

Mechanism of Si Laser Atomic Layer Epitaxy Using the Adsorption and Thermally-induced Reactions of Si_2H_6 on $\text{Si}(100) 2 \times 1$

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The combined technique of Si_2H_6 dosing and ArF-laser irradiation for a $\text{Si}(100) 2 \times 1$ surface is expected to realize Si atomic-layer epitaxy (ALE) on the basis of the investigation by electron energy loss spectroscopy (EELS) and reflection high energy electron diffraction (RHEED). ArF-laser irradiation is effective to evolve hydrogen without changing the time-averaged surface temperature. The adsorption process produces a $\text{Si}(100) (1 \times 1) :: 2\text{H}$ dihydride surface and is self-limiting at room temperature. Therefore, hydrogen plays an important role on this technique, having a potential to grow Si at low temperature.

1. INTRODUCTION

Atomic-layer epitaxy (ALE) is a thin film growth technique which contains a self-limiting process and realizes a single atomic layer controllability. This technique has been mainly applied to III-V and II-VI compound film growth so far, because alternating layer deposition of each element leads to the self-limiting process, and then ALE. Thus, relatively few results¹⁾ have been reported on IV group ALE. In a previous paper²⁾, we proposed a method for achieving Si ALE using ArF Eximer laser on $\text{Si}(100) 2 \times 1$ from Si_2H_6 , which has a potential to grow Si epitaxial film at low temperature. In this paper, we emphasize the role of hydrogen on this growth technique and discuss the key steps involved in it, describing recent results obtained in further investigation by electron energy loss spectroscopy (EELS) and reflection high energy electron diffraction (RHEED).

2. EXPERIMENTAL PROCEDURE

The EELS spectrometer consisting of a

cylindrical-mirror analyzer (CMA) and RHEED system used in these experiments were contained in a ultra-high-vacuum chamber with a base pressure of 2×10^{-10} Torr. EELS spectra were obtained using primary beam energies (E_p) of 75 and 100 eV, and RHEED patterns were observed with a 17kV electron beam and a glancing angle of approximately 2° . The Si substrates were $6 \times 20 \times 0.4$ mm in dimension cut from p-type $3-4 \Omega\text{-cm}$ $\text{Si}(100)$ wafers. The samples, cleaned by the heating process up to 1275K, exhibited 2×1 reconstructions typical of $\text{Si}(100) 2 \times 1$ surfaces. 99.98% pure Si_2H_6 was introduced on the sample surfaces through a gas doser for the adsorption and growth experiments.

3. EXPERIMENTAL RESULTS AND DISCUSSION

A typical EELS spectrum from a clean $\text{Si}(100) 2 \times 1$ surface with a primary energy (E_p) of 100 eV is shown in curve (a) of Figure 1. The assignments are based upon the first report by Rowe and Ibach. E_1 and E_2 are associated with bulk-band transitions while $\hbar\omega_s$ and $\hbar\omega_p$ are due to surface and bulk plasmons, respectively. S_1 peak has been ascribed to the dangling-bond states

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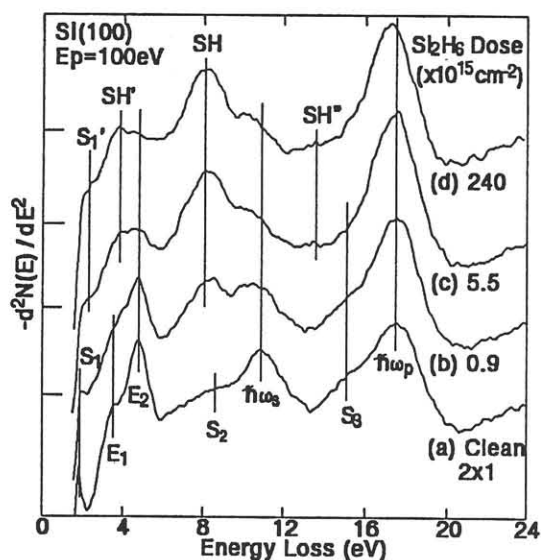


Figure 1. EELS spectra from a Si(100)2x1 surface after exposure at 300K to a Si₂H₆ dose of (a) 0, (b) $9 \times 10^{14} \text{ cm}^{-2}$, (c) $5.5 \times 10^{15} \text{ cm}^{-2}$, (d) $2.4 \times 10^{17} \text{ cm}^{-2}$.

in the 2x1 reconstruction surface, and transitions S₂ and S₃ are associated with back-bond states.

