

# Molecular Dynamics Simulation of Thermal Chemical Vapor Deposition for Hydrogenated Amorphous Silicon on Si (100) Substrate by Reactive Force-Field

1<sup>st</sup> Naoya Uene  
Graduate school of engineering  
Tohoku university  
Sendai, Japan  
uene@nanoint.ifs.tohoku.ac.jp

2<sup>nd</sup> Takuya Mabuchi  
Frontier research institute for  
interdisciplinary sciences  
Tohoku university  
Sendai, Japan  
mabuchi@tohoku.ac.jp

3<sup>rd</sup> Masaru Zaitso  
Research & development  
Japan advanced chemicals ltd.  
Sagamihara, Japan  
masaru.zaitso@japanadvancedchemicals.com

4<sup>th</sup> Shigeo Yasuhara  
Research & development  
Japan advanced chemicals ltd.  
Sagamihara, Japan  
shigeo.yasuhara@japanadvancedchemicals.com

5<sup>th</sup> Takashi Tokumasu  
Institute of fluid science  
Tohoku university  
Sendai, Japan  
tokumasu@ifs.tohoku.ac.jp

**Abstract**—We calculate a deposition process of hydrogenated amorphous silicon (a-Si:H) films on a silicon (100) substrate by reactive force-field molecular dynamics simulations. The influences of (a) substrate temperatures and (b) coverage of hydrogen atoms on the substrate on the adsorption probability are investigated, and it is found out that (a) the adsorption probability is almost constant for SiH<sub>2</sub> and SiH<sub>3</sub>, but decrease with increase in the substrate temperature for SiH<sub>4</sub>, (b) it decreases with the increase in hydrogen coverage.

**Keywords**—Chemical Vapor Deposition, Reactive Force-Field Molecular Dynamics Simulation, Reactive Sticking Coefficient, Surface-Covering Bonded Hydrogen, Surface Reaction

## I. INTRODUCTION

Chemical vapor deposition (CVD) is one of the common and powerful methods to form a high-quality thin film for advanced semiconductor devices. The film properties strongly depend on the process parameters such as substrate temperature, gas composition, gas pressure, and deposition time etc., therefore, understanding these influences is essential to obtain the desired physical properties. However, deposition phenomena in CVD process are complicated and difficult to understand, and trial and error by experiments are repeated. Predicting the microstructure and properties of thin films using a simulation is one of the most challenging project in material science [1][2]. The CVD process simulation should include all physical phenomena (mass transport) and chemical reactions (gas phase reaction and surface reaction) to analyze the phenomena over wide length and time scale accurately. Fast elementary processes (e.g. adsorption and diffusion of atoms on the surface) occur  $10^{-12} - 10^{-15}$  s and involve displacements of approximately  $10^{-10}$  m. The time for the deposition of approximately  $10^{-6}$  m thick in reaction chamber of approximately  $10^{-1}$  m in diameter requires usually  $10^2 - 10^4$  s [1]. It is not practical to simulate the development of film formation with capturing microscopic scale behavior because there are large gap between them even regarding the ever-increasing power of computer.

Multiscale modeling strategies are now becoming available to simulate entire CVD processes. Multiscale modeling strategies are realized by coupling together individual models at different length scales, i.e. the reactor scale model (macroscale) and the feature scale model (microscale).

1) *Reactor scale model*: The reactor scale model solves the governing equation of mass, momentum, heat, species transport to compute the flow, temperature, and species concentrations as functions of positions and time. Recent advances of computer performance have made it possible to solve it using a computational fluid dynamics (CFD) code.

2) *Feature scale model*: Various models have been proposed as a feature scale model [3][4][5]. Two approaches have been adapted (i.e. numerical and stochastic approach).

a) *numerical approach*: The numerical approach consists of ballistic model, a surface model, and a profile evolution algorithm. The transport of species has been dealt with by numerically solving continuum ballistic models when  $Kn > 1$ , continuum diffusion models when  $Kn \ll 1$ , and Boltzmann equations when  $Kn \sim 1$ , depending on the Knudsen number ( $Kn$ ). For the surface model, empirical expressions [6] for the surface reaction rate have been exploited. This approach is not universal because it is necessary to change the equation empirically depending on the composition of the gas.

b) *Stochastic approach*: Monte Carlo (MC) based models have been used for the transport of species and their interaction with the surface when  $Kn > 1$ . The concentrations of the various species, then the corresponding impingement rates at the surface, are estimated from a reactor scale model. The impingement rates are used as an input in feature scale model, which tracks surface events at the atomic scale (e.g. adsorption, desorption, reflection, and relaxation of surface atoms). As a result of MC simulation, the reactive sticking coefficient (RCS) can be obtained from statistical averages

for the reactivity of the various species. The RSCs are fed back into the reactor scale model and the process is repeated until convergence is obtained. In general, this approach has a larger computational cost than the numerical one because of time consuming MC simulations. It may become a more promising approach by improving the computer performance in the future because it can take into account molecular knowledge on the surface. However, surface reconstructions and multiple bonds between atoms were ignored because of the hypothesis [7].

