



# Dynamics of reactions inhibiting epitaxial growth of Si(100) surfaces via interaction with hydrogen chloride



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## ABSTRACT

The dynamics of reactions of HCl at growing Si(100) surfaces was investigated through computational methods, using clusters of different sizes and shapes. The analysis was conducted through Gaussian09 at the B3LYP/6-31G(d,p) level. It was found that adsorption of HCl on H-passivated dimers does not proceed as easily as on non-passivated dimers. In addition, analysis of reactions between HCl and a SiCl<sub>2</sub> moiety adsorbed on a surface dimer indicated that HCl can lead to detachment of the SiCl<sub>2</sub> moiety from the surface in the form of a SiCl<sub>2</sub> or a SiHCl<sub>3</sub> molecule, or to diffusion of the moiety to a neighboring dimer. However, when the dimer on which SiCl<sub>2</sub> adsorbs had been H-passivated prior to adsorption, the reaction of HCl with the SiCl<sub>2</sub> moiety becomes significantly more difficult. H-passivation of surface dimers seems thus to promote surface growth by protecting the surface against HCl adsorption and by preventing detachment or diffusion of the adsorbed SiCl<sub>2</sub> moiety, which is pointed out as an important intermediate in the growth mechanism. These results are in consonance with evidence found for the convenience of H-passivation of surface dimers prior to silicon deposition, already published in the literature.

## 1. Introduction

Epitaxial growth of Si(100) surfaces for producing semiconductor wafers can be achieved through CVD processes that use trichlorosilane (TCS, or SiHCl<sub>3</sub>) and hydrogen as source gases [1]. Many physical and chemical phenomena are involved in the epitaxial growth process, so that the elucidation of the mechanism is difficult. In the gas-phase, TCS is known to decompose mainly into SiCl<sub>2</sub> and HCl [2,3], and at the surface, the main species contributing to surface growth seems to be SiCl<sub>2</sub> when either TCS [1] or DCS (dichlorosilane, or SiH<sub>2</sub>Cl<sub>2</sub>) [4] is in the source gas, at least at high temperature. In previous work, we confirmed that SiCl<sub>2</sub> undergoes intradimer molecular adsorption on Si(100) surfaces with a small activation energy [5], and showed evidence that the adsorbed SiCl<sub>2</sub> can contribute to surface growth especially at high temperature and when the dimers on the surface are passivated with hydrogen atoms prior to the deposition process [6].

On the other hand, TCS decomposition in the gas-phase leads to the same amounts of SiCl<sub>2</sub> and HCl [2,3,7]. The former, as described above, contributes to surface growth, while the latter is a well-known etchant of silicon surfaces [8–10]. It is thus believed that HCl should not be allowed to react at the surface because it may inhibit surface growth in CVD reactors. Habuka et al. argued that when the growing silicon crystal substrate is rotated at high speed, the growth rate increases

because the rotation makes the HCl molecules that are formed near the hot surface go away from the surface by convection [11]. Some theoretical efforts to analyze HCl reactions at silicon surfaces have been reported in the literature [12,13], but the mechanism through which HCl reacts at Si(100) surfaces has not been elucidated yet.

In this work, we used clusters of silicon atoms as a proxy for the Si(100) surface, and investigated the dynamics of reactions that occur when HCl molecules attack the growing surface. We then compared the results obtained for the case when the surface dimers are passivated with H atoms with those obtained for the case when they are not passivated.

## 2. Methods

Because a crystal contains too many atoms on the two-dimensional surface as well as in the depth direction, its accurate reproduction by a computational model is difficult. The use of clusters of atoms that are formed by cutting a piece of the surface and passivating the resulting dangling bonds with hydrogen atoms is a strategy that has been shown to give good results. The validity of such a method has been extensively discussed in the literature. For example, Nakai et al. analyzed variations in energy density in the simulation of adsorption reactions of H<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and CO on Si(100) surfaces when clusters of different sizes were

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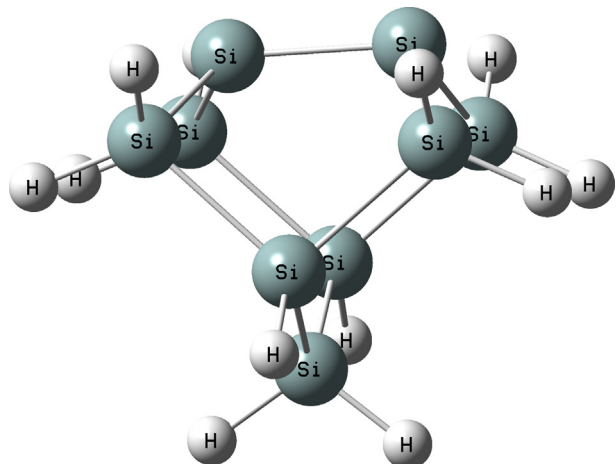
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**Table 1**  
Some of the clusters, in the non-passivated state, investigated in this work.

No. of dimers	Parallel (P)	Aligned (A)
1		Si <sub>9</sub> H <sub>12</sub>
2	Si <sub>15</sub> H <sub>16</sub>	Si <sub>31</sub> H <sub>32</sub>
3	Si <sub>21</sub> H <sub>20</sub>	Si <sub>45</sub> H <sub>44</sub>



**Fig. 1.** The cluster P1, which contains one non-passivated dimer on the surface.

used [14]. They showed that clusters containing three or four layers of silicon atoms led to predictions of adsorption energies consistent with experimental values. Other few examples of using clusters to model silicon surfaces include the analysis of adsorption reactions of chlorosilanes [15], disilanes [16], and SiO<sub>2</sub> [17], and the analysis of the dynamics of silicon surfaces having adsorbed H and Cl atoms [13].

