Silicon atomic layer growth using flash heating in CVD

M. Sakuraba, J. Murota, S. Ono

► To cite this version:

M. Sakuraba, J. Murota, S. Ono. Silicon atomic layer growth using flash heating in CVD. Journal de Physique IV Proceedings, 1993, 03 (C3), pp.C3-449-C3-456. 10.1051/jp4:1993362 . jpa-00251419

HAL Id: jpa-00251419

<https://hal.science/jpa-00251419>

Submitted on 1 Jan 1993

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Silicon atomic layer growth using flash heating in CVD

M. SAKURABA, J. MUROTA and S. ONO

*Laboratory for Microelectronics, Research Institute of Electrical Communication, Tohoku University,
2-1-1 Katahira, Aoba-ku, Sendai 980, Japan*

Abstract.—Si atomic layer growth on Si was investigated by heating the surface with a Xe flash lamp in an ultraclean low-pressure environment of SiH_4 or Si_2H_6 gas. In the case of SiH_4 , about 0.4 atomic layer deposition per single flash light shot was observed on Si(100) at a substrate temperature of 385°C and at a SiH_4 partial pressure of 500Pa. The adsorption process of SiH_4 can be explained quantitatively by Langmuir-type adsorption model, assuming that the total adsorption site density is equal to the surface atom density. It was found that the amount of adsorbed SiH_4 molecules is determined by the balance between adsorption and desorption of SiH_4 . In the case of Si_2H_6 , sub-monolayer growth of Si was observed at a substrate temperature of 320°C and under Si_2H_6 partial pressure of 300Pa. From the RHEED observation, epitaxial growth of Si films on Si(100) was confirmed to be realized at low temperatures such as 385°C and 320°C by using SiH_4 and Si_2H_6 , respectively, and the surface flatness of the deposited films was as good as that of the initial surface.

1.—Introduction.

Atomic layer epitaxy of Si and Ge in chemical vapour deposition(CVD) is attractive for the progress of future semiconductor devices, e.g. ultrasmall devices and hetero devices. In conventional CVD, surface adsorption and reaction of reactant gases proceed simultaneously. In order to achieve atomic layer control, it is important to separate the adsorption process and the reaction process. So far, in atomic layer epitaxy[1–4], the self-limiting process of gas adsorption has been employed using metal organic or chloride gases which form a strong chemical bond between surface atoms and adsorbed molecules. In order to prevent any contamination of deposited films, simple hydride gases such as GeH_4 , SiH_4 or Si_2H_6 without carbon or halogen should be used as the reactant gas. The studies of SiH_4 and Si_2H_6 adsorption process on Si surfaces in an ultrahigh vacuum have been reported[5]. However, atomic layer growth of Si using these hydride gases had not been reported so far. In the previous work, the atomic layer epitaxy of Ge using GeH_4 gas has been achieved by heating the surface with a Xe flash lamp in an ultraclean low-pressure environment[6–8]. In the present work, Si atomic

Fig.1.—Schematic diagram of an ultraclean RF-heated cold-wall low-pressure CVD system with Xe flash lamp.

layer growth process on Si substrate was investigated by the flash heating method, and sub-monolayer epitaxial growth of Si per shot of flash light has been achieved using SiH_4 and Si_2H_6 gases at 385°C and 320°C , respectively. Furthermore, the SiH_4 and Si_2H_6 adsorption mechanisms are discussed.

2.—Experimental.

