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Difference in the outermost layer between $TaB_2(0001)$ and $HfB_2(0001)$

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Atomic and electronic structures of $TaB_2(0001)$ and $HfB_2(0001)$ surfaces are investigated with use of the first-principles pseudopotential calculations. Our calculated surface formation energies indicate that the graphitic-boron-terminated $TaB_2(0001)$ surface is energetically more favorable, whereas the $HfB_2(0001)$ surface prefers termination with a close-packed Hf layer. These findings are consistent with experimental facts. We have also found the difference in the surface relaxation between them. The first interlayer spacing of the B-terminated TaB_2 surface is expanded by 0.39%. On the other hand, the outermost Hf-terminated HfB_2 surface is contracted by 4.8%. [S0163-1829(99)05147-4]

Metal borides exhibit multiple stoichiometries and crystal structures according to boron/metal ratio.[1] This originates in peculiar bonding of boron, which does not follow the conventional covalent bonding rules.[2] As the proportion of boron atoms to metal atoms increases in the metal borides, boron atoms form one-dimensional chains, two-dimensional nets, and three-dimensional clusters. These boron networks reinforce binding among metals and produce some properties such as high hardness, high-melting point, and chemical inertness as well as high-electric conductivity.

Among many metal borides, transition-metal diborides have received much attention since their atomic structure is not only simple but also unique.[3–7] These are layered compounds with a hexagonal AlB_2-type structure in which a graphitelike boron layer alternates with a close-packed metal layer.[8] Under room temperature and atmospheric pressure crystalline boron in the form of graphite does not exist. Then, the structure and the properties of the bulk transition-metal diborides have been discussed in terms of chemical bonding. Boron atoms form strong sp^2 bonds and interact with metal d orbitals. These chemical bondings are closely related to charge transfer between the boron and the metal atoms. Although two conflicting models have been proposed to explain different experiments,[4,5] it is now accepted that there is a small amount of charge transfer from the metal to the boron atoms.[6,7]

In addition to many studies of the bulk properties of the transition-metal diborides, comparable interest in their surface properties has been generated. Recently, atomic structures of $TaB_2(0001)$ and $HfB_2(0001)$ surfaces have been investigated by impact collision ion scattering spectroscopy (ICISS) experiments. The results showed the following remarkable difference between TaB_2 and HfB_2: The topmost layer of the $TaB_2(0001)$ surface is B and the first-interlayer spacing is expanded by 8.5%.[9] In the case of the $HfB_2(0001)$ the topmost layer is Hf.[10] There has been no experimental information about relaxation of the HfB_2 surface. The origin of the difference is an open question. In the present paper, we investigate atomic and electronic structures of the $TaB_2(0001)$ and the $HfB_2(0001)$ surfaces by using first-principles calculations and address the atomic structure problem from the standpoint of energetics. To our knowledge, there are no theoretical researches on metal diboride surfaces, so far.

Our calculation[11] is based on the local-density approximation in density functional theory. We used the Wigner interpolation formula for the exchange-correlation, and a norm-conserving pseudopotential. As for B, Hf, and Ta pseudopotentials, the optimized pseudopotentials originated from Troullier and Martins[12] were used in order to reduce the number of plane waves. Nonlocal parts of s,p (for B, Hf, and Ta), and d (for Hf and Ta) pseudopotentials were transformed to the Kleinman-Bylander separable form.[13] We first determine the equilibrium lattice constants of bulk TaB_2 and bulk HfB_2 by calculating total energies using the pseudopotentials. The obtained lattice constants are $a=3.08$ and $c=3.27$ Å $(c/a=1.06)$ for TaB_2 and $a=3.10$ and $c=3.40$ Å $(c/a=1.10)$ for HfB_2, which are close to the experimental values [$a=3.10$ and $c=3.23$ Å $(c/a=1.04)$ for TaB_2 and $a=3.14$ and $c=3.47$ Å $(c/a=1.11)$ for HfB_2].[8]

