Vol 13 No 6, June 2004
1009-1963/2004/13(06)/0932-06

Chinese Physics

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Chemisorption of Fe on Au-passivated Si(001) surface*

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(Received 30 June 2003; revised manuscript received 2 February 2004)

The chemisorption of one monolayer of Fe atoms on a Au-passivated Si(001) surface is studied by using the self-consistent tight-binding linear muffin-tin orbital method. The Fe adatom chemisorption on an ideal Si(001) surface is also considered for comparison. The chemisorption energy and layer projected density of states for a monolayer of Fe atoms on Au-passivated Si(001) surface are calculated and compared with that of the Fe atoms on an ideal Si(001) surface. The charge transfer is investigated. It is found that the most stable position is at the fourfold hollow site for the adsorbed Fe atoms, which might sit below the Au surface. Therefore there will be a Au–Fe mixed layer at the Fe/Au–Si(100) interface. It is found that the adsorbed Fe atoms cannot sit below the Si surface, indicating that a buffer layer of Au atoms may hinder the intermixing of Fe atoms and Si atoms at the Fe/Au–Si(001) interface effectively, which is in agreement with the experimental results.

Keywords: chemisorption, iron, gold, low index single crystal surface, passivation
PACC: 6830, 7115F, 7320A

1. Introduction

The ability to grow high-quality magnetic expitaxial thin films of 3d metals on semiconductor substrates is an important field, since for many technological applications as well as for fundamental physics studies one wants to exploit the magnetic anisotropy of the material. On the other hand, the growth of magnetic thin films offers unique opportunities for exploring the correlation between atomic structure and magnetic properties in these systems.[1]

The Fe/Si system continues to be of interest due to the possible incorporation of magnetic elements into silicide-integrated optoelectronic or microelectronic devices. A number of investigations dealing with the interlayer coupling in Fe–Si multilayer have been reported.[2–5] In particular, it was found that the growth at room temperature of a Fe layer on Si(001) substrate led to the formation of an intermixed phase at the Fe/Si(001) interface and subsequent growth of polycrystalline Fe overlayers.[6–9] Moreover, such interface interdiffusion has a strong influence on the magnetic behaviour of the deposited layer.[10]

The amorphous silicide at the interface,[6,9] strongly related to the dangling bonds at the Si(001) surface, will act as a strong interaction with Fe at the interface. In order to reduce intermixing at the Fe/Si(001) interface, a thin passivation layer on the semiconductor surface is highly desirable. In addition, S, Se or B passivation used in previous studies[11,12] gives rise to a rougher surface and it is not clearly established to what extent it can prevent silicide formation. Narusawa *et al*[13] claimed a saturation of the Si dangling bonds by the deposited Au where this saturation was followed by an interface reaction that started abruptly when the Au film exceeded a critical thickness of four monolayers (MLs). Ceelen *et al*[14] reported that the dimer reconstruction for the clean Si(001) surface disappeared during the deposition of Au which chemically reacted with the surface Si, breaking up the dimers and saturating the dangling bonds. Reference [15] reported that 2 MLs of Au atoms were used to passivate Si(001) so as to suppress Fe–Si reactions in Fe films grown on the Si(001) surface, and findings also pointed to a significant reduction of silicide formation.

*Project supported by the National Natural Science Foundation of China (Grant Nos 60276004 and 60290083), the Foundation for University Key Teachers from the Education Bureau of Henan Province, and the Natural Science Foundation of the Education Bureau of Henan Province, China (Grant No 2003140027).

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In view of the above discussions, a thin Au layer on Si(001) prior to the Fe adsorption acting as a diffusion barrier can prevent the reaction between Fe and Si atoms and the formation of silicide. In this paper, using the first principle calculation with the supercell approach, we study the electronic structure and adsorption properties of 1 ML Fe on Au-passivated Si(001) surface. The rest of the paper is organized as follows. In Section 2, we explain the model and the calculation method. The calculated results and discussions are presented in Section 3, and a brief summary is given in Section 4.

2. Model and calculation method

In this paper, the electronic structure of a monolayer of Fe atoms adsorbed on the Au-passivated Si(001) surface is studied by using the first-principle tight-binding linear muffin-tin orbital (TB-LMTO) method.[16−18] This method for calculation has been applied to deal with the adsorption properties of Mn on GaAs(001),[19] and the results obtained are in good agreement with experiments. Therefore, it is believed that the TB-LMTO method with the solid–vacuum supercell can be used to treat the present problem.

