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Chemisorption of Au on Si(001) surface*

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The chemisorption of one monolayer of Au atoms on an ideal Si(001) surface is studied by using the self-consistent tight binding linear muffin-tin orbital method. Energies of the adsorption system of a Au atom on different sites are calculated. It is found that the most stable position is A site (top site) for the adsorbed Au atoms above the Si(001) surface. It is possible for the adsorbed Au atoms to sit below the Si(001) surface at the B_1 site(bridge site), resulting in a Au–Si mixed layer. This is in agreement with the experiment results. The layer projected density of states is calculated and compared with that of the clean surface. The charge transfer is also investigated.

Keywords: chemisorption, gold, silicon, low index single crystal surface
PACC: 6820, 7115F, 7320A

1. Introduction

Chemical adsorption on the surface of a material is of fundamental interest in theory and technological applications. In recent years, studies of transition-metal atoms adsorbed on semiconductor substrates have attracted enormous experimental and theoretical interest.[1,2] However, investigation of metal atoms adsorbed on metal or semiconductor substrates has been relatively scarcer. The growth of ultra-thin films on metal or semiconductor substrates has been the subject of increasing interest in modern technology.[3] The Au/Si(001) system is an important model system for metal–semiconductor interactions.[4] Although much effort has been made to achieve a deep understanding of the electronic structure of a clean Si surface with adsorbed noble-metal in a variety of experiments,[5–8] the descriptions of the structure of the Au–Si interface remain controversial.[9]

At the initial stage of interface formation, the chemisorption of metal atoms on the semiconductor surface is important for understanding the properties of the interface. In recent papers, Ceelen *et al*[10] reported that the outermost layer consisted of a mixture of Au and Si atoms for the whole coverage of Au films on Si(001) at room temperature, and the critical coverage to induce intermixing was at most 0.25 monolayer (ML) for the Au film thickness up to 10MLs. Lu *et al*[11] observed that the dimer-induced Si(001) (2×1) reconstruction gradually changed to a (1×1) reconstruction during the deposition of Au atoms which chemically reacted with the surface Si atoms. Narusawa *et al*[12] claimed a saturation of the Si dangling bonds caused by the deposited Au atoms, and this saturation was followed by an interface reaction that started abruptly when the Au film thickness exceeded a critical value of 4MLs. Yang *et al*[9] supported that the outmost layer consisted of almost 100% Au for the coverage of above 1ML, and no intermixing in the outmost layer was reported for higher coverage. Florin *et al*[13] reported that 2MLs of Au atoms were used to passivate Si(001) to suppress Fe–Si reactions in Fe films grown on the Si(001) surfaces, and experimental observations found a significant reduction of silicide formation. In this paper, we make a first-principle calculation with the supercell approach to deal with the electronic structure and adsorption properties of 1ML Au on the Si(001) 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 structure of a monolayer of Au atoms adsorbed on the Si(001) surface is studied by

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using the first-principle tight binding linear muffin-tin orbital (TB-LMTO) method.[14−16] This method has been applied to deal with the adsorption properties of Co atoms on the Si(001) surface and Mn on the GaAs(001) surface by Wei,[17] Yang,[18] 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 can be used to treat the present problem.

For the adsorption of Au atoms on the Si(001) surface, 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 monolayer of Au atoms are placed on each side of the slab (see Fig.1(a)). In the region of the slab, there are five atomic layers of vacuum introduced in the supercell, which has a mirror symmetry with respect to the central layer of the solid films.

Four possible adsorption sites for a monolayer of Au atoms on the Si(001) surface are considered: namely, the 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 fourfold site (C) (see Fig.1(b)). The initial value of the distance between the Au monolayer and the surface is chosen in such a way that the bond length between the Au atom and its nearest-neighbour surface atom equals the sum of their covalent radii, which is similar to that used in Refs.[17,19].

