

# 5-6 Reactive Force-Field Molecular Dynamics Study of the Silicon-Germanium Deposition Processes by Plasma Enhanced Chemical Vapor Deposition

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**Abstract**— In order to form a SiGe thin film by chemical vapor deposition (CVD) with a suitable quality for advanced devices, the relationships between materials/process and structure/composition are needed to be clarified at the atomic level. We simulated SiGe CVD by using reactive force-field (ReaxFF) molecular dynamics simulations, especially on binary systems of SiH<sub>x</sub> + GeH<sub>x</sub>, and derived the influence of the substrate temperature and these ratios of gaseous species on the crystallinity and compositions in the thin films. The crystallinity increases as the substrate temperature increases, and the lowest crystallinity is obtained at the ratios of gaseous species 0.5 and 0.7 for the SiH<sub>3</sub> and SiH<sub>2</sub>, respectively. As the substrate temperature increases, the hydrogen content decreases while Si and Ge content tend to increase. These trends can be seen in relevant studies. Through this simulation we successfully observe that the reactivity of gaseous species greatly affects the crystallinity and compositions in the thin films.

**Keywords**— Chemical Vapor Deposition, Reactive Force-Field Molecular Dynamics Simulation, Silicon-Germanium, Thin Film Deposition

## I. INTRODUCTION

In the field of semiconductor manufacturing, chemical vapor deposition (CVD) and atomic layer deposition (ALD) are known as one of the common and powerful methods to deposit a high-quality thin film. In order to deposit promising thin films using CVD/ALD methods, the materials/process, structure/composition, and properties should be simultaneously optimized. For several decades, advances in semiconductor manufacturing have been increasing the number of materials and processes used for advanced device productions. As a result, an optimal combination should be selected from enormous number of options. This is hard issue and lead to increase the cost and development periods for device productions in the semiconductor manufacturing.

A new materials development tool called as “Materials integration” have appeared to deal with the hard issue. Materials integration aims to support the material development from an engineering viewpoint by combining all science and technology as shown in Fig. 1. In point of fact, some inorganic materials such as battery components have been successfully discovered for several years. Materials integration has also shown promising results in the semiconductor manufacturing. Chopra *et al.* developed a

software tool for creating plasma etch recipes based on physical models and Bayesian inference [1] and applied it to prediction of experimental results [2]. They showed that the etching rate of SiO<sub>2</sub> with CF<sub>4</sub>/Ar gases could be predicted. Suzuki *et al.* adopted machine learning approaches to optimize the plasma enhanced ALD process such as the uniformity [3]. They succeeded in achieving the target values and even outperforming the knowledgeable engineers. Chopra *et al.* and Suzuki *et al.* simply optimized only the process. The researches by Tanaka *et al.* are outstandingly noticeable from the viewpoint of simultaneous optimizing (co-optimization) materials and their processes [4]. They developed a predictive method to co-optimize by combining Bayesian optimization with data extracted from scientific papers, experimental data, and material databases. However, unfortunately, the results based on predictive model could not represent experimental results well.

Two approaches typically are known to improve the accuracy of materials integration; data-driven approach and physics-driven approach. The data-driven approach is based on correlations of material performance and structure extracted from systematically accumulated data. The physics-driven approach is based on the establishment of principles through elucidating controlling factors for material properties at each scale. Both approaches are necessary for all material development regardless of semiconductor manufacturing, and we selected latter. In order to proceed with the physics-driven

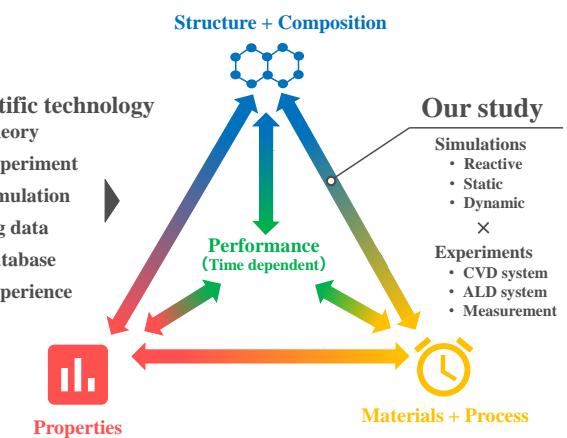


Fig. 1. A schematic diagram of Materials integration and our study position.

approach, the typical strategy is classifications into multi scale as shown in Fig. 2. At each scales, both physical dynamics and chemical reaction during CVD/ALD processes should be treated accurately. Reactive force-field (ReaxFF) MD simulations that is located between density functional theory (DFT), quantum mechanics (QM) calculations and empirical force-field (EFF) MD simulations can treat physical dynamics and chemical reactions [5].

