Theoretical study of interaction between atoms of Au, Ag, Cu and clean Si(111) surface

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Abstract

To evaluate the interactions between the atoms of Au, Ag and Cu and clean Si(111) surface, two types of silicon clusters Si4H7 and Si16H20 together with their metal complexes were studied by using hybrid (U)B3LYP density functional theory method. Optimized geometries and energies on different adsorption sites indicate that: (1) the binding energies at different adsorption sites are large (ranging from ~1.2 to 2.6 eV depend on the metal atoms and adsorption sites), suggesting a strong interaction between metal atom and silicon surface; (2) the most favorable adsorption site is the on top (T) site. Mulliken population analysis indicated that in the system of on top (T) site, a covalent bond is formed between metal atom and dangling bond of surface Si atom.

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1. Introduction

The growth of thin metal films on semiconductor surface has been and remains a subject of intense interest, both from a fundamental physics point-of-view and from its increasing importance for future device application [1–7]. As a model metal-semiconductor system, Au/Si system has been widely studied by many techniques including Auger electron spectroscopy [8–12], photoemission spectroscopy [10,11,13–16], low-energy electron diffraction [9,10,15], electron-energy-loss spectroscopy [9], and X-ray standing-wave spectroscopy [17], and a lot of interesting phenomena such as electromigration of metal atoms on silicon surface and interface reaction that substrate Si atom diffuse into Au films have been reported [18,19]. It is found that the electromigration is quite anisotropic that depends on the adsorbate structure and on the substrate structure [19], and the interface diffusion occurred only when the Au-overlayer thickness reaches a critical value of about two monolayers [20]. It means the electronic and geometric structure is strongly responsible for the surface interactions between metal atoms and semiconductor surfaces.

However, to our knowledge, very little theoretical work is available for the electronic and geometric structure of the Au/Si(111) system. Murayama et al. [21] investigated the bond structure of $\sqrt{3} \times \sqrt{3}$-Au/Si(111) by ab initio pseudopotential method in a local density approximation and reported that the surface is semi-metallic. The two bulk-Si valence bands and Au–Si hybridized conduction band overlap slightly at the center of the Brillouine zone. Due to the strong electronic-state hybridization between Au and Si, the charge redistribution occurs from d to s orbital around Au. Murayama et al. [22] studied the electronic structures and charge densities of $1 \times 1$-Au/Si(111) surfaces with and without on-top Si. They found that Au and top-layer Si produce the bonding and a larger charge...
transfer is seen from Si to Au. But the source of charge supply is different between two surfaces. The dangling bond of the on-top Si plays an important role in the interaction between clean Si(111) surface and metal atom. To gain an insight into the adsorption of a single metal atom on semiconductor surface, the present work gives a first-principles investigation of the interaction between metal atoms of Au, Ag and Cu and clean Si(111) surface, especially concentrating on the different adsorption sites.

2. Computational method

All calculations were carried out by using the Gaussian 98 program package. The hybrid (U)B3LYP density functional method was used, which includes Becke’s 3-parameter nonlocal-exchange functional [23] with the correlation functional of Lee et al. [24]. The effective-core-potential LANL2DZ basis set [25] is used for the atoms of Au, Ag and Cu. For Si atom, two basis sets were used: 6-31G(d) for Si4H7, and LANL2DZ basis set for Si16H20 cluster. For H atom, the standard 6-31G(d) basis set was used.

Miyoshi et al. [26] have used Si4H7 and Si4H10 cluster models to study the adsorption of Na and Mg atoms on clean Si(111) surface. It is reasonable to use Si4H7 and Si16H20 to model the interaction between the atoms of Au, Ag and Cu and Si(111) surface. The structures of Si4H7 and Si16H20 are shown in Fig. 1. As shown in Fig. 1, Si4H7 contains three Si atoms in the surface layer. Each surface Si atom has a dangling bond, where is an unpaired electron. All unsaturated bonds of the Si cluster other than the dangling bonds were terminated with hydrogen atoms. The structure of Si4H7 was fully optimized without any constraints.