We consider a deposition process of hydrogenated amorphous silicon (a-Si:H) films on a silicon (100) substrate by the thermal CVD using  $\text{SiH}_4$  as a precursor. a-Si:H are highly expected as potential materials applicable to electronic or optoelectronic thin-film devices such as thin-film transistors (TFT), photoreceptors, color sensors, and solar cells. The surface is covered with many hydrogen atoms before and during deposition processes. Understanding relationships between the structure, hydrogen coverage, morphology, and reactivity is very important as mentioned in many papers [8][9][10]. Here, we investigated influence of hydrogen atoms covering the substrate as a hydrogen coverage  $\theta$  and the substrate temperature  $T_S$  on the adsorption behaviors for each chemical species.  $\text{SiH}_4$ ,  $\text{SiH}_3$ , and  $\text{SiH}_2$  are selected as a chemical species because they have a possibility to form during the deposition processes using  $\text{SiH}_4$ . Many studies have reported that  $\text{SiH}_3$  is the dominant chemical species in the a-Si:H deposition process [8][11], but other chemical species cannot be ignored under high substrate temperatures [9].

Our study focuses on investigations of accurate molecular knowledge on the surface, and provides the data necessary for the construction of the feature scale model. For that purpose, we perform a reactive force-field molecular dynamics (ReaxFF MD) simulation that incorporates chemical reactions and molecular transport. Since the ReaxFF can reproduce the reaction path by the relation between bond order and bond distance more accurately, the CVD process can be handled with higher accuracy than MC and classical MD simulations. In addition, it is possible to perform calculations considering dynamics due to the smaller calculation cost compared with the quantum chemical simulations [12][13]. It is important for CVD processes to include dynamics knowledge such as molecular transport form.

## II. METHODS

### A. Reactive Force-Field (ReaxFF)

Molecular dynamics simulations were performed with the large-scale atomic/molecular massively parallel simulator (LAMMPS) MD packages using reactive force-field (ReaxFF) [14]. ReaxFF can describe bond-breaking and bond-formation events unlike general force-fields. In the ReaxFF formalism, each element is described by only one single atom type even within different chemical environment. In addition, the information of reactive sites or the bond connectivity is not defined before simulations. Instead, this information is derived from bond orders (BOs) that are calculated from interatomic distances. The BOs are repeatedly updated at every MD step. Our MD simulations were based on the ReaxFF potential which parameters are taken from the Si/Ge/H system [15]. We confirmed that inter- and intramolecular potential agree well with results from the density functional theory (DFT) calculation. DFT calculations are

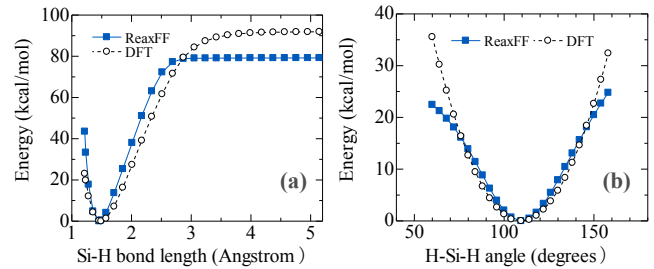


Fig. 1. Comparison between DFT (black open circles) and ReaxFF (blue solid squares) results for: (a) Si-H bond dissociation in  $\text{SiH}_4$  and (b) H-Si-H angle bending in  $\text{SiH}_4$ .

performed by using commercial software package BIOIVA Materials Studio. Results of inter-molecular potential in  $\text{SiH}_4$  obtained from DFT and ReaxFF are shown in Fig. 1.