Increasing the exposure of a Si(100) clean surface to Si₂H₆ at 300K, features of SH, SH', and SH'' appeared in the EELS spectra (Figure 1). The SH peak originates due to Si-H bond. The origin of SH'' peak is not clear. However, this might be attributed to the transition from -14.7 eV peak³⁾ in the He II energy distribution curve (EDC) obtained from a Si(100) (1x1)::2H dihydride surface. In the early stage of Si₂H₆ adsorption (curve (b)), the S₁ peak decreased drastically, and the half-order RHEED diffraction spots decreased in intensity with respect to the integral spots. After exposing the Si(100)2x1 surface to saturation doses ($240 \times 10^{15} \text{ cm}^{-2}$) of Si₂H₆ at 300K, the RHEED patterns became sharp 1x1. The S-H peak position of 8 eV in the corresponding EELS spectrum (curve (d)) is assigned to the dihydride phase⁴⁾. The spectrum is also in good agreement with the previously reported spectrum⁵⁾ obtained from the dihydride surface formed using atomic-H. These results strongly suggest that the initial adsorption sites are the dangling-bonds

and the dimer bonds are gradually ruptured with increasing exposure. In the saturation dose of Si₂H₆, uniform dihydride phase is formed at room temperature. Therefore, the SH' is also considered to be attributed to the dihydride surface structure. The SH peak intensities, normalized using the intensity at the saturation coverage, are plotted as a function of Si₂H₆ dose in Figure 2. Even after the nearly saturation exposure of a $5.5 \times 10^{15} \text{ cm}^{-2}$ dose, about fifty times as large as this dose was further required to obtain the 1x1 RHEED pattern, implying that the maximum number of the adsorption layer is controlled to be almost one. Therefore, the hydrogen, terminating on the dihydride surface, tends to prohibit multiple layer adsorption of Si. Figure 3 shows side views of a Si(100) surface in the Si₂H₆ adsorption process described above.

After reaching the saturation coverage, the sample surfaces annealed at progressively higher temperatures for 12 or 15 minutes (Figure 4). Heating the samples up to 615K resulted in the reduction of the SH peak intensity and shift up to 8.7 eV from 8.0 eV. This surface corresponds primarily to Si(100) (2x1)::H monohydride surface⁴⁾ (Figure 3 (d)). Si(100) surfaces exposed to atomic-H at above 575K for 1 min⁶⁾ or at 525K for 1 min³⁾ have been reported to exhibit also mainly

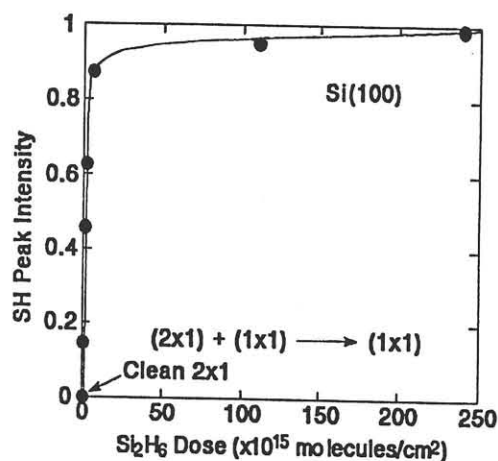


Figure 2. Change in the SH EELS peak intensity and the RHEED pattern as a function of Si₂H₆ dose. These SH intensities are normalized using the intensity at the saturation coverage.

monohydride phase. Therefore, changes in the SH peak intensities between curves (c) and (d) in Figure 4 signals the evolution of hydrogen from the surface with mainly monohydride phase. This process limits epitaxial growth rate in a $\text{Si}_2\text{H}_6/\text{Si}(100)$ system. Figure 5 shows EELS spectra obtained from $\text{Si}(100)$ surfaces exposed to Si_2H_6 at various temperatures. At 725K, Si was grown epitaxially evidenced by the retention of the initial clean-surface EELS spectra together with the observation of a 2x1 RHEED pattern. Considerable hydrogen still remains on the surfaces grown at under 575K (curves (d) and (e)).