For the adsorption of Fe on Au-passivated Si(001) surface, a standard supercell model is shown in Fig.1. A total of 16 layers are assembled to form the system for calculation, including a slab of eight silicon layers that is used to simulate the substrate, a monolayer of Au atoms on each side of the slab that is treated as buffer layers, and an adsorbed monolayer of Fe atoms that is put on one side of the slab. In the region of the slab, there are five atomic layers of vacuum introduced in the supercell.

Four possible adsorption geometries for a monolayer of Fe on the substrate, namely a top site (A), two bridge sites (B_1 with a Si atom on the fourth atomic layer below it, and B_2 with a Si atom on the second atomic layer below it) and a fourfold site (C) are considered (see Fig.1(b)). The initial value of the distance between the Fe monolayer and the surface is chosen in such a way that the bond length between the Fe atom and its nearest-neighbour surface atom equals the sum of their covalent radii. In practical calculations, the $3d^6 4s^2$ states of Fe, $5d^{10}\ 6s^1$ states of Au and $3s^2\ 3p^2$ states of Si are treated as valence bands. The rest of the occupied levels are frozen. The Brillouin zone (BZ) integration is performed by the tetrahedron technique. A grid of 196 $\boldsymbol{k}$ points in the BZ is used in the irreducible BZ to construct the tetrahedrons.

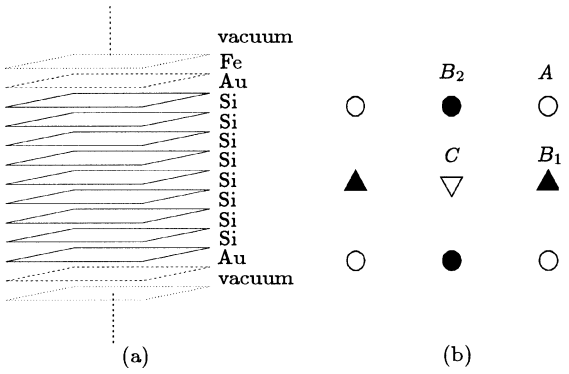


Fig.1. Illustration of the supercell we used for Fe adsorption on Au-passivated Si(001) surface (a) and the adsorption geometries (b). The labels A, B_1, B_2, and C denote the adsorption sites for Fe on the top site, two bridge sites (B_1 with a Si atom on the fourth atomic layer below it and B_2, with a Si on the second atomic layer below it) and the fourfold site, respectively. Open circle, solid circle, inverted empty triangle and solid triangle represent first, second, third and fourth layers of Si atoms, respectively.

In an attempt to hinder silicide formation, a monolayer of Au atoms is introduced to saturate the dangling bonds on the slab. Since in the experimental[13−15] studies for the Si(001) surface, the number of electronically active dangling bond states can be reduced dramatically by Au passivation, this method will be expected to improve the slab calculation and to be able to deal with the present problem theoretically. Our calculation shows that the most stable position of the Au atoms is at the top site at a distance of 0.2407 nm above the Si(001) surface.[20] Therefore, the Au atoms are set at those sites on each side of the slab.

3. Results and discussion

3.1. Fe adsorption on Si(001) surface

In order to better understand the electronic structure of one monolayer of Fe atoms on Au-passivated Si(001) surface, first, we study 1 ML Fe atoms on an ideal Si(001) surface for comparison. The model for calculation is similar to Fig.1. It includes eight silicon layers, a monolayer of Au atoms to saturate one face of the slab to simplify the calculation procedures, one adsorbed monolayer of Fe atoms, and six layers of vacuum. A similar model has been used in Ref.[19].

The variations of the total energy E_{tot} of the supercell with the vertical distance (D) of the adatoms from the surfaces are calculated. The minimum values of E_{tot} corresponding to D of different adsorbed sites are listed in Table 1. The energies listed in Table 1 are given relative to the lowest value of the total energy for Fe atoms adsorbed on the fourfold site. Table 1 shows clearly that, among the adsorption sites considered here, the most stable position of the Fe atom is at the fourfold hollow. In the following, only the C site adsorption is discussed. Figure 2 gives the curve of the total energy E_{tot} of the system versus the vertical distance D when the Fe atom is adsorbed on the fourfold site. It shows that the most stable adsorption occurs at the C site at a distance of 0.0258 nm above the surface. There exist a barrier at the Si surface and a local minimum at C_1 below the surface, therefore a Fe and Si mixed layer might exist at the Fe/Si(001) interface, which is in agreement with the experimental results.[6,9]

Table 1. Calculated total energy E_{tot} of the supercell versus the vertical distance D of the adatoms from the Si surface.