Our final objective is to clarify the relationship between materials/process and structure/composition in thin films at the atomic level on CVD/ALD processes (see Fig. 1). As an example, we focused on a silicon-germanium (SiGe) thin film deposited by PECVD using SiH<sub>4</sub> and GeH<sub>4</sub>, and H<sub>2</sub>. The SiGe thin films, such as hydrogenated amorphous SiGe (a-SiGe:H) and hydrogenated microcrystalline SiGe ( $\mu$ -c-SiGe:H), are known as a potential material for thin film solar cells [6], micro-electro-mechanical systems (MEMS) [7], and biomedical applications [8]. In the experiment, flow rates of SiH<sub>4</sub> and GeH<sub>4</sub> were changed to control the composition of Si and Ge in the thin film. At that time, various gaseous species that have a different reactivity are formed in the plasma. The different reactivity affects the structure/composition of the thin film, but the influence is not clear enough. To achieve a specific ratios of gaseous species experimentally is not easy, however this is an important aspect to optimize the deposition process. The SiH<sub>3</sub>, SiH<sub>2</sub>, GeH<sub>3</sub>, and GeH<sub>2</sub> are suggested that they have a dominant effect on thin film deposition [9]. In this paper, we considered binary systems as shown in Fig. 3 and analyzed the influence of the substrate temperature and these ratios of gaseous species on the crystallinity and compositions in the thin films at the atomic level by ReaxFF MD simulations.

## II. METHODS

### A. Simulation details

ReaxFF MD simulations were performed to simulate the SiGe deposition processes with large-scale atomic/molecular massively parallel simulator (LAMMPS) [10]. An existing parameter set [11] was modified to match the dissociation energies in gaseous species because bond formation and breaking are particularly important in this study. The substrate was Si (100)-(2×1), and the size of the simulation box was 30.72 Å × 26.88 Å × 45.00 Å. A periodic boundary condition was applied in the *x* and *y* directions, and a fixed boundary condition was applied in the *z* direction. The first bottom layer of the substrate was fixed, and second and third layers were controlled constantly at desired temperature by the Berendsen

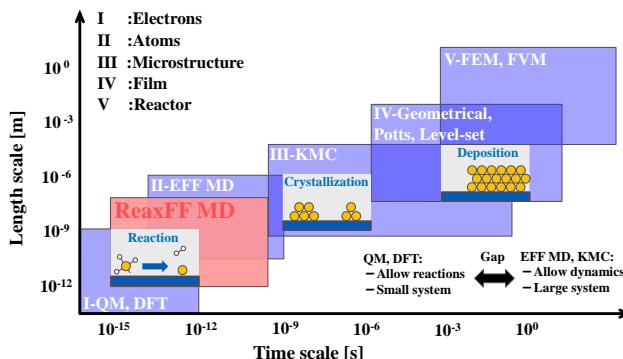


Fig. 2. Multiscale approach in CVD/ALD processes based on the physics driven approaches.

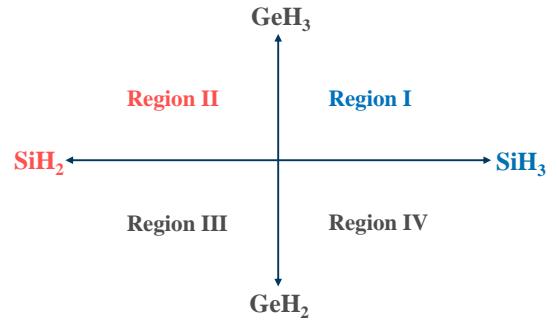


Fig. 3. A binary system of gaseous species ratios that dominates the deposition for SiGe thin film. Region I and II are described in this paper.

