

Surface Hydrogen Effects on Ge Surface Segregation During Gas Source MBE

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Using RHEED intensity oscillations, temperature dependence of Ge surface segregation during Si-GSMBE was studied, and it was found that surface hydrogen may act as a growth-controlling surfactant. Comparison with solid source growth results suggests that hydrogen significantly suppresses the Ge segregation. Segregation kinetics were examined through simulation studies, and the results indicate that the addition of surface hydrogen to the system inhibits segregation due to a lowering of the Gibbs heat of segregation.

1. Introduction

The epitaxial Si/Si_{1-x}Ge_x interface is of considerable research interest because of the possibility of tailoring the band gap of Si_{1-x}Ge_x based heterostructures. As a consequence, there has been a great deal of activity in this field to understand the parameters which govern the growth process in the Si_{1-x}Ge_x system, not only for technological advances but also for fundamental studies of strained layer epitaxy.

Silicon gas source molecular beam epitaxy (Si-GSMBE) is widely recognized as a subject of rapidly growing importance. Growth from gaseous hydride sources provides a clean growth process and pioneers new processing technologies. What remains unclear, however, is how the presence of hydrogen in Si-GSMBE will influence the growth processes.

Measurement of reflection-high-energy-electron diffraction (RHEED) intensity oscillations has been shown by the present authors¹⁾ to be an excellent probe for high resolution studies of Ge surface segregation during Si-GSMBE growth of Si/Si_{1-x}Ge_x. The Ge surface segregation can be monitored *in-situ* via a gradual growth rate change at the heterointerface which is caused by an increasing hydrogen desorption rate due to the presence of surface Ge at growth temperatures below 600°C.

In this paper we report an investigation of surface hydrogen effects on Ge surface segregation during gas source MBE growth of Si/Si_{1-x}Ge_x heterostructures. Using the novel RHEED technique, temperature studies of Ge surface segregation during GSMBE have been conducted and reveal that the segregation is significantly suppressed when compared to growth from solid sources at substrate temperatures below 600°C.

2. Experimental Procedure

All experiments were carried out in a purpose-built MBE system which has been modified to accommodate the hydrides of both Si and Ge (SiH₄, Si₂H₆, GeH₄). Si(001) substrates were prepared by a modified Shiraki etch and the resulting thin surface oxide film was thermally removed. Details of the Si substrate preparation and the RHEED arrangement have been reported elsewhere.²⁾

The growth experiments proceeded as follows: After the buffer layer deposition, 50 Å of Si_{1-x}Ge_x was grown at 560 °C. The substrate was then flashed to 800°C for 2 min to promote surface relaxation as well as remove surface hydrogen. Following annealing, the substrate temperature was lowered to the overlayer growth temperature, and the Si layers were grown on the Si_{1-x}Ge_x alloy while the RHEED intensity oscillations were monitored.

3. Results and Discussion

Figure 1 shows RHEED intensity oscillations of the specular beam obtained in the [010] azimuth during Si overlayer growth on Si_{0.93}Ge_{0.07} at 560°C using a Si₂H₆ beam flux of 3.4×10^{15} molecules cm⁻²s⁻¹. It is apparent from the figure that the period of the oscillations increased gradually during the Si overlayer growth. The gradual frequency change indicates a decreasing growth rate (GR) as Si is deposited and following ~ 20 MLs of Si overlayer growth the GR approaches the typical Si on Si homoepitaxial value observed at 560°C.

The change in growth rate (Δ GR) during Si overlayer growth below 600°C can be attributed to a *gradual* decrease in the number of centres from which hydrogen can desorb easily. These centres can be equated with Ge surface atoms resulting from Ge segregation effects which are known to occur in