In the present surface calculations, we have employed a repeated slab geometry with seven MB_2 $(M=\text{Ta, Hf})$ (1×1) layers separated by a vacuum region equivalent to seven MB_2 layers thickness. The alternate metal and boron layers representing metal-terminated (B-terminated) surfaces are composed of four metal (B) layers and three B (metal) layers. We have used a plane-wave basis set to expand the electronic wave function at each k point. The cutoff energy of the plane-wave basis is 64 Ry. The surface Brillouin zone is divided into 4×4 meshes and 16 inequivalent k points are used for the k-space integration. We have determined equilibrium atomic positions in the surface layers by the first-principles molecular dynamics (FPMD).[14] We adopt a steepest-descent type of algorithm for the electronic degrees of freedom[15] and ordinary molecular dynamics for the ionic motion. All the atoms in the slab are relaxed. The convergence criterion for forces acting on each atom in the unit cell is 1.0×10^{-3} hartree/bohr.

Table I shows the calculated geometry optimization results of the M-terminated $MB_2(0001)$ surfaces and the

TABLE I. Calculated surface relaxations, $\Delta d_{12}/d_{bulk}$ and $\Delta d_{23}/d_{bulk}$, and work functions, Φ, for $HfB_2(0001)$ and $TaB_2(0001)$ surfaces, compared with experiments (Refs. 9 and 22).

	$\Delta d_{12}/d_{bulk}$	$\Delta d_{23}/d_{bulk}$	Φ (eV)
Hf-terminated HfB_2 ($a=3.10$ Å)	-4.8%	$+0.89\%$	5.28
B-terminated HfB_2 ($a=3.10$ Å)	-7.2%	$+2.0\%$	6.30
Ta-terminated TaB_2 ($a=3.08$ Å)	-8.9%	$+0.55\%$	4.79
B-terminated TaB_2 ($a=3.08$ Å)	$+0.29\%$	-2.5%	6.48
B-terminated TaB_2 ($a=3.06$ Å)	$+0.39\%$	-2.5%	6.48
B-terminated TaB_2 (experiments)	$+8.5\%$		6.0

B-terminated $MB_2(0001)$ surfaces. We used the calculated lattice constants of bulk HfB_2 ($a=3.10$, $c=3.40$ Å) and TaB_2 ($a=3.08$, $c=3.27$ Å) as the lattice constants in the slab calculations. The outermost interlayer spacings of Hf-terminated HfB_2 and B-terminated HfB_2 are contracted by 4.8% and 7.2%, respectively. The second interlayer spacings are correspondingly expanded by 0.89% and 2.0%, respectively. On the other hand, a little expansion of the topmost layer spacing (0.29%) has been found on the B-terminated TaB_2 surface while the outermost Ta-terminated TaB_2 surface is contracted by 8.9%. The second interlayer spacings of the B-terminated and the Ta-terminated surfaces are correspondingly contracted (2.5%) and expanded (0.55%), respectively. The oscillatory relaxations in HfB_2 and TaB_2 have also been found in other metal surfaces.[16] There is a noticeable difference between HfB_2 and TaB_2. Although there is a discrepancy between our calculations and the ICISS experiments for the relaxation of the B-terminated TaB_2 surface, it seems that the stabilized topmost surfaces have small relaxations. In other words, the Hf-terminated $HfB_2(0001)$ surface and the B-terminated TaB_2 (0001) are likely to be stable without introducing large relaxation.

