First-principles study of electronic properties and stability of Nb_5SiB_2 (001) surface*

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The density functional calculations are performed to study the electronic structure and stability of Nb_5SiB_2 (001) surface with different terminations. The calculated cleavage energies along the (001) planes in Nb_5SiB_2 are 5.015 $J \cdot m^{-2}$ and 6.593 $J \cdot m^{-2}$ with the break of Nb–Si and Nb–NbB bonds, respectively. There exists a close correlation between the surface relaxation including surface ripple and the cleavage energy: the larger the cleavage energy, the larger the surface relaxation. Moreover, the surface stability of the Nb_5SiB_2 (001) with different terminations has been investigated by the chemical potential phase diagram. From a thermodynamics point of view, the four terminations can be stabilized under different conditions. In chemical potential space, NbB (Nb) and Nb (Si) terminations are just stable in a small area, whereas Si (Nb) and Nb (NbB) terminations are stable in a large area (the letters in brackets represent the subsurface atoms).

Keywords: first principles, Nb_5SiB_2 surface, electronic properties, surface stability

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1. Introduction

With high melting points and relatively low densities, the Nb–Si based alloys have been extensively studied as the candidate structural materials at high temperatures in the next generation. Nevertheless, Nb_5Si_3 has severe brittleness at ambient temperature. In order to overcome this frailty, ductile metal Nb phase has been introduced to form the Nbss/Nb_5Si_3 in situ composites (Nbss: Nb Solid Solution).[1−6] In these studies, the main purpose was to balance the room-temperature toughness and high-temperature strength as well as the oxidation resistance. It has been proved that alloying and suitable heat treatments are effective means, which have resulted in a significant improvement in the properties of the composites. The influence of alloying by the addition of Ti, Ta, Cr, Al, Mo, Hf and Sn on the microstructure, the mechanical property and the oxidation behaviour of Nb–Nb_5Si_3 in situ composites have been investigated.[7−11] The result showed that the addition of Ti and/or Mo can enhance the fracture toughness of the Nb–Si binary system, while the improvement in oxidation resistance can be achieved by the addition of Ti, Hf, Sn or their combinative addition. However, the addition of Mo caused a decrease in oxidation resistance, but an increase in hardness by 10% was obtained.[8,12,13]

Boron was used to improve the mechanical properties and the oxidation behaviours of Nb–Si alloys. The results showed that B improved both the room-temperature toughness and the high-temperature strength.[14] In the ternary system Nb–Si–B there exists $Nb_5Si_{3-x}B_x$ phase ($0 < x \leq 2$), named T_2, which is isostructural with α-Nb_5Si_3.[1,15] Considering the Nb_5SiB_2 stoichiometry, two boron atoms substitute two silicon atoms at the 8h Wyckoff position sites of Nb_5Si_3. These studies concentrated on the phase equilibrium, the solidification pathway and the preparation of T_2 phase.[16] An investigation of superconducting properties of the $Nb_5Si_{3-x}B_x$ phase has also been carried out.[17] In fact, the understanding of surface properties such as surface energy, stability and adhesion, is crucial for applications. However, few experimental quantitative studies about surface properties have been carried out.

First-principles calculations are widely used in the study of bulk materials,[18−20] as well as surfaces and interfaces,[21−24] providing much information that can not be obtained by experiments. In this study, we investigate the surface properties of (1×1) Nb_5SiB_2 (001) with different terminations by density functional

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theory (DFT).

2. Calculation method and models

The DFT calculations were performed with the Vienna *ab initio* simulation package (VASP),[25−27] employing projector augmented wave (PAW) pseudopotentials[28,29] and the PW91 generalized gradient approximation (GGA) exchange correlation functional.[30] We tested kinetic-energy cutoff and k-point sampling convergence for all supercells and verified the accuracy of the computational methods by calculating the bulk Nb_5SiB_2. As a result of the convergence tests, we used the kinetic-energy cutoff of 400 eV. The calculated lattice constants of Nb_5SiB_2 are $a = 6.278$ Å (1 Å = 0.1 nm), $c = 11.712$ Å, and $c/a = 1.866$, which are in good agreement with experimental values ($a = 6.232$ Å, $c = 11.616$ Å, and $c/a = 1.864$).[31] Besides, we considered only very simple (1×1) cells, and have not explored possible surface reconstructions.

