Molecular-dynamics simulations of solid-phase epitaxy of Si: Growth mechanisms

T. Motooka and K. Nisihira
Department of Materials Science and Engineering, Kyushu University, Hakozaki, Fukuoka 812-8581, Japan

S. Munetoh, K. Moriguchi, and A. Shintani
Advanced Technology Research Laboratories, Sumitomo Metal Industries, Ltd., Hyougo 660, Japan
(Received 1 October 1999)

Crystal-growth processes of Si during solid phase epitaxy (SPE) in the [001] direction have been investigated based on molecular-dynamics (MD) simulations using the Tersoff potential. A tetragonal cell including an amorphous/crystalline (a/c) Si interface composed of up to 4096 atoms was taken as the starting system. From the Arrhenius plot of the growth rates obtained by MD simulations, we have found that the activation energy of SPE at lower temperatures is in good agreement with the experimental value (≈2.7 eV), while it becomes lower at higher temperatures. This can be attributed to the difference in the a/c interface structure and SPE mechanism. In the low-temperature region, the a/c interface is essentially (001) and the rate-limiting step is two-dimensional nucleation on the (001) a/c interface. On the other hand, the a/c interface is predominantly composed of {111} facets in the high-temperature region and the rate-limiting step is presumably a diffusion process of Si to be trapped at the kink sites associated with these facets.

I. INTRODUCTION

Solid phase epitaxy (SPE) of Si is one of the basic processes in Si microelectronics fabrication technologies. Various experimental works were carried out to determine the growth rate of thermal SPE by using furnace and laser annealing, and the activation energy was found to be ≈2.7 eV.[1] Recently, extensive investigations have been performed on ion-beam-induced epitaxial crystallization (IBIEC) where ion-beam-induced defects play an important role for crystallization, and the activation energy is found to be varied from 0.18 to 0.40 eV depending on ion mass and temperature.[2] Based on these results, it is generally believed that crystallization occurs at amorphous/crystal (a/c) Si interfaces in both thermal SPE and IBIEC processes. However, the atomistic mechanism of crystallization at the a/c interface is not well understood.

In this paper, we have investigated crystal-growth processes in SPE based on molecular-dynamics (MD) simulations by employing the Tersoff interatomic potential of Si.[3] Although the Tersoff potential gives rise to high melting temperature 2547 K,[4] it can well reproduce structural properties of *a*-Si (Ref. 5) and liquid Si,[6] and thus it is considered to be useful to describe crystallization processes of Si. Atomic movements at the a/c interfaces were visualized and the activation energy was determined, and the atomistic mechanism of crystallization at the a/c interface was proposed.

II. METHOD

MD simulations have been performed using a MD cell including an a/c interface as illustrated in Fig. 1. The typical MD cell size is $21.7\times21.7\times43.4\,\text{Å}^3$ (tetragonal prism) and the number of Si atoms, 1024, was determined by using the crystalline Si density, 2.33 g/cm^3. Atomic movements were determined by solving Langevin equations

$$m\ddot{\mathbf{r}}_i(t)=\mathbf{F}_i(t)-m\gamma\dot{\mathbf{r}}_i(t)+\mathbf{R}_i(t),$$

where m is the atomic mass, $\mathbf{r}_i(t)$ the position vector of the ith atom at time t, $\mathbf{F}_i(t)$ the interatomic force calculated by the Tersoff potential, and γ and $\mathbf{R}_i(t)$ are the friction constant and random force to control temperature, respectively. We employed the scheme developed by van Gunsteren and Berendsen for numerical integrations of the Langevin equation.[7] The time step for the integration was set at 0.001 ps and the friction constant γ was chosen to be 5 (ps)$^{-1}$.