We discuss quantitatively the stability of the HfB_2 and the TaB_2 surfaces. Since the B-terminated and the metal-terminated surface models contain the different number of B and metal atoms, we have calculated their surface formation energies as a function of the chemical potential of one of the constituents, B, within the thermodynamically allowed range at $T=0$ K.[17] The surface formation energy can be expressed as $\Omega=(E_{total}-\Sigma_i n_i \mu_i)/(2S)$, where E_{total} is the total energy of the slab and n_i and μ_i are the number and the chemical potential of the ith constituents, respectively. S is the surface area. The factor $\frac{1}{2}$ accounts for two equivalent surfaces per the slab. The chemical potential of B is restricted within the range, $\mu_{B(bulk)}-\frac{1}{2}\Delta H \leqslant \mu_B \leqslant \mu_{B(bulk)}$, which is determined by the constraints, $\mu_B \leqslant \mu_{B(bulk)}$, $\mu_M \leqslant \mu_{M(bulk)}$, $\mu_M+2\mu_B \leqslant \mu_{MB_2(bulk)}$, and the heat of formation, $\Delta H=\mu_{M(bulk)}+2\mu_{B(bulk)}-\mu_{MB_2(bulk)}$. We have obtained $\mu_{M(bulk)}, \mu_{B(bulk)}$, and $\mu_{MB_2(bulk)}$ from the total energies per atom of bulk Hf(hcp), bulk Ta(bcc), bulk α-B_{12}(rhombohedron) and those per MB_2 of bulk HfB_2 and bulk TaB_2, respectively. Our calculated heats of formation of HfB_2 and TaB_2, $\Delta H_{HfB_2}=3.46$ and $\Delta H_{TaB_2}=2.08$ eV, are in good agreement with experimental values ($\Delta H^{exp}_{HfB_2}=3.4$ and $\Delta H^{exp}_{TaB_2}=2.0$ eV).[1] Figure 1 shows relative surface formation energies of TaB_2 and HfB_2 as a function of the chemical potential of B: $\mu_B-\mu_{B(bulk)}$. Over wide range of allowed chemical potentials, the B-terminated $TaB_2(0001)$ surface is more stable than the Ta-terminated $TaB_2(0001)$ surface. On the other hand, the Hf-terminated $HfB_2(0001)$ surface is more favorable than the B-terminated $HfB_2(0001)$ surface. Here, we must consider relation between the chemical potential and the experimental condition. Hayami *et al.* reported that the HfB_2 clean surface, which is terminated by a flat (1×1) Hf layer is obtained by heating at 1900°C. This surface turns into a structure in which Hf atoms are adsorbed on a flat Hf layer after once heating over 2000°C. They interpreted that this irreversible structural change is due to desorption of boron atoms from the subsurface.[10] On the other hand, TaB_2 clean surface obtained after heating at 1730°C is terminated by a graphitic boron layer.[9] Even after once heating above 1730°C a Ta-terminated surface has never been observed. This is probably due to segregation of boron atoms from inner layers to the outermost layer following desorption of the first-layer boron atoms.[18] We speculate that the different behavior of boron atoms between HfB_2 and TaB_2 arises from difference in strength of the B-B bond. As stated later, the B-B π bond of TaB_2 is tighter than that of HfB_2, since charge is more transferred from Ta to B than from Hf to B. Anyway, these facts suggest that an Hf-rich condition can be easily achieved in the HfB_2 surface and

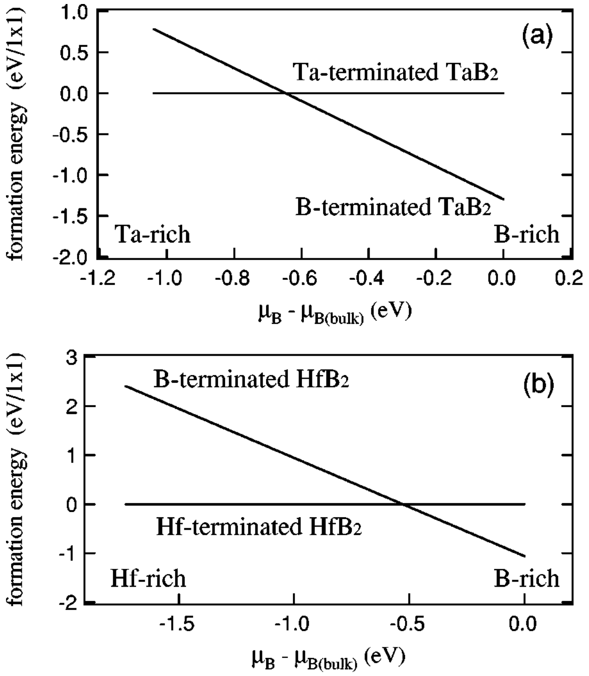

FIG. 1. Surface formation energies per (1×1) lateral unit cell for (a) $TaB_2(0001)$ surfaces and (b) $HfB_2(0001)$ surfaces as a funciton of the chemical potential of B. The chemical potentials, $\mu_B-\mu_{B(bulk)}$, range (a) from B-rich limit, 0 eV, to Ta-rich limit, $-\frac{1}{2}\Delta H_{TaB_2}=-1.04$ eV and (b) from B-rich limit, 0 eV, to Hf-rich limit, $-\frac{1}{2}\Delta H_{HfB_2}=-1.73$ eV.