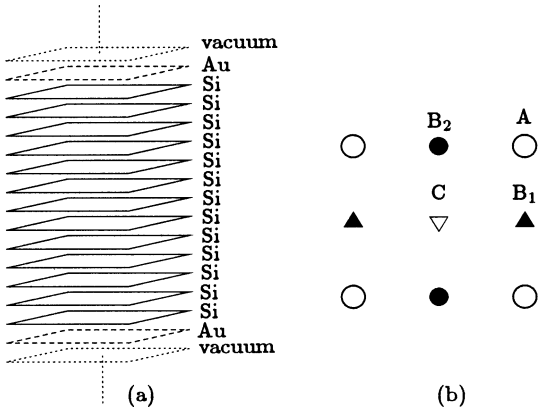


Fig.1. Illustration of the supercell used for Au adsorption on Si(001) surface (a) and the adsorption geometries (b). The symbols A, B_1, B_2, and C denote the adsorption sites for Au on the top site, two bridge sites (B_1 with a Si atom on the fourth atomic layer below it and B_2 with a Si on the second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

In practical calculations, the $5d^{10}6s^1$ state of Au and the $3s^2$ $3p^2$ states of Si are treated as valence bands. The rest of the occupied levels are considered frozen. The Brillouin zone (BZ) integration was 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.

3. Calculated results and discussion

3.1. Adsorption energy

For the adsorption of a monolayer Au on Si(001) surface, we calculate the variations of the total energy (denoted as $E_{\rm tot}$) of the supercell versus vertical distance (D) of the adatoms from the surface. Each of the minimum values of $E_{\rm tot}$ corresponding to D with the different absorbed site is given in Table 1. The listed energies in Table 1 are relative to the lowest value of the total energy for Au adsorbed on the top site (i.e. site A in Fig.1(b)). From Table 1, we can easily conclude that, among the adsorption sites considered here, the most stable position of the Au atom is the A site above the surface with a Au–Si bond length ($d_{\rm Au--Si}$) of 0.2407nm.

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

Site	A	B_1	B_2	C
D/nm	0.2407	0.1457	0.1457	0.0258
$E_{\rm tot}$/eV	0.0000	0.2480	2.3240	0.2160

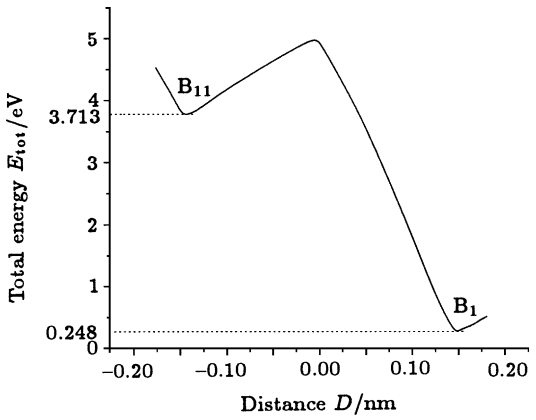


Fig.2. The bridge site (i.e. site B_1 in Fig.1(b)) total energy $E_{\rm tot}$ (eV) of the Au/Si(001) system versus the vertical distance D (nm) of the adatoms from the Si surface. The local minimum position of the B_1 is denoted as B_{11}. The energy values are also relative to the minimum $E_{\rm tot}$ of the A site.

For the case of putting Au atoms below the Si (001) surface, our study shows that only the B_1 site exists in a stable position. The position is found with a distance of 0.1358nm from the Si(001) surface (this position is denoted as B_{11}) and adsorption energy 3.173eV (the value is also relative to the minimum E_{tot} of the A site). By studying all the E_{tot} of the B_1 site (including the E_{tot} of Au atoms sitting above the surface), Fig.2 can be obtained. Figure 2 shows the curve of the total energy E_{tot} of the system versus vertical distance (D) when Au is absorbed on the B_1 site. Clearly, there exists a barrier at the Si(001) surface and a local minimum at B_{11} below the surface. Due to the existence of the B_{11} site, we can conclude that a few of the Au atoms can penetrate the barrier and sit at the position of B_{11}. Therefore, an Au and Si atom mixed layer might exist at the Au/Si(001) interface which is in agreement with the experimental results.[10]

According to the above discussion, in the following, we will consider the roles of A site and B_{11} site for monolayer Au atoms adsorbed on the Si(001) surface.

3.2. Project density of states

The layer project density of states (LPDOS) for the clean Si(001) system and the Au adsorbed system are shown in Fig.3. The density of states (DOS) for the bulk is shown by a dashed line for comparison. The zero-point energy (vertical line in the figures) is aligned at the Fermi level. From the three figures it can be seen that the LPDOS of the middle layer is bulk-like. This also indicates that the model of supercell is reasonable for simulating the Au/Si(001) system.