thermostat. The temperature was not controlled on the fourth and subsequent layers to prevent direct influences of changing the velocity of atom due to the temperature control on the surface reaction. The range of the substrate temperature was set at 800 K–1500 K. 2000 gaseous molecules with the velocity corresponding to 1300 K in the *z* direction were impinged one by one onto the substrate surface every 7.5 ps. Ratios of SiH<sub>3</sub> and GeH<sub>3</sub> were selected and then, GeH<sub>3</sub> flow rate  $X_{\text{GeH}_3}$  was defined. The change of ratios of SiH<sub>3</sub> and GeH<sub>3</sub> corresponds to deposit films at various germanium contents by changing the gaseous composition (SiH<sub>4</sub>, GeH<sub>4</sub> and, H<sub>2</sub>). The initial position of the gaseous species was set at 10 Å from the top of the Si substrate in the *z* direction, and that in the in-plane (*x*-*y*) was randomly set. The initial position of gaseous molecules is changed from the surface with the constant velocity 1–2 Å/ns to prevent the interaction with the deposited atoms at initial condition. The Velocity-Verlet algorithm was used for time integration with a 0.25 fs time step. A pre-thermal annealing for 7.5 ps and a post-thermal annealing for 60 ps were performed before and after the deposition to equilibrate the substrate and deposited thin films.

### B. Analysis details

Open visualization tool (OVITO) was used to analyze the structure and compositions in thin films [12]. In the case of SiGe thin films, the structure is mainly cubic diamond. The identify diamond structure algorithm was used to find atoms that is arranged in cubic diamond lattice. Using the algorithm, the local environment of each atom was analyzed up to the second neighbor shell to determine the four local structural type as a cubic diamond, 1st neighbor, 2nd neighbor, and others. These detail definition and algorithms for identifications are described in the reference [13]. As a structure, we evaluated the crystallinity ( $C_d$ ) that was defined like following equation;

$$C_d = (\text{Cubic} + \text{1st neighbor} + \text{2nd neighbor}) / N_{\text{depo}} \quad [1]$$

Where, the cubic diamond, 1st neighbor, and 2nd neighbor represent the number of classified atoms as mentioned above. The atomic content as a composition were calculated for each atom by dividing the number of remained Si/Ge/H atoms by the number of total atoms ( $N_{\text{depo}}$ ) in thin films as follows ( $x$  is H, Si, or Ge atom);

$$x \text{ content} = x \text{ atoms} / N_{\text{depo}} \quad [2]$$

### III. RESULTS AND DISCUSSION

In this paper, only the region I and II in fig. 3 are described (i.e.,  $\text{SiH}_3 + \text{GeH}_3$  or  $\text{SiH}_2 + \text{GeH}_3$ ). Fig. 4 shows the deposited thin films with various ratios of gaseous species  $X_{\text{GeH}_3}$  ( $= \text{GeH}_3 / (\text{SiH}_x + \text{GeH}_3)$ ) and substrate temperatures. Here,  $x$  is 2 or 3. These snapshots were taken from the final configurations.

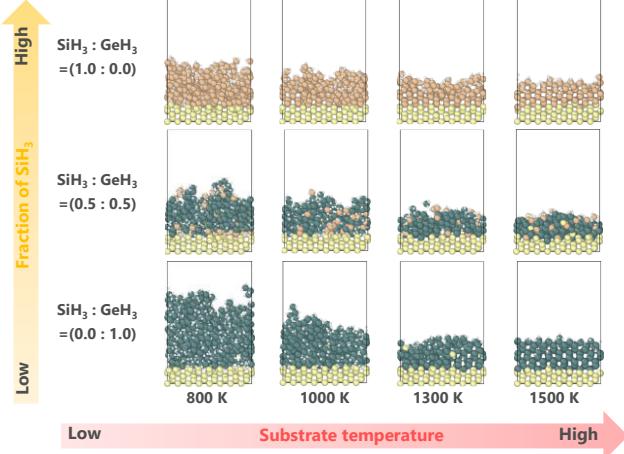


Fig. 4. Snapshots of the deposited thin films with various ratios of  $\text{SiH}_3$  and  $\text{GeH}_3$   $X_{\text{GeH}_3}$  and the substrate temperatures. The white, beige, yellow, and deep green represent added H atom, added Si atom, substrate Si atoms, and added Ge atoms, respectively.