The initial a/c interface was prepared by attaching eight *c*-Si(001) layers to a block of bulk *a*-Si obtained by rapid quenching of liquid Si.[5] The MD cell was preannealed at 1000 K for 20 ps and then heated at various temperatures between 1450 and 2000 K for crystallization at the a/c interface. In order to examine atomic motions during SPE growth, atomic coordinates contained in the central region including the diagonal (110) plane of the tetragonal cell with a thickness of 10 Å were projected on the (110) plane. In order to determine the SPE rate, we have examined the cell size dependence of the growth rate at 2000 K using a larger MD cell with a size of $43.4\times43.4\times43.4\,\text{Å}^3$ made by combining the four small MD cells described above. Since no appreciable change was found in the growth rates between the small and large MD cells including 1024 and 4096 atoms, respectively, we show the simulation results obtained by using the small MD cell.

III. RESULTS AND DISCUSSIONS

Figure 2 shows an example of the simulated SPE processes annealed at 1800 K. These simulations indicated that the a/c interface was rough for the temperatures larger than 1600 K, while it was rather flat for the temperatures less than 1550 K. The a/c interface position was defined as a middle in the rough interface. Figures 3(a) and 3(b) show the a/c inter-

 ©2000 The American Physical Society

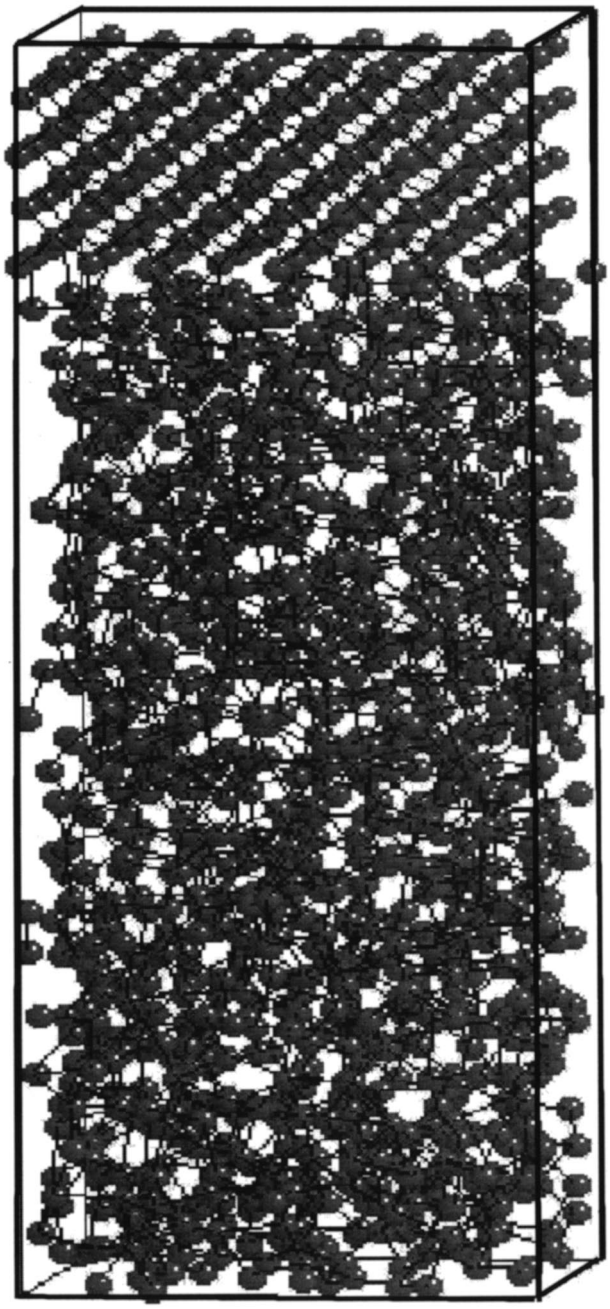

FIG. 1. MD cell with an a/c interface.

