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The chemisorption of Mg on the Si (100)-(2 × 1) surface

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Abstract: The adsorption of a half monolayer of Mg atoms on the Si (100)-(2 × 1) surface is studied by using the self-consistent tight binding linear muffin-tin orbital method. Energies of the adsorption systems of Mg atoms on the different sites are calculated. It has been found that the adsorbed Mg atoms are more favorable on the cave site above the surface than any other sites on the Si (100)-(2 × 1) surface and a metastable shallow site also exists above the surface. This is in agreement with the experimental results. The charge transfer and the layer projected density of states are also studied.

Key words: silicon; chemisorption; supercell; magnesium; low index single crystal surface
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1. Introduction

Adsorption of overlayers of Mg atoms on silicon surfaces has been a subject of growing interest during the last decade because of its importance in technological applications such as the efficient photocathodes and thermionic energy converters. The understanding of Mg adsorption on the Si (100) surface has been an especially interesting problem to investigate because of the possible use of Si substrates for the growth of Mg_2Si films[1]. Although much effort has been made to achieve an in depth understanding of the electronic structure of a clean Si (100) surface with the adsorbed Mg atoms in a variety of experiments[2−6], the descriptions of the most stable site of Mg adsorption on the Si (100) surface remain controversial.

At the initial stage of interface formation, the chemisorption of Mg atoms on the Si (100) surface is important for understanding the properties of the system. In the recent papers, Kawashima *et al.*[2] reported that Mg atoms were adsorbed on the hollow site (valley-bridge site, in their notation) for the coverage of 1, 1/3, 1/4, 1/6, and 0 monolayer (ML), respectively. Cho *et al.*[3] observed that the most preferable adsorption site for both 1/2 and 1/3 ML coverage is the cave site between two dimers (bridge site, in their notation). Hutchison *et al.*[4], in their scanning tunneling microscope (STM) results for the low coverage-Mg–Si (100) case, have reported three types of adsorption geometries at room temperature. Type Ⅰ is the most favorable phase and it refers to a single Mg atom adsorbed on a cave site. Kubo *et al.*[5] supported that two Mg atoms adsorbed on the adjacent hollow sites at room temperature. In addition, for the annealed case at high temperature, they have claimed a single Mg atom adsorbed on the neighboring shallow site or two Mg atoms adsorbed on the cave sites. In this paper, we make a first-principle calculation with the supercell approach to deal with the electronic structure and adsorption properties of a half monolayer (i.e., 2 Mg atoms per 2 × 1 unit cell) of Mg on the Si (100)-(2 × 1) surface. The rest of the paper is organized as follows. In Section 2, we give the model and the calculation method. The calculated results and discussion are presented in Section 3, and a brief summary is given in Section 4.

2. The model and calculation method

The electronic structures and adsorption properties of a half monolayer of Mg on the Si (100)-(2 × 1) surface are studied by using the first principle tight binding linear muffin-tin orbital (TB-LMTO) method[7−9] with the supercell approach. This method has been applied to deal with the adsorption properties of Co atoms on the Si (100) surface[10] and Co on the H-passivated Si (100) surface[11], respectively, and the obtained results are in good agreement with the experimental results. Therefore, it is believed that the TB-LMTO method with the solid-vacuum supercell approach can be used to treat the present problem.

The standard supercell model used for the calculation is similar to those used in Refs. [10] and [11]. The adsorption of a half monolayer of Mg atoms on the Si (100)-(2 × 1) surface is considered in the present work. A total of 20 layers are assembled to form the system for calculation, including a slab of thirteen silicon layers that is used to simulate the substrate. A half monolayer of Mg atoms is placed on each side of the slab (see Fig. 1(a)). In the region of the slab, there are five atomic layers vacuum introduced in the supercell. Test calculation with a thicker vacuum layer (equivalent to nine atomic layers) and a thicker substrate (equivalent to seventeen silicon layers) show that the present model is reasonable to give convincing results. The supercell has mirror symmetry with respect to the central layer of the solid films.