Site	A	B_1	B_2	C
D/nm	0.2358	0.2008	0.1308	0.0258
E_{tot}/eV	2.380	7.658	7.582	0.000

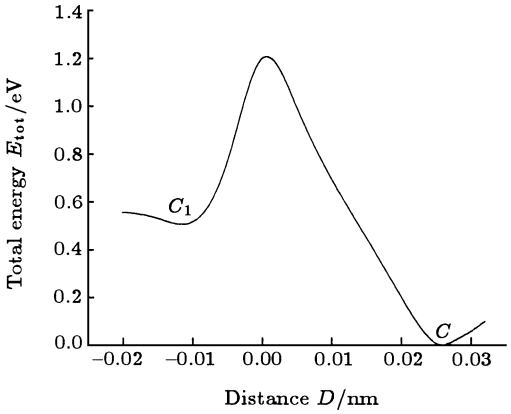


Fig.2. Total energy E_{tot} of Fe/Si(001) system versus the vertical distance D of the adatoms from the Si surface.

The layer project density of states (LPDOS) for the clean Si(001) system and the Fe adsorbed system are shown in Fig.3, in which the density of states (DOS) for the bulk is shown by the dashed line for comparison and the zero-point energy (vertical line) is aligned at the Fermi level. From the figures it can be seen that the LPDOS of the middle layer is bulk-like, which indicates that the model of supercell is reasonable for simulating the Fe/Si(001) system. From Fig.3(a), which is the LPDOS of the clean Si(001) surface, by removing the Fe layer, it can be seen that the surface layer is quite different from the bulk one. A high sharp peak A appears at the Fermi level with a large tail in the energy gap, which corresponds to the Si dangling bond states contributed mainly by Si 3p state. Another peak B appears at about 7.5 eV below the Fermi level. In contrast to peak A, peak B is a resonant state mainly contributed by the Si 3s state. The adsorption of Fe atoms on the Si(001) surface has strong effects on the LPDOS in the surface layer (Fig.3(b)). Peak A disappears completely after the adsorption, while peak B decreases and shifts down. These results are mainly attributed to the interaction of Fe 3d with Si 3p in the surface layer. The bonding of the Fe 4s state with Si 3s, 3p states and that of Si 3s with the Fe 3d, 4s states are weak.

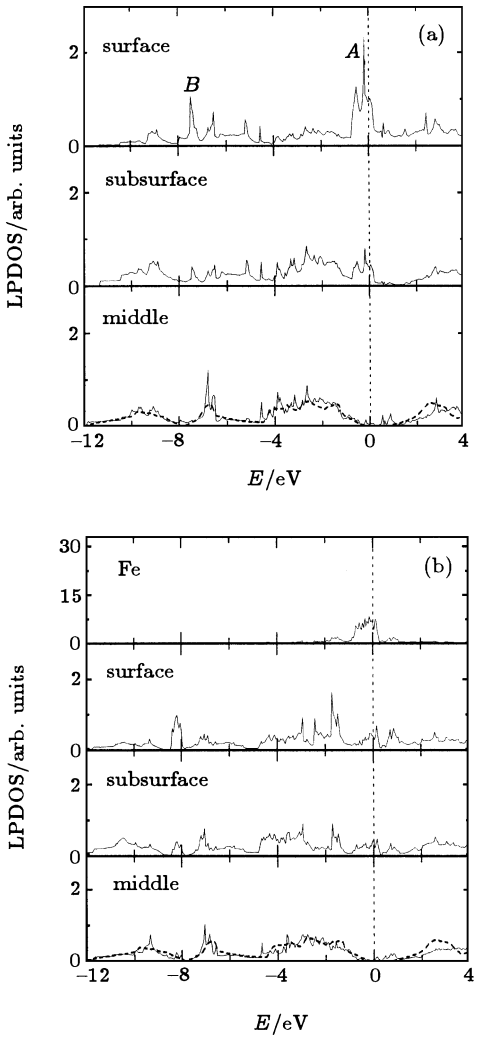


Fig.3. LPDOS for the system of clean (a) and Fe adsorbed (b) Si(001) surfaces. The vertical line indicates the Fermi level and the dashed line is the LPDOS for the bulk.

3.2. Fe adsorption on the Au-passivated Si(001) surface

In an attempt to hinder Fe and Si intermixing, one monolayer of Au atoms is treated as the buffer layer prior to the Fe adsorption. The model for calculation is shown in Fig.1(a).

