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Silicon atomic layer growth controlled by flash heating in chemical vapor deposition using SiH₄ gas

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The separation between surface adsorption and reaction of SiH₄ on a Si substrate has been investigated by heating the surface with a Xe flash lamp in an ultraclean low-pressure environment. About 0.4 atomic-layer epitaxy per flash-lamp light shot was observed on Si(100) at a substrate temperature of 385 °C and at SiH₄ partial pressure of 500 Pa. The dependencies of SiH₄ surface coverage on the SiH₄ partial pressure and shot-to-shot time interval are expressed by the Langmuir adsorption type equation, assuming that the total adsorption site density is equal to the surface atom density.

Atomic-layer growth control of Si and Ge on Si in chemical vapor deposition (CVD) is attractive for the progress in future semiconductor devices, e.g., ultrasmall devices and heterodevices. In conventional CVD, surface adsorption and the reaction of reactant gases proceed simultaneously. In order to perform atomic-layer growth, it is important to separate the adsorption and the reaction. So far, in atomic-layer epitaxy,¹⁻⁴ the self-limiting process of gas adsorption has been employed using metalorganic or chloride gases which form a strong chemical bond between surface atoms and adsorbed molecules. In order to prevent any contamination into a grown film, simple reactant gases without carbon or halogen such as GeH₄ and SiH₄ should be used. The studies on SiH₄ adsorption on a Si surface in ultrahigh vacuum have been reported.⁵ However, atomic-layer growth of Si has not been reported so far. In our previous work, atomic-layer growth of Ge using a GeH₄ gas had been achieved by flash heating the surface with a Xe flash lamp in an ultraclean low-pressure environment.⁶⁻⁸ In the present work, the separation between surface adsorption and reaction of SiH₄ gas on a Si substrate was investigated by the same flash heating method, and submonolayer growth of Si per flash-lamp light shot has been achieved below 400 °C. Furthermore, the SiH₄ adsorption mechanism is discussed.

The Si depositions were carried out using SiH₄ in an ultraclean rf-heated, cold-wall low-pressure CVD system,

as schematically shown in Fig. 1.⁶⁻⁸ With gate valves, turbomolecular pumps, and a load-lock chamber, the system is ultrahigh vacuum compatible. A substrate is set into the load-lock chamber and transported into the reactor under ultraclean Ar purge and evacuation. During the evacuation, Ar gas is flowing continuously to avoid contamination from the exhaust line.⁹ The deposition time sequence after the substrate was placed on the susceptor in the reactor is shown in Fig. 2. While heating the substrate, SiH₄ gas is introduced into the reactor and then SiH₄ molecules adsorbed at the surface are decomposed by Xe flash-lamp light shots (duration about 1 ms, 20 J/cm²). The lamp light shots were incident perpendicularly upon the substrate at shot-to-shot intervals of a few tens of seconds. Here, the moisture levels of Ar and SiH₄ gases at the reactor inlet were 10 ppb or lower. The substrate surface temperature prior to the light incidence was measured by an optical pyrometer. The substrates used were 1.25 in.-diam *p*-type wafers of 2–20 Ω cm with mirror-polished (100) and (111) surfaces. Before loading the substrates into the load-lock chamber, they were cleaned in several cycles in a 4:1 solution of H₂SO₄ and H₂O₂, high purity DI water, 2% HF with a final rinse in DI water. The deposited thickness was measured by Tencor Alpha step. The structure of the film surface was evaluated by electron diffraction.

Figure 3 shows the substrate temperature dependence of the deposited film thickness per flash-lamp light shot

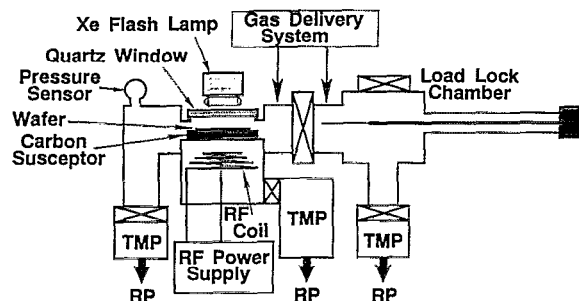


FIG. 1. Schematic diagram of an ultraclean rf-heated, cold-wall low-pressure CVD system with a Xe flash lamp.

