PHYSICAL REVIEW B VOLUME 47, NUMBER 23 15 JUNE 1993-I

Si crystal growth mediated by synchrotron-radiation-stimulated hydrogen desorption

Housei Akazawa, Yuichi Utsumi, Tsuneo Urisu,* and Masao Nagase
NTT LSI Laboratories, 3-1, Morinosato-Wakamiya, Atsugi, Kanagawa 243-01, Japan

(Received 1 March 1993)

Si crystal growth on Ge(100) resulting from surface photochemical reaction is achieved using atomic layer epitaxy, alternating disilane exposure, and irradiation with synchrotron radiation. Self-limiting chemisorption with fractional SiH_x coverage and partial hydrogen removal in stimulated desorption results in a constant growth rate of 0.2 ML/cycle below thermal growth temperatures. The effects of gas and adsorbate excitation in photochemical vapor deposition are experimentally separated.

Photoepitaxy using synchrotron radiation (SR) is a new nonthermal technique in the developing field of crystal growth.[1] Since both surface and gas excitation effects contribute to the reaction kinetics in conventional chemical vapor deposition (CVD), experimental separation of these two channels is an important subject in photochemistry. In this paper, we have applied atomic layer epitaxy (ALE) to map out the surface process: Si crystal growth mediated by SR-stimulated desorption of surface hydrogen atoms.[2] This purely electronic process achieves region-selective deposition below the thermal growth temperature. Comparison between thermal and stimulated desorption demonstrates the nature of SR-ALE, and the growth mechanism in SR-CVD due to the gas excitation effect is clearly presented in relation to SR-ALE.

We performed our experiments using Beam Line 1C at the Photon Factory of the National Laboratories for High Energy Physics. SR from the storage ring was perpendicularly focused onto the sample placed inside the ultrahigh vacuum (minimum pressure of 5×10^{-10} Torr) reaction chamber. The use of intense nonmonochromatized photons, having an energy distribution from 1 to 1000 eV with a peak at 100 eV, was essential to growing films with a measurable thickness. The photon flux and power density at the target were 2.3×10^{16} photons sec^{-1} and 5 W cm^{-2}, respectively, at a ring current of 100 mA. Measurement using an infrared thermal video system confirmed that the surface temperature increased only 30 °C in the irradiated region and 10 °C in the surrounding region.

99.99% pure disilane was exposed with a pulse nozzle. The pressure in the chamber was varied from 5×10^{-3} to 2×10^{-3} Torr when the nozzle was opened. Gas exposure for a time period T_1 was automatically alternated with SR irradiation for a time period T_2 in the ALE mode, according to the timing chart shown in Fig. 1. After the nozzle was closed, a 15-sec exhaust interval was sufficient for the pressure to return to the background pressure (7×10^{-8} Torr). The residual disilane ambient is negligible for SR excitation.

Thermal desorption of native oxide covering Si(100) and Ge(100) (Ref. 3) wafers produced clear, double-domain (2×1), reflection high-energy electron-diffraction (RHEED) patterns. Auger electron spectroscopy (AES) showed no detectable contaminants, such as carbon and oxygen, before or after growth. Two-dimensional growth on Si(100) was confirmed down to 200 °C, although growth rate measurement is practically impossible in the ALE mode. Thus, Ge(100) substrates were used simply because of the requirement for precise thickness measurement of a thin Si film by an optical method. The light reflectance curve within 400–800 nm was best fitted to the theoretical one assuming a flat Si overlayer. The Si crystal layer on Ge(100) during the initial growth stage, however, consists of islands having [311] facets due to the lattice mismatch between Si and Ge. The curve fitting gives the average thickness (±10% relative uncertainty) over the corrugated Si area based on the linear relationship between the thickness and the degree of dispersion in the light reflectance versus wavelength curve. For coalesced, thick Si film grown by SR-CVD, the measured thickness using the optical method and using a stylus step profiler agreed within ±10%. From this calibration, we estimate the absolute thickness accuracy to be within ±30% at most. The SR-CVD growth rates on Ge(100) and Si(100) under the same conditions were shown to be similar for several data points.