From Fig.3 (a), i.e. the LPDOS of the clean Si(001) surface, it can be seen that the first and the second layers are greatly different from the bulk one. On the first 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 mainly by the Si $3p^2$ state with a little part from Si $3s^2$ state. Another large sharp peak (B) appears at about 7.5eV below the Fermi level. In contrast to peak (A), peak (B) is in a resonance state mainly contributed by the Si $3s^2$ state with a little part from Si $3p^2$ states. The two peaks get damped rapidly on the second layer.

Comparing with the LPDOS of the clean surface, we see from Fig.3(b) that the following results can be obtained for the case of Au adsorbed on A site. In the Au adsorbed layer, there is a noticeable peak at $\sim$3.5eV below E_F The LPDOS in the middle layer changes slightly; this means that the middle layer is quite bulk-like and the presently used supercell is reasonable for simulating the surface problem. The changes in LPDOS in the surface layer are quite noticeable due to the Au adsorption. The peak (A) decreases greatly after adsorption and pervades the region from -4.5eV to 1.5eV, and peak (B) decreases obviously, too. The above results are due to the fact that the adsorbed Au atoms interact with the surface atoms and partially saturate the dangling bonds of the surface atoms. This is in agreement with the experiment.[11,12] Moreover, the interaction between Au atoms and the surface atoms is mainly due to the bonding of Au $5d^{10}$ states with $3p^2$ states of the surface Si atoms. The bonding of the Au $6s^1$ states with Si $3s^2$ and $3p^2$ states and that of Si $3s^2$ with the Au $5d^{10}$ and $6s^1$ states are weak. This is a general behaviour of metals on the silicon substrates.

Comparing Figs.3(a) and (b) with Fig.3(c), i.e. the LPDOS of Au absorbed on the B_{11} site, we can obtain the following results. For the Au adsorbed layer, there is a peak at $\sim$7.5eV below E_F. Comparing Fig.3(b) with Fig.3(c), this peak is lower and shifts down below E_F. The changes in LPDOS in the surface layer are no more noticeable than that in Fig.3(b) for the Au adsorption. The peaks (A) and (B) decrease slightly after adsorption compared with Fig.3(a). In contrast to peak (B), peak (A) decreases apparently. The reason for the above facts is that the bonding of the adsorbed Au atoms $5d^{10}$ states interact with that of surface Si atoms $3p^2$ states. But this interaction is not stronger than that of A site. This result is the main reason that the LPDOS of Au absorbed on the B site is different from that of the A site. Moreover, this result also indicates that the Au atoms density at the B_{11} site is diluted; therefore, a small number of Au atoms can be absorbed on this position. This conclusion explains theoretically the problem that the Au–Si intermixing cannot easily be observed and the thickness of silicide cannot easily be confirmed experimentally. At the same time, the bonding of the Au $6s^1$ states with Si 3s and 3p states and that of Si 3s with the Au 5d and 6s states are very weak.