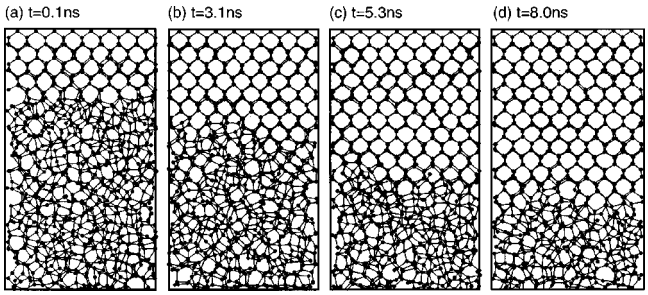

FIG. 2. Typical MD simulation results of SPE growth. The MD cell is annealed at 1800 K and changes in the atomic coordinates annealed after (a) 0.1 ns, (b) 3.1 ns, (c) 5.3 ns, and (d) 8.0 ns are shown.

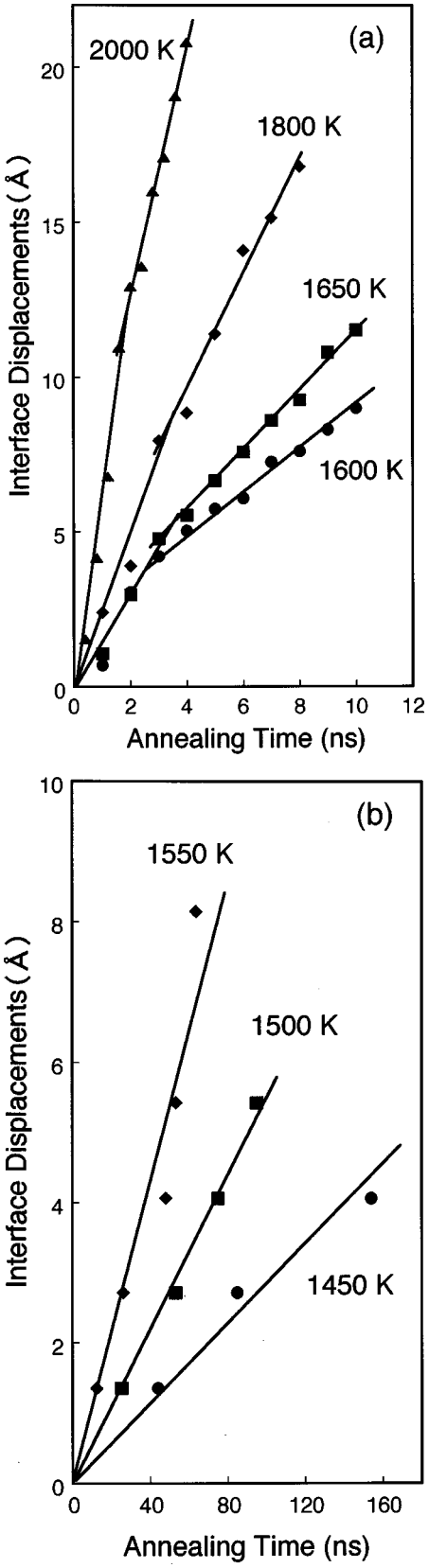

FIG. 3. Interface displacements as a function of annealing time: (a) higher and (b) lower temperature regions.

face displacements in the [001] direction as a function of annealing time in the higher and lower temperature regions, respectively. The initial growth rates were generally larger in the high-temperature region [see Fig. 3(a)] probably due to

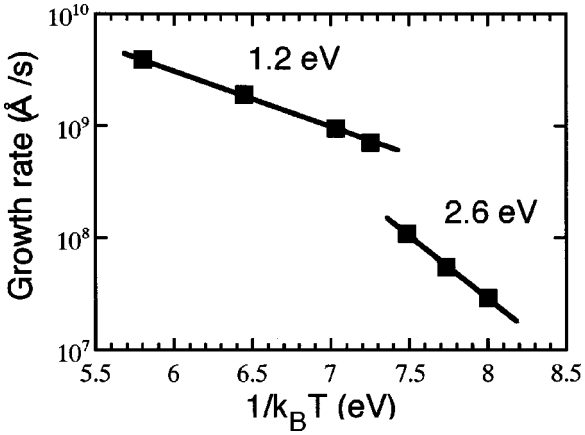

FIG. 4. Arrhenius plot of the [001] SPE growth rates.

