Reactive Force-Field Molecular Dynamics Study of the Effect of Gaseous Species on Silicon-Germanium Alloy Growth by PECVD Techniques

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

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

3rd Masaru Zaitsu
Rsearch & development
Japan advanced chemicals ltd.
Sagamihara, Japan
masaru.zaitsu
@japanadvancedchemicals.com

4th Shigeo Yasuhara
Rsearch & development
Japan advanced chemicals ltd.
Sagamihara, Japan
shigeo.yasuhara
@japanadvancedchemicals.com

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

Abstract—**We simulated the growth of SiGe alloys by using reactive force-field (ReaxFF) molecular dynamics simulations in binary systems of SiH_x and GeH_x and identify the effect of gaseous species on the compositions and crystallinity in alloys. The compositions in alloys could be estimated if compositions of gaseous species can be identified because of the observation of the linear increase in Ge content in alloys. Supplying GeH_2 decreased the crystallinity compared to GeH_3. The mechanism is described by the mobility and reactivity of the gaseous species and surface structures. These results suggest that the mobility and reactivity of both surface and gaseous species are essential in identifying the effect of gaseous species on composition and crystallinity.**

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

I. INTRODUCTION

In the field of semiconductors, the growth of compound semiconductors continues to be an important topic in materials development. Chemical vapor deposition (CVD) and atomic layer deposition (ALD) are standard and powerful methods to grow a high-quality thin film. Establishing the relation between material/process and composition/structure is essential to growing good thin films using CVD/ALD methods as shown in Fig.1. The complex reaction dynamics in the growth process should be clarified for this goal.

Numerical simulations have been widely used, as shown in Fig. 2 since experimental observation of such complex reaction dynamics is difficult even with state-of-the-art equipments. In particular, multi-scale simulations, including kinetic Monte Carlo (KMC) methods, are currently being used successfully[1]–[3]. The simulation can describe the time evolution of lattice-based thin film growth by ignoring the thermal motion of atoms and introducing a stochastic surface reaction model. The simulation has the advantage of predicting useful outputs, such as the thickness of the grown thin film, the distribution of byproducts, and the chemical composition and surface morphology of the thin film can be compared with experimental results. On the other hand, the limited reactions under some geometric configurations have been taking into modeling due to the poor availability of reliable surface data [4]. In general, current multi-scale simulations, including the KMC method, take only the geometric configurations with the lowest activation energy at the transition state into the model stochastically.

However, in the natural growth process, the atoms which consist of the surface are thermally moving, and reaction dynamics occur in all geometric configurations. Therefore, we believe that the description of the thermal motion of atoms and the treatment of processes involving reaction dynamics in all geometrical configurations are the key to the future development of numerical simulations. Our goal is to clarify the reaction dynamics in thin film growth using numerical simulations to establish the relation between material/process and composition/structure in CVD and ALD techniques.

In this study, silicon-germanium (SiGe) alloy growth was selected as a relatively simple process. SiGe alloys, such as hydrogenated amorphous SiGe (a-SiGe:H) and hydrogenated microcrystalline SiGe (μc-SiGe:H), have been known as a potential material for thin-film solar cells [5], micro-electro-mechanical systems (MEMS) [6], and biomedical applications [7]. Plasma enhanced chemical vapor deposition (PECVD) is a common technique to grow SiGe alloys. Even in the SiGe alloy growth, understanding the relationship between process parameters and composition and structure is essential for improving device performance. In SiGe MOSFETs, the SiGe alloy is incorporated in the channel and used to give improved device property [8]. However, the excess of Ge content in the
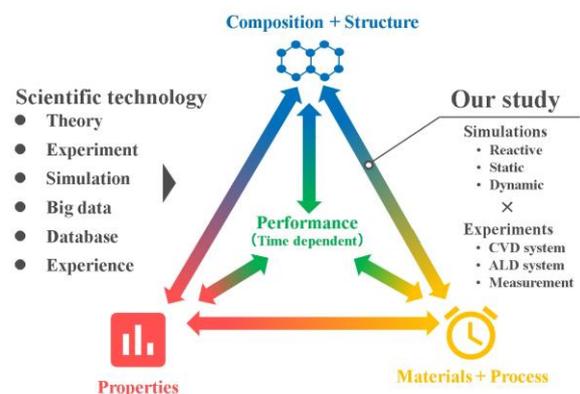

Fig. 1. A schematic diagram of Materials integration and our study position.

