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Full Length Article

Novel pathways for elimination of chlorine atoms from growing Si(100) surfaces in CVD reactors

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ABSTRACT

Reactions leading to elimination of chlorine atoms from growing Si(100) surfaces were simulated using clusters of silicon atoms of different sizes and shapes, and at the UB3LYP/6–31 g(d,p) level of theory. The reactions of type $SiCl_2(s) + 2\ H_2(g)$, where (s) indicates an adsorbed species at the surface and (g) a gas-phase species, were found to proceed in two steps: $SiCl_2(s) + H_2(g) \rightarrow SiHCl(s) + HCl(g)$ and $SiHCl(s) + H_2(g) \rightarrow SiH_2(s) + HCl(g)$, each having activation energies around 55 kcal/mol, a value which is comparable to experimental values published in the literature. In addition, the results suggested that H-passivation of Si(100) surfaces support reactions leading to canonical epitaxial growth, providing a plausible explanation for the convenience of passivating the surfaces prior to silicon deposition. The reactions analyzed here can therefore be seen as important steps in the mechanism of epitaxial growth of Si(100) surfaces.

1. Introduction

Epitaxial growth of silicon crystals, which is of great interest for the electronics and photovoltaics industries, is usually performed in CVD (chemical vapor deposition) reactors that use gaseous silane or chlorinated silanes as silicon precursors [1]. The chlorinated silanes dichlorosilane (SiH_2Cl_2, DCS) and trichlorosilane ($SiHCl_3$, TCS) are preferable to silane (SiH_4) because chlorine binds to silicon more strongly than silicon itself, preventing nucleation of silicon particles in the gas phase and allowing for lower operating temperatures [2].

The performance of a CVD reactor depends on many chemical and physical factors. As for the chemistry involved, evidence for the importance of reactions of $SiCl_2$ at the growing silicon surfaces has been reported for various systems (Refs. [3–6] are just some examples of reports published by different research groups, along three decades). The mechanism of $SiCl_2$ formation in the gas phase from chlorosilanes and its kinetics are well-known [7,8], and the proposed rate coefficients have been adopted in reaction models that were able to reproduce accurately experimental results obtained for the gas-phase [9]. Furthermore, $SiCl_2$ has been shown to adsorb easily on silicon surfaces, confirming the relevance of this species in the epitaxial growth of silicon [10]. The chlorine atoms in the adsorbed $SiCl_2$ hinder further growth reactions to proceed, and therefore the elimination of these surface chlorine atoms is expected to be important. Reaction R1, shown below, has been pointed out as the rate-determining step in the surface growth process in a CVD reactor that used DCS as the precursor and H_2 as the carrier gas [11].

$$SiCl_2(s) + H_2(g) \rightarrow Si(s) + 2HCl(g) \tag{R1}$$

In the above reaction, (s) indicates a species adsorbed at the surface and (g) a gas-phase molecule. In their pioneering work, Oshita et al. studied R1 both experimentally and theoretically [11]. They estimated that the activation energy of R1 was between 40 and 50 kcal/mol, experimentally; in addition, by adopting a small cluster of silicon atoms to model the surface, they determined the activation energy theoretically and obtained the value of 110 kcal/mol. The authors attributed the discrepancy between the experimental and theoretical activation energies to the fact that the transition state had to be determined by keeping the silicon atoms in the cluster fixed at positions that corresponded to the bulk structure (it was not practical at the time to conduct a full optimization). To the best of our knowledge, no further theoretical studies on the above reaction have been published, in spite of its practical importance. This lack of attention to R1 can be attributed to the fact that $SiCl_2$ has been thought to adsorb dissociatively on silicon surfaces, following the reaction shown below:

$$SiCl_2(s) + 2Si(s) \rightarrow 2Si(b) + 2SiCl(s) \tag{R2}$$

where Si(b) denotes a bulk silicon atom (an atom which is or is about to be incorporated in the crystalline structure of silicon). If R2 occurs and SiCl(s) is formed, then R1 does not proceed, because $SiCl_2(s)$ would not be formed. R2 does appear in kinetic models

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proposed recently to be used for prediction of silicon growth rates [12,13] (these models do not consider R1). However, the molecular adsorption of $SiCl_2$ on Si(100) surfaces has been shown to proceed easily [10,14], with formation of $SiCl_2$(s). Therefore, reaction R1 deserves further attention, and in this work we analyzed it theoretically, using silicon clusters of various sizes and shapes to model the silicon surface, and through full optimizations. As a result, the elimination of chlorine atoms from $SiCl_2$(s) was found to proceed in two steps, instead of the single step shown by R1. The reaction dynamics of chlorine elimination found in this work reveals pathways that not only are novel and consistent with experimental observations, but also shed light on the role of hydrogen molecules in the epitaxial growth of silicon.

2. Methods

The dynamics of the reaction between $SiCl_2$(s) and H_2 was conducted in the same way as in previous work on the adsorption reactions of H_2 and HCl [15], and of $SiCl_2$ [10] on Si(100) surfaces. As before, we used clusters of silicon atoms to model the silicon surface, and these clusters have structures that depend on whether the dimers on their surface are parallel to each other (P clusters) or aligned (A clusters). A parallel cluster having three dimers (P3) was found to reproduce activation energies of adsorption fairly accurately [15].