One SR-ALE growth run on Ge(100) took about 10 h, beginning at a ring current of 350 mA and finishing at 250 mA. Between 100 and 300 growth cycles were conducted and between 30- and 80-Å-thick Si crystals were grown. Although the halo background in RHEED pat-

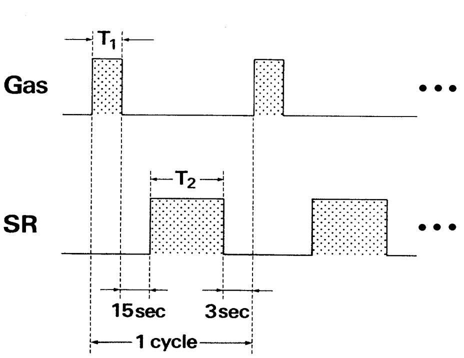

FIG. 1. Gas exposure and SR irradiation timing chart for ALE growth.

0163-1829/93/47(23)/15946(4)/$06.00

terns strengthened as the low-temperature limit of epitaxy was approached,[4,5] spots representing island growth were observed on the Ge(100) down to 220 °C, both with SR-CVD and SR-ALE. This implies that the local registration of the Si adatom is conserved with respect to the underlying crystal, although insufficient thermal reordering occurs. In the nonirradiated region, the RHEED pattern exhibits a disilane-saturated Ge(100) surface with weakened half-order streaks, representing a mixed dihydride and monohydride $[(1\times1){:}2H+(2\times1){:}H]$ chemisorbed surface.[6]

Figure 2(a) shows the dependence of the growth rate per ALE cycle on substrate temperature, where $T_1=20$ sec and $T_2=262$ sec, and the Si monolayer thickness is 1.36 Å. At temperatures below $T_s=350\,^\circ\mathrm{C}$, no Si film is grown in the nonirradiated region because the thermal desorption rate of hydrogen is actually zero. The hydrogen-terminated surface is inactive and inhibits more disilane from being chemisorbed. Consequently, constant-layer Si growth in the irradiated region proceeds through self-limiting chemisorption, followed by reactivation of the Si surface due to photostimulated desorption of any surface hydrogen atoms. This result represents the first Si epitaxial growth mediated by an electronic process. Above $T_s=350\,^\circ\mathrm{C}$, the growth rate increases steeply with temperature in both the irradiated and nonirradiated regions. This thermal growth begins at the same temperature at which H_2 desorbs from dihydride on Si(100) (corresponding to the β_2 peak), as shown in Fig. 2(b), and also from dihydride on porous Si.[7] This ensures that a Si-covered Ge substrate can actually be regarded as a Si substrate. By monitoring the Ge (52 eV) AES signal and measuring the depth profile using secondary-ion mass spectroscopy (SIMS), we confirmed that there was no Ge segregation and no intermixing at the interface within the temperature range of Fig. 2(a). This is due to the surfactant effect of hydrogen atoms, which is characteristic in CVD.[8] With parameters of $T_1=20$ sec and $T_2=82$ sec, the constant growth rate below 350 °C in the irradiated region was much lower than at $T_2=262$ sec because of the insufficient irradiation time. The general tendency in temperature dependence was similar, however, to that shown in Fig. 2(a).

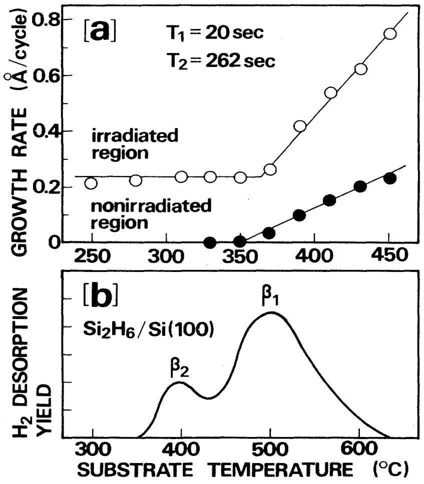

FIG. 2. (a) SR-ALE growth rate vs substrate temperature. (b) Thermal hydrogen desorption spectrum from disilane chemisorbed Si(100).

Figure 3(a) shows the dependence of the ALE growth rate at $T_2=262$ sec and $T_2=350\,^\circ\mathrm{C}$ on the gas exposure time. It is apparent that the growth rate is constant at 0.24 Å/cycle, confirming self-limiting chemisorption. This result also indicates that 5 sec of disilane exposure is enough to compensate for the hydrogen-removed "active" sites with newly chemisorbing species.