The Si (100)-(2 × 1) surface model used for the calculation is similar to those used in Refs. [12]. Five possible adsorption geometries for a half monolayer of Mg atoms on the Si (100)-(2 × 1) surface, namely, the cave site (C), the hollow site (H), the pedestal site (P), the bridge site (B) and the shallow site (S) are considered (see Fig. 1(b)). The initial value of

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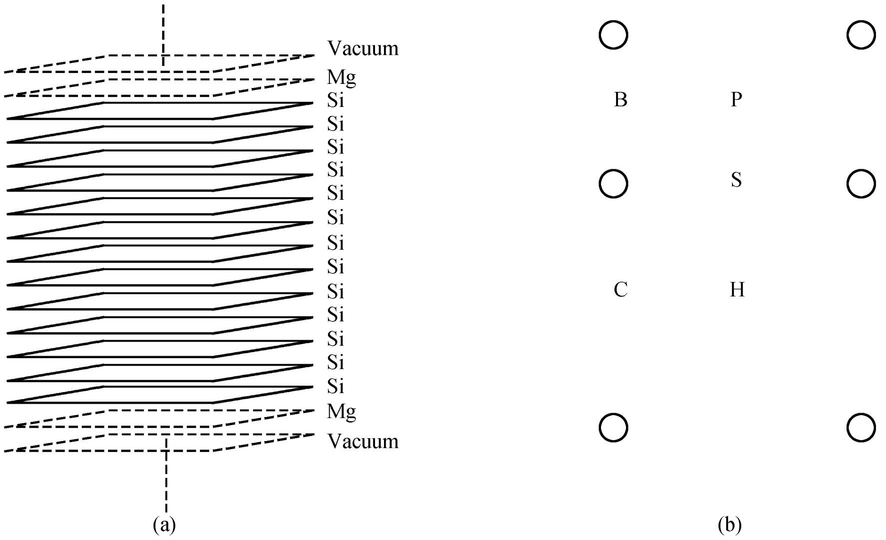

Fig. 1. (a) Illustration of the present supercell for Mg adsorption used on the Si (100)-(2 × 1) surface and (b) the adsorption geometries. The labels C, H, P, B and S denote the adsorption sites for Mg on the cave site, the hollow site, the pedestal site, the bridge site and the shallow site, respectively. Open circles represent the first layer of Si.

Table 1. The calculated total energy E_{tot} of the supercell versus the vertical distance D of the adatoms from the Si surfaces.

Site	Cave	Hollow	Pedestal	Bridge	Shallow
D (nm)	0.072	0.053	0.132	0.201	0.180
E_{tot} (eV)	0.000	1.113	1.234	0.607	0.198

distance between the Mg layer and the substrate is chosen in such a way that the bond lengths between the Mg atom and its nearest-neighbor surface atoms equal the sum of their covalent radii. In the calculation, the valence electrons in the neutral configurations are $3s^2$ for Mg and $3s^2$ $3p^2$ for Si. The rest of the occupied levels are frozen. The Brilliouin zone (BZ) integration was performed by the tetrahedron technique. A grid of 105 k points in the Brilliouin zone is used in the irreducible BZ to construct the tetrahedrons.

3. Results and discussion

3.1. Adsorption energy

The variations of the total energy (denoted as E_{tot}) of the supercell versus vertical distance (D) of the adatoms from the surface are calculated. The D values correspond to the heights measured from Si dimers of Mg adatoms on cave, hollow, pedestal, bridge, and shallow site, respectively. The minimum values of E_{tot} corresponding to D with different absorbed sites are given in Table 1. The energies listed in Table 1 are relative to the lowest value of the total energy for Mg adsorbed on the cave site (i.e. site C in Fig. 1(b)). Table 1 shows clearly that, among the adsorption sites considered here, the most stable position of the Mg atom is on the cave site with a distance 0.072 nm above the surface. This result is in agreement with experiments[3, 4]. The resulting Mg–Si bond length on the cave site is 0.267 nm, which is very close to the result (0.268 nm) of Shaltaf[1]. Kawashima *et al.*[2] reported that Mg atoms were adsorbed on the hollow site (valley-bridge site, in their notation) for the coverage of 1, 1/3, 1/4, 1/6, and 0 monolayer (ML), respectively. In our calculation, the hollow site is unstable and the total energy of Mg on the hollow site is 1.113 eV larger than that of the cave site. Shaltaf *et al.*[1] using the package fhi98pp calculated the adsorption of Mg on the Si (100)-(2 × 1) surface and suggested that adsorption takes place on the cave site, and the conclusion is the same with us. Kubo *et al.*[5] have claimed a single Mg atom adsorbed on the neighboring shallow site or two Mg atoms adsorbed on the cave sites. Our results suggested that the shallow site is a metastable site with a distance 0.18 nm above the surface and the total energy of Mg on the shallow site was found to be 0.198 eV larger than that of the cave site, which is in agreement with the experimental results[5].

According to the above discussion, in the following, we will consider the roles of the cave site and the shallow site for a half monolayer of Mg atoms adsorbed on the Si (100)-(2 × 1) surface.