Si deposition on Si was carried out using SiH_4 or Si_2H_6 in an ultraclean RF-heated cold-wall low-pressure CVD system as schematically shown in Figure 1. The system was made ultrahigh vacuum compatible with gate valves, turbo molecular pumps and a load-lock chamber. Moisture levels of used Ar, SiH_4 and Si_2H_6 gases at the reactor

Fig.2.—Typical deposition sequence after setting the samples on the susceptor in the reactor.

inlet were 10ppb or lower. The substrates are set into the load-lock chamber and transported into the reactor under evacuation with a simultaneous ultraclean Ar gas flow to avoid contamination from the exhaust line[9]. A typical deposition time sequence after the substrates were placed on the susceptor is shown in Figure 2. While heating the substrates, SiH_4 or Si_2H_6 gas is introduced into the reactor and then SiH_4 or Si_2H_6 molecules adsorbed at the surface are decomposed by Xe flash lamp light shots (duration about 1msec, 20 J/cm^2). The flash light shots were incident perpendicularly upon substrates. The shot to shot interval was of a few tens of seconds. The substrate surface temperature prior the light incidence was measured by an optical pyrometer. The substrates used were p-type Si wafers of $2\text{--}20\Omega\text{-cm}$ with a mirror polished (100) surface. Before loading the substrates into the load-lock chamber, they were cleaned in several cycles in a 4:1 solution of H_2SO_4 and H_2O_2 , high purity DI water, 2% HF with a final rinse in DI water. The deposited thickness, after repetition of hundreds cycles of flash shots, was measured by Tencor Alpha Step. The structure of the film surface was evaluated by reflection high-energy electron diffraction (RHEED).

3.-Results and discussion.

Figure 3 shows the substrate temperature dependence of the deposited film thickness per shot of flash light. In the case of SiH_4 gas, the deposited thickness per shot of flash light is found to be about $0.4\text{\AA}$, which is independent of the substrate temperature in the substrate temperature range of $385\text{--}395^\circ\text{C}$, on Si(100) at a SiH_4 partial pressure of 300Pa and at a shot to shot time interval of 40sec. It should be noted that the increase in the deposited thickness per shot of flash light observed at substrate temperatures above

Fig.3.-Substrate temperature dependence of the deposited Si film thickness per flash light shot on Si(100) surface. The SiH_4 or Si_2H_6 partial pressure is 300Pa. Arrows show no deposition.

Fig.4.—Shot to shot time interval dependence of deposited Si film thickness per flash light shot at the SiH_4 partial pressures of 100–500Pa on Si(100) substrate at a substrate temperature of 385°C.

400°C may 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 of flash light on Si(100). It is found that the deposited thickness initially increases and saturates with the time interval. This saturation means that continuous SiH_4 decomposition during the flash light shot interval scarcely occurs. As shown in the figure, the thicknesses on Si(100) in the saturation region are about 0.12Å, 0.40Å and 0.55Å for 100Pa, 300Pa and 500Pa, respectively. This means that the saturated amount of adsorbed SiH_4 molecules is determined by the balance between adsorption and desorption of SiH_4 on the surface.

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

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

where Q_{SiH_4} and Q_s are the densities of the surface site at which SiH_4 is adsorbed, and not adsorbed, respectively. It is also assumed that the adsorption of atomic hydrogen or other species is negligibly small compared with Q_{SiH_4} or has no influence on the SiH_4 adsorption. Assuming that the SiH_4 adsorption process is based on the Langmuir-type adsorption, the surface coverage velocity of SiH_4 is given by

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

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 the equation (2) gives

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

where τ is the shot to shot time interval. The deposited thickness per shot of flash light can be expressed by a product of atomic layer thickness (d_{AL}) and surface coverage (Q_{SiH_4}/N , N is the surface atom density) as the following Langmuir-type equation.

$$\begin{aligned} (\text{Deposited thickness / shot}) &= d_{\text{AL}} \frac{Q_{\text{SiH}_4}}{N} \\ &= d_{\text{AL}} \frac{n_0}{N} \frac{k_1 P_{\text{SiH}_4}}{k_1 P_{\text{SiH}_4} + k_{-1}} [1 - \exp\{-(k_1 P_{\text{SiH}_4} + k_{-1}) \tau\}]. \end{aligned} \quad (4)$$