inadequate equilibration of the a/c interfaces, while the growth rate becomes very low and constant-speed layer-by-layer growth is observed in the low-temperature region [see Fig. 3(b)]. Thus, in the high-temperature region, the growth rates were determined by using the linear parts following those of the initial growth. Figure 4 shows the Arrehnius plot of these SPE growth rates. There exist two activation energies: 2.6 eV determined in the lower temperature region and 1.2 eV in the higher temperature region. The former is in good agreement with the experimental value, ≈2.7 eV obtained in thermal SPE, while no experimental value corresponds to the latter and some interpretation of this value will be given below.

Figure 5 shows typical snapshots of the SPE processes annealed at 1450 and 2000 K. These snapshots clearly suggest that layer-by-layer crystallization occurs along the (001) and (111) planes at 1450 and 2000 K, respectively. From these MD simulation results, we can envisage the SPE growth mechanisms in the lower and higher temperature regions as shown schematically in Fig. 6. In the lower temperature region, the a/c interface is essentially (001) with a

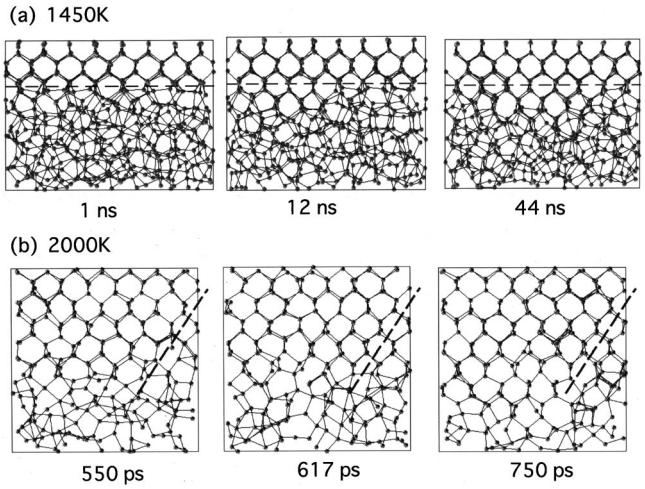

FIG. 5. Typical snapshots of atomic movements during SPE growth at (a) 1450 and (b) 2000 K obtained by MD simulations. The dashed lines indicate the a/c interfaces where crystallization can be observed.

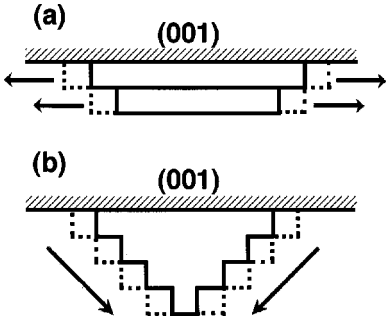

FIG. 6. Schematic diagram of the rate-limiting steps for (a) lower and (b) higher temperature SPE crystallization in the [001] direction.

small portion of (111) edges, and the rate-limiting step of crystallization can be considered to be two-dimensional nucleation on the (001) a/c interface which gives rise to the activation energy, 2.6 eV. This is consistent with the experimental fact that the SPE rate in the [111] direction is much slower,[8] since two-dimensional nucleation would be more difficult on the (111) interface than on the (001).