As shown in Fig. 1(a), the Nb_5SiB_2 bulk has a $D8_1$ symmetry with a complicated stacking sequence. It can be determined that there are two groups of niobium atoms in a Nb_5SiB_2 conventional cell according to the atomic geometry positions, while all the Si atoms are equivalent and all the B atoms are also equivalent. Therefore, the $Nb_5SiB_2(001)$ surface has four different terminations as shown in Figs. 1(b)–1(e). The four surfaces are of Nb and B mixture NbB(Nb), pure Nb(Si), pure Si(Nb) and pure Nb(NbB), which are denoted by S1, S2, S3, and S4, respectively. The letters in brackets represent the subsurface atoms. All the Nb_5SiB_2 (001) terminations were simulated using symmetrical slabs with 9 or 11 atomic layers separated by a vacuum region of 15 Å.

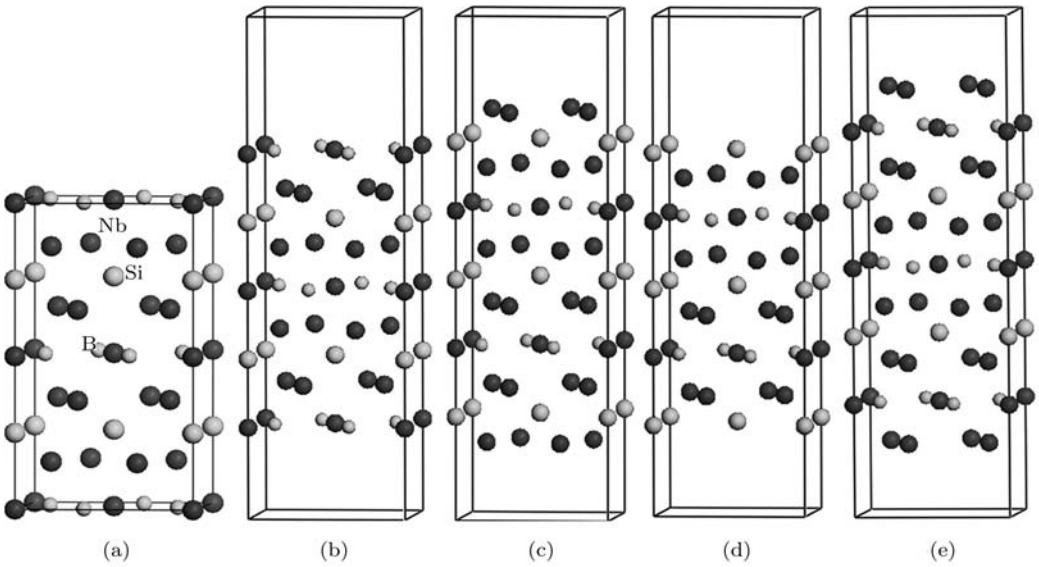


Fig. 1. Atomic structure models: (a) bulk Nb_5SiB_2, (b)–(e) Nb_5SiB_2 (001) surface models, with (b) NbB(Nb) termination denoted by S1, (c) Nb(Si) termination by S2, (d) Si(Nb) termination by S3, and (e) Nb(NbB) termination by S4. The letters in brackets represent the subsurface atoms.

3. Results and discussion

3.1. Cleavage energy

The bond strength of bulk Nb_5SiB_2 is described in terms of the cleavage energy, which is calculated by two complementary parts of the surfaces. The cleavage energy is defined as the energy to split the bulk into two complementary parts of the surfaces:[23,32−34]

$$E_{\rm cl}^{X+Y} = \frac{1}{2S_0}(E_{\rm slab}^{X} + E_{\rm slab}^{Y} - nE_{\rm Nb_5SiB_2}^{\rm bulk}). \quad (1)$$

Here, $E_{\rm cl}^{X+Y}$ denotes the cleavage energy and S_0 is the surface area of slab X or slab Y. The surface area of slab X is the same as that of slab Y. $E_{\rm slab}^{X}$ and $E_{\rm slab}^{Y}$ are the total energies of the two complementary surfaces which have been relaxed with fixed surface area. $E_{\rm Nb_5SiB_2}^{\rm bulk}$ is the total energy of bulk Nb_5SiB_2 of a unit cell and n is the total number of bulk units in the two slabs. Table 1 lists the calculated cleavage energies and the interlayer distances between (001) planes in the bulk Nb_5SiB_2.