### B. Calculation System

We report results of simulations that each chemical species impact on the hydrogenated Si (100) substrates. The substrate was composed of  $(2 \times 2 \times 1)$  Si lattice and has about

15 Å vacuum region above the substrate. Beyond the distance gas molecules are not affected by the surface. The periodic boundary conditions are applied for the  $x, y$  directions, and the free boundary condition is applied for the  $z$  direction. The velocity Verlet algorithm with a step of 0.25 fs that can describe the fast-chemical reaction was used. The number of surface-covering bonded hydrogen atoms on the Si substrate were chosen to 0, 9, 18, 27, and 36, which corresponds to the hydrogen coverage  $\theta$  of 0.00, 0.25, 0.50, 0.75, and 1.00, respectively. To mimic the bulk behavior of Si substrate, the one bottom layer was fixed and the other layers were maintained in a constant temperature of 500-1000 K in 100 K intervals using the Nose-Hoover thermostat. The initial position of each chemical species is set at the height of 10 Å above hydrogen atoms on the substrate ( $x$  and  $y$  coordinates are random). The incident velocity of each chemical species is set at 0.00394094, 0.004004278, and 0.004070771 Å/fs for  $\text{SiH}_4$ ,  $\text{SiH}_3$ , and  $\text{SiH}_2$  respectively (corresponding to the most probable speed of 300 K for each chemical species). Each chemical species has only an incident velocity normal to the surface. Our calculation system with chemical species and surface conditions of each hydrogen coverage are shown in Fig. 2 and 3. After the 15 ps NVT simulation from the start of incidence, we judged the adsorption according to the bonding state. The case where Si atom constituting a  $\text{SiH}_x$  forms bonds on the substrate (i.e. Si-Si bond) until the end of simulations is defined as the adsorption. 2000 times simulations are performed for each condition and then, an adsorption probability is calculated. In general, the more we calculate, the

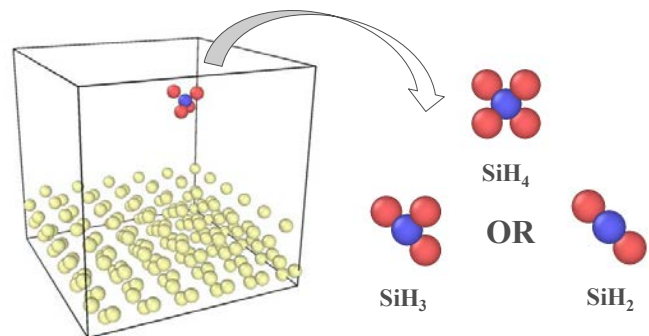


Fig. 2. Calculation system with chemical species.

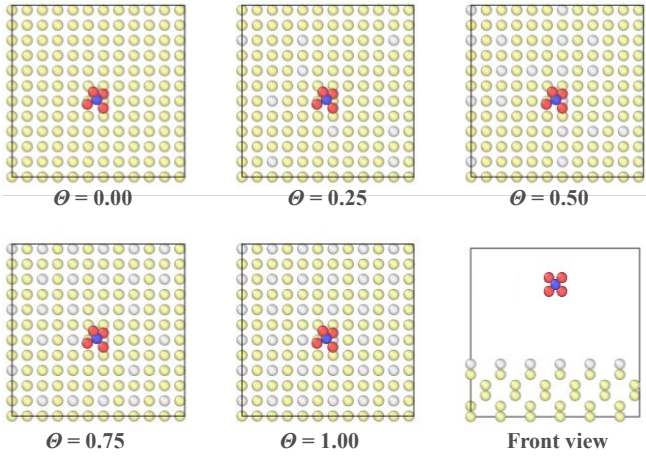


Fig. 3. Surface conditions of each hydrogen coverage ( $\text{Si}_{\text{substrate}}$  : yellow,  $\text{H}_{\text{adsorption}}$  : white,  $\text{Si}_{\text{precursor}}$  : blue, and  $\text{H}_{\text{precursor}}$  : red).

more accurate results will be obtained. However, long time and many times simulation lead to high costs. We increased the number of calculations by 1 ps and determined the calculation conditions so that the change in adsorption probability converges within  $\pm 5.00\%$ .

### III. RESULTS AND DISCUSSION

#### A. Substrate Temperature

Fig. 4 (a), (b) shows the result of the substrate temperature dependence on the adsorption probability when the hydrogen coverage = 0.00 and 0.25, respectively. The adsorption probabilities of  $\text{SiH}_2$  and  $\text{SiH}_3$  are almost constant regardless of the substrate temperature. This trend is consistent with the experimental values of the surface reaction probability  $\beta$  obtained from Time-resolved cavity ringdown spectroscopy ( $\tau$ -CRDS) [16]. In addition, the values at the hydrogen coverage of 1.0 agree well with the previously reported experimental values (0.3 for  $\text{SiH}_3$  and 0.6 for  $\text{SiH}_2$ ) [16]. For  $\text{SiH}_4$ , it tends to decrease as the substrate temperature increases. These results suggest that an increase in substrate temperature has the effect of preventing adaptation to the incident precursor. It is related to the fact that the thermal accommodation coefficient in kinetics theory of gases decreases with the increase in wall temperature [17]. However, the degree of influence differs depending on the chemical species.  $\text{SiH}_2$  and  $\text{SiH}_3$  which have relatively strong reactivity are less affected by the decrease in adsorption probability as the substrate temperature increases.  $\text{SiH}_4$  is strongly affected because it is a relatively stable chemical species compared with  $\text{SiH}_2$  and  $\text{SiH}_3$ .