For $\tau \rightarrow \infty$,

$$\frac{d_{\text{AL}}}{(\text{Deposited thickness / shot})} = \frac{N}{n_0} \frac{k_{-1}}{k_1} \frac{1}{P_{\text{SiH}_4}} + \frac{N}{n_0}. \quad (5)$$

Figure 5 shows the $(P_{\text{SiH}_4})^{-1}$ dependence of the inverse of deposited thickness per shot of flash light in the saturation regions in Figure 4. It is found that data in Figure 5 can be described by the equation (5) with $N/n_0=1$. Therefore, it is considered that the total adsorption site density n_0 is equal to the surface atom density N and one SiH_4 molecule can occupy only one adsorption site. Solid curves shown in Figure 4 are obtained from

Fig.5.—The $(P_{\text{SiH}_4})^{-1}$ dependence of the inverse of deposited thickness per flash light shot in the saturation region. The shot to shot time interval is 60sec.

the equation (4) using the following parameters, $d_{AL}=1.36\text{\AA}$, $k_1=7.0\times 10^{-5}\text{ Pa}^{-1}\text{sec}^{-1}$, $k_{-1}=5.2\times 10^{-2}\text{ sec}^{-1}$ on Si (100) with $n_0=N$. The calculated curves are in good agreement with the experimental data. Consequently, the adsorption process of SiH_4 can be explained quantitatively by Langmuir-type adsorption model, assuming that the total adsorption site density is equal to the surface atom density.

Figure 6(a) shows the typical RHEED pattern taken from the film deposited on Si(100) surface by flash heating at the substrate temperature of 385°C using SiH_4 gas. All the films deposited at 385°C were epitaxial and smooth as determined by similar streak pattern to the above. The RHEED pattern of Figure 6(a) has weak 2-fold streaks beside bright fundamental 1×1 -streaks, although only bright fundamental 1×1 -streaks are observed on Si(100) surface after the wet cleaning as shown in Figure 6(b). A similar RHEED pattern to Figure 6(a) was also obtained when the film was deposited by flash heating CVD after the double-domain 2×1 reconstructed surface (Figure 6(c)) was formed by continuous thermal decomposition of SiH_4 at 580°C . In other words, the 2×1 reconstructed surface is mostly transformed into the 1×1 non-reconstructed surface by flash heating CVD under the conditions of high SiH_4 partial pressure and of low-temperature

Fig.6.—Typical RHEED patterns taken from [011] azimuth for (a) the Si film deposited with 500shots, the shot to shot time interval 24sec, at the substrate temperature 385°C and the SiH_4 partial pressure 300Pa, (b) non-reconstructed Si(100)- 1×1 surface after wet cleaning as stated in Experimental and (c) reconstructed Si(100)- 2×1 surface formed by continuous thermal decomposition of SiH_4 at 580°C .

Fig.7.—Typical RHEED pattern for the Si film deposited at the substrate temperature of 320°C on Si(100) surface with 500shots, the shot to shot time interval 20sec, the Si_2H_6 partial pressure 300Pa.

below 400°C. Therefore, it is suggested that, at a high SiH_4 partial pressure, the adsorption of Si-hydrides suppresses the surface atom reconstruction.

In the case of Si_2H_6 gas in Figure 3, the Si deposition can be observed in the substrate temperatures above 320°C. Above 330°C, the deposited thickness per shot of flash light increases with the substrate temperature. As shown in Figure 3, the substrate temperature dependence of deposited thickness per shot of flash light has an energy of about 1.6eV, which is equal to the activation energy of deposition rate in thermal CVD[10–11]. Therefore, it is considered that the continuous thermal decomposition of Si_2H_6 during the time interval between flash light shots, is dominant. However, at the substrate temperature range of 320–330°C, the deposited thickness per shot of flash light scarcely depends on the substrate temperature. The deposited thickness per shot of flash light at the Si_2H_6 partial pressure of 300Pa is found to be about 0.16Å and 0.23Å under the shot to shot time interval of 20sec and 40sec, respectively.