Si16H20 cluster was cut from a bulk Si(111) surface. It has four layers with four Si atoms in each layer. Each surface Si atom has a dangling bond, which is an unpaired electron. All unsaturated bonds of the Si cluster other than the dangling bonds were terminated with hydrogen atoms. The structure of the Si16H20 cluster was optimized with all the silicon atoms fixed.

The density functional theory (DFT) is useful only for the system dominated by a single electronic configuration. So, we used complete-active-space self-consistent-field (CASSCF) calculations to confirm that the electronic states of the cluster (Si4H7 as the example) and their complexes with Au can be described by a single configuration.

3. Results and discussions

To model the interaction between Si4H7 surface and atoms of Au, Ag and Cu, we considered three adsorption sites: on-top (T1), bridge (B) and threefold filled (F), as shown in Fig. 2. In the calculations, only the distances between silicon surface and metal atoms (Au, Ag, or Cu) (h) were optimized, i.e., the geometry parameters of Si4H7 moiety were fixed and the metal atom was kept in a σ plane (Fig. 2).

In the CASSCF calculation, all the dangling bonds of the surface Si atoms and s valence orbital of the Au atom were treated as active space. Thus, the active electrons are 3 and 4 for Si4H7 and Au–Si4H7 complexes, respectively. The optimized Si–Si and Si–H bond distance in Si4H7 were 2.354 and 1.479 Å, respectively, which agree well with the experimental values in bulk silicon and hydrogen silicides (2.35 and 1.48 Å, respectively). The coefficient of the dominant configuration is 0.9999, which means the electronic configuration can be described by a single one. The calculated structural parameters, binding energies and coefficients of the dominant configuration of Au–Si4H7 are

Fig. 1. Model clusters for clean Si(111) surface: (a) Si4H7, (b) Si16H20.

Fig. 2. Adsorption sites considered in this work. (a) Top view of the Si4H7 model, with T, F and B denoting the on top, three-fold filled and bridge adsorption sites, respectively; (b) Au atom adsorbed on the T site with the optimized Au–Si1 distance being 2.34 Å; (c) Au atom adsorbed on the F site having the optimized Au–Si1 distance of 2.72 Å; (d) Au atom adsorbed on B site, with the optimized distance between Au and the midpoint of Si3 and Si4 being 1.87 Å.
shown in Table 1. As shown in Table 1, the on-top (T) site has the maximal binding energy and corresponds to the minimal bond distance between Au atom and surface Si atom. Whereas, the threefold filled (F) site has the minimal binding energy and corresponds to the maximal bond distance between Au atom and surface Si atom. We also found the coefficients of the dominant configuration for the on-top (T1) site is 0.9946 and therefore its electronic state can be described by a single one. But the coefficients of the dominant configuration for the bridge (B) and threefold filled (F) are 0.9556 and 0.9126, respectively, so it is only an approximate to describe these two models by a single configuration.

For simplicity, in the following calculation, the structure of SiH7 and M–SiH7 complexes were performed by B3LYP method at 6-31G(d) level. The optimized Si–Si and Si–H bond distance in SiH7 were 2.348 and 1.493 Å, which agree well CASSCF results, respectively.

Calculated potential energy curve at different adsorption sites is shown in Fig. 3. Fig. 3 shows that the on-top (T) site is the most favorable adsorption site, which shows the same situation in binding energies with the CASSCF results in Table 1. It also agrees well with the results of Na–SiH7 given by CASSCF, MRSDCI and MRSDCI + Q calculation and Au/Si(100) system studied by self-consistent tight binding linear muffin-tin orbital method [26,27]. The calculated structural parameters and binding energies are shown in Table 2. As shown in Table 2, the on-top (T) site has the maximal binding energy, which corresponds to the minimal bond distance between metal atom and surface Si atom. The smaller the distance between metal atom and surface Si is, the larger the binding energy will be. Table 2 also shows that the atoms of Au, Ag and Cu have the completely same situation at different adsorption sites.