#### A. Crystallinity

Fig. 5 shows the crystallinity as a function of the substrate temperature for ratios of  $\text{SiH}_3$  and  $\text{GeH}_3$   $X_{\text{GeH}_3}$ . The crystallinity  $C_d$  increases as the substrate temperature increases. The  $\text{SiH}_3$  and  $\text{GeH}_3$  more overcome the energy barrier from local minimum to global minimum (on lattice) with increasing the substrate temperature. As a result, higher crystal structure (more compact thin film) are obtained at high substrate temperature. These tendencies are related to experimental study for the deposition of a-SiGe:H [17]. Fig. 6 shows the crystallinity as a function of the  $X_{\text{GeH}_3}$  in the case of  $\text{SiH}_2$  and  $\text{SiH}_3$ . The insets represent the atomic configuration. The lowest crystallinity is obtained at the  $X_{\text{GeH}_3}$  0.5 and 0.7 for the  $\text{SiH}_3$  and  $\text{SiH}_2$ , respectively. The crystallinity at the  $X_{\text{GeH}_3}$  1.0 is comparable to pure Si films ( $X_{\text{GeH}_3}$  0.0). This reflect that the uniform ratios of gaseous species are preferable for the highest crystallinity. It may lead

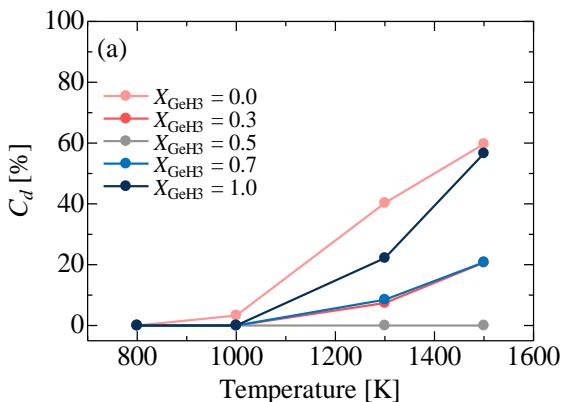


Fig. 5. Crystallinity as a function of the substrate temperature for various ratios of  $\text{SiH}_3$  and  $\text{GeH}_3$   $X_{\text{GeH}_3}$ .

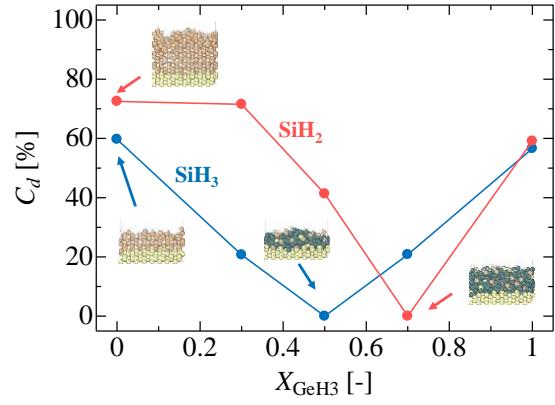


Fig. 6. Crystallinity as a function of the  $X_{\text{GeH}_3}$  when the substrate temperature is 1500 K.

to the less difference of lattice constant in the films (Si: 5.43 Å, Ge: 5.68 Å). The crystallinity is related to the microstructure parameter  $R^*$  as measured with Fourier transform infrared (FTIR) spectroscopy. Please note that the microstructure parameter decreases at void-less films, thus it has opposite meanings with the crystallinity. Our trends can be quantitatively compared with the experimental ones reported in a literature [14].

#### B. Composition

Fig. 7 shows the hydrogen content as a function of the substrate temperature for various ratios of  $\text{SiH}_3$  and  $\text{GeH}_3$   $X_{\text{GeH}_3}$ . The hydrogen content decreases as the substrate temperature increases. While silicon and germanium content tend to increase with increasing substrate temperature (not shown here). The reason is more  $\text{H}_2$  are formed and desorbed from the surface at higher substrate temperature, resulting in an increase in the silicon and germanium content. Fig. 8 shows Si and Ge content as a function of the  $X_{\text{GeH}_3}$ . The increase of Ge content is remarkable with respect to  $X_{\text{GeH}_3}$  in the case of  $\text{SiH}_3$ . In other words, Ge atoms were preferentially incorporated into the film compared with Si atoms. This Ge preferential incorporation from the gas phase into the film is typically observed during the deposition process for SiGe thin films [14]. Please note that the binding energy of Ge-H (2.97 eV/bond) is lower than that of Si-H (3.20 eV/bond) in gaseous species, therefore,  $\text{GeH}_3$  is easier to dissociate than  $\text{SiH}_3$  on the surface during surface diffusions and preferentially incorporated into the film.

