Interaction of HfCl$_4$ precursor with H$_2$O terminated Si (001) surface: First principles study

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ABSTRACT

We investigated the reaction of HfCl$_4$ molecules with a H$_2$O terminated Si (001)-2×1 surface using density functional theory to understand the initial stage of atomic layer deposition (ALD) of HfO$_2$. Half monolayer of H$_2$O molecules were adsorbed on the buckled-down Si atoms of the Si dimers of the Si (001)-2×1 surface below the dissociation temperature of H$_2$O and were dissociated into H and OH at room temperature. This process could make uniform and well-aligned -H and -OH's on the Si (001) substrate. The reaction of a HfCl$_4$ molecule was more favorable with -OH than -H. The reaction of the HfCl$_4$ molecule with the -OH generated a HCl molecule, and the remaining HfCl$_3$ was attached to the O atom. The first reaction of the HfCl$_4$ molecule with –OH produced 0.21 eV energy benefit. The reaction of the second HfCl$_4$ molecule with the most adjacent –OH of the first one produced 0.28 eV energy benefit. The third and fourth molecules showed same tendency with the first and second ones. The energy differences of the fifth and sixth HfCl$_4$ reactions were -0.01 eV, 0.06 eV, respectively. Therefore, we found that the saturation Hf coverage was approximately 5/8 of the available –OH’s, which was $2.08 \times 10^{14}$ Hf /cm$^2$. The result was well-matched with the experimental study of other group.

INTRODUCTION

The complementary metal oxide semiconductor (CMOS) device is the most important electronic device in microelectronic industry. Silicon dioxide (SiO$_2$) is used extensively as dielectric materials. However, SiO$_2$ is so thin that the tunneling leakage current becomes too high. 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 (HfO$_2$) is considered to be the most promising candidate due to its relatively high permittivity, good thermal stability, and compatibility with dual metal integration. One of the best advantages for SiO$_2$ is that it can be grown by thermal oxidation; whereas, high-$k$ oxides must be deposited. Atomic layer deposition (ALD) technique is a desirable process to form HfO$_2$ because it shows good conformality and uniformity over large areas.

Green et al. studied the efficacy of various underlayers for nucleation and growth of atomic layer deposited HfO$_2$ films. The use of a chemical oxide underlayer led to good HfO$_2$ nucleation with linear growth rate and almost no barrier. In contrast, the growth on H-terminated Si was characterized by a large barrier to nucleation and growth. It indicated that the initial preparation of the Si surface decided the film quality. Willis et al. confirmed that a one-cycle ALD growth reaction on H$_2$O terminated Si (001)-2×1 surface was shown to lead successful nucleation, and the saturation Hf coverage was measured to be $2.08 \times 10^{14}$ Hf /cm$^2$.
In this study, we employed a first principles calculation to investigate the initial ALD mechanism of HfO$_2$ on H$_2$O-terminated Si (001) -2×1 surface. We used 4×4 Si surface that is covered with H’s and OH’s.

**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-points mesh of 2×2×1 produced well converged results.

*Figure 1.* (a) A uniform H- and OH-terminated Si surface and (b) HfCl$_4$. Oxygen atoms are shown in red, hydrogen atoms in white, silicon substrate atoms in yellow, hafnium as the largest atoms in brown, and chlorines in green.

Figure 1 (a) shows a uniform H- and OH-terminated Si surface. This surface could be obtained through the 1/2 monolayer water molecule adsorption below the dissociation temperature of H$_2$O and dissociation above the dissociation temperature. There are eight H’s and OH’s in this 4×4 Si (001) surface. Figure 2 (b) shows a HfCl$_4$ molecule. The distance between Cl and Hf atom was calculated to be 2.31 Å.

**RESULTS AND DISCUSSION**

The reactions of the HfCl$_4$ molecule with -H and -OH are shown in figure 2 (a). The reaction of the HfCl$_4$ molecule with -H was endothermic by 1.59 eV. In contrast, the reaction of the HfCl$_4$ molecule with -OH was exothermic by -0.17 eV. Therefore, the reaction of the HfCl$_4$ molecule was more favorable with -OH than -H. This result was well-matched with the experimental studies of other groups. When the HfCl$_4$ molecule was reacted with -OH, a HCl molecule was generated and the resulting HfCl$_3$ was attached to the O atom. The free energy could be influenced by the configuration of HfCl$_3$ with respect to the Si surface. Figure 2 (b) shows the energy difference as a function of the HfCl$_3$ angle. We obtained an optimal configuration of HfCl$_3$ at the angle of 180°.
Figure 2. (a) The reactions of the HfCl$_4$ molecule with -H and -OH, and (b) the energy difference as a function of the HfCl$_3$ angle.

After the reaction of the first HfCl$_4$ with -OH, there were seven available -OH’s on this 4$x$4 Si (001) surface for further reaction with other HfCl$_4$. We calculated the reaction of the next HfCl$_4$ molecules with OH’s. Figure 3 shows the relative energy as a function of the number of the HfCl$_4$ molecules. The reaction of the second HfCl$_4$ molecule was favorable with the most adjacent -OH of the first one and it formed a pair with first one. The reaction of the third and fourth HfCl$_4$ molecule showed the same tendency with the first and second ones. The energy differences of the fifth and sixth HfCl$_4$ reactions were -0.01 eV, 0.06 eV, respectively. There were two points at this result. First, the energy differences of the second and fourth HfCl$_4$ reactions were a little higher than the first and third ones. Second, the reactions of HfCl$_4$ molecules were favorable up to fifth HfCl$_4$ and the reaction of sixth HfCl$_4$ molecule was endothermic by 0.06 eV.