The dependence of the growth rate on the SR irradiation time at $T_1=20$ sec is shown in Fig. 3(b), for $T_s=350\,^\circ\mathrm{C}$ and 430 °C. At $T_s=350\,^\circ\mathrm{C}$, the growth rate increases linearly up to 180 sec irradiation time and then saturates. The quantum yield for the unsaturated regime is estimated to be 1×10^{-6} Si atoms growth per incident photon, a typical efficiency for SR-stimulated desorption.[9] At $T_s=430\,^\circ\mathrm{C}$, a parallel thermal desorption mechanism increases the rate. These results (Figs. 2 and 3) clearly demonstrate that the growth rate reaches a plateau at 0.24 Å/cycle (corresponding to about 0.2 ML/cycle) for a wide range of the three parameters: T_s, T_1, and T_2. This saturation behavior is also seen for the SR intensity in the uniform thickness profile around the center of the beam spot.

The following scheme has been shown to describe the disilane chemisorption process on both clean Si(100) (Ref. 10) and clean Si(111) (Ref. 11), although their surface structures are considerably different.

$$\mathrm{Si_2H_6}(g)\leftrightarrows\mathrm{Si_2H_6}(a)\rightarrow2\mathrm{SiH_3}(a)\rightarrow2\mathrm{SiH_2}(a)+2\mathrm{H}(a)\ , \tag{1}$$

where (g) and (a) denote gas and absorbate, respectively. $Si_2H_6(a)$ is a weakly trapped molecule on the surface which dissociates to become $SiH_3(a)$. This $SiH_3(a)$ then releases a hydrogen atom to an adjacent Si atom. The resulting dihydride and monohydride are the dominant surface species below 350 °C. Moreover, it is known that hydrogen atoms on Si(311) (Ref. 12), and even on porus Si

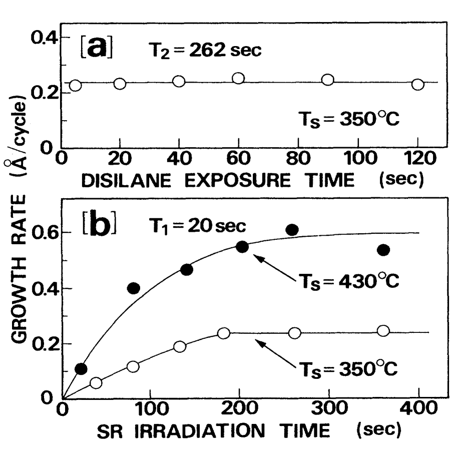

FIG. 3. (a) SR-ALE growth rate vs gas exposure time. (b) SR-ALE growth rate vs SR irradiation time.

(Ref. 17) exist as monohydrides and dihydrides. It is therefore reasonable to expect that with the self-limiting chemisorption on the faceted Si as growth proceeds on the Ge(100), the surface becomes terminated with silicon monohydrides and dihydrides, although the relative population may be different from that on a flat plane.

The onset of thermal growth just above 350 °C with recombinative hydrogen desorption from dihydride indicates that a monohydride surface is not self-limiting with respect to disilane chemisorption. Reactive sticking is therefore possible at local hydrogen-depleted sites. In SR-ALE, direct excitation with vacuum ultraviolet light is effective for the $\mathrm{SiH}_x(a)$ ($x=1$ and 2), since the $\mathrm{Si_2H_6}(g)$ and $\mathrm{Si_2H_6}(a)$ disappear during the exhaust period. H^+ desorption occurs according to the Knotek-Feibelman mechanism involving Si core hole creation.[13] Valence electronic excitation due to secondary electrons can also induce desorption of hydrogen atoms. Redesorption of $\mathrm{SiH}_x(a)$ ($x=1$ and 2) itself is unlikely because it requires the breaking of two Si-Si back bonds. In any case, even partial hydrogen removal promotes some disilane chemisorption during the next gas exposure step, similar to the chemisorption onto the monohydride surface just above 350 °C.

It is generally accepted that filling up to dangling-bond sites with hydrogen atoms and steric hindrance at dissociative chemisorption limit the saturation coverage of SiH_x below 1 monolayer. Thermal ALE with disilane exposure and annealing using KrF excimer laser irradiation shows a constant growth rate of 0.4 ML/cycle on Si(100).[14] With trisilane exposure and direct heating of the substrate, a 0.8-ML/cycle was achieved on Si(111).[15] Considering that annealing causes complete hydrogen desorption, a 0.4-ML/cycle gives the upper limit of the growth rate in disilane ALE. The 0.2-ML/cycle in SR-ALE therefore suggests the partial hydrogen removal ability of stimulated desorption.

