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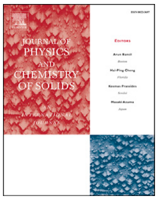

Insight into the structural and electronic properties of orthorhombic Cr_3C_2 (001) surface

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ABSTRACT

By using the first-principle calculations, the surface relaxation, surface energies and work functions, surface electronic structure of orthorhombic Cr_3C_2 (001) surface have been calculated. The LDA computed values of surface energy and work function for the stoichiometric Cr_3C_2 (001) surface are 4.13 J/m^2 and 4.4 eV, respectively. Results of the relaxed structure indicate that the major effect of atomic relaxations is in the top two layers, and the largest rumpling locates at the second layer. The Cr_3C_2 (001) surface has a stronger metallic character than the bulk duo to the appearance of the surface state. Mulliken population analysis also demonstrates the strong increase in the Cr-Cr metallic bonding on the top surface and considerable covalency for C-Cr bonding.

1. Introduction

Chromium carbides (Cr-C) thin films have been playing a significant role in a variety of industrial applications owing to their excellent properties such as high hardness, good wear resistance and excellent corrosion resistance [1–4]. For corrosion resistance, Cr-C films are highly effective to protect metallic materials from chemical attack by forming a passive film of chromium oxide at elevated temperatures in air likewise during oxidation in aqueous solutions [5]. In the field of proton exchange membrane fuel cells (PEMFCs), Cr-C films have attracted lots of academic interests and are regarded as a promising material system for corrosion prevention of metal bipolar plates [6–9]. For instance, Yi et al. [7] developed multilayered Cr-C films on stainless steel (SS316L) sheet which is an important candidate material of bipolar plates in proton exchange membrane fuel cells (PEMFCs). They revealed that the corrosion resistance of multilayered Cr-C films attained 11.1% of performance increase than a-C films and accorded with the DOE's 2020 technical targets. As generally known, the Cr-C thin films have larger surface areas than the bulk. Therefore, it is of great importance to understand the surface properties of Cr-C thin films and the related physical and chemical properties affected by surfaces.

To date, many efforts on the structure and properties of Cr-C thin films have been performed [10–13]. It is reported that most of Cr-C films with different carbon contents exhibit an amorphous structure, which can be described as a “two phase” structure: one amorphous CrC_x phase and one amorphous a-C phase [10]. Meanwhile, the physical and chemical properties of the Cr-C films are obviously correlated to the carbon content [11]. However, the significant surface properties of Cr-C thin films are rarely reported and not yet quite clearly understood.

In the Cr-C system there is three stable crystallographic phases (Cr_3C_2, Cr_7C_3, $Cr_{23}C_6$) and several metastable crystallographic phases, such as CrC and Cr_3C [14,15]. Particularly, Cr_3C_2 phase is one of the most important components of the Cr-C films and has been given the most attention by researchers. Cr_3C_2 has an orthorhombic crystal structure that is commonly found in transition metal carbides, and is similar in structure to FeC_3 and β-Mo_2C [16–18]. According to Chiou et al. [19], the FeC_3 (001) surface has the lowest surface energy among various surfaces, and thus is the most stable surface. Similarly, Asara et al. [20] revealed that the β-Mo_2C (001) surface is the most stable one. In general, the close-packed surface of a crystal is considered as the most stable surface. Using first-principles calculations, in our work, the close-packed Cr_3C_2 (001) surface is confirmed indeed to have a lower surface energy than that of the other low-index surfaces.

Hence, in this paper, we focus on the orthorhombic Cr_3C_2 (001) surface with the aim to obtain the basic information about the surface structural and electronic properties of Cr_3C_2 phase. Periodic surface models with first-principles methods were used to check the structural features of the surface. The next section describes the model geometries and computational methods of this study. In the third section, we discuss the bulk properties, surface energies and work functions, surface

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relaxations and rumplings, surface electronic properties of orthorhombic Cr_3C_2 (001) surface. In the last section, we summarize our conclusions.

2. Methods

2.1. Computational methods

All calculations were performed using plane wave pseudopotential method as implemented in Cambridge sequential total energy package (CASTEP) [21]. By using Kohn–Sham equation [22] together with the self-consistent field (SCF) method to achieve the electronic minimization, the ground state can be found. Furthermore, the minimum total energy of the system was achieved to implement the geometry optimization using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) algorithm [23]. The SCF convergence threshold was set 5.0×10^{-7} eV/atom, and the convergence tolerance were set as energy for 5.0×10^{-6} eV/atom, maximum force for 0.01 eV/Å. The atomic configurations of Cr and C generated from the ultrasoft pseudopotential were $3s^2 3p^6 3d^5 4s^1$ and $2s^2 2p^2$, respectively. The generalized gradient approximation of PBE (GGA-PBE) and local-density approximation (LDA) were used to treat the exchange-correlation energy [24]. The wave functions are expanded in plane wave up to a cutoff energy of 550 eV. Brillouin zone sampling [25] was employed using Monkhorst-Pack k-points meshes of 8 × 4 × 16 and 8 × 4 × 1 for bulk and surface calculations, respectively.