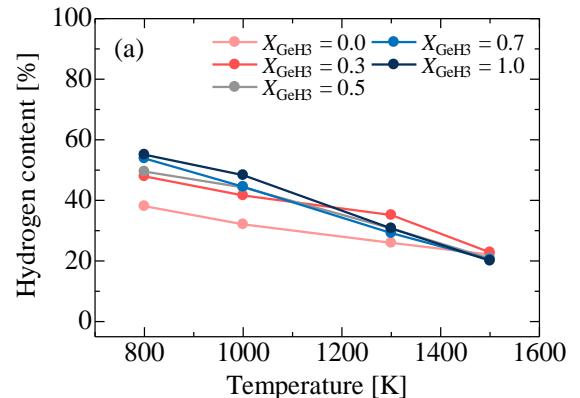


Fig. 7. Hydrogen content as a function of the substrate temperature for various ratios of  $\text{SiH}_3$  and  $\text{GeH}_3$   $X_{\text{GeH}_3}$ .

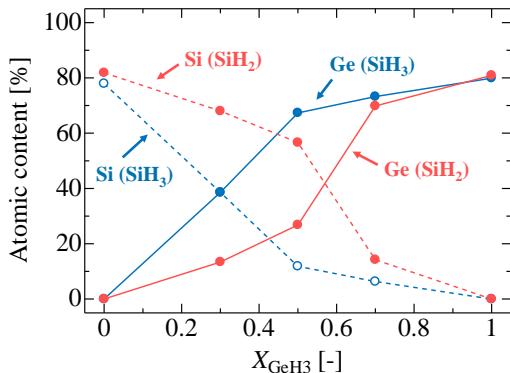


Fig. 8. Si and Ge content as a function of the ratios of  $X_{GeH3}$  when the substrate temperature is 1500 K.

On the other hands, in the case of  $SiH_2$ , the Ge content gradually goes up with respect to  $X_{GeH3}$  comparing to the case of  $SiH_3$ . This gradual increase may be originated from the difference of reactivity between  $SiH_3$  and  $SiH_2$ .  $SiH_2$  can be incorporated into the film without dissociation of Si–H bond. These results suggest that the Ge preferential incorporation from the gas phase into the film is also depend on the ratios of gaseous species in plasmas.

#### IV. CONCLUSIONS

We investigated SiGe thin film deposition with various ratios of  $SiH_3$ ,  $SiH_2$ , and  $GeH_3$  using ReaxFF MD simulations. The crystallinity and atomic contents in the deposited thin films were analyzed as a structure and compositions. The crystallinity  $C_d$  increased as the substrate temperature increases and could be explained by the higher mobility of  $SiH_x$  and  $GeH_x$  on the surface at elevated substrate temperature. The lowest crystallinity was obtained at the ratios of gaseous species  $X_{GeH3}$  0.5 and 0.7 for the  $SiH_3$  and  $SiH_2$ , respectively. The crystallinity at the  $X_{GeH3}$  1.0 was comparable to pure Si films ( $X_{GeH3}$  0.0). This reflect that the uniform ratios of gaseous species are preferable for the highest crystallinity. The hydrogen content decreased as the substrate temperature increases, while silicon and germanium content tended to increase with increasing substrate temperature. The reason is more  $H_2$  molecules were formed and desorbed from the surface at higher substrate temperature, resulting in an increase in silicon and germanium content. In the case of  $SiH_3$ , Ge atoms were preferentially incorporated into the film compared with Si atoms. The reason is originated from lower binding energy of Ge–H (2.97 eV/bond) than Si–H (3.20 eV/bond) in gaseous species. These tendencies in this paper were in good agreement with relevant studies. On the other hands, in the case of  $SiH_2$ , the Ge content gradually went up with respect to the  $X_{GeH3}$  comparing to the  $SiH_3$ . It was originated from the difference of reactivity between  $SiH_3$  and  $SiH_2$ .  $SiH_2$  can be incorporated into the film without dissociation of Si–H bond. These results suggest that the Ge preferential incorporation from the gas phase into the film is also depend on the ratios of gaseous species in plasmas.

Finally, we observed that the substrate temperature and ratios of gaseous species affect the structure/composition of the thin film, obviously. Our simulation is promising to optimize the deposition process for high-quality thin films.

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