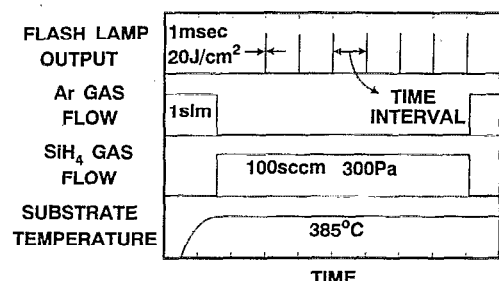


FIG. 2. Typical process sequence for atomic-layer growth of Si after the samples were placed on the susceptor in the reactor.

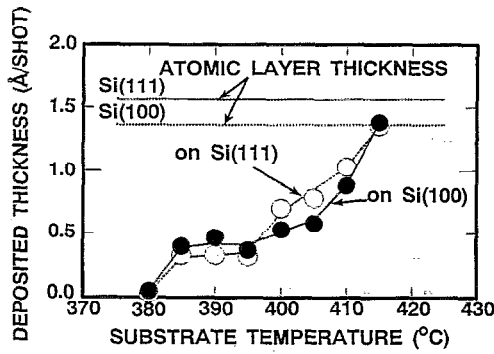


FIG. 3. Substrate temperature dependence of the deposited Si film thickness per flash-lamp light shot. The shot-to-shot time interval was 40 s and the SiH_4 partial pressure 300 Pa.

under the shot-to-shot time interval of 40 s and the SiH_4 partial pressure of 300 Pa. In the substrate temperature range of 385–395 °C, the deposited thickness per shot is independent of the substrate temperature and is found to be about 0.4 Å on Si(100) and 0.3 Å on Si(111), respectively. The anomalous increase in the deposited Si film thickness at substrate temperatures above 400 °C can be explained by continuous SiH_4 decomposition during the interval between flash light shots.

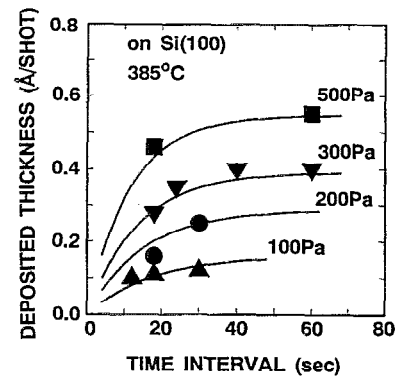
Figure 4 shows the shot-to-shot time-interval dependence of the deposited film thickness per shot (a) on Si(100) and (b) on Si(111) at a substrate temperature of 385 °C. It is found that the deposited thickness increases and saturates with the time interval. This saturation means that continuous SiH_4 decomposition during the interval scarcely occurs. As shown in the figure, the thicknesses on Si(100) in the saturation region are about 0.12, 0.40, and 0.55 Å for 100, 300, and 500 Pa, respectively, and slightly thicker than those on Si(111). This means that the saturated amount of adsorbed SiH_4 molecules is determined by the balance between adsorption and desorption of SiH_4 , and depends on the substrate orientation. It should be noted that streak and Kikuchi lines were observed for the atomically deposited films on Si(100), but halo pattern on Si(111) in electron diffraction measurements.

Now, assuming that a SiH_4 molecule is adsorbed at a single adsorption site, the total adsorption site density at surface n_0 can be described by

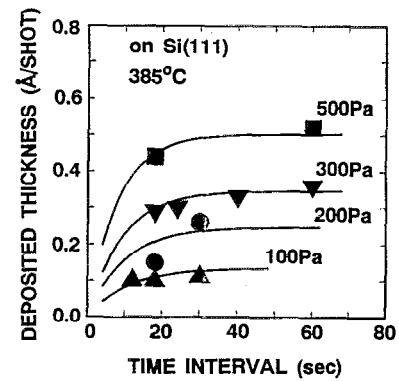
$$n_0 = Q_s + Q_{\text{SiH}_4} \quad (1)$$