SiGe alloy has deteriorated the device characteristics because of defects caused by the lattice mismatch between the Si (0.543 nm) and Ge (0.566 nm) [9]. This is an excellent example of how the gaseous composition as a process parameter affects composition and structure in alloys.

The fact that gaseous species affect composition and structure is not surprising, given that thin-film growth results from many collisions of abundant gaseous species onto the surface. Specifically, neutrals (SiH_4, GeH_4, H_2), radicals (such as SiH_3, GeH_3, SiH_2, GeH_2, H), ions (such as SiH_2^+, GeH_3^+, H^+) exists in the gas phase. After that, they collide with the surface, and a part of them become the alloys. SiH_3, SiH_2, SiH, GeH_3, and GeH_2 are regarded as dominant gaseous species when the SiGe alloys are grown [10]. However, the effects of gaseous composition on composition and structure in alloys have not been understood enough because of the difficulty of generating the specific gaseous species. The aspect will also be helpful for other potential materials such as SiC, GaN, InP, and SiGeC. This study aims to identify the effects of each gaseous species on composition and crystallinity in SiGe alloys and understand the mechanism by simulations.

II. METHODS

A. Simulation details

Reactive Force-Field molecular dynamics (ReaxFF MD) simulation is a powerful technique for observing thin film growth and understanding the growth mechanism. The simulations were performed to grow SiGe alloys with a large-scale atomic/molecular massively parallel simulator (LAMMPS) [11]. Although the accessible spatial and time scale is limited compared to the kinetic monte carlo (KMC) model (see Fig. 2), ReaxFF MD can evaluate and explicitly compositions and crystallinity because the atomic positions are not limited to lattice positions. Thus, this approach has potential progress in multi-scale modeling, which is expected to integrate from the reactor scale to the atomic scale comprehensively. An existing parameter set [12] was modified to match the dissociation energies in gaseous species because bond formation and breaking are critical 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 the second and third layers were controlled constantly at the desired temperature by the Berendsen thermostat. The temperature was not controlled on the fourth and subsequent layers to minimize di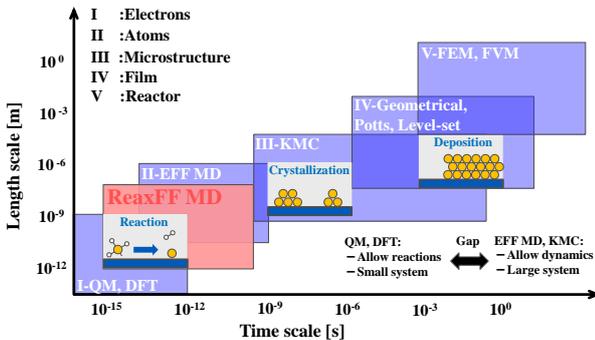rect influences of changing the velocity of substrate atoms on the surface reactions. The substrate temperature was set at 1500 K to accelerate the reactions for a short period.

We considered a binary system, as shown in Fig. 3. The SiGe alloys were mainly grown by SiH_3 or SiH_2. As Ge gaseous species, GeH_3 or GeH_2 were replaced for Si gaseous species up to 20% fractions (i.e., Ge gaseous species ratio). All gaseous species with the velocity corresponding to 1300 K in the z direction impinged one by one onto the substrate surface every 5.5 ps. An initial position of gaseous species was set at 10 Å from the top of Si atoms in the z direction, and that in the in-plane (x-y) was randomly chosen. Then, the insertion volume of gaseous molecules moved up with a constant velocity of 1–2 Å/ns from the surface. The movement enables to prevent the interaction of molecules at an initial position with the grown surface. The Velocity-Verlet algorithm was used for time integration with a 0.25 fs time step. The SiGe alloys were grown until the total number of Si and Ge atoms was 400 (± 5%). Pre-thermal annealing for 7.5 ps and post-thermal annealing for 60 ps were performed before and after the growth to equilibrate the substrate and grown SiGe alloys. Three times of calculations were performed for each system to evaluate the results accurately.