#### B. Hydrogen Coverage

In Fig. 5 (a), (b) show the result of the hydrogen coverage dependence on the adsorption probability when the substrate temperature = 500 K and 1000 K. The adsorption probabilities decreased with increasing the hydrogen coverage. These results indicate that the hydrogen coverage inhibits the reactivity. It is considered that the adsorption probability decreases with the increase of the hydrogen coverage because the dangling bond is occupied by the surface-covering bonded hydrogen atom.

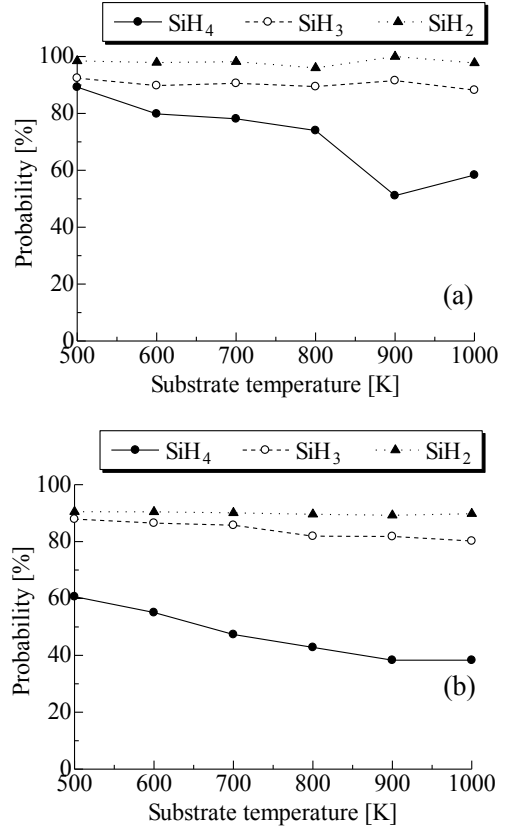


Fig. 4. Substrate temperature dependence of the adsorption probability. (a) Hydrogen coverage = 0.00 and (b) Hydrogen coverage = 0.25

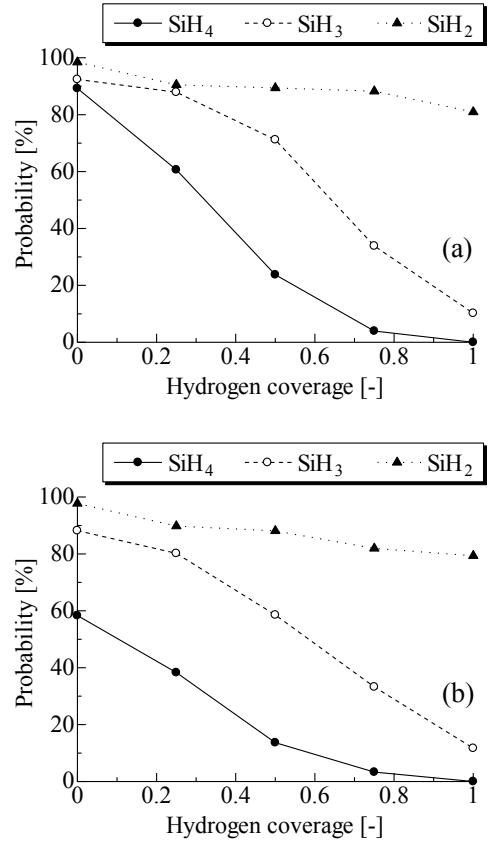


Fig. 5. Hydrogen coverage dependence of the adsorption probability. (a) Substrate temperature = 500K and (b) Substrate temperature = 1000K

#### IV. CONCLUSIONS

An influence of (a) substrate temperatures, (b) hydrogen coverage on the adsorption probability are investigated by using ReaxFF MD simulations.

We found that (a) the adsorption probability is almost constant for SiH<sub>2</sub> and SiH<sub>3</sub>, but decrease with increase in the substrate temperature for SiH<sub>4</sub>, (b) it decreases with the increase in hydrogen coverage. It is well known that the deposition rate generally increases as the substrate temperature increases. However, our results show that increasing the substrate temperature leads to a decrease in reactivity depending on the chemical species. We think that it is related to the thermal accommodation coefficient decreases with the increase in wall temperature. From these results, it is suggested the reason why the reactivity increases with increasing the substrate temperature is that the surface-covering bonded hydrogen atoms are eliminated on the substrate.

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