Applied Surface Science 392 (2017) 410–417

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Analysis of the dynamics of reactions of $SiCl_2$ at Si(100) surfaces

Keisuke Anzai [1], Nílson Kunioshi *, Akio Fuwa

Graduate School of Creative Science and Engineering, Waseda University, 3–4–1 Ohkubo, Shinjuku-ku, Tokyo 169-8555, Japan

ARTICLE INFO

Article history:
Received 11 May 2016
Received in revised form 29 June 2016
Accepted 11 September 2016
Available online 12 September 2016

Keywords:
Silicon surface growth
Cluster model
Reaction dynamics
Molecular orbital method

ABSTRACT

The dynamics of reactions of $SiCl_2$ at Si(100) surfaces was investigated through the molecular orbital method at the B3LYP/6-31G(d,p) level of theory, with the surface being modeled using clusters of silicon atoms. The intradimer adsorption of a $SiCl_2$ molecule proceeded with no energy barrier, and in the structure of the product of the adsorption reaction the Si atom of the $SiCl_2$ adsorbate formed a triangular structure with the two Si atoms of the surface dimer, in agreement with theoretical predictions published recently in the literature for a small cluster. However, the dynamics reported in this work indicates that $SiCl_2$ undergoes molecular adsorption at the silicon surface, in contrast with the dissociative adsorption suggested by some available kinetic models. Intradimer adsorption of a second $SiCl_2$ molecule, and interdimer adsorptions of a first, a second, and a third $SiCl_2$ molecule were also seen to proceed without significant energy barriers, suggesting that the formation of the first additional layer of silicon atoms on the surface would be fast if the adsorption of $SiCl_2$ were the only type of reaction proceeding in the system. The diffusion of the $SiCl_2$ adsorbate over the surface and its desorption from the surface were found to have comparable activation energies, so that these reactions are expected to compete at high temperatures.

1. Introduction

Thin films of crystalline silicon can be grown on silicon substrates of lower grade [1], and allow for smaller consumption of highly pure silicon by the photovoltaic industry, because most of the optical absorption occurs up to a depth of around 30 μm from the crystal surface [2]. The formation of single crystalline silicon films can be obtained by chemical deposition of gaseous precursors such as trichlorosilane ($SiHCl_3$, or TCS) on silicon substrates, but the process requires accurate control of many factors [3]. A better understanding of each of these factors is needed for enabling the production of low cost and high quality silicon films to supply the growing photovoltaic industry.

In fact, the mechanism of epitaxial growth of silicon surfaces inside CVD chambers is quite complex, with simultaneous occurrence of many chemical and physical events. Chemical reactions of adsorption (chemisorption) and desorption, stabilization of gaseous species near the surface (physisorption), and transport phenomena related to convection, diffusion and thermal conduction, all interact and are expected to affect surface growth in positive or negative ways, depending on the conditions [4–6]. As for the surface chemistry involved, $SiCl_2$ has been pointed out as the main adsorbate contributing to the epitaxial growth of the silicon surface in a CVD chamber in which TCS and excess of hydrogen are used as the source gases [7]. $SiCl_2$ can reach significant concentrations in the gas phase from reactions of TCS [8,9]. Furthermore, molecular hydrogen coming from the gas phase can react with the adsorbed $SiCl_2$ and release two molecules of HCl, making the surface available for further growth reactions; such a reaction has been identified as the rate-determining step in the surface growth inside a CVD chamber where SiH_2Cl_2 was used as the precursor gas [10].

In spite of the relevance of $SiCl_2$ reactions at silicon surfaces, very few studies on the detailed chemistry of these reactions have been reported in the literature. One of the few examples is the theoretical study of Ohshita et al. [11]. That pioneer theoretical approach was accurate at the time, but silicon atoms were shown later to form dimers on the surface [12], and this surface structure may influence the reaction dynamics significantly. Kinetic models made available in the literature for prediction of surface growth rates do include reactions related to the adsorption of $SiCl_2$:

$$SiCl_2 + 2Si(s) \rightarrow SiCl(s) + Cl(s)$$

$$SiCl_2 + 2Si(s) \rightarrow Si(b) + 2SiCl(s)$$

* Corresponding author.
E-mail address: nilson@waseda.jp (N. Kunioshi).
[1] Present address: Mizuho Aero-Engine Works, IHI Corporation, 229 Tonogaya, Mizuho-machi, Nishitama-gun, Tokyo 190-1297, Japan.