On the other hand, in the higher temperature region, the a/c interface is predominantly composed of [111] facets and the rate-limiting step is a trapping process of Si at the kink sites associated with these facets. Thus, the activation energy 1.2 eV may correspond to the surface diffusion barrier on the (111) surface. Abrink, Broudy, and McCarthy[9] estimated, based on molecular beam epitaxy (MBE) experiments, this barrier height to be about 0.2 eV for ⟨112⟩ diffusion on a step-free {111} plateau, while Joyce, Bradley, and Booker[10] gave a value of ~2 eV from their nucleation experiments by gas-source MBE. However, it should be noted that the Tersoff potential gives rise to high melting temperature (2547 K), while it can well reproduce thermodynamic properties such as the Gibbs free energy and thermal expansion coefficient in the temperature region less than ≈1500 K.[11] Therefore, we must conclude that it is not appropriate to use the Tersoff potential for correct estimation of the activation energy in the higher temperature region larger than 1500 K. The poor nature of the Tersoff potential in this temperature region may also cause the abruptness of the change from high- to low-temperature behavior in Fig. 4. Nevertheless, we believe, there is a general trend that the structure of the a/c interface changes from a flat (001)-like surface to a rough surface composed of {111} facets during SPE growth of Si in the [001] direction as annealing temperature increases. In fact, similar rough surfaces can be observed in the solid/liquid interface obtained by local laser heating of polycrystalline Si thin films on quartz substrates capped by deposited SiO_2 films.[12] These results also suggest that the low activation energy ~0.3 eV observed in IBIEC may well be due to not only ion-beam-induced defects as generally considered but also structural change at the a/c interface during ion-beam irradiation.

IV. CONCLUSION

We have shown layer-by-layer crystallization processes at the amorphous/crystalline (a/c) Si interface during SPE by

using MD simulations. It was found that the atomistic mechanism of SPE growth was different in the lower and higher temperature region. In lower temperatures, the rate-limiting step is two-dimensional nucleation on the amorphous/crystal Si(001) interface and the activation energy is found to be 2.6 eV which is in good agreement with the experimental value of thermal SPE. On the other hand, in higher temperatures, {111} facets are formed at the a/c interface and the rate-limiting step is considered to be a diffusion process of Si on the (111) plane which may result in a lower activation energy.

ACKNOWLEDGMENTS

This work was supported by JSPS Research for the Future Program in the Area of Atomic Scale Surface and Interface Dynamics under the project ''Dynamic Behavior of Silicon Atoms, Lattice Defects, and Impurities near Silicon Melt-crystal Interface.'' Part of this work is the result of ''Technology for Production of High Quality Crystal,'' which is supported by the New Energy and Industrial Technology Development Organization (NEDO) through the Japan Space Utilization Promotion Center (JSUP) in the program of the Ministry of International Trade and Industry (MITI).

[1] G. L. Olson and J. A. Roth, Mater. Sci. Rep. **3**, 1 (1988).
[2] A. Kinomura, J. S. Williams, and K. Fujii, Phys. Rev. B **59**, 15 214 (1999).
[3] J. Tersoff, Phys. Rev. B **37**, 6991 (1988).
[4] S. J. Cook and P. Clancy, Phys. Rev. B **53**, 7176 (1996).
[5] M. Ishimaru, S. Munetoh, and T. Motooka, Phys. Rev. B **56**, 15 133 (1997).
[6] M. Ishimaru, K. Yoshida, T. Kumamoto, and T. Motooka, Phys. Rev. B **54**, 4638 (1996).
[7] W. F. van Gunsteren and H. J. C. Berendsen, Mol. Phys. **45**, 637 (1982).
[8] J. S. Custer, A. Battaglia, M. Saggio, and F. Priolo, Phys. Rev. Lett. **69**, 780 (1992).
[9] H. C. Abrink, R. M. Broudy, and G. P. McCarthy, J. Appl. Phys. **39**, 4673 (1968).
[10] R. A. Joyce, R. R. Bradley, and G. R. Booker, Philos. Mag. **15**, 1167 (1967).
[11] L. Porter, S. Yip, M. Yamaguchi, H. Kaburaki, and M. Tang, J. Appl. Phys. **81**, 96 (1997).
[12] U. Landman, W. D. Luedtke, R. N. Barnett, C. L. Cleveland, M. W. Ribarsky, E. Arnold, S. Ramesh, H. Baumgart, A. Martinez, and B. Khan, Phys. Rev. Lett. **56**, 155 (1986).