Adsorption and Reaction of Hf Precursor With Two Hydroxyls on Si (100) Surface: 
First Principles Study

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ABSTRACT

Density functional theory was used to investigate the adsorption and reaction of HfCl₄ with two hydroxyls on Si (001)-2×1 surface in atomic layer deposition (ALD) process. When H₂O molecules are adsorbed on Si (001) surface at room temperature, they are dissociated into hydrogens and hydroxyl groups. There are two dissociation pathways; inter-dimer dissociation and intra-dimer dissociation. The activation energies of these pathways can be converted to the reaction probabilities. The probability for inter-dimer dissociation is ca. 67 % and the probability for intra-dimer dissociation is ca. 33 %. We prepared a reasonable Si substrate which consisted of six inter-dimer dissociated H₂O molecules and two intra-dimer dissociated H₂O molecules. The HfCl₄ must react with two hydroxyls to be a bulk-like structure. There were five reaction pathways where HfCl₄ can react with two hydroxyls on; inter-dimer, intra-dimer, cross-dimer, inter-row, and cross-row. Inter-row, inter-dimer and intra-dimer were relatively stable among the five reaction pathways based on the energy difference. The electron densities between O and Hf in these three reactions were higher than the others and they had shorter Hf-O and O-O bond lengths than the other two reaction pathways. The electron density and Hf-O, O-O bond lengths had influence on the energy difference.

INTRODUCTION

The complementary metal oxide semiconductor (CMOS) device is the most important electronic device in microelectronic industry. Silicon dioxide (SiO₂) is used extensively as dielectric materials. However, SiO₂ is so thin that the tunneling leakage current becomes too high.¹ High-k materials have received much attention recently in microelectronics because high-k gate dielectrics can significantly suppress the tunneling leakage current in CMOS devices. Among various high-k materials, hafnium dioxide (HfO₂) is considered to be the most promising candidate due to its relatively high permittivity, good thermal stability, and compatibility with dual metal integration.² The great advantage of SiO₂ is that it can be grown by thermal oxidation. In contrast, high-k oxides must be deposited.² Atomic layer deposition (ALD) technique is a desirable process to form HfO₂ because it shows good conformality and uniformity over large areas.³,⁴

Willis et al. studied a reaction of HfCl₄ with H₂O terminated Si (001)-2×1 using density functional theory calculation.⁵ The model predicted a saturation coverage of (2.05±0.05) × 10¹⁴Hf/cm² and the main factor which limited the reactant coverage was found to be a preferred reaction at two hydroxyl sites. They demonstrated the surface made up of roughly equal numbers of OHFCl₃ and (O)₂HfCl₂. Tang et al. performed density functional theory calculation to investigate an interface state of Si:HfO₂.⁶ They calculated several interface models of Si:HfO₂ and found the most favorable interface structure.
The HfCl$_4$ should react with two hydroxyls to form a bulk-like structure in ALD for HfO$_2$. In this study, we calculated the reaction of HfCl$_4$ with various two hydroxyls sites on Si (001) - 2×1 based on density functional theory.

**CALCULATION**

Density functional theory (DFT) calculations were performed using the Vienna *ab-initio* Simulation Package (VASP) code with the projector augmented wave (PAW) potentials and the generalized gradient approximation (GGA). The residual minimization scheme direct inversion in the iterative subspace (RMM-DIIS) was used for calculating the ground state of electrons. A cutoff energy was 450 eV for the plane wave expansion of the wave functions and Monk-horst pack k-point mesh 2×2×1 produced well converged results.

When H$_2$O molecules are adsorbed on Si (001) surface at room temperature, they are dissociated with hydrogens and hydroxyls. There are two dissociation pathways; inter-dimer dissociation and intra-dimer dissociation. The activation energies of these pathways could be converted to the reaction probabilities. It was approximately 2:1. Figure 1 (a) shows H$_2$O terminated Si (001) surface which was formed by 6 inter-dimer dissociations and 2 intra-dimer dissociations.

![Figure 1](image)

**Figure 1.** (a) H$_2$O terminated Si (001) surface which is formed by 6 inter-dimer dissociations and 2 intra-dimer dissociations and (b) an interface of tetragonal-HfO$_2$ and Si.