Table 1. Cleavage energies (in J/m^2) and layer distances (in Å) between different (001) layers in bulk Nb_5SiB_2 and α-Nb_5Si_3.

	layer-layer	cleavage energy/(J/m^2)	layer distance/Å	
Nb_5SiB_2	Nb–NbB	6.593	1.611	present work
	Nb–Si	5.015	1.317	
Nb_5Si_3	Nb–NbSi	5.787	1.774	Ref. [34]
	Nb–Si	5.103	1.216	

Among the four termination surfaces, S1 and S2 are one type of complementary pair, which is generated by the splitting of the NbB–Nb bonds whereas S3 and S4 are the other type of complementary surface which is generated by the splitting of the Nb–Si bonds along the (001) plane. For the Nb_5SiB_2 system, it can be seen from Table 1 that the cleavage energy between Nb and Si planes (5.015 J/m^2) is smaller than that between Nb and NbB planes (6.593 J/m^2), though the interlayer distance between the Nb and Si planes (1.317 Å) is smaller than that between Nb and NbB planes (1.611 Å). The result directly indicates that the Nb–Si bond is the most energetically favourable cleavage point. Therefore, it can be predicted that when the tensile stress is imposed on Nb_5SiB_2 along the [001] direction, the break will take place in the Nb–Si bond. This can be easily understood from their electronegativity difference. The electronegativities of Nb, Si, and B atoms are 1.6, 1.9, and 2.04, respectively.[35] The electronegativity difference between Nb and B (0.44) is greater than that between Nb and Si (0.30), which leads to the stronger interaction between Nb and NbB planes.

We have investigated the cleavage energies of corresponding bonds of α-Nb_5Si_3.[34] Comparing the Nb_5SiB_2 system with the α-Nb_5Si_3 system, the cleavage energies between Nb and Si planes in both systems are smaller than those between NbB and Nb planes and between NbSi and Nb planes. The cleavage energy of Nb–Si in Nb_5SiB_2 is a little smaller than that in α-Nb_5Si_3, while the cleavage energy between Nb and NbB planes in Nb_5SiB_2 is much larger than that between Nb and NbSi planes in α-Nb_5Si_3. The bond strength difference in Nb_5SiB_2 is much greater than that in α-Nb_5Si_3 system.

3.2. Surface structure

The interlayer relaxation can be evaluated by $\Delta = (d - d_0)100/d_0$. Here d and d_0 denote the interlayer distances of the relaxed surface and bulk materials, respectively. We also calculated the surface ripples between Nb and B of the top layer for S1 surface as well as the energy differences between relaxed and fixed surface structures for the four surfaces. The calculated interlayer relaxations together with the surface ripples and the energy differences between relaxed and fixed surface structures are listed in Table 2.

Table 2. Interlayer relaxations. Δ_{12}, Δ_{23} and Δ_{34} of the Nb_5SiB_2 (001) surface with different surface terminations together with surface ripples (in Å) and energy differences (in eV) between relaxed and fixed surface structures. Note that S1, S2, S3 and S4 surfaces have the same surface areas.

	models			
properties	S1	S2	S3	S4
Δ_{12}/%	–3.48	–9.49	–10.4	–4.59
Δ_{23}/%	1.21	–1.75	–0.56	0.12
Δ_{34}/%	–1.37	0.99	–0.68	0.68
Ripple/Å	0.303	–	–	–
ΔE/eV	–1.981	–1.213	–0.728	–0.271

For the top layer, the interlayer distances of the four optimized surface models contract compared with those of bulk Nb_5SiB_2. The S2 and the S3 surfaces contract by about 9.49% and 10.4%, respectively, while the S1 and the S4 surfaces contract just by about 3.48% and 4.59%, much smaller than the S2 and the S3 surfaces. At first glance, it seems that the S1 and the S4 surfaces are more stable than the S2 and the S3 surfaces. However, the energy differences between relaxed and fixed surface structures are −1.981 eV, −1.213 eV, −0.728 eV and –0.271 eV for S1, S2, S3 and S4 surfaces, respectively. From the energy point of view, S3 and S4 surfaces are more stable than S1 and S2 surfaces. Furthermore, the relaxations of S1 and S2 surfaces are concerned with the top three layers, while S3 and S4 surfaces are concerned only with the top layer. In addition, the surface ripple in the first layer of S1 surface attains to 0.303 Å and Nb atoms are upward according the atomic structure after optimization. Considering the atomic structure relaxation and energy variation caused by structure relaxation, it can be predicted that the S3 and the