http://dx.doi.org/10.1016/j.apsusc.2016.09.039
0169-4332/

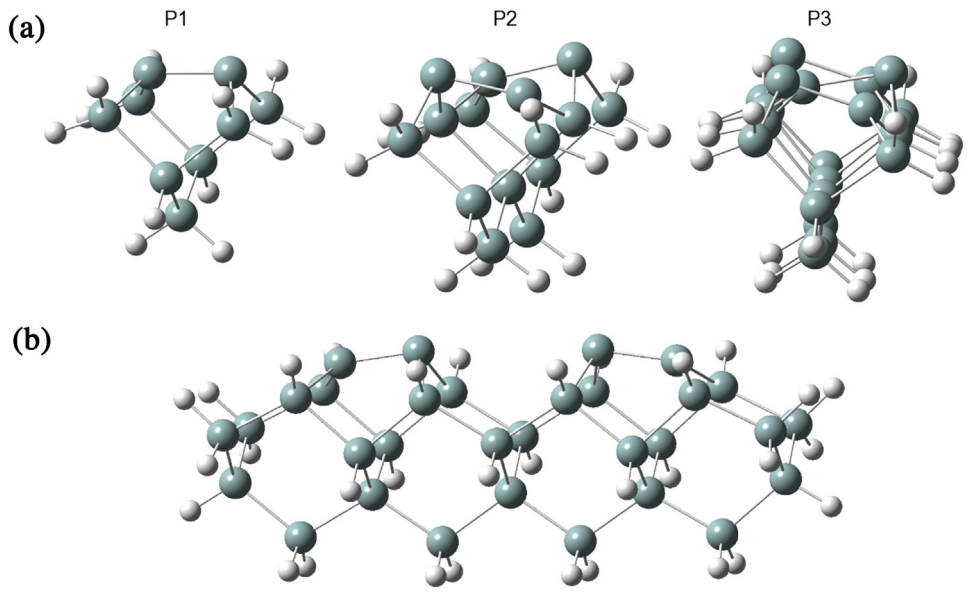

Fig. 1. The clusters used in this work to model the silicon surface: the parallel clusters P1, P2 and P3 (a), and the aligned cluster A2 (b). The darkest spheres represent silicon atoms, and the smallest spheres hydrogen atoms.

are examples of reactions that have been included in kinetic models published recently [6,13]. In the reactions above, the suffix (s) indicates a moiety attached to the surface, and Si(b) means a bulk silicon atom. Both reactions suggest that $SiCl_2$ adsorbs dissociatively and leads to the formation of SiCl(s), but this does not agree with the recent theoretical predictions of Xu et al. [14], which suggest a molecular adsorption forming $SiCl_2$(s).

With the aim to achieve a better understanding of the surface chemistry involved in the silicon surface epitaxial growth, in this work we analyzed the dynamics of reactions of $SiCl_2$ on Si(100) surfaces. Clusters were used to model the surface in the same way as that described in our previous work on the adsorption reactions of H_2 and HCl [15]. The results obtained in the present work showed that the adsorption of $SiCl_2$ on Si(100) surfaces proceed without energy barriers and followed a molecular adsorption dynamics rather than the dissociative dynamics of the two reactions shown above. Furthermore, adsorption of a second and a third $SiCl_2$ molecule in the vicinity of the first adsorption site were also seen to proceed without large barriers, and the diffusion of an adsorbed $SiCl_2$ molecule over the silicon surface was also analyzed. The implications of the results obtained in this work for the elucidation of the mechanism of epitaxial growth of silicon surfaces are discussed in detail.

2. Methods

The calculations were conducted in the same way as in a previous work on the adsorption reactions of H_2 and HCl on Si(100) surfaces [15], where the effect of size and shape of the clusters on the calculated activation energies was determined. In that work, we considered clusters having dimers that were parallel to each other on the surface (P clusters) and clusters where the surface dimers were aligned (A clusters), and found that the P3 cluster (a P cluster with 3 dimers on the surface) was sufficient for fairly accurate calculations. Still, in order to guarantee that the size was large enough and led to accurate results under a broad range of reaction conditions, a cluster that had 3 dimers parallel to each other and 3 dimers aligned on its surface was considered, and this cluster ($Si_{57}H_{52}$) led to the best agreement with experimental activation energies and tilt angles [15].

Table 1
Clusters investigated in this work.

No. of dimers on the surface	Parallel (P)	Aligned (A)
1	Si_9H_{12}	
2	$Si_{15}H_{16}$	$Si_{31}H_{32}$
3	$Si_{21}H_{20}$	–
4	$Si_{27}H_{24}$	–
5	$Si_{57}H_{52}$	

Following the procedures adopted previously, the silicon atoms on the surface of all clusters were not passivated (no H termination) while the peripheral silicon atoms in lower layers were H-terminated. The full optimization (with all variables allowed to vary) of structures ($SiCl_2$ and clusters before reaction, transition states, and products after reaction), and the calculation of vibrational frequencies and activation energies were conducted at the B3LYP/6-31G(d,p) level (the validity of this level is discussed in [15]), with the zero-point energies being evaluated from the vibrational frequencies with no corrections. All calculations were performed using Gaussian09 [16].

Table 1 lists the clusters considered in this work. The cluster with 5 dimers on the surface is the cluster that has, on its surface, 3 dimers parallel to each other and 3 dimers aligned in a row.

Clusters P1 to P3 are the same as the "small clusters" used by Santos et al. [17] to model the Si(100) surface, and are depicted in Fig. 1(a). A2, the only aligned cluster investigated in this work, is shown in Fig. 1(b). It can be seen from the optimized structures of P2, P3 and A2 of Fig. 1 that dimers buckle in alternate directions so that they are actually not perfectly parallel nor aligned.

3. Results and discussion

Among the many types of reactions that $SiCl_2$ undergoes at Si(100) surfaces, we have analyzed intradimer and interdimer adsorption, and diffusion over the surface.

3.1. Intradimer adsorption of $SiCl_2$

The silicon surface was modeled using clusters of different sizes and shapes. In a previous work we found that clusters having sur-