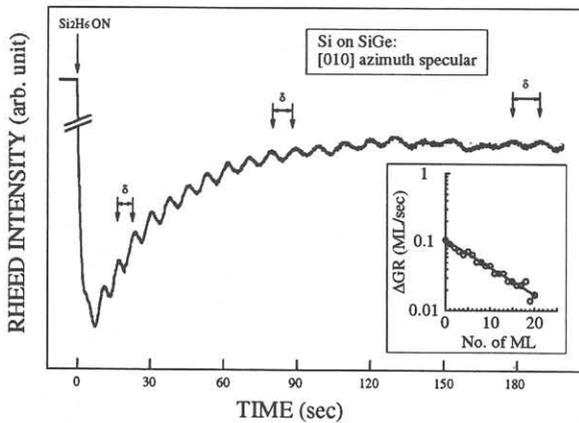


Fig. 1. RHEED intensity oscillations observed during Si growth on $\text{Si}_{1-x}\text{Ge}_x$ at a substrate temperature of 560°C . The inset shows the decrease of the growth rate change and the fit from Eq. (1) (solid line).

$\text{Si}/\text{Si}_{1-x}\text{Ge}_x$ heterostructures.

Assuming that the Ge segregation occurs in the equilibrium regime, we have previously modelled Si on $\text{Si}_{1-x}\text{Ge}_x$ growth behaviour using a mass balance segregation model¹⁾ of the form

$$N_{\text{Ge}} = B \cdot \exp\left(-\frac{x}{\lambda}\right) \quad (1)$$

where N_{Ge} is the surface Ge concentration, λ is the segregation decay length, and B is a constant. The model assumes that the observed ΔGR is proportional to the surface Ge concentration, *i.e.*

$$\Delta\text{GR} = \alpha \cdot N_{\text{Ge}} \quad (2)$$

Given that in the temperature range studied ($T_g < 600^\circ\text{C}$) the growth rate-limiting step is hydrogen desorption from the growing surface, this assumption appears to be reasonable and is consistent with recent TPD studies of deuterium from $\text{Si}_{1-x}\text{Ge}_x$ by Ning and Crowell.³⁾ They have found that deuterium desorption proceeds via first-order desorption kinetics with respect to Ge surface concentration. As shown in the inset in Fig. 1, it was revealed that the simple exponential form, Eq. (1), fits well the observed ΔGR decay.

The good agreement between model and data implies that by analyzing the gradual recovery in detail, we can achieve, with monolayer resolution, an *in-situ* investigation of dynamical aspects of the Ge segregation.

Using this technique, we have investigated the influence of the substrate temperature on the Ge surface segregation in GSMBE. Figure 2 shows the temperature dependence of the Ge segregation profiles. Here, a Si overlayer was again grown on $\text{Si}_{0.93}\text{Ge}_{0.07}$ alloy at different temperatures; $T_g = 560, 540,$ and 520°C . In Fig. 2, the normalized Ge surface concentrations are calculated from the GR change of the Si overlayer at each substrate temperature using Eq. (2). For comparison, the results of Si/Ge growth from conventional solid source MBE (SSMBE) by Nakagawa and Miyao⁴⁾ are also shown (solid lines). In their experiments, Si overlayers were deposited on three monolayers of Ge and the segregation profiles were examined *ex-situ* by XPS. For comparison with

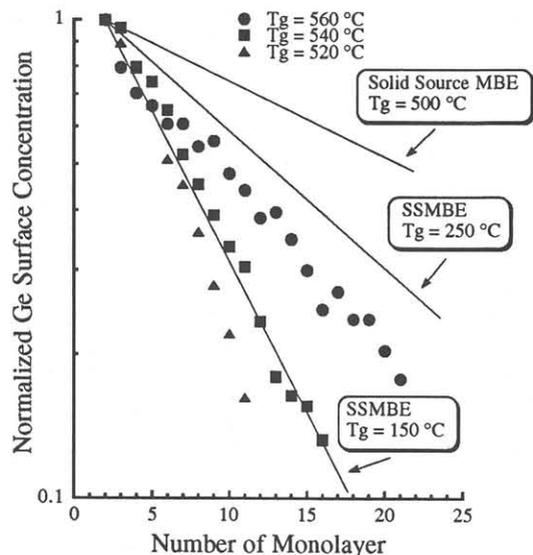


Fig. 2. Temperature dependence of the Ge segregation during GSMBE. The data for solid source MBE (solid lines) follow Nakagawa and Miyao (ref. 4).