S4 surfaces are more stable than S1 and S2 surfaces. There is close correlation between the cleavage energy and the surface relaxation including surface ripple: the larger the cleavage energy, the larger the surface relaxation, which is consistent with the result of Zhang and Wang.[32]

3.3. Derivation of surface energy

The thermodynamic stability of a given surface is determined by its surface energy. The thermodynamics formalism is employed by the following scheme.[32,36–40] The surface energy γ with neglecting the TS term and pressure term contributions can be defined as

$$\gamma = \frac{1}{2S_0}[E_{\rm slab} - N_{\rm Nb}\mu_{\rm Nb} - N_{\rm Si}\mu_{\rm Si} - N_{\rm B}\mu_{\rm B}], \quad (2)$$

where S_0 is the surface area; $E_{\rm slab}$ denotes the total energy of the surface slab; $N_{\rm Nb}$, $N_{\rm Si}$ and $N_{\rm B}$ are the numbers of Nb, Si and B atoms in the slab respectively; $\mu_{\rm Nb}$, $\mu_{\rm Si}$ and $\mu_{\rm Si}$ refer to the chemical potentials of Nb, Si and B respectively.

The total chemical potentials $\mu_{\rm Nb_5SiB_2}$ of the surface system are in equilibrium with that of bulk $E^{\rm bulk}_{\rm Nb_5SiB_2}$, i.e.

$$\mu_{\rm Nb_5SiB_2} = E^{\rm bulk}_{\rm Nb_5SiB_2}, \quad (3)$$

and then the chemical potential of the Nb_5SiB_2 surface system can be expressed as

$$\mu_{\rm Nb_5SiB_2} = 5\mu_{\rm Nb} + \mu_{\rm Si} + 2\mu_{\rm B}. \quad (4)$$

With Eq. (4), the surface energy of a ternary compound can be described as a function of chemical potentials of B and Si. Therefore, Eq. (2) becomes

$$\gamma = \frac{1}{2S_0}\left[E_{\rm slab} - \frac{1}{20}N_{\rm Nb}E^{\rm bulk}_{\rm Nb_5SiB_2} - \left(N_{\rm B} - \frac{2}{5}N_{\rm Nb}\right)\mu_{\rm B} - \left(N_{\rm Si} - \frac{1}{5}N_{\rm Nb}\right)\mu_{\rm Si}\right]. \quad (5)$$

The variation of surface condition may be represented by the deviation of the actual chemical potential from these bulk values,

$$\Delta\mu_{\rm Nb} = \mu_{\rm Nb} - E^{\rm bulk}_{\rm Nb}, \quad \Delta\mu_{\rm Si} = \mu_{\rm Si} - E^{\rm bulk}_{\rm Si}, \quad \text{and} \quad \Delta\mu_{\rm B} = \mu_{\rm B} - E^{\rm bulk}_{\rm B}. \quad (6)$$

Combining Eqs. (2)–(6), the surface energy becomes

$$\gamma = \sigma - \frac{1}{2S_0}\left[\left(N_{\rm B} - \frac{2}{5}N_{\rm Nb}\right)\Delta\mu_{\rm B} + \left(N_{\rm Si} - \frac{1}{5}N_{\rm Nb}\right)\Delta\mu_{\rm Si}\right], \quad (7)$$

where

$$\sigma = \frac{1}{2S_0}\left[E_{\rm slab} - \frac{1}{20}N_{\rm Nb}E^{\rm bulk}_{\rm Nb_5SiB_2} - \left(N_{\rm B} - \frac{2}{5}N_{\rm Nb}\right)E^{\rm bulk}_{\rm B} - \left(N_{\rm Si} - \frac{1}{5}N_{\rm Nb}\right)E^{\rm bulk}_{\rm Si}\right], \quad (8)$$

with σ being the surface energy when the chemical potentials of B and Si equal those of the pure bulk B and pure bulk Si, respectively. In a similar way to that in the above process, we can also give the surface energy as a function of $\Delta\mu_{\rm Nb}$ and $\Delta\mu_{\rm Si}$ as well as $\Delta\mu_{\rm Nb}$ and $\Delta\mu_{\rm B}$.