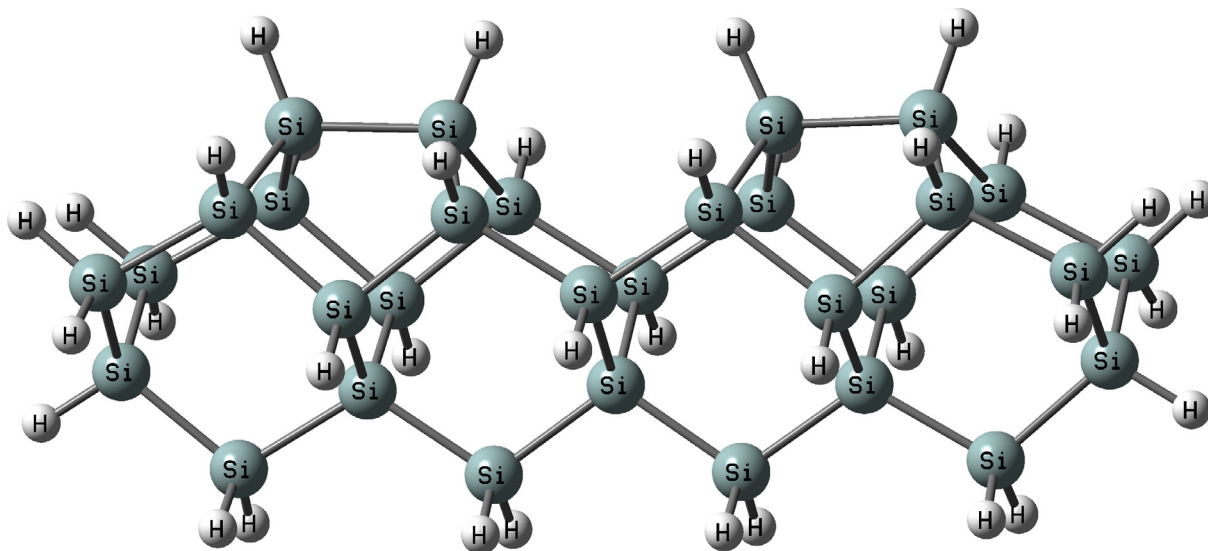
The authors of the present work have also used clusters of various sizes and shapes to analyze the adsorption of H<sub>2</sub> and HCl on the Si(100) surface, and found that the calculated activation energies depended slightly on the cluster size and shape [18]. When the clusters contained surface dimers that were aligned to each other, they were called A2, A3, etc., where “A” stands for aligned, and “2” and “3” indicate the number of dimers on the surface. And when the dimers were parallel to each other, the clusters were called P2, P3, etc., with “P” standing for parallel. Table 1 shows the number of Si and H atoms in some clusters where the dimers are not passivated with H atoms (H passivation of

dimers will lead to an increase of 2 per dimer in the number of H atoms in a cluster). Results obtained in previous work showed that calculations performed through Gaussian09 [19] at the B3LYP/6-31G(d,p) level were able to reproduce experimental activation energies accurately when the clusters had the proper size and shape [18]. It was also seen that the smallest cluster was not able to reproduce the steric effects that arise in the elimination of chlorine atoms from the growing silicon surface, so that clusters containing more than one dimer were needed for accurate analysis of the reaction dynamics [6].

In the present work, similar methods to those employed previously [5,6,18] were adopted to analyze the dynamics of reactions of HCl at growing Si(100) surfaces. The intradimer adsorption of HCl on a clean Si(100) surface has already been shown to proceed with no activation energy [18]; here, we first study the adsorption of HCl on H-passivated dimers, and compare the results with those obtained for non-passivated dimers. In addition, from evidence published in the literature [1,3,4] and findings of our previous work [6], we assumed that the product of the intradimer adsorption of a SiCl<sub>2</sub> molecule on the Si(100) surface constitutes an important stage in the growth process. We thus investigate how HCl reacts with the growing surface after this stage, when the surface dimers are H-passivated and when they are not passivated.

In the determination of activation energies, the zero-point energies were included and obtained from unscaled vibration frequencies calculated at the B3LYP/6-31G(d,p) level. The transition states were confirmed to have a single imaginary frequency and, when needed, IRC (intrinsic reaction coordinate) calculations were performed to verify that the located transition states linked the reactants to the products of the reactions investigated.

Some of the clusters used in the present work, obtained in previous work [5,6,18] by structure optimization, are shown in Figs. 1–3. Fig. 1 shows the P1 cluster, the smallest cluster that contains only one dimer; it should be noted that the chemical bonds that were cut to make the cluster are passivated with H atoms, while the surface dimer is not passivated. The cluster A2H4, containing two aligned, H-passivated dimers on the surface is depicted in Fig. 2, and Fig. 3 shows the cluster A2SiCl<sub>2</sub>, which results from molecular intradimer adsorption of SiCl<sub>2</sub> on a non-passivated surface dimer of an A2 cluster; the structure shown in Fig. 3 is in agreement with predictions made by Xu et al. [20] and depicts an important stage in the growing process of Si(100) surfaces. Hereafter, we refer to the clusters that contain H-passivated dimers on their surface as dimer passivated clusters.



**Fig. 2.** The cluster A2H4, which contains two aligned, H-passivated dimers on the surface.

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