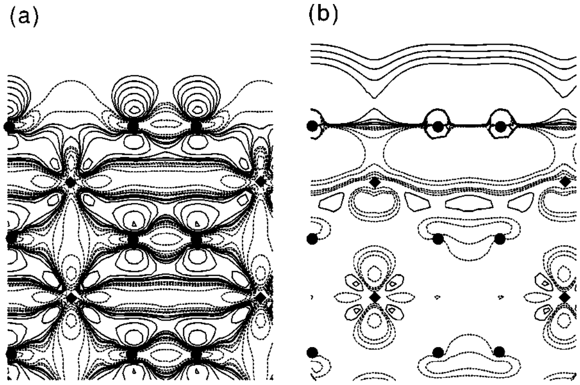

FIG. 2. Contour maps of difference charge densities for the B-terminated TaB_2 surface, (a) $\Delta\rho=\rho$ (relaxed TaB_2 seven-layer slab)$-\rho$(boron four-layer slab)$-\rho$(Ta three-layer slab) and (b) $\Delta\rho'=\rho$(relaxed TaB_2 slab)$-\rho$(unrelaxed TaB_2 slab). The contours are drawn for the $(11\bar{2}0)$ plane normal to the surface. Solid and dotted lines indicate the amount of accumulated and depleted charges, respectively. Solid circles and solid diamonds denote boron and metal atoms, respectively.

B-rich condition in the TaB_2 surface. Therefore, our calculated results are well consistent with the experimental findings.

Relaxation at simple metal surfaces has been understood in terms of two pictures: One is the conventional Finnis-Heine (FH) picture, which is based on smoothing of the surface charge density corrugation.[19] The other is the Feibelman's chemical picture, which is based on bond-order bond-length correlation.[20] The former cannot explain the expansion of the first-interlayer spacing found in Be(0001) (Ref. 21) and the large contraction of outermost layer spacing found in hexagonal close-packed Ti and Zr surfaces.[20] Therefore, the FH picture is unlikely to be applied to the present study. First, let us discuss the relaxation of the TaB_2 surfaces. In order to gain some insight into origin of the outward relaxation of the B-terminated TaB_2 surface, we have investigated charge state of it. We have found that charge transfer from the second Ta layer to the topmost B layer occurs and the charge between B atoms in the first layer increases. This phenomenon suggests that the chemical bonds between the B atoms in the first layer are strengthened and that the B-B bond length gets shortened. In our calculations, however, since each layer has a (1×1) lateral periodicity, the atomic positions in the plane is determined by the lateral lattice constants. Therefore we performed FPMD calculations at various lateral lattice constants a and optimized the atomic configurations along the surface normal. When the lateral lattice constant is reduced to 3.06 Å, the surface formation energy of the B-terminated TaB_2 surface is lowered by 0.12 eV/bohr^2 and the topmost layer is more expanded by 0.39% (see Table I) than the result calculated with $a=3.08$ Å. The second interlayer spacing of the B-terminated TaB_2 surface is contracted by 2.5%. The results support our anticipation. Figure 2(a) shows the contour map of the difference charge density for the B-terminated TaB_2 surface ($a=3.06$ Å), $\Delta\rho=\rho$ (B-terminated TaB_2 seven-layer slab)$-\rho$(graphitic boron four-layer slab)$-\rho$(Ta three-layer slab). Calculations of the graphitic boron four-layer slab and the Ta three-layer slab were performed with the same cell size, atomic position, number of k points and cutoff energies as the TaB_2 seven-layer slab. The $\Delta\rho$ plots indicate the charge accumulation in π orbitals of the B layers and the formation of Ta-B bonds. In particular, the charge increment in the outermost B layer, extending into the vacuum, is remarkable. This phenomenon corresponds to large calculated work function of 6.48 eV, which is in good agreement with an experimental value[9,22] (see Table I). Considering that bonding π orbitals of the graphitic boron are originally empty, the incremental charge in the π orbitals strengthen the chemical bonds in the first boron layer of the B-terminated TaB_2 surface. The consequence is that the bonds between the first and the second layers is weakened and that the first interlayer spacing is expanded. This can be clearly seen by the charge redistribution map shown in Fig. 2(b). This map displays the difference between the charge density of the relaxed and unrelaxed surfaces. As the outermost boron layer expands, there are a charge depletion between the first and the second layers and a charge increment out of the surface. In the case of the Ta-terminated surface, the surface formation energy is not lowered by changing the lateral lattice constant.