2.2. Models

As shown in Fig. 1 and Table 1, the Cr_3C_2 unit cell where there are twelve Cr atoms and eight C atoms is built according to the literature [16]. The unit cell is orthorhombic and its space group is Pnma with three sets of Cr atoms (Cr1, Cr2, Cr3) and two sets of C atoms (C1, C2) occupying fourfold positions in the system. As shown in Fig. 2, a symmetric slab was used to ensure surfaces on both sides of the slab being equivalent and eliminate spurious dipole effects. Along the [001] direction in the crystal structure of Cr_3C_2, the atomic stacking sequence is –Cr_6C_4–Cr_6C_4–, and each atomic layer of the slab is stoichiometric and nonpolar. The vacuum layer of 14 Å is enough to avoid the interactions between the slab and its periodic images. Repeated Cr_6C_4-terminated (1 × 1) slabs with 5, 7, 9 layers were employed. All atoms in the slab were fully relaxed to a force tolerance of 0.01 eV/Å during the surface geometry optimization.

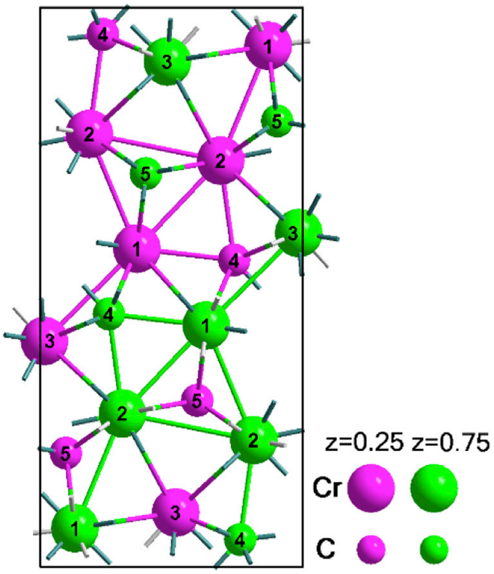

Fig. 1. The unit cell structure of Cr_3C_2 projected on (001).

Table 1
The LDA and GGA computed lattice parameters of bulk Cr_3C_2 compared with previous studies.

Atom positions [16]	Lattice constant (Å)			Species
Cr (4c)	a	b	c	
(0.3683,0.5685,0.2500)	5.525	11.468	2.827	Exp [16].
(0.6794,0.7260,0.2500)	5.480	11.455	2.789	Present (GGA)
(0.0167,0.4016,0.2500)	5.374	11.286	2.749	Present (LDA)
C (4a)	5.540	11.494	2.833	Exp [15].
(0.7424,0.5476,0.2500)	5.48	11.47	2.79	Cal.(GGA) [26]
(0.8971,0.7952,-0.2500)	5.38	11.28	2.75	Cal.(LDA) [26]
	5.473	11.468	2.790	Cal.(GGA) [27]
	5.379	11.284	2.750	Cal.(LDA) [27]

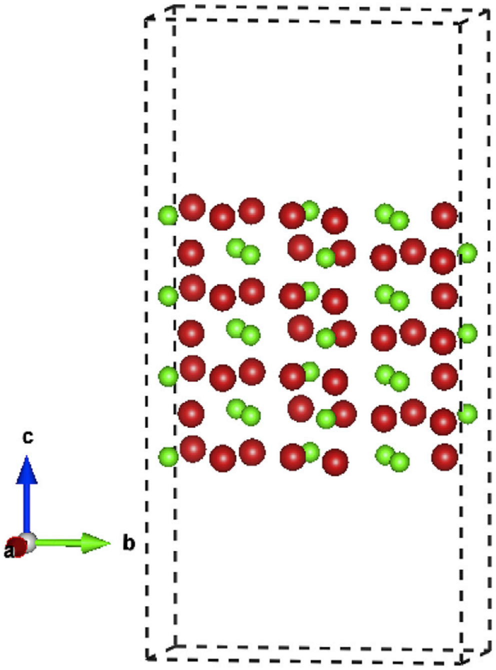

Fig. 2. Schematic illustration of Cr_3C_2 (001) surface model: seven-layer slab with stoichiometric Cr_6C_4-terminated surfaces at top and bottom. The red spheres stand for Cr atoms, the green spheres represent C atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3. Results and discussion

3.1. Bulk properties

The bulk lattice parameters of the orthorhombic Cr_3C_2 were optimized and listed in Table 1, compared with previous theoretical and experimental values. Our computed lattice constants are in good agreement (~1%–3%) with the experimental values and are consistent with previously reported LDA and GGA results.

As shown in Fig. 3, near the Fermi level, the DOS of bulk Cr_3C_2 are mainly attributed to Cr 3d states and C 2p states. The C 2p orbitals are overlapped with the Cr 3d orbitals, which demonstrates a high degree of p–d hybridization between C and Cr atoms forming polar covalent bonds. Moreover, there are strong metallic bonds among the Cr atoms mainly owing to the 3d electrons of chromium, of which contribution to the DOS approximately is 68.5% within the energy window from −7 to 6 eV. Similarly, these characteristics were previously observed for transition-metal carbides, such as FeC_3 and β-Mo_2C, in which metallic and covalent mixture bond states are always expected [28,29].