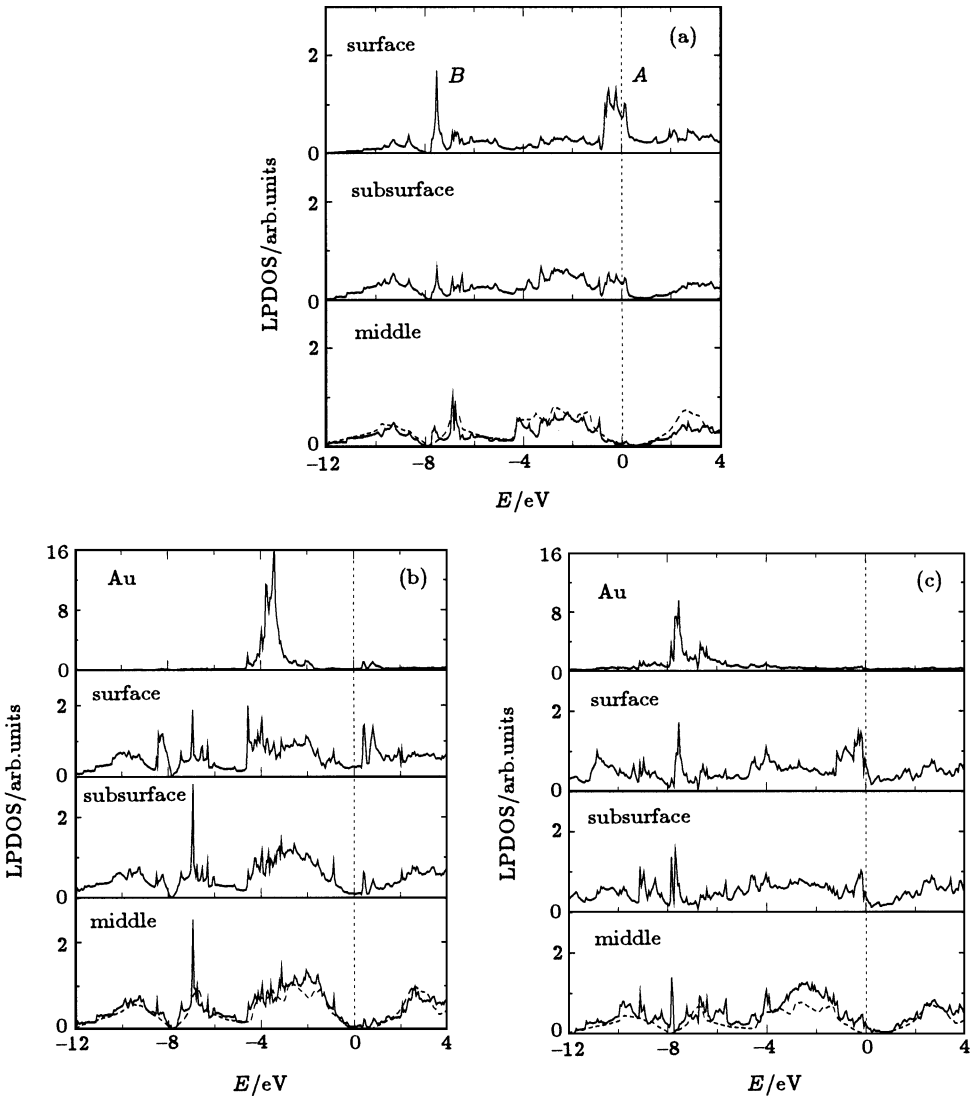


Fig.3. The LPDOS for (a) the clean Si(001) surface, (b) Au adsorbed on A site and (c) Au adsorbed on B_{11} site. The vertical line indicates the Fermi level and the dashed line is the LPDOS for the bulk.

3.3. Charge transfer

Usually, chemisorptions are accompanied by charge transfer between the adsorbates and the substrate. Table 2 lists 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 a 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 layer and empty spheres in vacuum. Clearly, the second layer gains 0.12 electrons. The layer effective charges for Au atoms adsorbed on Si(001) surface are also given in Table 2. Compared with the clean surface, for the case of Au adsorbed on A site, the surface layer gains 0.61 electrons and the subsurface loses 0.07 electrons. There are in total about 0.54 electrons transferred from the adsorbed Au atoms to the substrate. For the case of Au atoms adsorbed on B_{11} site, compared with the clean surface, the surface layer gains 0.18 electrons and the subsurface gains 0.26 electrons. Therefore, about 0.44 electrons are transferred from the adsorbed Au atoms to the substrate. In contrast, the charges transferred from Au atoms to the substrate for the A site adsorption are more than that of the B_{11} site adsorption. This result shows that the Au–Si interaction for the B_{11} site adsorption is weaker than that of A site adsorption, indicating that

the density of Au atoms at the B_{11} site is diluted. From Table 2, it can also be seen that the effective charges on the third and the middle layers are almost unaffected by the adsorption of the two cases, showing that the thickness of the slab is reasonable.

Table 2. The layer effective charges (in unit of electron) in the unit cell for the clean and Au-adsorbed surfaces. Here the affective 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
	Au adsorbed layer				
(A site)	–0.90	–0.12	0.05	0.00	0.00
(B_{11} site)	–0.53	–0.55	0.38	–0.01	0.00

4. Summary

In summary, the chemisorption of one monolayer of Au adatoms on the Si(001) surface is studied by using the self-consistent TB-LMTO method. The Au adatoms adsorbed on both the top site and the bridge site are considered separately. It has been found that the adsorbed Au atoms might sit at the top site above the surface. At the same time, an Au and Si mixed layer exists at the Au/Si(001) interface. The LPDOS in the clean surface decreases significantly after the adsorption of Au atoms on the top site above the surface, since the dangling bonds of the surface Si atoms are partially saturated by the adsorbed Au atoms.

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