B. Analysis details

The open visualization tool (OVITO) [13] was used to analyze the composition and crystallinity in SiGe alloys. The structure of the SiGe alloys is mainly cubic diamond. The identify diamond structure algorithm was used to find atoms that exist on a cubic diamond lattice. The local environment of each atom was analyzed up to the second neighbor shell to determine the four local structural types as a cubic diamond, 1st neighbor, 2nd neighbor, and others. As a structure, we evaluated the crystallinity (C_d) that was defined as the following equation;

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

Where the cubic, 1st neighbor, and 2nd neighbor represent the number of classified atoms as mentioned above. More detailed definitions and algorithms for identifications are described in the reference [14]. The composition was obtained by dividing the number of specified atoms by the total number of Si and Ge atoms in alloys as follows;

$$x \text{ content} = x \text{ atoms} / (\text{Si} + \text{Ge atoms}) \qquad (2)$$
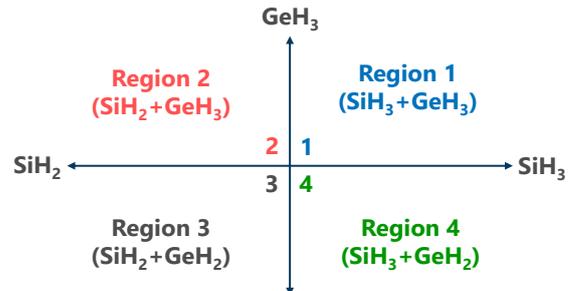

Fig. 2. Simulation methods for the CVD/ALD processes at each length and time scale.

Fig. 3. A binary system of gaseous species that dominates the growth for SiGe alloys.

III. RESULTS

A. Composition

Fig. 4 shows the Ge content in alloys as a function of the Ge gaseous species ratio. A linear increase in Ge content in alloys was observed in all regions. Our results suggest that the compositions in alloys could be estimated if gaseous compositions can be identified. However, please note that other gaseous species should be considered for optimizing whole PECVD processes. One remarkable result is that the preferential incorporation of Ge atoms from GeH_2 is much higher than GeH_3. For instance, typical Ge content in SiGe alloys in efficient thermoelectric applications is up to 30% [15]. Compared to regions 1 with 4, GeH_2 can achieve the same Ge content in alloys with a supply of approximately one-third of GeH_3. GeH_2 has multiple pathways to chemisorption on the surface, forming the Si-Si, Si-Ge, and Ge-Ge bond. GeH_2 having high reactivity can be chemisorbed on the surface when GeH_2 collides with a bare Si or Ge atom and even a terminated H atom by taking into the gaseous species side. Please note that GeH_2 typically forms a bond with the Si or Ge atom under the collided H atom. However, GeH_3 having high mobility desorbed as GeH_4 by H abstraction or just bounded as GeH_3. Besides, GeH_3 may be desorbed during surface diffusions by receiving energies due to its high mobility even if GeH_3 directly collided with Si or Ge surface atoms. The composition strongly affects both the mobility and reactivity of gaseous species on the growth surface.

B. Crystallinity

Fig. 5 shows the crystallinity as a function of the Ge gaseous species ratio. Here, we will focus on decreasing the crystallinity with an increase of the Ge gaseous species ratio. The most significant decrease in crystallinity was observed in region 4, followed by region 3. There was almost no tendency of decrease in region 2 and 1. This result qualitatively shows that the supply of GeH_2 decreased the crystallinity compared to GeH_3.

Interestingly, the decrease in crystallinity was considerable in region 4. These results mean that the crystallinity of the thin film grown from SiH_3 tends to quickly decrease by supplying GeH_2, but that of the thin film grown by SiH_2 does not decrease. We think the mechanism is also caused by the mobility and reactivity of the gaseous species on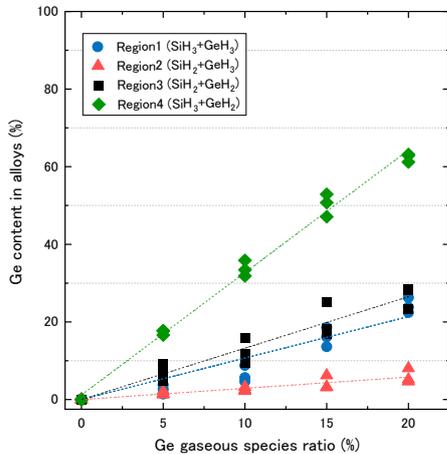 the surface and the surface structure. During thin film growth from SiH_2, the typical hydrogen loss paths from the film, such as surface hydrogen abstraction or desorption of interstitial hydrogen after diffusions to the surface, are not active [16]. Hence, hydrogen loss from the film is limited, and the surface exhibits a high H coverage. On the other hand, during thin film growth from SiH_3, the surface exhibits low H coverage because some hydrogen loss paths are active. The hydrogen coverage of the surface tend to determine the stable surface structure [17]. The monohydride structure could be mainly observed on the surface grown by SiH_3, while the dihydride structure observed grown by SiH_2 (see Fig. 6). In other words, the surface grown by SiH_2 means a higher hydrogen coverage and a lower surface reactivity than that of SiH_3. In fact, the hydrogen contents in the alloys in regions 2 and 3 were higher than that in region 1 and 4 (not shown here). Therefore, the crystallinity is quickly decreased by highly reactive Ge gaseous species because the surface reactivity is high, and the networks are dissociated.

