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First-principles study of the (001) and (110) surfaces of superhard ReB_2

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ABSTRACT

Structural relaxations, electronic properties, and surface energies of ReB_2 (001) and (110) surfaces with various terminations are investigated with a first-principles method. It is found that the surface interatomic spacings of ReB_2 (001) and (110) surfaces are different from those of the bulk structure. The vertical spacings between the first and second layers of the studied surfaces are contracted. The (001)-Re surface is likely to be stable without introducing a large relaxation. Among these surfaces, only the (110) surface has surface rumpling, and the Re atoms on its first layer are apt to move inward. After atomic relaxation, some covalent bonds formed by the outmost atoms of the relaxed surfaces are shorter than those of the bulk system, which indicates that the covalent B–B and Re–B bonds of the surface layer have been strengthened. An analysis of surface energies shows that after relaxation, the (001)-Re surface is more stable than other types of surfaces.

1. Introduction

For the past several decades, researchers have searched for superhard materials that can be used in place of diamond. Thus far, scientists have primarily focused on exploring covalent compounds formed by transition metals and light elements [1–5]. Among them, ReB_2 synthesized under ambient pressure was reported to be an ultra-incompressible and superhard material (hardness ≥ 40 GPa) [6]. Several theoretical studies on the electrical, thermal, and elastic properties of bulk ReB_2 have been reported [7–9]. However, there is no theoretical investigation of the surface properties of ReB_2. Under certain conditions, the hardness of many materials can be increased when synthesized as a film [10]. Moreover, the surface properties are important for thin-film coating and catalysis. Thus, theoretical and experimental studies on the surface structure of transition-metal diborides with the AlB_2 structure have been performed [11–13]. The crystal structure of ReB_2 is very different from those of transition metal diborides, in which the boron atoms are buckled, and Re is located on top of the B atom in ReB_2 [8]. Therefore, to build a more realistic model for interfaces related to ReB_2, it is necessary to investigate its surface properties. An experimental report on superhard ReB_2 crystals revealed that a maximum hardness value of 40.5 ± 2.4 GPa can be obtained along (002), which is approximately 6% higher than the hardness of the (hk0) plane under low loading conditions [14]. In this work, we aim to offer a deeper understanding of the ReB_2 surface by exploring the stability and relaxation of these surfaces.

2. Computational detail

The calculations presented in this study were performed with the density functional theory, using the projector-augmented wave (PAW) method [15,16], as implemented in the Vienna *ab initio* simulation package [17-19]. The generalized gradient approximation (GGA) [20] was used with the PAW potential. A plane wave cutoff energy of 500 eV was employed throughout. The structure was relaxed with the conjugate-gradient algorithm method, which ensured that the forces on the atoms were smaller than 0.02 eV/Å. Before starting the surface calculation, we optimized the bulk structure of the hexagonal ReB_2 phase, and the optimized lattice parameters ($a = 2.914$ Å and $c = 7.5$ Å) agree well with the experimental values ($a = 2.897$ Å and $c = 7.475$ Å) [21] and the previous theoretical calculation results ($a = 2.913$ Å and $c = 7.506$ Å [4], $a = 2.9007$ Å and $c = 7.4777$ Å [8]). The calculated large bulk modulus (340 GPa) and shear modulus (301 GPa) also agree with previously calculated theoretical values [4,8]. The high bulk modulus of ReB_2 indicates that it can strongly resist a volume change caused by an applied load. Its high shear modulus shows its strong resistance against a shape change. Therefore, ReB_2 should have a high hardness, as has been confirmed by experimental work [6]. The following surface optimizations are all based on the bulk geometry. To model the surfaces of ReB_2, the well-known slab approach was used, in which periodic boundary conditions are applied to the surface supercell including a slab of atomic layers and a vacuum region. In the present work, 2×2 and 1×1 unit cells are used for the (001) and (110) surfaces of ReB_2, respectively. The (001) surfaces of ReB_2 are terminated by a layer with Re atoms and with another one or two layers of B atoms (labeled as (001)-Re, (001)-B, and (001)-BB, respectively), and its (110) surface is terminated by one layer with four B

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atoms and two Re atoms (labeled as (110)). The *k*-points of 7×7×1, 5×5×1, 5×5×1, and 1×6×9 were generated using the Monkhorst–Pack mesh in the irreducible Brillouin zone, and 13, 9, 11, and 9 atomic layers were used in the slabs of the (001)-Re, (001)-B, (001)-BB, and (110) surfaces, respectively. The thickness of the vacuum layer is 10 Å, which is enough to avoid interactions between periodic slabs of atomic layers. To study the surface relaxation, we optimized the atomic positions in several near-surface planes for the (001)-Re (from 1 to 6), (001)-B (from 1 to 4), (001)-BB (from 1 to 5), and (110) (from 1 to 4) surfaces, while the remaining bottom layers were fixed.

3. Results and discussion

Because the number of nearest neighbors for the atoms at the surface layer is less than that of the atoms in the bulk, it is unlikely that they will remain at their precise bulk-truncated positions. Rather, the atoms are likely to move in response to their new environment. In our calculations, both the (001) and (110) surfaces of ReB_2 with various termination layers were simulated, and we used an idealized model for a perfect and flat surface. The side and top views of the optimized surface structures are shown in Fig. 1.