Figure 7 shows the typical RHEED pattern from the films deposited on Si(100) surfaces by flash heating at the substrate temperature of 320°C using Si_2H_6 gas. This 1×1-streak pattern is the same as the pattern observed from Si(100) surface as shown in Figure 6(b). Therefore, it is considered that the initial flat surface was maintained during flash heating CVD at 320°C.

4.—Conclusions.

Si atomic layer growth processes on Si substrates were investigated by flash heating CVD. The deposited thickness per shot of flash light is independent of the substrate temperatures in the ranges of 385–395°C for SiH_4 and 320–330°C for Si_2H_6 . In the case of SiH_4 , the deposited thickness per shot of flash light increased and saturated with the time interval and the saturated thicknesses on Si(100) were about 0.12Å, 0.40Å and 0.55Å for 100Pa, 300Pa and 500Pa, respectively. The adsorption process of SiH_4 can be explained quantitatively by Langmuir-type adsorption model, assuming that the total adsorption site density is equal to the surface atom density. In the case of Si_2H_6 , sub-

monolayer growth of Si was observed at the substrate temperature of 320°C under Si₂H₆ partial pressure of 300Pa. But, for the Si₂H₆ surface adsorption process, further investigations will be necessary. From the RHEED observation, it is confirmed that, by using flash heating CVD, epitaxial growth of Si films on Si(100) was realized at temperatures such as 385°C and 320°C by using SiH₄ and Si₂H₆, respectively, and the surface flatness of the deposited films was as good as that of the initial surface. Furthermore, from the transformation of the streaks in the RHEED pattern, it is suggested that the adsorption of Si-hydrides suppresses the surface atom reconstruction.

Acknowledgments.

The authors wish to express their thanks to Profs. Yasuji Sawada and Takashi Matsuura for their advice and encouragement in executing this study. The CVD reactor was provided by Kokusai Electric Co., Ltd. The study was carried out in the Superclean Room of the Laboratory for Microelectronics, Research Institute of Electrical Communication, Tohoku University, and was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan.

References.

- [1] Suntola T., Antson J., Pakkala A. and Lindfors S., Soc. Information Display (SID'80) Digest (1980) 109.
- [2] Nishizawa J., Abe H. and Kurabayashi T., *J. Electrochem. Soc.* **132** (1985) 1197.
- [3] Takahashi Y., Ishii H. and Fujinaga K., *ibid.* **136** (1989) 1826.
- [4] Takahashi Y. and Urisu T., Extended Abstracts 22nd (1990 Intern.) Conf. on Solid State Devices and Materials, Sendai (1990) 917.
- [5] Gates S. M., *Surface Sci.* **195** (1988) 307.
- [6] Sakuraba M., Murota J., Mikoshiba N. and Ono S., *J. Crystal Growth* **115** (1991) 79.
- [7] Murota J., Sakuraba M., Mikoshiba N. and Ono S., *J. Phys. IV France* **1** (1991) C2-803.
- [8] Sakuraba M., Murota J., Mikoshiba N. and Ono S., Extended Abstracts 23rd (1991 Intern.) Conf. on Solid State Devices and Materials, Yokohama (1991) 147.
- [9] Murota J., Furuno M., Kato M., Mikoshiba N., Ono S., Kurokawa H., Sato T., Nakamura N. and Ikeda F., The Electrochem. Soc. Extended Abstracts, Fall Meeting, Seattle, WA (1990) 576.
- [10] Mishima Y., Hirose M., Osaka Y., Nagamine S., Ashida Y., Kitagawa N. and Isogaya K., *Jpn. J. Appl. Phys.* **22** (1984) L46.
- [11] Nakayama S., Yonezawa H. and Murota J., *Jpn. J. Appl. Phys.* **23** (1984) L493.