In summary, we were able to qualitatively show that the gaseous composition has a significant effect on the composition and structure of the grown thin film. Experiments have difficulty reproducing such specific gaseous species compositions, and multi-scale simulations, including the KMC method, basically cannot evaluate the crystallinity due to the lattice-based thin film growth. The fact that we can quantitatively evaluate crystallinity by reproducing the thermal motion of atoms and treating reaction dynamics shows the originality of our simulation.

IV. CONCLUSIONS

We identified the effects of gaseous species on composition and crystallinity in SiGe alloys and understood mechanisms using ReaxFF MD simulations. For compositions, our results suggest that the compositions in alloys could be estimated if compositions of gaseous species can be identified because of the observation of the linear increase in Ge content in alloys. For structure, we quantitatively showed the supplying the GeH_2 decreased the crystallinity compared to GeH_3. Also, we showed that the thin film grown from SiH_3 tends to quickly decrease by supplying GeH_2, but the thin film grown by SiH_2 does not decrease. The mechanism is described by the mobility and reactivity of the gaseous species and surface structures. Our results suggest that considerations of the mobility and reactivity of gaseous species on the surface

Fig. 4 The Ge content in alloys as a function of the Ge content in gas phase. The dotted line is a guide to eye.
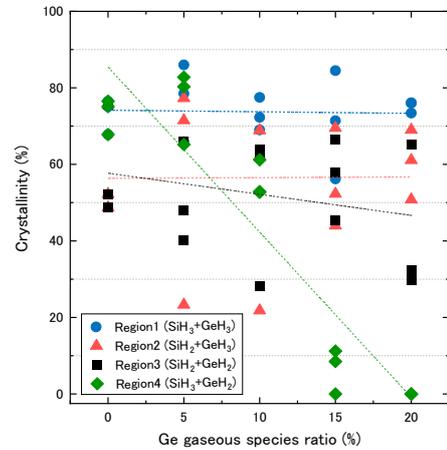

Fig. 5 The crystallinity as a function of the Ge content in gas phase. The dotted line is a guide to eye.
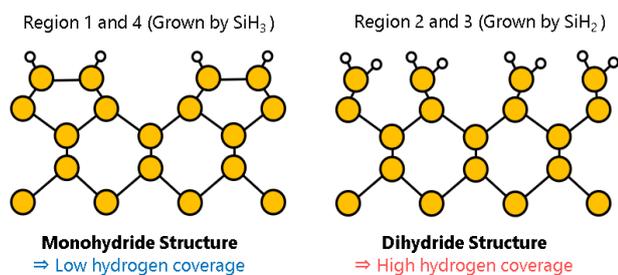
Fig. 6 Hydrogen structures on the surface grown by SiH_3 and SiH_2.

are essential in understanding the effect of gaseous species on film qualities. Lastly, clarifying the reaction dynamics in thin-film growth using numerical simulations will help to establish the relation between material/process and composition/structure in CVD/ALD techniques. Our simulation will be adapted for SiC, InP, GaAs, and other potential materials in the future.

ACKNOWLEDGMENT

REFERENCES

[1]   V. Günther, F. Mauß, C. Klauer, and C. Schlawitschek, "Kinetic Monte Carlo simulation of the epitaxial growth of Si(100)," *Phys. Status Solidi Curr. Top. Solid State Phys.*, vol. 9, no. 10–11, pp. 1955–1962, 2012, doi: 10.1002/pssc.201200340.

[2]   M. Crose, W. Zhang, A. Tran, and P. D. Christofides, "Run-to-run control of PECVD systems: Application to a multiscale three-dimensional CFD model of silicon thin film deposition," *AIChE J.*, vol. 65, no. 7, 2019, doi: 10.1002/aic.16400.