3.2. Project density of states

In the calculation, we use the slab model to represent the supercell. Mg adatoms and Si exist in different layers. The densities of states (DOS) for different layers are calculated separately. This is called the layer project density of states (LPDOS). The LPDOS for the clean Si (100)-(2 × 1) system and the Mg adsorbed system are shown in Fig. 2. The DOS for the bulk Si is also calculated by using a separate bulk Si system which is shown by a dashed line for comparison. The zero-point energy (vertical line in the figure) is aligned at the Fermi level. From the figures it can be seen that the LPDOS of the middle layer is bulk-like. This also indicates that the model of the supercell is reasonable for simulating the Mg/Si (100)-(2 × 1) system.

From Fig. 2(a), i.e. the LPDOS of the clean Si (100)-(2 ×

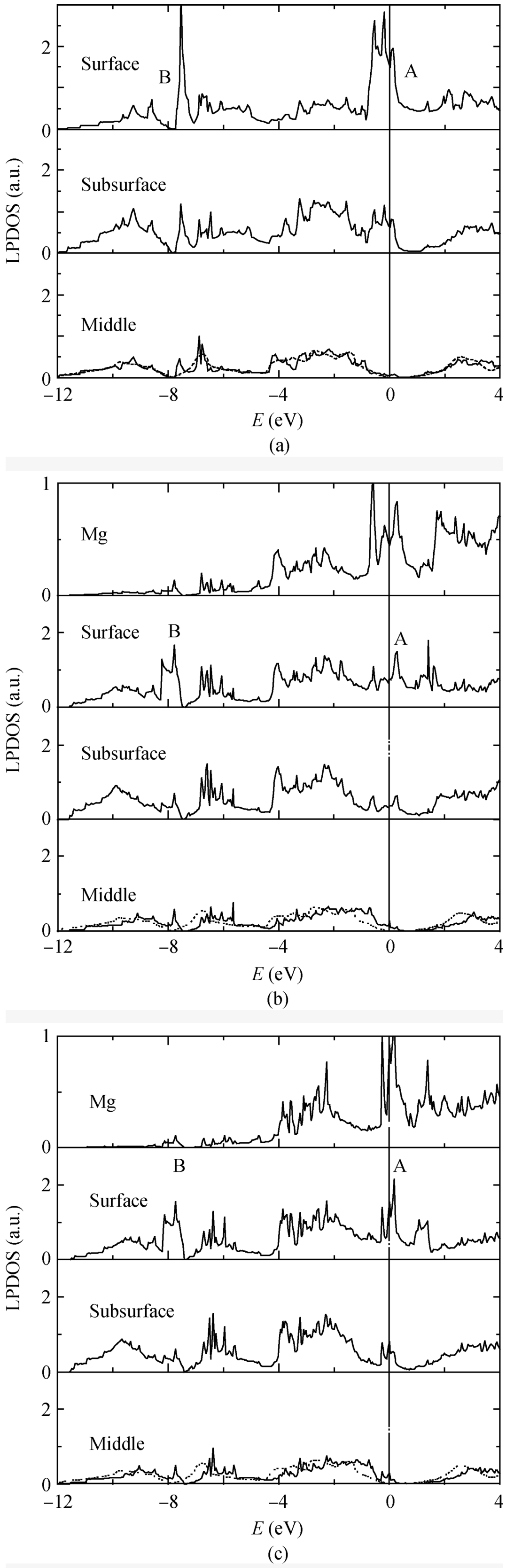

Fig. 2. The LPDOS for (a) the clean Si (100)-(2 × 1) surface, (b) Mg adsorbed on cave site, and (c) Mg adsorbed on shallow site. The vertical line indicates the Fermi level and the dashed line is the LPDOS for the bulk.

1) surface, it can be seen that the LPDOS for the surface layer and the subsurface layer is greatly different from the bulk one. On the surface layer, a high peak (A) appears at the Fermi level with a large tail in the energy gap, which corresponds to the Si dangling bond states contributed to mainly by Si $3p^2$ states with a little part from Si $3s^2$ states. Another large sharp peak (B) appears at about 7.5 eV below the Fermi level. In contrast to peak (A), peak (B) is a resonance state mainly contributed to by the Si $3s^2$ states with a little part from Si $3p^2$ states. The two peaks get damped rapidly on the subsurface layer.

Comparing with the LPDOS of the clean surface, we see from Fig. 2(b) that the following results can be obtained for the case of Mg adsorbed on the cave site. The LPDOS in the middle layer changes slightly, which means that the middle layer is quite bulk-like and the presently used supercell is reasonable to simulate the surface problem. The changes in LPDOS in surface layer are quite noticeable due to the Mg adsorption. The peak A disappears completely after adsorption, the state pervades the area from –4.5 to 2 eV, and the peak B decreases and shifts down from –7.4 to –8.2 eV. These results are due to the fact that adsorbed Mg atoms interact with surface atoms and partially saturate the dangling bonds of the surface atoms. This is in agreement with the experiment[13]. Moreover, the interaction between Mg atoms and the surface atoms is due to the bonding of Mg $3s^2$ states with $3p^2$ states of surface Si atoms. Bonding of the Mg $3s^2$ states with the Si $3s^2$ states is weak. This is a general behavior of metal on the silicon substrate.

