density Functional Theory (DFT) [15–17]. The CASTEP code based on a plane wave expansion technology in reciprocal space was used [18]. Generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) approach was used for exchange–correlation energy calculations [19]. A special **k** point sampling method proposed by Monkhorst–Pack was used for the energy integration in the first irreducible Brillouin zone [20]. In the calculation, the kinetic energy cut-off value was selected as 340 eV, which was sufficient to obtain the reliable results. The **k** point mesh was selected as $10\times10\times1$. All atoms were relaxed to their equilibrium positions when the change in energy on each atom between successive steps was converged to 1×10^{-5} eV/atom. The forces

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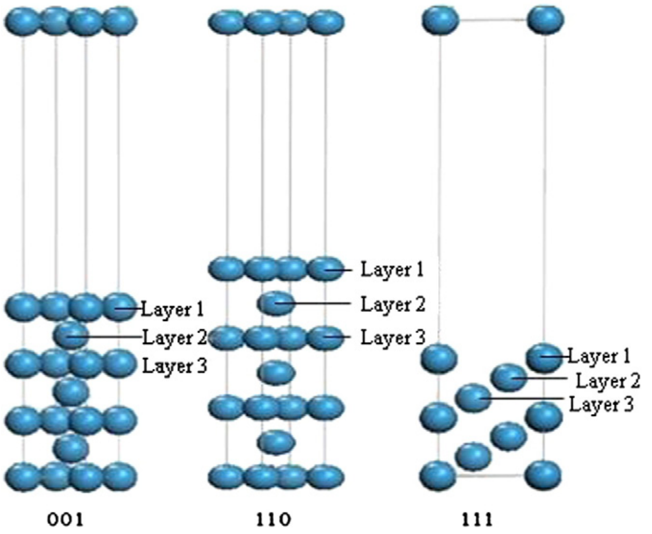

Fig. 1. Schematic view of supercells for W surfaces.

on each atom were converged to 0.03 eV/Å, the stress on each atom was converged to 0.05 GPa and the displacement was converged to 0.001 Å.

The W(001), (110) and (111) slabs are created based on the above optimized bulk geometries. 7 atomic layers are chose in the calculations in this work. Fig. 1 gives schematic view of supercells for W surfaces. To avoid the interaction between repeated slabs, a uniform vacuum width of 16 Å is employed. The slabs are fully relaxed until the system energy achieved the minimum.

To ensure the reliability of this work, the lattice constant and Young's modulus of W bulk are calculated. The theoretical and experimental tests are summarized in Table 1. The result indicates that our theoretical values are in agreement with experimental test.

3. Results and discussion

3.1. Surface relaxation

In the relaxation process, due to lack of neighbor atoms, the surface atoms are in an unstable state. They will deviate from the original location to other locations, thereby achieving a more stable structure.

In order to describe the relaxation of surface atoms quantitatively, the formula was defined as:

$$\Delta_{ij} = \frac{l'_{ij} - l^0_{ij}}{l^0_{ij}} \times 100\% \tag{1}$$

where Δ_{ij} is the relative percentage change of the interlayer spacing between ith and jth layers relative to the unrelaxed interlayer spacing. l'_{ij} is the relaxed interlayer spacing between ith and jth and l^0_{ij} is unrelaxed interlayer spacing. In Tables 2 and 3, "−" represents contraction and "+" represents expansion of interlayer spacing.

Table 2 lists the theoretical and experimental relaxation results of the W(110). The surface atomic relaxation results of our work are −2.778, −0.850 and −0.667, respectively. Compared with the experimental results, our calculated relaxation quantities are all located in error range of the experimental data. However, for the majority of metals, the measurement process of surface relaxation is exceedingly complex. And the experimental condition is also limited by a host of elements such as experimental temperature, pressure, and certain errors caused by operators, thereby producing some deviation between experiment and theoretical simulation. As a consequence, the measured results through experiments have some uncertainty. At the same time, it is acknowledged that this calculation method used in the current framework of Density Functional Theory (DFT) provides an accurate estimation to measure surface relaxation, thus more effectively guiding the future experiment.

Table 1
Lattice constant and Young's modulus of W bulk.

	Lattice constant (Å) a = b = c	Young's modulus (GPa)
This work	3.168	352.46
Experiment	3.165 [21]	394.23 [22]

Table 2
Atomic relaxations of W(110) surface and the comparison with available experiments.

	Δ_{12}	Δ_{23}	Δ_{34}
LEED exp. [23]	0.0 ± 4.5	–	–
HEIS exp. [24]	0.0 ± 1.8	0.0 ± 1.8	–
This work	−2.778	−0.850	−0.667

Table 3 compares the relaxation of W on three low index surfaces. It is clear that three surfaces have different relaxation levels. The layer distance of 1st and 4th is defined as $\Delta d_{14} = \Delta d_{12} + \Delta d_{23} + \Delta d_{34}$, thereby getting hold of $|\Delta_{14}(110)| < |\Delta_{14}(111)| < |\Delta_{14}(001)|$. Obviously, the relaxation of W(110) surface is the smallest among three surfaces, which indicates that W(110) surface is the most stable surface.

3.2. Surface energy

The surface energy is a crucial indicator for the stability of surface structure, which is determined as follows [25]:

$$E_{surf} = \frac{1}{2A}(E_{slab} - nE_{bulk}) \tag{2}$$

where E_{slab} is the total energy of the slab and E_{bulk} is the energy of the bulk per formula unit W. A is defined as unit surface area and n is the total number of formula units W in the slab. The surface energies of W on three low index surfaces are calculated and displayed in Table 4. From Table 4, it is clear that the calculated values are 0.248, 0.194 and 0.232 eV/Å^2, respectively, which is similar with previous experimental result (0.1768 eV/Å^2). Due to the lack of precise measuring technology and the limitation of experimental conditions, the certain variation between experiment and theory is acceptable.

The order of surface energies is $E_{surf}(110) < E_{surf}(111) < E_{surf}(001)$, which has the same trend with the order of relaxation quantities of $|\Delta_{14}(110)| < |\Delta_{14}(111)| < |\Delta_{14}(001)|$. W(110) surface has the smallest surface energy, indicating that W(110) surface is the most stable and would be helpful to make a perfect two-dimensional system. W(110) can stably exist in a composite interface.

3.3. Density of state

To further illustrate the W(110) stability among different surfaces, the total density of states (DOS) and partial density of states (PDOS) of the bulk and 7 atomic-layered slab are calculated and shown in Fig. 2. It is clear that the largest contribution to the total density of

Table 3
Relaxation results of W on three low index surfaces.

Source	Δ_{12}	Δ_{23}	Δ_{34}	Δ_{14}
W(001)	−8.803	−3.983	−0.998	−13.78
W(110)	−2.778	−0.852	−0.667	−4.297
W(111)	−8.119	−10.38	+11.87	−6.629