Previously, the silicon atoms on the surface of our clusters were not passivated (no H termination), while the peripheral silicon atoms in lower layers were H-terminated. In this work, in addition to those clusters (hereafter referred to as non-passivated clusters), we also use clusters whose dimers are H-passivated, and compare the results with those obtained with the non-passivated clusters.

Table 1 lists some of the non-passivated clusters used in this work. The optimization of these clusters has been conducted in a previous work [15]. Fig. 1 shows P3, a cluster having three dimers parallel to each other on the surface. It can be seen that the dimers are tilted, in agreement with previous theoretical predictions [16,17] and experimental observations [18,19].

Table 1
Some of the non-passivated clusters considered in this work.

No. of dimers	Parallel (P)	Aligned (A)
1	Si_9H_{12}	
2	$Si_{15}H_{16}$	$Si_{31}H_{32}$
3	$Si_{21}H_{20}$	–

The structure shown in Fig. 2 corresponds to a cluster P1 after molecular adsorption of a $SiCl_2$ molecule on its dimer, optimized in a previous work [10].

As before, full optimization (with all variables allowed to vary) of structures (H_2, $SiCl_2$, and HCl molecules, clusters before and after reaction, and transition states), and calculation of vibrational frequencies and activation energies were conducted at the B3LYP/6-31G(d,p) level (the accuracy and validity of this approach has been discussed to some extent in Ref. [15]), with the zero-point energies (ZPE) being evaluated from the vibrational frequencies with no corrections. All calculations were performed using Gaussian09 [20]. The transition states were identified by verification of the movement of atoms in the vibration mode having the unique

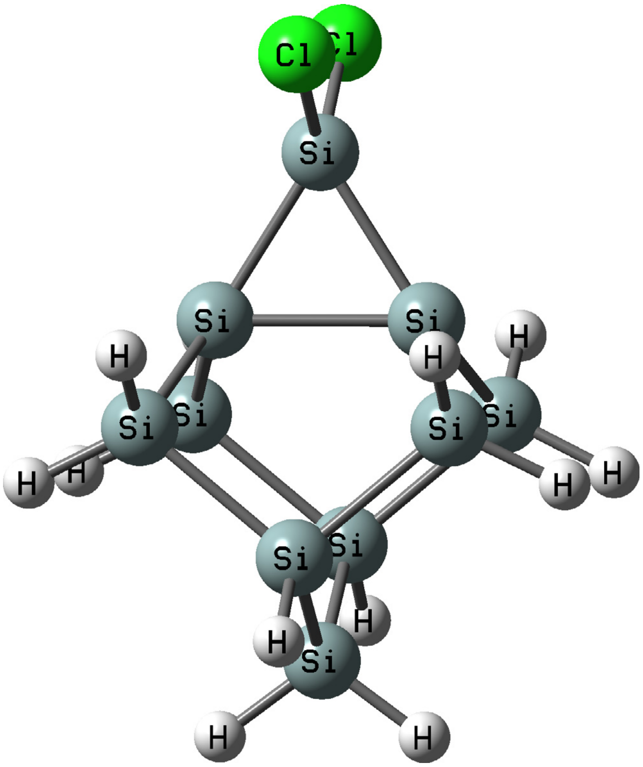

Fig. 2. Optimized structure of P1$SiCl_2$, which results from intradimer adsorption of $SiCl_2$ on P1.

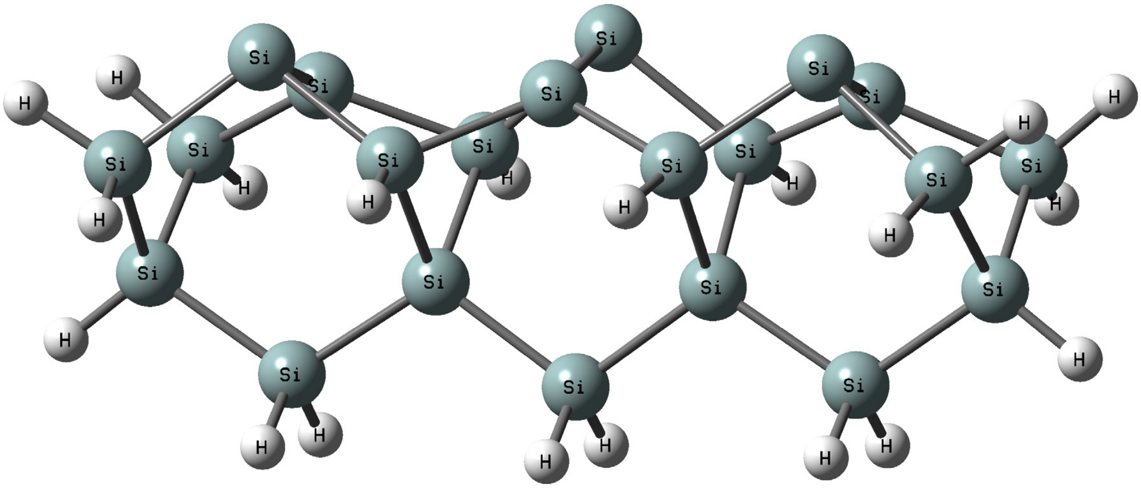

Fig. 1. Optimized structure of the non-passivated P3 cluster, showing buckled dimers on the surface.