For the adsorption of a monolayer of Fe atoms on Au-passivated Si(001) surface, each of the minimum $E_{\rm tot}$ values corresponding to D with the different adsorbed sites are given in Table 2, in which the listed energies are relative to the lowest value of the $E_{\rm tot}$ for the Fe atom adsorbed on the C_1 site (i.e. C site below the Au surface in Fig.1(b)). From Table 2, it can be easily concluded that, among the adsorption sites considered here, the most stable position of the Fe atom is at the C_1 site below the Au surface and at distance of 0.0992 nm from the Si surface. The large difference between the total energies for Fe (at B_1, B_2, and C) above the Au surface and for Fe (at C_1) below the Au surface demonstrates that it is possible for Fe atoms to sit below the Au surface. By calculation, we find that there is an energy barrier at the Au–Si surface. A mixed layer of Au–Fe might exist at the Fe/Si(001) interface. While setting Fe below the Si surface, no stable position can be obtained, which shows that there cannot exist a Fe–Si mixed layer at the interface. This indicates that the buffer layer of Au can effectively prevent Fe–Si intermixing. This result is in agreement with the experiment.[15]

Table 2. The calculated total energy $E_{\rm tot}$ of the supercell versus the vertical distance D of the adatoms from the Si surface.

Site	B_1	B_2	C	C_1
D/nm	0.3765	0.5318	0.3516	0.0992
$E_{\rm tot}$/eV	2.924	9.153	1.564	0.000

For the top site (i.e. A site in Fig.1(b)) adsorption, no stable position can be found. Table 2 does not give the case of the top site adsorption.

According to the above discussion, in the following, the C and C_1 site adsorptions are considered for a monolayer of Fe adsorption on the Au-passivated Si(001) surface.

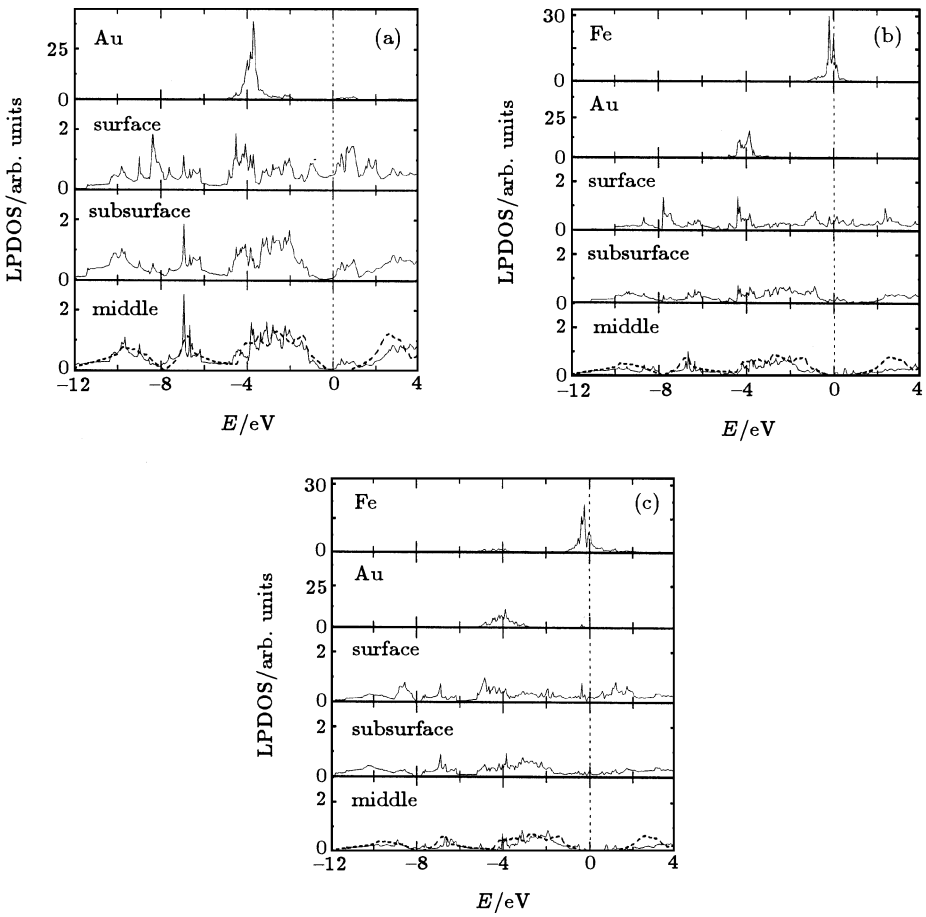


Fig.4. LPDOS for the system of clean surface (a), Fe adsorbed on C site (b) and on C_1 site (c) for the Au–Si(001) surface. The vertical line indicates the Fermi level and the dashed line is the LPDOS for the bulk.