**DISCUSSION**

Figure 1 (b) shows an interface of tetragonal-HfO$_2$ and Si. This interface was the most stable among several interfaces of tetragonal-HfO$_2$ and Si. Hf atoms located between two oxygen atoms which were on Si atoms. We concluded that HfCl$_4$ should react with two hydroxyls to be bulk-like structure. The reaction was calculated by the following equation.

$$\text{HfCl}_4 + 2 \text{OH-Si} \rightarrow \text{HfCl}_2\text{-O-Si} + 2\text{HCl}$$
There were five reaction pathways of HfCl\textsubscript{4} for reacting with two hydroxyls; cross-dimer, cross-row, inter-dimer, intra-dimer, and inter-row. Figure 2 shows the configuration of each reaction pathways.

![Figure 2](image)

**Figure 2.** The reactions of HfCl\textsubscript{4} with two hydroxyls on Si (001) surface (a) cross-dimer, (b) cross-row, (c) inter-dimer, (d) intra-dimer, and inter-row.

**Table 1.** Bond lengths, bond angles, and energy differences of the each reaction.

<table>
<thead>
<tr>
<th>Pathway</th>
<th>Hf-O (Å)</th>
<th>Cl-O (Å)</th>
<th>Hf-Cl (Å)</th>
<th>Hf-O-Hf (°)</th>
<th>O-O (°)</th>
<th>ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) cross-dimer</td>
<td>1.98</td>
<td>2.35</td>
<td>2.33</td>
<td>113.71</td>
<td>97.29</td>
<td>0.79</td>
</tr>
<tr>
<td>(b) cross-row</td>
<td>2.20</td>
<td>2.34</td>
<td>2.68</td>
<td>111.94</td>
<td>91.50</td>
<td>1.09</td>
</tr>
<tr>
<td>(c) inter-dimer</td>
<td>1.98</td>
<td>2.04</td>
<td>2.34</td>
<td>114.79</td>
<td>114.79</td>
<td>0.30</td>
</tr>
<tr>
<td>(d) intra-dimer</td>
<td>1.98</td>
<td>2.67</td>
<td>2.57</td>
<td>105.92</td>
<td>115.06</td>
<td>0.51</td>
</tr>
<tr>
<td>(e) inter-row</td>
<td>1.98</td>
<td>2.39</td>
<td>2.54</td>
<td>111.93</td>
<td>108.90</td>
<td>0.53</td>
</tr>
</tbody>
</table>

| HfCl\textsubscript{2} molecule | 2.31              | 105.7             |

Table 1 shows bond lengths, bond angles, and energy differences of the each reaction. The reactions classified into two groups based on energy difference. Inter-dimer, intra-dimer, and inter-row were a group of favorable reactions and the others were a group of relatively unfavorable reactions. Bond lengths of Hf-O in favorable reactions were equally 1.93Å and bond lengths of O-O were shorter than the others. We compared the bond length of Hf-Cl and the bond angle of Cl-Hf-Cl with HfCl\textsubscript{4} molecule. The favorable reactions had relatively similar bond length of Hf-Cl and bond angle of Cl-Hf-Cl with HfCl\textsubscript{4} molecule. This result indicated that the configuration of HfCl\textsubscript{2} and oxygen atoms decided the stability of the reaction.
Figure 3. (a) The line profile of the electron density from O(1) to O(2); O(1)-Hf-O(2) and (b) the expansion of square. The isosurface level was $0.08 \alpha_0^{-3}$. ($\alpha_0$: Bohr radius)

Figure 4 shows the line profile of the electron density. The electron density was measured by the visualization for electronic and structural analysis (VESTA) and the isosurface level was $0.08 \alpha_0^{-3}$ ($\alpha_0$: Bohr radius). The electron densities of O(1)-Hf and O(2)-Hf were almost same. The square of figure 4 (a) was enlarged into figure 4 (b). Cross-dimer and cross-row reaction (classified unfavorable reactions) had lower electron densities of Hf-O than the others. It meant that the Hf-O bonds of cross-dimer and cross-row were weak, resulting in further energy increase.

CONCLUSIONS

The reaction of HfCl$_4$ with two hydroxyls on Si (001)-2×1 surface was investigated using DFT calculation. There were five reaction pathways of HfCl$_4$ for reacting with two hydroxyls. The reactions classified into two groups based on energy difference. The favorable reactions had short bond lengths of Hf-O and O-O than the others and they had similar bond length of Hf-Cl and bond angle of Cl-Hf-Cl with HfCl$_4$ molecule. The relatively unfavorable reactions had lower electron densities of Hf-O than the others. These results indicated the configuration of HfCl$_2$ and oxygen atoms, the electron density of Hf-O decided the stability of the reaction.

REFERENCES