To verify this point, we prepared a disilane-saturated Ge(100) surface with 10^6-langmuir exposure at 200 °C, which exhibits a similar RHEED pattern to the one observed in the nonirradiated regions after SR-ALE growth. With SR irradiation, half-order streaks in a zero-order Laue zone gradually emerged, although the diffraction spots in the $\frac{1}{2}$ and first-order Laue zone were unclear even after 30 min of irradiation. Hydrogen desorption by annealing above 500 °C, however, produced a RHEED pattern almost identical to that from clean Ge(100). This observation indicates that while stimulated desorption almost certainly occurs, some hydrogen atoms persist in remaining, hindering the attainment of a well-ordered (2×1) surface.[16] Similarly, it has been shown by thermal desorption spectroscopy confined to the irradiated region that dideuteride is more active in stimulated desorption than monodeuterium chemisorbed on Si(100), but only about half the deuterium can be removed, even after 8 h of SR irradiation.[17]

The influence of the limited hydrogen removal ability of the electronic process and the importance of thermal assistance can be clearly seen in Fig. 3(b). The steep increase and saturation in the growth rate with irradiation time indicates that most of the hydrogen desorption occurs during the long irradiation time and not during the gas exposure time, at both $T_s=350\,^\circ\mathrm{C}$ and $T_s=430\,^\circ\mathrm{C}$. At $T_s=350\,^\circ\mathrm{C}$, only 0.2 ML of SiH_x can newly chemisorb during each cycle due to the incomplete hydrogen removal. The remaining hydrogen atoms reduce the effective number of available sites for chemisorption. At $T_s=430\,^\circ\mathrm{C}$, however, the stimulated desorption and thermal process (thermal desorption and possibly thermal diffusion) together remove a much larger amount of hydrogen, thus facilitating chemisorption of about 0.4 ML of SiH_x for each cycle.

The next question is why hydrogen atoms cannot be removed completely by just the stimulated desorption. The efficiency of stimulated desorption is generally determined by the lifetime of a valence hole, which is primarily dependent on the local electronic structure. Indeed, the cross section depends on the species, as observed in Ref. 17. Site specifically alone, however, cannot explain the limitation on the number of removable hydrogen atoms. With decreasing hydrogen coverage, dangling bonds recover and thus the surface state gradually emerges.[6] As a result, the nonlocalized valence electrons exert a drastic increase in the quenching of valence holes, leading to the steep drop of stimulated desorption probability.

We next consider the SR-CVD mechanism in relation to SR-ALE. Figure 4(a) shows the temperature dependence of the SR-CVD rate along with the thermal growth rate without SR irradiation, under 1.3×10^{-3} Torr of ambient disilane. The activation energy obtained from the thermal growth data is $E_a=43$ kcal/mol. This is close to the value for hydrogen desorption from silicon dihydride[12] and supports our reaction model described above. The onset of thermal growth in SR-CVD again occurs at $T_s=350\,^\circ\mathrm{C}$. The minimum growth rate around 350 °C is more than an order of magnitude higher than the constant growth rate in SR-ALE. Obviously, another non-

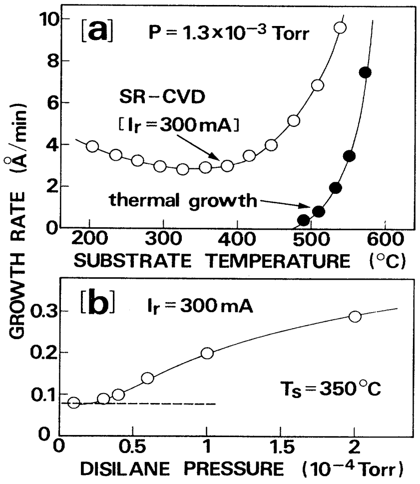

FIG. 4. (a) SR-CVD rate and thermal growth rate vs substrate temperature normalized by ring current of 300 mA. (b) SR-CVD rate vs disilane pressure. The broken line shows the corresponding SR-ALE growth rate assuming one minute of SR irradiation.

thermal growth mechanism must operate in SR-CVD. If SR is irradiated in the presence of gas, $Si_2H_6(g)$ and $Si_2H_6(a)$ are ionized and decomposed. Core excitation of $Si_2H_6(g)$ effectively produces highly reactive species such as $Si^+(g)$ and $SiH^+(g)$. Fewer hydrogen atoms are bonded to these species, so they can stick directly to the surface and contribute to growth. The second growth channel is photolysis of $Si_2H_6(a)$, which follows the hydrogenated Si-network formation. The gradual growth-rate increase with decreasing temperature below 300 °C can be interpreted as due to the increasing residence time of $Si_2H_6(a)$, which increases the cross section of photoexcitation. The growth rate depends on the amount of $Si_2H_6(a)$ and $Si_2H_6(g)$, and it is proportional to the pressure.