Table 2 also shows that the binding energies of Au–SiH7 at the three adsorption sites are larger than that of Ag–SiH7 and Cu–SiH7, i.e., Au atom corresponds to the strongest interaction with surface Si atom while Ag atom corresponds to the weakest one. We refer it to their different electronic structures and strong relativistic effect of Au atom. Because of the relativistic effect of Au atom, the energy of orbital 5d increase and that of orbital 6s decrease, and the energy gap between them is very small. So, the electronic configuration of Au atom can be roughly described as [Xe]4f14(5d, 6s)11 [28]. It has the tendency to accept one electron to become the more stabilized configuration as [Xe]4f14(5d, 6s)12. The calculated results supported this viewpoint. In the on-top (T) site adsorbed complex (Au–SiH7), the net charge of Au atom is −0.28 unit electron, which means a large amount of electrons transferred from SiH7 to Au atom. In contrast to Au–SiH7, the net charges of Ag and Cu in the complexes of Cu–SiH7 and Ag–SiH7 (on top site) are 0.006 and 0.002, respectively. This is because the relativistic effect of Ag and Cu is very weak and the energy gap between orbital 4d and 5s of Ag, or orbital 3d and 4s of Cu are relatively large, and mainly the orbital interaction between the dangling bond of surface Si and the orbital 4s of Cu and 5s of Ag occurs. Besides, the energy of orbital 4s of Cu is

### Table 1
Calculated structural parameters for Au–SiH7 complexes by CASSCF method

<table>
<thead>
<tr>
<th>Sites</th>
<th>( h_b (\text{Å}) )^a</th>
<th>( R_{b} (\text{Au–Si} (\text{Å}) )^b</th>
<th>( E_b (\text{eV}) )^c</th>
<th>( C_i )^d</th>
</tr>
</thead>
<tbody>
<tr>
<td>On-top (T)</td>
<td>2.39</td>
<td>2.39</td>
<td>1.84</td>
<td>0.9946</td>
</tr>
<tr>
<td>Threefold filled (F)</td>
<td>2.31</td>
<td>3.21(3.09)</td>
<td>0.37</td>
<td>0.9126</td>
</tr>
<tr>
<td>Bridge (B)</td>
<td>2.08</td>
<td>2.84</td>
<td>0.81</td>
<td>0.9556</td>
</tr>
</tbody>
</table>

^a\( h_b \) denotes the distance between the Au atom and the Si(111) surface.

^b\( R_{b} \) is the minimal distance between a Au atom and surface Si atom.

^c Value in parenthesis is the distance between the Au atom and the second layer Si atom.

^d \( C_i \) is the coefficient of dominant configuration.

### Table 2
Calculated structural parameters for M–SiH7 (M = Au, Ag and Cu) complexes by B3LYP method

<table>
<thead>
<tr>
<th>Sites</th>
<th>( h_b (\text{Å}) )^a</th>
<th>( R_{b}(M–Si) (\text{Å}) )^b</th>
<th>( E_b (\text{eV}) )^c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>On-top (T)</td>
<td>2.34</td>
<td>2.34</td>
<td>2.64</td>
</tr>
<tr>
<td>Threefold filled (F)</td>
<td>1.94</td>
<td>2.95 (2.72)</td>
<td>1.61</td>
</tr>
<tr>
<td>Bridge (B)</td>
<td>1.87</td>
<td>2.68</td>
<td>2.04</td>
</tr>
<tr>
<td>Ag</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>On-top (T)</td>
<td>2.44</td>
<td>2.44</td>
<td>1.83</td>
</tr>
<tr>
<td>Threefold filled (F)</td>
<td>2.07</td>
<td>3.03 (2.84)</td>
<td>1.27</td>
</tr>
<tr>
<td>Bridge (B)</td>
<td>2.01</td>
<td>2.78</td>
<td>1.46</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>On-top (T)</td>
<td>2.27</td>
<td>2.27</td>
<td>2.21</td>
</tr>
<tr>
<td>Threefold filled (F)</td>
<td>1.75</td>
<td>2.83 (2.53)</td>
<td>1.89</td>
</tr>
<tr>
<td>Bridge (B)</td>
<td>1.74</td>
<td>2.59</td>
<td>1.69</td>
</tr>
</tbody>
</table>

^a\( h_b \) denotes the distance between the metal atom and the Si(111) surface.

^b\( R_{b} \) is the minimal distance between a metal atom and surface Si atom.

^c Value in parenthesis is the distance between the metal atom and the second layer Si atom.