The LPDOS for the clean system, which is obtained by removing the Fe layer, and the Fe adsorbed system are shown in Fig.4. The DOS for the bulk is shown by the dashed line for comparison. The zero-point energy is marked by a vertical line at the Fermi level. The LPDOS of the middle layer is bulk-like, which indicates that the model of supercell is reasonable for simulating the Fe/Au–Si(001) system.

From Fig.4(a), which is the LPDOS of the clean surface, compared with Fig.3(a), it can be seen that the changes in LPDOS of the surface layer are noticeable. The peak at the Fermi level damps rapidly, which is due to the Au adsorption, i.e. the adsorbed Au atoms interacting with the surface Si atoms and partial saturation of the dangling bonds of the surface atoms. Moreover, it is mainly the bonding of Au 5d state with Si 3p state. From Figs.4(b) and (c), the following results can be obtained for Fe adsorbed on Au-passivated Si(001) surface. For the Fe adlayer, compared with Fig.3(b), the two peaks become thin and tall, which is due to the fact that the adsorbed Fe atoms and Au atoms in the buffer layer are situated very close and the valence electrons of Fe atoms are repulsed by Au. Because of this interaction, the LPDOS of the Au layer also has small changes. 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 for simulating the surface problem.

Usually, chemisorptions are accompanied by charge transfer between the adsorbates and the substrate. Table 3 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 in the corresponding layers in the unit cell. It is found from Table 3 that, for the clean surface, the effective charges in the surface are negative. This means that the surface Si atom transfers some of its electrons to the second layer and empty sphere in the vacuum. Clearly, the second layer gains 0.05 electrons. The layer effective charges for Fe adsorbed on the Si(001) surface are given in Table 3, too. Compared with the clean surface, for the case of Fe adsorption on C site, the surface layer gains 0.24 electrons and the subsurface loses 0.07 electrons. Therefore, there are totally about 0.17 electrons transferred from the adsorbed Fe atom to the substrate. For the Fe adsorption on the C_1 site, the surface layer gains 0.12 electrons and the subsurface gains 0.13 electrons. Therefore the sum of charges transferred is 0.25 electrons. From Table 3, it also can be seen that the effective charges on the third and the middle layers are almost unaffected by the adsorption in the two cases, showing that the thickness of the slab is reasonable.

Table 3. The layer effective charges (in units of electron) in the unit cell for the clean and Fe adsorbed surfaces. Here the effective charge denotes the sum of the effective charges of all atoms and empty spheres inside the layer.

Site	Adlayer	Surface	Subsurface	Third layer	Middle layer
	clean surface	−0.47	0.05	0.00	0.00
	adsorbed layer				
C	Fe −0.72	−0.23	−0.02	0.02	0.00
	Au −0.52				
C_1	Fe −0.58	−0.35	0.18	0.03	0.00
	Au −0.92				

4. Summary

In summary, the chemisorption of Fe adatoms on the Au-passivated Si(001) surface has been studied by the TB-LMTO method. An effective method of using a monolayer of Au atoms to passivate the dangling bonds of the slab is introduced, which makes it possible to use Au atoms as buffer layers as well as to simplify the supercell to simulate the Si(001) surface. The Fe adatoms adsorbed on both the ideal and passivated Si(001) surfaces are considered separately. The total adsorption energy calculation and the analysis of the layer projected density of states are studied in this paper. It is found that, for the adsorbed Fe adatoms on the ideal Si(001) surface, the Fe atoms sit at the C site and a Fe–Si mixed layer may exist at the Fe/Si interface, while for Fe adsorption on the Au-passivated Si(001) surface, the Fe atoms are favourable on the C site and Fe atoms might sit below the Au surface. Therefore, a Au–Fe mixed layer may exist in the Fe/Au–Si (001) interface region. The

adsorbed Fe atoms cannot exist below the Si surface and there is no Fe–Si mixed layer. From the above discussion, we can conclude that using a Au buffer layer can effectively hinder the Fe–Si intermixing at the interface, which proves the possibility of growing high-quality magnetic expitaxial Fe films on noble metal-passivation Si(001) surface theoretically.

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