On the other hand, the growth rate by pure photodesorption is derived from the pressure dependence of the SR-CVD rate shown in Fig. 4(b), in which substrate excitation dominates. The growth rate asymptotically approaches an offset of 0.08 Å/min in the zero pressure limit. This value coincides with the efficiency of the unsaturated regime (0.24 Å/180 sec) in SR-ALE at $T_s = 350\,^\circ\text{C}$ [Fig. 4(b)]. SR-CVD under pressures of less than 10^{-5} Torr of ambient disilane is therefore like SR-ALE: the surface is always saturated with $SiH_x(a)$ and only $SiH_x(a)$ excitation is effective.

In conclusion, Si crystal growth mediated by SR-stimulated hydrogen desorption has been presented in the very low-temperature regime. Submonolayer SiH_x saturation and partial hydrogen desorption yield a 0.2 ML/cycle. The relation between SR-CVD and SR-ALE is explained consistently by separating the surface and gas excitation processes.

We would like to thank T. Sakai, J. Takahashi, and H. Yokoyama for their helpful comments. We also thank the staff of the Photon Factory for their support of our experiments.

---

[*] Present address: Institute for Molecular Science, Myodaiji, Okazaki 444, Japan.

[1] Y. Utsumi, J. Takahashi, H. Akazawa, and T. Urisu, Jpn. J. Appl. Phys. **30**, 3195 (1991).

[2] The term ALE originally indicated layer-by-layer (1 ML/cycle) growth, but for group-IV semiconductors, ALE is often extended to denote fractional layer growth achieved by alternating gas exposure and ligand desorption.

[3] R. A. Ludder, G. G. Fountain, and R. J. Markunas, J. Appl. Phys. **60**, 3519 (1986).

[4] H. Kawabata, H. Ueba, and C. Tatsuyama, J. Appl. Phys. **66**, 634 (1989).

[5] D. J. Eaglesham, H. J. Gossmann, and M. Cerullo, Phys. Rev. Lett. **65**, 1227 (1990); D. J. Eaglesham and M. Cerullo, Appl. Phys. Lett. **58**, 2276 (1991).

[6] Y. Suda, D. Lubben, T. Motooka, and J. E. Greene, J. Vac. Sci. Technol. B **7**, 1171 (1989).

[7] P. Gupta, V. L. Colvin, and S. M. George, Phys. Rev. B **37**, 8234 (1988).

[8] M. Copel and R. M. Tromp, Appl. Phys. Lett. **58**, 2648 (1991).

[9] M. L. Knotek, V. O. Jones, and V. Rehn, Phys. Rev. Lett. **43**, 300 (1979).

[10] F. Bozoso and Ph. Avouris, Phys. Rev. B **38**, 3943 (1988).

[11] R. Imbihl, J. E. Demuth, S. M. Gates, and B. A. Scott, Phys. Rev. B **39**, 5222 (1989).

[12] U. Myler, P. Althainz, and K. Jacobi, Surf. Sci. **251/252**, 607 (1991).

[13] M. L. Knotek and P. J. Feibelman, Phys. Rev. B **40**, 964 (1978).

[14] D. Lubben, R. Tsu, T. R. Bramblett, and J. E. Greene, J. Vac. Sci. Technol. A **9**, 3003 (1991).

[15] S. Imai, S. Takagi, O. Sugiura, and M. Matsumura, Jpn. J. Appl. Phys. **30**, 3646 (1991).

[16] D. S. Lin, E. S. Hirschorn, T. C. Chiang, R. Tsu, D. Lubben, and J. E. Greene, Phys. Rev. B **45**, 3494 (1992).

[17] I. Nishiyama, Y. Teraoka, and F. Uesugi, *Extended Abstract of the 52nd Autumn Meeting of the Japan Society of Applied Physics* (Japan Society of Applied Physics, Tokyo, 1991), p. 576.