^d \( E_b = E_{\text{complex}} -(E_{\text{silicon}}+E_{\text{metal}}) \). All the binding energies \( (E_b) \) including the zero point energy (ZPE) correction.
more close to that of the dangling bond of surface Si, and therefore displays a stronger interaction with the dangling bond of Si than that of Ag atom.

For comparing, the Mulliken population analysis of Au–Si4H7 cluster is listed in Table 3. From Table 3, one can see that all the Au atoms at the three adsorption sites are negative charged, which implies that the electron transfer occurs from Si(111) moiety to Au atom. The on-top (T) site corresponds to the least electron transfer, whereas the threefold filled (F) site corresponds to the most one. The electron transfers are not consistent with the binding energies. Our calculation also reveals that in the system of on-top (T) site, the electron transfer mainly occurs from Si2 to Au. But in the system of bridge (B) and threefold filled (F) sites, the electron transfer occurs from the two and three neighboring surface Si atom, respectively. The overlap population is a measure of the shared electronic density between two atoms. A large positive value indicates the atoms in question are bonded, a large negative value indicates the atoms are in an anti-bonded state. Table 3 shows that in the system of on-top (T) site the overlap population of Au–Si2 is as large as 0.34, which is comparable to that (0.31) of normal Si–Si bonds in Si4H7 cluster. Natural bonding orbitals (NBO) analysis shows that the bonding orbital of Au–Si2 consists of Si orbitals 48% (s: 17%, p: 83%) and Au orbitals 52% (s: 90%, d: 9%). But in the system of bridge (B) site, the overlap population of Au–Si3 and Au–Si4 bonds are only 0.12, which are much smaller than that of Au–Si2 bond in the system of on-top (T) site. As for the system of threefold filled (F) site, the very small value (0.06) of overlap population indicates a non-bonded state between Au atom and surface Si atom.

To verify the cluster-size dependence of calculated results, we used a larger model cluster (Si16H20) and considered five adsorption sites: on-top of Si2 (T1), bridge (B1 and B2), threefold filled (F) and on-top of Si8 (T2), as shown in Fig. 4. Calculated potential energy curves for metal atoms of Au, Ag and Cu at different adsorption sites are shown in Fig. 4 as well. The similar conclusion as M–SiH7 complexes can be drawn that the on-top (T1 and T2) sites are the most favorable adsorption sites and threefold filled (F) site corresponds to the highest total energy. We also noted that T2 adsorption site has a little lower total energy than that of T1. This can be explained by the strain effect of the two hydrogen atoms in the neighboring silicon atoms (Si3 and Si4).

Table 3

<table>
<thead>
<tr>
<th>Sites</th>
<th>Net charge of Au atom</th>
<th>Overlap population/bond*</th>
</tr>
</thead>
<tbody>
<tr>
<td>On-top (T)</td>
<td>−0.28</td>
<td>Au–Si2: 0.34</td>
</tr>
<tr>
<td>Threefold filled (F)</td>
<td>−0.58</td>
<td>Au–Si2: 0.06, Au–Si3: 0.06, Au–Si4: 0.06</td>
</tr>
<tr>
<td>Bridge (B)</td>
<td>−0.57</td>
<td>Au–Si1: 0.12, Au–Si6: 0.12</td>
</tr>
</tbody>
</table>

* Only the values between surface Si and Au atoms were listed. The overlap population of the normal Si–Si bonds in Si4H7 cluster is 0.31.

Table 4

<table>
<thead>
<tr>
<th>Adsorption sites</th>
<th>Relative energies (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>Ag</td>
</tr>
<tr>
<td>T1</td>
<td>B1, B2</td>
</tr>
<tr>
<td>F</td>
<td>T2</td>
</tr>
</tbody>
</table>

Fig. 4. Adsorption sites of metal atoms on the surface of Si16H20 and potential energies of M–Si16H20 complexes at different sites. (a) Top view of Si16H20 and five adsorption sites: T1, B1, B2, F and T2; (b) side view of Au–Si16H20 (T1 adsorption site); (c) potential energy curves at different adsorption sites.
On-top of Si 8 (T2) 2.29 2.29 2.37
Bridge of Si 5 and Si 6 (B2) 2.05 2.80 1.50
Threefold filled (F) 2.12 3.07 (2.90) 1.20
On-top of Si 8 (T2) 2.38 2.38 2.62

