The Study of Coordination Adsorption Effect that CO Adsorption on 4H-SiC (001) Surface about Different Placement Angles

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Abstract. The bond structure, electron density difference, density of state, orbits of CO adsorption on 4H-SiC surface of different placement angles are calculated using the plane wave ultra-soft pseudo-potential based on density functional theory. The calculation results show that placement angles have no effect on adsorption process and the optimization results are basically same. It clear reveals that the main interaction in the process of adsorption comes from the 2p orbit of carbon atom and 3s and 3p orbit of silicon atom. CO would get electron not just from the silicon atom but other silicon atoms which are near it in the process of adsorption.

Introduction

SiC, as the new type third generation semiconductor materials, has more superior performance than Si and GaAs which represent the first and second generation semiconductor materials, respectively. The adsorption properties of SiC surface have been studied by many scholars in recent years [1-3]. Jin [4] has studied the surfaces property from the β-SiC (111) derived structure and its water molecule adsorption by first-principles. James Westover [5] has studied metallization of the β-SiC (100)-3×2 surface by a DFT investigation, which revealed that metallization could be achieved via hydrogen atoms occupying the second silicon layer. Du [6] has studied the mechanism of hydrogen production via water splitting on 3C-SiC’s different surfaces, which indicated that the adsorption behavior of water molecule could take place on 3C-SiC’s different surfaces and it leads to the surface reconstruction. Although there are most study on SiC surface, the study of coordination adsorption effect that CO adsorption on 4H-SiC (001) surface about different placement angles are fewer.

The purpose of this paper is to study the coordination adsorption effect that CO adsorption on 4H-SiC (001) surface. According to DFT (density functional theory), CO adsorption on 4H-SiC (001) surface models are set up by CASTEP (Cambridge serial total energy package). By geometry optimization and quantum calculation, we will obtain the bond structure, electronic orbital and density of states of models to analyze the coordination adsorption effect.

Simulation Theories

In this work, CASTEP [7-8] (Cambridge serial total energy package) package in Materials Studio software is used for calculation. The adsorption models are contrastively calculated through the first principles and DFT (density functional theory). To obtain better adsorption state, we selected GGA(Generalized Gradient Approximation) PBE (Perdew, Burke and Emzerhof) method [9-14] of ultrasoft pseudopotentials [15-17] in calculation. For an economical calculation, simulation was performed using 400eV cut off energy and a 4×3×1 k-point sampling grid. The convergence precision in iterative process was 2.0×10^-6eV/atom. A (2×3) surface unit cell with a slab of one layer thickness was selected as the model. This slab was repeated periodically with a 10Å of vacuum region between the slabs. Four different angles that CO adsorption on 4H-SiC(001) surface are set to study coordination adsorption effect, adding atoms fixed direction when we made models to analyze its angled effects, as shown in Figure 1. From Figure 1(a), we can see carbon of CO have bonded two neighbor silicon atoms.
The Calculation Results and Discussion

Bond Structure Change

After geometry optimization, we can obtain the models as shown in Figure 2. Comparing Figure 2 with Figure 1, the bond structure of models has obvious change. Some data of bond structure are measured, as listed in Table 1.

![Figure 2. Four different angles between CO and 4H-SiC (001) surface after geometry optimization.](image)

<table>
<thead>
<tr>
<th>Angle (°)</th>
<th>C-O bond(Å)</th>
<th>C-Si bond(Å)</th>
<th>A₁(°)</th>
<th>A₂(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>45(°)</td>
<td>1.201</td>
<td>2.072</td>
<td>48.572</td>
<td>85.977</td>
</tr>
<tr>
<td>60(°)</td>
<td>1.200</td>
<td>2.076</td>
<td>48.910</td>
<td>85.100</td>
</tr>
<tr>
<td>75(°)</td>
<td>1.201</td>
<td>2.104</td>
<td>49.905</td>
<td>85.913</td>
</tr>
<tr>
<td>90(°)</td>
<td>1.201</td>
<td>2.095</td>
<td>48.831</td>
<td>87.188</td>
</tr>
</tbody>
</table>

* A₁ is the angle between C-Si bond and 4H-SiC(001) surface
* A₂ is the angle between O-C bond and 4H-SiC(001) surface

Electron Density Difference Analysis

On the basis of the calculated results, we obtained the electron density difference that shows in Figure 3 and definite amounts are listed in Table 2. Red and blue represent getting electron and losing electron respectively. The atoms of O and C get electron from silicon atom of 4H-SiC (001). An interesting characteristic in electron transfer is that the electron change is mainly identical of four different placement angles, as shown in Table 2. When CO adsorb on 4H-SiC (001) surface, we can reach, that the electron transfer condition never mind with placement angle. Comparing with atomic orbital charge population before and after adsorption, it clear reveals that the main
interaction in the process of adsorption comes from the 2p orbit of carbon atom and 3s and 3p orbit of silicon atom. Look through, the electron that CO got are more than the electron that silicon atom lost which bond with carbon atom. So, CO would get electron from other silicon atom which is near it in the process of adsorption.

Figure 3. Electron density difference of four different angles.