3.1. The structural relaxations of clean ReB_2 (001) surfaces

There are three types of termination that were considered for the (001) surface: (001)-Re, (001)-B, and (001)-BB surfaces. They are all trigonal with a space group of 156. Only the positions of the atoms along the normal surface have changed, and no rumpling appears on the ReB_2 (001) surface for the three types of surface structures. Table 1 illustrates our calculated atomic displacements, δz_n, (relative to the ideal positions) as a percentage of the bulk lattice parameter for the (001) surfaces, where n denotes the sequence number of an atomic layer away from the surface. The sign of δz_n is positive for a displacement toward the vacuum and negative toward the bulk. Table 1 shows that atoms of the same layers have an equivalent change for the same sign. We also find that the first-layer Re (B) atoms always move inward by relaxation, while the second-layer atoms move outward. Consequently, the distance between the first and second layers decreases. Moreover, the atomic displacements of the first-layer atoms are larger than those of the second-layer atoms for the (001)-Re and (001)-B surfaces, and the displacements of the first-layer atoms are comparable to those of the second-layer atoms for the (001)-BB surface. Hence, the largest relaxation occurs on the surface layers for the (001) surfaces with -Re, -B, and -BB terminations.

To obtain detailed information on atomic relaxation in each of the atomic layers, the fractional change in displacement between neighboring layers ($\delta d_{n,\ n+1}/d_{un}$) and the length of the shortest surface covalent bonds (d_{Re-B} and d_{B-B}) after relaxation of the ReB_2 (001) surface are also listed in Table 1. $\delta d_{n,\ n+1}/d_{un}$ denotes the fractional change due to relaxation in the distance between the n and n+1 layers as a percentage of the unrelaxed layer spacing. If $\delta d_{n,\ n+1}/d_{un}$ is negative, it indicates that the distance between the n and n+1 layers decreases by relaxation. Otherwise, the distance between adjacent layers increases. The results show that the vertical spacings between the first and second layers for the relaxed (001) surfaces

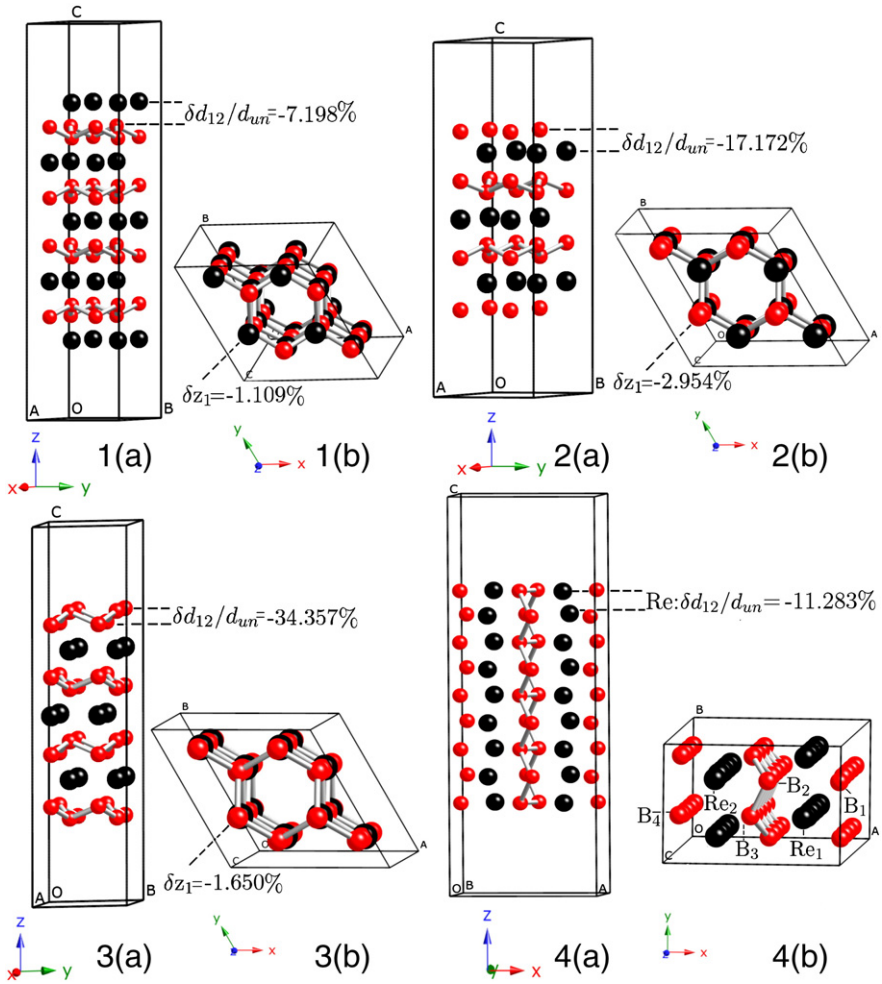

Fig. 1. The side and top views of the slab models of the ReB_2 (001)-Re, (001)-B, (001)-BB, and (110) surface structures. The black and the red colored spheres represent the Re and B atoms, respectively.