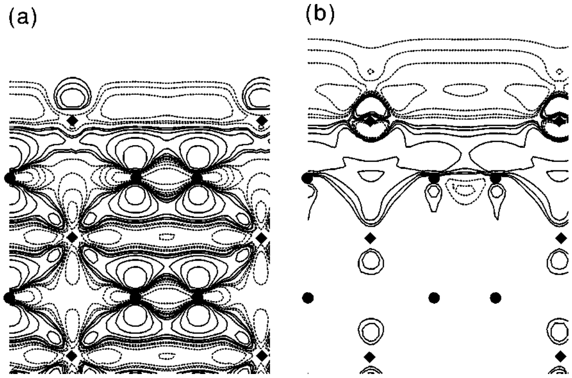

FIG. 3. Contour maps of difference charge densities for the Hf-terminated HfB_2 surface, (a)$\Delta\rho=\rho$(relaxed HfB_2 seven-layer slab)$-\rho$(boron three-layer slab)$-\rho$(Hf four-layer slab) and (b) $\Delta\rho'=\rho$(relaxed HfB_2 slab)$-\rho$(unrelaxed HfB_2 slab).

As to HfB_2, both the B-terminated and the Hf-terminated surfaces have minimum surface formation energies at the bulk lateral lattice constant. Therefore, even if the first layer of HfB_2 is B, the B-B bonds in the first layer does not get shortened. The transferred charge from the second Hf layer to the first layer is too small to strengthen the B-B bonds, since valence of Hf is four, while that of Ta is five. As shown in Table I, both the B-terminated and the Hf-terminated surfaces exhibit large inward relaxations. The latter, which is energetically more favorable and has been experimentally observed, has smaller relaxation than the former. Figure 3(a) shows the contour map of the difference charge density for the Hf-terminated HfB_2 surface, $\Delta\rho=\rho$ (Hf-terminated HfB_2 seven-layer slab)$-\rho$(graphitic boron three-layer slab)$-\rho$(Hf four-layer slab). We can see that the charge is accumulated in π orbitals of the B layers and that the B-Hf bonds are formed. Figure 3(b) shows the difference between the charge density of the relaxed and unrelaxed surfaces of the Hf-terminated HfB_2. The incremental charge is accumulated in the interlayer region between the first Hf and the second B layers. Therefore, the interlayer bonds are strengthened and the first-interlayer spacing is contracted.

Finally, we address the large difference between our calculations ($\Delta d_{12}/d_{bulk}=+0.39\%$) and the experiments ($\Delta d_{12}/d_{bulk}=+8.5\%$) for the relaxation of the B-terminated TaB_2 surface. There are some reports that the discrepancies in the Rh(001) and the Be(0001) surface relaxations between theoretical and measured results are due to neglect of thermal expansion.[23,24] Our small outward relaxation was determined by the total energy calculations at the temperature of 0 K. The effect of the zero-point vibrations has not also been taken into account. The large outward relaxation was obtained by the ICISS experiments at room temperature. The thermal vibrations at room temperature may increase the outermost layer spacing. This is the future problem.

In summary, our first-principles calculations show that the graphitic-boron-layer termination is energetically more favorable for the $TaB_2(0001)$ surface, whereas the Hf-layer termination is for the $HfB_2(0001)$ surface. We have also found the remarkable difference in the surface relaxation between them. These are closely related to the amount of charge transfer from the metal to the boron atoms, which brings about the difference in strength of chemical bonds between B-B and B-Hf or B-Ta.

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