The combination of Eq. (6) with Eq. (4) gives

$$5\Delta\mu_{\rm Nb} + \Delta\mu_{\rm Si} + 2\Delta\mu_{\rm B} = -E^{\rm f}_{\rm Nb_5SiB_2}, \quad (9)$$

where $E^{\rm f}_{\rm Nb_5Sib_2}$ is the formation energy, determined by the difference between the total energy of Nb, Si and B elements in their bulk phase and the total energy of bulk. The calculated formation energy is 5.10 eV obtained from the following formula:

$$E^{\rm f}_{\rm Nb_5SiB_2} = 5E^{\rm bulk}_{\rm Nb} + E^{\rm bulk}_{\rm Si} + 2E^{\rm bulk}_{\rm B} - E^{\rm bulk}_{\rm Nb_5SiB_2}. \quad (10)$$

Since Si-rich (or Nb-rich and B-rich) preparation conditions are fixed by $\Delta\mu_{\rm Si} = 0$ (or $\Delta\mu_{\rm Nb} = 0$ and $\Delta\mu_{\rm B} = 0$), one finds that the surface can be in equilibrium with its surroundings only when the chemical potentials are within both upper and lower bounds. We can obtain the upper and the lower bounds of chemical potential for element Nb (Si or B) by setting $\Delta\mu_{\rm Si} = 0$, $\Delta\mu_{\rm B} = 0$ ($\Delta\mu_{\rm Nb} = 0$, $\Delta\mu_{\rm B} = 0$ or $\Delta\mu_{\rm Nb} = 0$, $\Delta\mu_{\rm Si} = 0$) in the following equation:

$$-E^{\rm f}_{\rm Nb_5SiB_2} \leq 5\Delta\mu_{\rm Nb} + \Delta\mu_{\rm Si} + 2\Delta\mu_{\rm B} \leq 0. \quad (11)$$

We can obtain the chemical potential ranges of Nb, Si and B to be -1.02 eV $\leq \Delta\mu_{\rm Nb} \leq 0$ eV, -5.10 eV $\leq \Delta\mu_{\rm Si} \leq 0$ eV and -2.55 eV $\leq \Delta\mu_{\rm B} \leq 0$ eV, respectively.

3.4. Surface stability of Nb_5SiB_2 (001) with different terminations

The surface energies each as a function of $\Delta\mu_B$ are shown in Fig. 2(a) under the condition of Si-rich ($\Delta\mu_{Si} = 0$). It can be clearly seen that the surface energies of the Si(Nb) and Nb(NbB) terminations are independent of $\Delta\mu_B$, while in the case of the other two terminations, the surface energies are linearly dependent on $\Delta\mu_B$. The surface energy of the Si(Nb) termination is the lowest and NbB(Nb) is the highest over the almost entire range of chemical potential of $\Delta\mu_B$, which indicates that Si(Nb) is more stable than the others and the NbB(Nb) surface is the most unfavourable surface in the case of Si-rich condition.