Comparing Figs. 2(a) and 2(b) with Fig. 2(c), i.e. the LPDOS of Mg adsorbed on the shallow site, we can obtain the following results. The changes in LPDOS in the surface layer are no more noticeable than that in Fig. 2(b) for the Mg adsorption. The peaks A and B decrease slightly after adsorption compared with Fig. 2(a). In contrast to peak B, peak A apparently decreases. The reason for the above facts is that the bonding of the adsorbed Mg atoms $3s^2$ states interact with that of surface Si atoms $3p^2$ states. But this interaction is not stronger than that of the cave site. This result is the main reason that the LPDOS of Mg adsorbed on the shallow site is different from that of the cave site. Moreover, this result also indicates that the Mg atoms density at the shallow site is diluted; therefore, a small number of Mg atoms can be adsorbed on this position. This conclusion explains theoretically the problem that only Kubo *et al.*[5] have claimed a single Mg atom adsorbed on the shallow site for the annealed case at high temperature experimentally. At the same time, bonding of the Mg $3s^2$ states with Si $3s^2$ states is very weak.

3.3. Charge transfer

Usually, chemisorptions are accompanied by charge transfer between the adsorbates and the substrate. In fact, it is the electron cloud transfer and overlap, not the isolated electrons transfer. Therefore it is called effective charges. Table 2 gives the layer effective charges (defined as the atomic charges relative to the neutral configurations), which are obtained from the sums of the effective charges of all atoms and empty spheres on the corresponding layers in the unit cell.

It is found from Table 2 that, for the clean surface, the effective charges in the surface are negative. This means that the surface Si atoms transfer some of their electrons to the second

Table 2. The layer effective charges (in the unit of electron) in the unit cell for the clean and Mg adsorbed surfaces. Here the effective charges denote the sum of the effective charges of all atoms and empty spheres inside the layer.

Adlayer		Surface	Subsurface	Third layer	Middle layer
Clean surface		−0.73	0.12	0.03	0.00
Mg adsorbed layer					
(Cave site)	−1.01	0.36	0.03	−0.01	0.00
(Shallow site)	−0.95	0.29	0.05	−0.02	0.00

layer and empty spheres in the vacuum. Clearly, the second layer gains 0.12 electrons. The layer effective charges for Mg atoms adsorbed on the Si (100)-(2 × 1) surface are given in Table 2, too. Compared with the clean surface, for the case of Mg adsorbed on the cave site, the surface layer gains 1.09 electrons, the second layer loses 0.09 electrons and the third layer loses 0.04 electrons. Therefore, in total about 0.96 electrons are transferred from the adsorbed Mg atoms to the substrate. This means the adsorbed Mg atoms transfer some of their electrons to the empty spheres in the vacuum. For the case of Mg adsorbed on the shallow site, compared with the clean surface, the surface layer gains 1.02 electrons, the second layer loses 0.07 electrons and the third layer loses 0.05 electrons. There are in total about 0.90 electrons transferred from the adsorbed Mg atoms to the substrate. In contrast, the charges transferred from Mg atoms to the substrate for the cave site adsorption are more than that of the shallow site adsorption. The result shows that the Mg–Si interaction for the shallow site adsorption is weaker than that of the cave site adsorption, indicating that the density of Mg atoms at the shallow site is diluted. From Table 2, it also can be seen that the effective charges on the third and middle layers are almost unaffected by the adsorption of the two cases, showing that the thickness of the slab is reasonable.

4. Conclusion

In summary, the electronic structures and adsorption properties of a half monolayer of Mg atoms on the Si (100)-(2 × 1) surface have been studied by using the self-consistent TB-LMTO method. Through the total adsorption energy calculation, the analysis of the layer projected density and the charge distribution, it has been found that the adsorbed Mg atoms are more favorable on the cave site above the surface than any other sites on the Si (100)-(2 × 1) surface. The LPDOS in the clean surface decrease significantly after Mg adsorbed on the cave site above the surface, since the dangling bonds of the surface Si atoms are partially saturated by the adsorbed Mg atoms. The $3s^2$ states of Mg atoms mainly bond with $3p^2$ states of the surface Si atoms, and the other bonding is weak.

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