[3]   O. Babahani, S. Hadjadj, F. Khelfaoui, H. O. Kebaili, and S. Lemkeddem, "Monte Carlo Simulation of Chemical Reactions in Plasma Enhanced Chemical Vapor Deposition: from Microscopic View to Macroscopic Results," *Silicon*, vol. 11, no. 3, pp. 1267–1274, 2019, doi: 10.1007/s12633-018-9916-y.

[4]   D. Marinov, C. Teixeira, and V. Guerra, "Deterministic and Monte Carlo methods for simulation of plasma-surface interactions," *Plasma Process. Polym.*, vol. 14, no. 1–2, pp. 1–18, 2017, doi: 10.1002/ppap.201600175.

[5]   Z. Yu *et al.*, "Improved power conversion efficiency in radial junction thin film solar cells based on amorphous silicon germanium alloys," *J. Alloys Compd.*, vol. 803, no. 30, pp. 260–264, 2019, doi: 10.1016/j.jallcom.2019.06.276.

[6]   Q. Wang and H. Vogt, "With PECVD Deposited Poly-SiGe and Poly-Ge Forming Contacts Between MEMS and Electronics," *J.*

[7]   F. L. Huerta *et al.*, "Biocompatibility and surface properties of hydrogenated amorphous silicon-germanium thin films prepared by LF-PECVD," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 628, no. 1, p. 012003, 2019, doi: 10.1088/1757-899X/628/1/012003.

[8]   Y. M. Haddara, P. Ashburn, and D. M. Bagnall, "Silicon-Germanium: Properties, Growth and Applications," in *Springer Handbook of Electronic and Photonic Materials.*, 2017, pp. 523–541.

[9]   C. Ismael, K. Andrey, M. Saraí, Zarate-Galvez Hiram E., M. Svetlana, and K. Yuri, "Study of Si and Ge Atoms Termination Using H-Dilution in SiGe : H Alloys Deposited by Radio Frequency (13.56 MHz) Plasma Discharge at Low Temperature," *Materials (Basel).*, vol. 13, no. 5, p. 1045, 2020.

[10]   L. Zhao, R. Hunsperger, and S. Hegedus, "Modeling and experimental study of SiH4/GeH4/H2 gas discharge for hydrogenated silicon germanium deposition by RF PECVD," in *Materials Research Society Symposium Proceedings*, 2012, vol. 1426, pp. 403–408, doi: 10.1557/opl.2012.841.

[11]   S. Plimpton, "Fast Parallel Algorithms for Short-Range Molecular Dynamics," *J. Comput. Phys.*, vol. 117, pp. 1–19, 1995, doi: 10.1006/jcph.1995.1039.

[12]   G. Psofogiannakis and A. C. T. Van Duin, "Development of a ReaxFF reactive force field for Si/Ge/H systems and application to atomic hydrogen bombardment of Si, Ge, and SiGe (100) surfaces," *Surf. Sci.*, vol. 646, pp. 253–260, 2016, doi: 10.1016/j.susc.2015.08.019.

[13]   A. Stukowski, "Visualization and analysis of atomistic simulation data with OVITO-the Open Visualization Tool," *Model. Simul. Mater. Sci. Eng.*, vol. 18, no. 1, p. 015012, 2010, doi: 10.1088/0965-0393/18/1/015012.

[14]   E. Maras, O. Trushin, A. Stukowski, T. Ala-Nissila, and H. Jónsson, "Global transition path search for dislocation formation in Ge on Si(001)," *Comput. Phys. Commun.*, vol. 205, pp. 13–21, 2016, doi: 10.1016/j.cpc.2016.04.001.

[15]   J. A. Pérez-Taborda, O. Caballero-Calero, and M. Martín-González, "Silicon-Germanium (SiGe) Nanostructures for Thermoelectric Devices: Recent Advances and New Approaches to High Thermoelectric Efficiency," in *New Research on Silicon: Structure, Properties, Technology*, 2017, pp. 183–206.

[16]   S. Sriraman, E. S. Aydil, and D. Maroudas, "Growth and characterization of hydrogenated amorphous silicon thin films from SiH2 radical precursor: Atomic-scale analysis," *J. Appl. Phys.*, vol. 95, no. 4, pp. 1792–1805, 2004, doi: 10.1063/1.1636512.

[17]   A. . Fallis, "Structure of Si(100)H: Dependence on the H chemical potential," *J. Chem. Inf. Model.*, vol. 44, no. 3, pp. 1419–1422, 1991, doi: 10.1017/CBO9781107415324.004.