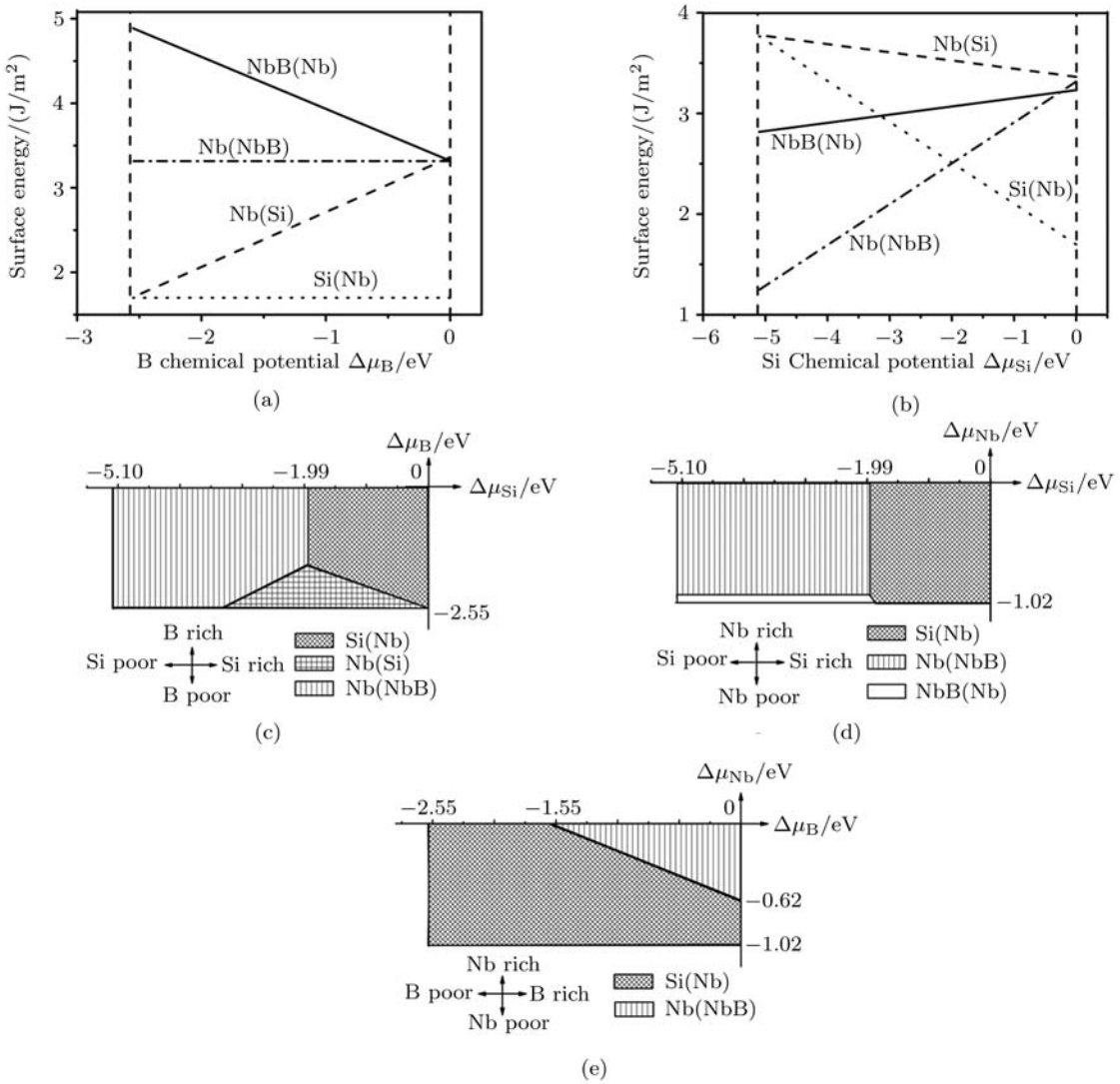


Fig. 2. Surface energies (in $J \cdot m^{-2}$) and surface stabilities of Nb_5SiB_2 system. Panel (a) is for surface energy as a function of $\Delta\mu_B$ (with $\Delta\mu_{Si} = 0$), panel (b) for surface energy as a function of $\Delta\mu_{Si}$ (with $\Delta\mu_B = 0$), panel (c) for surface diagram as a function of $\Delta\mu_B$ and $\Delta\mu_{Si}$, panel (d) for surface diagram as a function of $\Delta\mu_{Nb}$ and $\Delta\mu_{Si}$, and panel (e) for surface diagram as a function of $\Delta\mu_B$ and $\Delta\mu_{Nb}$.

Figure 2(b) shows the variations in the surface energy of each termination as a function of $\Delta\mu_{Si}$ under B-rich condition ($\Delta\mu_B = 0$). It can be found that the surface energies of all the four terminations are linearly dependent on $\Delta\mu_{Si}$. In the Si-poor case, the Nb(NbB) termination is more stable than the others. With the increase of $\Delta\mu_{Si}$, the stability of the Nb(NbB) decreases, and the Si(Nb) termination becomes the most stable one.

The surface energies of each termination as a function of $\Delta\mu_B$ and $\Delta\mu_{Si}$ are calculated, and phase diagram composed of the most stable surfaces is shown in Fig. 2(c). The whole range of surface stability diagram is divided into three parts:, i.e., Si(Nb), Nb(NbB) and Nb(Si) terminations. When $\Delta\mu_{Si}$ is high, corresponding to Si-rich condition, Si(Nb) surface is the most

stable one. Under Si-poor condition, the most stable surface is the Nb(NbB) surface. A small area of Nb(Si) surface appears in the surface diagram. The NbB(Nb) termination does not appear.