Table 2. Atomic orbital charge population of four different angles.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>S</th>
<th>P</th>
<th>Charge(e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>clean</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>1.84</td>
<td>4.58</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>1.68</td>
<td>1.91</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>1.14</td>
<td>1.82</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>1.83</td>
<td>4.56</td>
<td>-0.39</td>
</tr>
<tr>
<td>45(°)</td>
<td>C</td>
<td>1.29</td>
<td>2.72</td>
</tr>
<tr>
<td>Si</td>
<td>1.06</td>
<td>1.79</td>
<td>1.15</td>
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<tr>
<td>O</td>
<td>1.83</td>
<td>4.56</td>
<td>-0.39</td>
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<tr>
<td>60(°)</td>
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<td>2.73</td>
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<tr>
<td>Si</td>
<td>1.06</td>
<td>1.79</td>
<td>1.15</td>
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<tr>
<td>O</td>
<td>1.83</td>
<td>4.55</td>
<td>-0.39</td>
</tr>
<tr>
<td>75(°)</td>
<td>C</td>
<td>1.30</td>
<td>2.71</td>
</tr>
<tr>
<td>Si</td>
<td>1.08</td>
<td>1.79</td>
<td>1.14</td>
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<tr>
<td>90(°)</td>
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<td>2.71</td>
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<tr>
<td>Si</td>
<td>1.07</td>
<td>1.78</td>
<td>1.14</td>
</tr>
</tbody>
</table>

The electrons of 2s from O in 4 complexes keep a constant, 1.83, which show that the 2σ orbital takes few actions in the bonding process. Contrary, 2π(px, py, pz) orbitals taking accepter which obtain mainly some electrons from C (and partly from Si) take positively part in this process. C-O bond length increases in complex 4 evidences this point of view.

**Density of State Analysis.** To get more study the property of CO adsorption on 4H-SiC (001) surface in different placement angles, we have obtained the density of state after calculation, as shown Figure 4 and Figure 5. DOS (Density of states), including PDOS (partial DOS), can provide a fundamental understanding of the adsorbate-substrate interaction.

Figure 4. Density of states of oxygen molecule before adsorption and that at four different placement angles after adsorption respectively (a) CO; (b) 45°; (c) 60°; (d) 75°; (e) 90°.
As shown in Figure 4, we can see that it is mainly contributed of P orbit of CO molecule near Fermi energy. In the Figure 4 (a), electron peak shows a strong activity at 0 eV. Compared Figure 4 (a) with (b)-(e), there are new waves produced and the waves move to low energy location, which shows there are new chemical bonds produced and the system is more stable after adsorption than before adsorption.

![Figure 5](image)

Figure 5. The DOS of CO adsorption on 4H-SiC (001) surface of four different angles. 
(a) Clean surface (b) 45°; (c) 60°; (d) 75°; (e) 90°.

Figure 5 (a) shows the density of states of clean 4H-SiC (001) surface. (b)-(e) represent the density of states of the whole system in the process of CO adsorption on 4H-SiC (001) surface at four different placement angles respectively. The first electron peak in Figure 5 (b)-(e) has move to high energy location in varying degrees. It is the result of the influence of distance that the oxygen atom leaves 4H-SiC (001) surface. At -8eV, the waves become smoothness especial in Figure 5(c).

**Orbits Analysis.** Known by us, the electronic configuration of CO is (1σ)2(2σ)2(3σ)2(4σ)2(1π)4(5σ)2(2π)0 (6σ)0.

![Image of HOMO and LUMO](image)

Figure 6. The HOMO and LUMO of CO adsorption on 4H-SiC (001) surface of four different angles.

From the chemical activity for the different initial angles, the highest occupied orbitals and the lowest unoccupied orbital were analyzed in detail. The hybrid orbital of s,p of SiC interacts with pz of C to change to bonding orbital. The lowest unoccupied orbital py of O interacts with py in C to become to exhibit a repulse effect to explain the increasing LOCS. The interactions of orbital of Figure 6(b) and (c) are similar to the orbital above. C atom gets electron from Si when its Pπ orbital interacts with corresponding orbital in Si, meanwhile, O atom also gives some electrons to C atom to increase its negative electron, meanwhile, anti-bonding in C-Si is weaken duo a long distance.
between them. In Figure 6(d), C-O keeps an initial perpendicular pose for the interactions from C counteracting with interaction from O atom. O lose some electrons in this process, which pz orbital obtains some electrons from pz of C atom, C gets some electrons from Si and takes as receiver, the transaction in Figure 6(b) and (c) is similar, interestingly, O gets some electrons when it loses some electrons. But it loses some electrons in fact. In Figure 6(d), O and C will lose some electrons to Si bulk which leads a more active Si surface. Common trait in four complex is that coordination covalent bond was strengthened in CO adsorbed process which would need a bigger space. This is main reason for the perpendicular adsorption structure.

Conclusions
The calculation results show that placement angles have no effect on adsorption process and the optimization results are basically same. It clear reveals that the main interaction in the process of adsorption comes from the 2p orbit of carbon atom and 3s and 3p orbit of silicon atom. CO would get electron not just from the silicon atom which bond with it but other silicon atoms which are near it in the process of adsorption.

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References