Here, Q_s is the density of surface sites, where SiH_4 and other species are not adsorbed, and Q_{SiH_4} is the site density of adsorbed SiH_4 . It is also assumed that the adsorption of atomic hydrogen or other species is negligibly small compared with Q_s and Q_{SiH_4} . Then, the surface coverage velocity of SiH_4 is given by

$$\begin{aligned} \frac{dQ_{\text{SiH}_4}}{dt} &= k_1 P_{\text{SiH}_4} Q_s - k_{-1} Q_{\text{SiH}_4} \\ &= k_1 P_{\text{SiH}_4} n_0 - (k_1 P_{\text{SiH}_4} + k_{-1}) Q_{\text{SiH}_4}, \end{aligned} \quad (2)$$



(a)



(b)

FIG. 4. Shot-to-shot time-interval dependence of deposited Si film thickness per flash-lamp light shot for the SiH_4 partial pressures of 100–500 Pa (a) on Si(100) and (b) on Si(111) substrates at a substrate temperature of 385 °C.

where k_1 and k_{-1} are the rate constants of SiH_4 adsorption and desorption, respectively, P_{SiH_4} is the SiH_4 partial pressure. Assuming that $Q_{\text{SiH}_4} = 0$ at $t=0$, the integration of Eq. (2) gives

$$Q_{\text{SiH}_4} = \frac{k_1 P_{\text{SiH}_4} n_0}{k_1 P_{\text{SiH}_4} + k_{-1}} \{1 - \exp[-(k_1 P_{\text{SiH}_4} + k_{-1})t]\}. \quad (3)$$

The deposited thickness per shot (d_L) can be expressed by a product of the atomic-layer thickness (d_{AL}) and the surface coverage (Q_{SiH_4}/N , N is the surface Si atom density) as follows:

$$\begin{aligned} d_L &= d_{\text{AL}} \frac{Q_{\text{SiH}_4}}{N} \\ &= d_{\text{AL}} \frac{n_0}{N} \cdot \frac{k_1 P_{\text{SiH}_4}}{k_1 P_{\text{SiH}_4} + k_{-1}} \\ &\quad \times \{1 - \exp[-(k_1 P_{\text{SiH}_4} + k_{-1})t]\}. \end{aligned} \quad (4)$$

The solid curves shown in Fig. 4 are calculated from Eq. (4) using the following parameters, $d_{\text{AL}} = 1.36$ Å, $k_1 = 7.0 \times 10^{-5}$ Pa $^{-1}$ s $^{-1}$, $k_{-1} = 5.2 \times 10^{-2}$ s $^{-1}$ on Si(100), and

$d_{\text{AL}}=1.57 \text{ \AA}$, $k_1=8.0 \times 10^{-5} \text{ Pa}^{-1} \text{ s}^{-1}$, $k_{-1}=8.5 \times 10^{-2} \text{ s}^{-1}$ on Si(111) with $n_0=N$. The calculated curves are in good agreement with the experimental data. Using Eq. (4) with the above parameters, the single-atomic-layer growth per shot is expected in the SiH_4 partial pressure range of above a few thousand Pa. This expectation suggests that the total adsorption site density is equal to the surface atom density and a SiH_4 molecule occupies only one adsorption site.

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- ¹T. Suntola, J. Antson, A. Pakkala, and S. Lindfors, Society of Information Display (SID'80) Digest, 1980, p. 109.
- ²J. Nishizawa, H. Abe, and T. Kurabayashi, J. Electrochem. Soc. **132**, 1197 (1985).
- ³Y. Takahashi, H. Ishii, and K. Fujinaga, J. Electrochem. Soc. **136**, 1826 (1989).
- ⁴Y. Takahashi and T. Urisu, *Extended Abstracts of 1990 International Conference on Solid State Devices and Materials*, Sendai, Japan (The Japan Society of Applied Physics, Tokyo, 1990), p. 917.
- ⁵S. M. Gates, Surf. Sci. **195**, 307 (1988).
- ⁶J. Murota, M. Sakuraba, N. Mikoshiba, and S. Ono, J. Phys. IV **1**, C2-803 (1991).
- ⁷M. Sakuraba, J. Murota, N. Mikoshiba, and S. Ono, J. Cryst. Growth **115**, 79 (1991).
- ⁸M. Sakuraba, J. Murota, N. Mikoshiba, and S. Ono, *Extended Abstracts of 1991 International Conference on Solid State Devices and Materials, Yokohama, Japan* (The Japan Society of Applied Physics, Tokyo, 1991), p. 147.
- ⁹J. Murota, M. Kato, R. Kircher, and S. Ono, J. Phys. IV **1**, C2-795 (1991).