The ArF-laser irradiation with a single 20 ns pulse is found to be very effective to evolve the hydrogen. Figure 6 shows EELS spectra obtained after exposing a $\text{Si}(100)2\times 1$ surface at 300K to Si_2H_6 and then ArF-laser irradiating it with 1 pulse at 300K or 525K. While the sample was heated

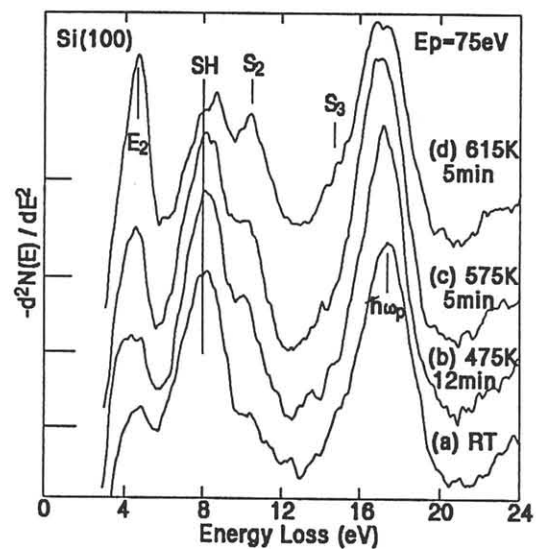


Figure 4. EELS spectra from (a) a Si_2H_6 -exposed $\text{Si}(100)$ surface, and from a Si_2H_6 -exposed $\text{Si}(100)$ surface following (b) a 12 min anneal at 475K, (c) a 5 min anneal at 575K and (d) a 5 min anneal at 615K.

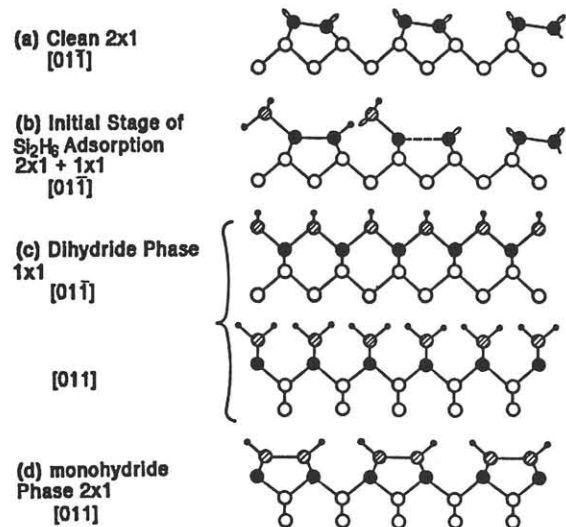


Figure 3. Side views of a $\text{Si}(100)$ surface in the Si_2H_6 -adsorption and annealing process; (a) clean 2x1, (b) initial stage of Si_2H_6 adsorption, (c) dihydride phase formation after Si_2H_6 saturation exposure, (d) monohydride phase formation after annealing the dihydride surface at around 600K for 5 min. Perpendicular directions to the side views are indicated below each title.

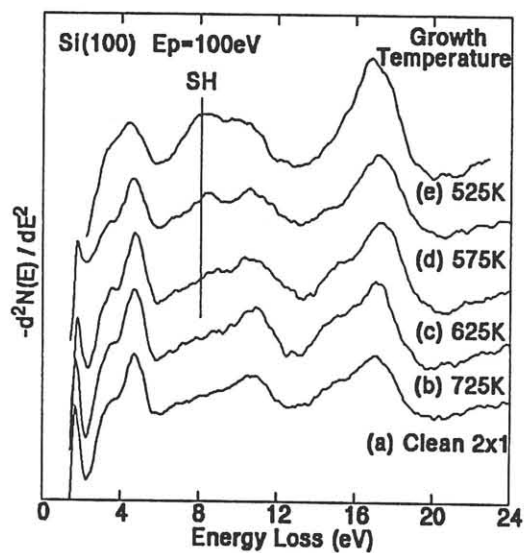


Figure 5. EELS spectra from (a) a $\text{Si}(100)2\times 1$ surface, after exposing a $\text{Si}(100)2\times 1$ surface to a Si_2H_6 dose of $1\times 10^{16} \text{ cm}^{-2}$ at (b) 725K, (c) 625K, (d) 575K and (e) 525K.