Ag
On-top of Si 1 (T1) 2.47 2.47 1.93
Bridge of Si 3 and Si 4 (B1) 2.27 2.53 1.75
Bridge of Si 3 and Si 6 (B3) 1.75 2.60 1.91
Threefold filled (F) 2.12 3.07 (2.90) 1.20
On-top of Si 8 (T2) 2.47 2.47 1.98

Cu
On-top of Si 1 (T1) 2.28 2.28 2.35
Bridge of Si 3 and Si 4 (B1) 2.06 2.34 2.15
Bridge of Si 3 and Si 6 (B3) 1.75 2.60 1.91
Threefold filled (F) 1.78 2.84 (2.57) 1.56
On-top of Si 8 (T2) 2.29 2.29 2.37

Table 5
Mulliken population analysis of Au–Si16H20 cluster at different adsorption sites

<table>
<thead>
<tr>
<th>Sites</th>
<th>Net charge of Au atom</th>
<th>Overlap population/bond*</th>
</tr>
</thead>
<tbody>
<tr>
<td>On-top of Si 1 (T1)</td>
<td>−0.075</td>
<td>Si2–Au (bonded): 0.32</td>
</tr>
<tr>
<td>Bridge of Si 3 and Si 4 (B1)</td>
<td>−0.172</td>
<td>Si3–Au(bonded): 0.29, Si3–Au(non-bonded): −0.12</td>
</tr>
<tr>
<td>Bridge of Si 3 and Si 6 (B3)</td>
<td>−0.306</td>
<td>Si3–Au(bonded): 0.17, Si6–Au(bonded): 0.17</td>
</tr>
<tr>
<td>Threefold filled (F)</td>
<td>−0.327</td>
<td>Si3–Au(bonded): 0.08, Si6–Au(bonded): 0.08, Si4–Au(bonded): 0.06, Si6–Au(non-bonded): −0.24</td>
</tr>
<tr>
<td>On-top of Si 8 (T2)</td>
<td>−0.226</td>
<td>Si8–Au(bonded): 0.29</td>
</tr>
</tbody>
</table>

The overlap population of the normal Si–Si bonds in Si16H20 cluster is 0.29.

Si8 have large positive charges, it is easy to understand that Au atom will possess more negative charge when Au atom was adsorbed on the threefold filled (F) site. The overlap populations for Au–Si 3 (T1 site), Au–Si 6 (B3 site) and Au–Si 8 (T2 site) are 0.32, 0.29 and 0.29, respectively, which are comparable to that of the normal Si-Si bonds (0.29) in Si16H20 cluster, indicating a covalent bond between Au atom and Si atom. But in threefold filled (F) site, the overlap populations between Au and Si atom are very small, suggesting a non-bond state between them.

By comparing Tables 2 and 4 we can see that the binding energies are weakly depend on the size of the cluster but strongly depend on the adsorption site. Although the charges of Si atoms at the clean surface are different in the two different size models, the binding energy only changes a little. For example, in the on-top site models, the binding energy in Si4H7 cluster is 2.64 eV, which is very close to that of T 1 (2.57 eV) and T 2 (2.62 eV) adsorption sites in Si16H20 cluster.

4. Conclusions

To model the interactions between clean Si(111) surface and atoms of Au, Ag and Cu, the M–Si4H7 and M–Si16H20 complexes were studied by using hybrid (U)B3LYP density functional theory method.

Our calculation reveals strong interactions between atoms of Au, Ag and Cu and clean Si(111) surface with large binding energies ranging from ~1.2 to 2.6 eV depend on adsorption sites and different metal atoms. The most favorable adsorption site is the on top (T) site. The Mulliken population analysis indicated that in the system of on top (T) sites, a covalent bond is formed between metal atom and dangling bond of surface Si atom. But in the system of threefold filled (F) site, only non-bonded states are formed between metal atoms and surface Si atom, implying a very weak interaction between metal atoms and silicon surface.

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References