Figure 3. The relative energy as a function of the number of the HfCl$_4$ molecules.

Figure 4 shows the line profile of the electron density between two atoms. 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). When the second HfCl$_4$ reacted with a -OH, it
formed a pair with the first one, resulting in sharing Cl atoms. The electron density from Hf(1) to Cl(2) was lower than that from Cl(1) to Hf(1). It meant that the Hf atom shared the rest of electrons with the other Cl atom that was shared with Hf(2). It was confirmed that the electron density from Hf(1) to Cl(2) and from Hf(2) to Cl(2) were exactly the same. Therefore, we believe that the sharing of Cl atoms from Hf atoms results in the further energy reduction.

Figure 4. The line profile of the electron density from Cl(1) to Cl(3); Cl(1)-Hf(1)-Cl(2)-Hf(2)-Cl(3). The isosurface level was $0.08 \alpha_0^{-3}$ ($\alpha_0$: Bohr radius)

Table 1. Distances and angles of HfCl$_3$, OH-terminated Si substrate, and the interface of HfCl$_3$-OH terminated Si substrate as a function of the number of HfCl$_4$.

<table>
<thead>
<tr>
<th></th>
<th>1st HfCl$_3$</th>
<th>2nd HfCl$_3$</th>
<th>3rd HfCl$_3$</th>
<th>4th HfCl$_3$</th>
<th>5th HfCl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf-Cl (Å)</td>
<td>2.33</td>
<td>2.33</td>
<td>2.33</td>
<td>2.34</td>
<td>2.31</td>
</tr>
<tr>
<td>$\angle$ Cl-Hf-Cl (°)</td>
<td>110.14</td>
<td>149.90</td>
<td>111.06</td>
<td>149.10</td>
<td><strong>123.44</strong></td>
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<tr>
<td>Si-Si</td>
<td>2.44</td>
<td>2.43</td>
<td>2.46</td>
<td>2.45</td>
<td>2.48</td>
</tr>
<tr>
<td>Si-O</td>
<td>1.69</td>
<td>1.69</td>
<td>1.69</td>
<td>1.69</td>
<td>1.67</td>
</tr>
<tr>
<td>$\angle$ Si-Si-O</td>
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<td>108.85</td>
<td>108.53</td>
<td>109.47</td>
<td><strong>119.65</strong></td>
</tr>
<tr>
<td>Hf-O</td>
<td>1.90</td>
<td>1.89</td>
<td>1.90</td>
<td>1.89</td>
<td><strong>1.93</strong></td>
</tr>
<tr>
<td>$\angle$ Si-O-Hf</td>
<td>164.88</td>
<td>166.57</td>
<td>165.51</td>
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<td><strong>173.02</strong></td>
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<td>$\angle$ O-Hf-Cl</td>
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<td>109.46</td>
<td>104.37</td>
<td><strong>114.01</strong></td>
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<td></td>
<td>105.38</td>
<td>100.26</td>
<td>106.02</td>
<td>100.95</td>
<td>103.24</td>
</tr>
</tbody>
</table>
The configurations as a function of the number of the HfCl₄ molecules were shown in table 1. It consists of three parts; the HfCl₃, OH-terminated Si, and the interface of HfCl₃-OH terminated Si substrate. The first HfCl₃ showed almost same configuration with the third one and the second HfCl₃ showed almost same configuration with the fourth one. There was no significant change of the substrate and the interface up to the reaction of the fourth HfCl₄. However, the reaction of the fifth HfCl₄ caused lots of change in HfCl₃, the substrate, and the interface compared to previous ones. Two pairs of HfCl₃’s (the first one and the second one, the third one and the fourth one) were so favorable that the fifth HfCl₃ suffered the repulsion force caused by the previous four HfCl₃’s due to the steric hindrance, resulting in significantly reduced energy reduction. The endothermic reaction of the sixth HfCl₄ was explained by the same reasoning. In the 4×4 Si surface size, therefore, the reactions of HfCl₄ molecules were favorable up to fifth HfCl₄. It demonstrated that the saturation Hf coverage was calculated to be $2.08 \times 10^{14}$ Hf/cm² and this result was well-matched with the experimental data of other group.

CONCLUSIONS

We performed a density functional theory study to investigate the reaction of HfCl₄ with H₂O-terminated Si (001)-2×1 surface. The reaction of the HfCl₄ molecule was more favorable with -OH than -H. When even numbers of the HfCl₄ molecules reacted –OH’s on the surface, the molecules shared some Cl atoms, resulting in further energy reduction. In 4×4 Si surface size, the reactions of HfCl₄ molecules were favorable up to fifth HfCl₄. The calculated saturation Hf coverage was $2.08 \times 10^{14}$ Hf/cm² and was well-matched with the experimental data.

REFERENCES