at 525K, 1 pulse 120 mJ cm^{-2} ArF-laser irradiation evolved the hydrogen completely (curve (d)). The reestablishment of the initial clean-surface EELS spectra, together with the observation of a 2×1 RHEED pattern, indicates that monolayer of Si was epitaxially grown. The rise in temperature during the 20 ns ArF-laser irradiation with a power density of 120 mJ cm^{-2} is calculated to be 300K with the order of $1 \mu\text{s}$ decay time. Thus, even if this irradiation is repeated, for example, at around 1 Hz, the time-averaged temperature rise is negligible. Complete hydrogen evolution from the monohydride phase using the pulsed ArF-laser means the second layer is ready to start growing. If the surface is again exposed to the Si_2H_6 saturation dose, dihydride phase, which provides the second layer of Si, will be formed. These two key steps are expected to lead to low temperature Si ALE.

4. SUMMARY AND CONCLUSIONS

After exposing a $\text{Si}(100)2 \times 1$ clean surface to Si_2H_6 of $2.5 \times 10^{17} \text{ cm}^{-2}$ dose, a uniform dihydride

surface is formed. This adsorption process is found to be essentially self-limiting at room temperature. Hydrogen evolution from a monohydride phase converted from the dihydride phase is a rate limiting process for Si epitaxy in a $\text{Si}_2\text{H}_6/\text{Si}(100)$ system. In order to evolve the hydrogen effectively from the Si_2H_6 exposed surface, at least 725K thermal heating is required. On the other hand, pulsed ArF-laser irradiation is very effective to evolve the hydrogen keeping the average surface temperature almost constant. The combined technique of the self-limiting adsorption of Si_2H_6 on $\text{Si}(100)2 \times 1$ and ArF-laser irradiation is suggested to provide low temperature Si ALE.

5. REFERENCES

- 1) Y.Takahashi, Y.Sese, and T.Urisu; Extended Abstracts (The 36th Spring Meeting; The Japan Society of Applied Physics and Related Societies, 1989)p.254.
- 2) Y.Suda, D.Lubben, T.Motooka and J.E.Greene, to be published in J. Vac. Sci. Technol., Sep./Oct.(1989).
- 3) Ciraci, R.Butz, E.M.Oelling and H.Wagner, Phys. Rev. **B30**, 711(1984).
- 4) Y.Suda, D.Lubben, T.Motooka and J.E.Greene, to be published in J. Vac. Sci. Technol.
- 5) H.H.Madden, Surf. Sci. **105**, 129(1981).
- 6) J.A.Schaefer, F.Stucki, J.A.Anderson, G.J.Lapeyre and W.Göpel, Surf. Sci. **140**, 207(1984).

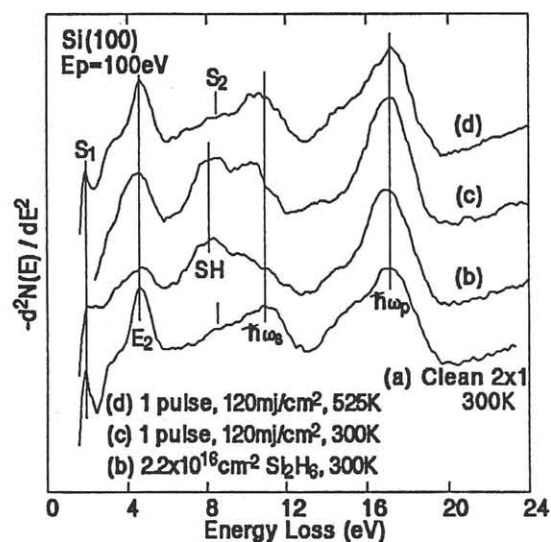


Figure 6. EELS spectra from (a) a clean $\text{Si}(100) 2 \times 1$ surface, (b) after exposing a $\text{Si}(100)2 \times 1$ surface at 300K to Si_2H_6