The surface stability as a function of $\Delta\mu_{\mathrm{Nb}}$ and $\Delta\mu_{\mathrm{Si}}$ ($\Delta\mu_{\mathrm{Nb}}$ and $\Delta\mu_{\mathrm{B}}$) is also given in Fig. 2(d) (Fig. 2(e)). It can be seen that Si(Nb) and Nb(NbB) surfaces cover very large area while NbB(Nb) surfaces cover a small area. This means Si(Nb) and Nb(NbB) surfaces are more stable than NbB(Nb) termination, which is consistent with results of surface structure relaxation.

3.5. Density of states

Figure 3 shows the local densities of states (LDOSs) of the top two layers of the Nb_5SiB_2 (001) surface with different terminations compared with those of the corresponding atoms in the bulk. For NbB(Nb) termination surface (S1), the energy levels of top and second layer of atoms are all shifted toward the higher energy. The energy level of top layer atom is shifted toward the higher energy while the energy level of subsurface atom is shifted slightly toward the lower energy for Nb(Si) termination S2 surface. The energy levels of surface and subsurface layer atoms of Nb(NbB) termination S4 surface change a little compared with that of the corresponding bulk atoms. The change of energy level of surface atoms of S4 surface is less than that of S1 surface, which implies that the S4 termination is more stable than the S1 termination. This is consistent with the previous analysis.

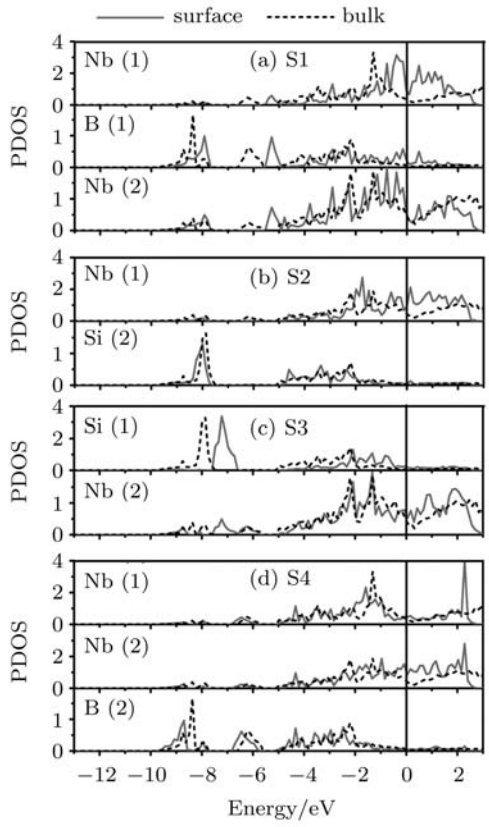


Fig. 3. The local densities of states (LDOSs) of the top two surface layers of Nb_5SiB_2 (001) surface with different terminations compared with those of the corresponding atoms in the bulk Nb_5SiB_2 (short dash line). The solid lines correspond to the LDOSs of the surface models. Panel (a) is for S1, panel (b) for S2, panel (c) for S3, and panel (d) for S4. The number (1) or (2) in bracket denotes the atom in the top layer or subsurface. The Fermi level is shifted to zero.

4. Conclusion

In this work, we have presented a density functional theory study of the $(1 \times 1)Nb_5SiB_2(001)$ surface properties using the Vienna *ab initio* simulation package (VASP). Based on the calculations of the four termination models, the cleavage energies, the surface relaxation and the surface stability are clearly understood from an atomic point of view. The calculated cleavage energies of bulk Nb_5SiB_2 are 5.015 $\mathrm{J \cdot m^{-2}}$ and 6.593 $\mathrm{J \cdot m^{-2}}$ for Nb–Si and Nb–NbB bonds along the (001) planes, respectively, which indicates that the Nb–Si bond is a more energetically favourable cleavage point. The structure relaxations of NbB(Nb) and Nb(Si) surfaces are concerned with the top three layers, whereas Si(Nb) and Nb(NbB) terminations only with concerning the top layer. There is a large surface ripple (0.303 Å) in the first layer of NbB(Nb) surface, and Nb atoms are upward according the atomic structure after optimization. There is close correlation between the cleavage energy and the surface relaxation including surface ripple: the larger the cleavage energy, the larger the surface relaxation. Moreover, the stabilities of the (1×1) Nb_5SiB_2 (001) surfaces with different terminations are investigated. From the viewpoint of thermodynamics, the four terminations can be stabilized under different conditions, Si(Nb) and Nb(NbB) terminations are stable in a very large area, while NbB(Nb) and Nb(Si) terminations are stable just in a small area.

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