our results, their data are normalized to the same concentration range. It appears in the figure that the Ge segregation is drastically suppressed in GSMBE compared to SSMBE. This change in the segregation behaviour may be understood in terms of the recently reported "surfactant" effect of surface hydrogen,^{5,6)} which is produced by the dissociation of Si_2H_6 and GeH_4 and passivates the surface during growth when $T_g < 600^\circ\text{C}$. Several authors⁵⁻⁷⁾ have pointed out the important role of surface hydrogen in providing sharp interfaces. Surface hydrogen may influence the segregation kinetics during the growth of $\text{Si}/\text{Si}_{1-x}\text{Ge}_x$ heterostructures, resulting in the suppression of Ge surface segregation.

To elucidate the detailed mechanism of the hydrogen "surfactant" effect, we have conducted simulation studies of Ge surface segregation during Si-GSMBE. Following Fukatsu *et al.*⁸⁾ and Godbey and Ancona,⁹⁾ the two-site exchange model¹⁰⁾ as depicted in Fig. 3 was employed. For solid source MBE growth, Fukatsu *et al.*⁸⁾ have estimated the kinetic barrier, E_1 , and the Gibbs heat of Ge surface segregation, ΔG_{seg} , to be 1.63 ± 0.1 and 0.28 ± 0.1 eV, respectively, from XPS results⁴⁾ and SIMS data.

There are two possible mechanisms of reducing the segregation decay length: by increasing E_1 , or by reducing ΔG_{seg} . Increasing the kinetic barrier, E_1 , results in kinetically-limited segregation.¹⁰⁾ During low temperature GSMBE using a constant beam flux, the GR changes continually due to Ge segregation effects. Thus, under appropriate conditions growth may occur in both the equilibrium and kinetically-limited regimes. With a large E_1 , segregation is kinetically-limited at a sufficiently fast GR, but during GSMBE of Si on $\text{Si}_{1-x}\text{Ge}_x$, as growth proceeds N_{Ge} decreases and therefore the GR becomes slower until segregation enters the equilibrium regime. This non-constant GR effect results in the observation of two segregation regimes in a single profile significantly altering the segregation decay curve. This gives rise to

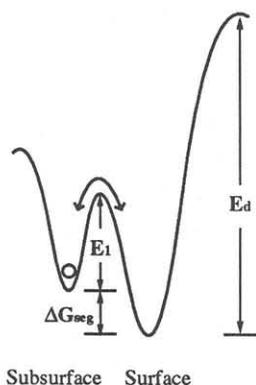


Fig. 3. Schematic energy diagram of the two-site-exchange model.

quite dissimilar experimental and theoretical segregation profiles.

On the other hand, simulation results found by decreasing the Gibbs heat of segregation, ΔG_{seg} , are shown in Fig. 4. Here ΔG_{seg} values are adjusted to best fit the experimental segregation decay length at each temperature. As seen in the figure, the simulated segregation reproduces the observed profiles quite satisfactorily giving $\Delta G_{seg} = 0.19, 0.15,$ and 0.13 eV at 560, 540, and 520°C, respectively.

From the simulation studies of segregation profiles, it appears that Ge segregation is suppressed during the GSMBE growth of Si/Si_{1-x}Ge_x heterostructures due to the reduction of Gibbs heat of segregation, ΔG_{seg} , rather than due to kinetic effects. This is a reasonable conclusion considering that it is the energetics of surface dangling bonds on the growing surface which give rise to ΔG_{seg} .^{11,12)} During GSMBE growth, surface adsorbed hydrogen passivates these dangling bonds, reducing ΔG_{seg} and making the surface inert for the interchange between Si and Ge atoms. In the temperature range studied here, the coverage of surface hydrogen significantly changes as a function of substrate temperature.¹³⁾ In this case it is likely that segregation occurs freely at bare surface sites, while little or no segregation occurs on hydrogen covered sites. In this sense, the observed reduced ΔG_{seg} is assumed to be an *average* or *effective* Gibbs energy over all the surface sites. It is the change in the surface hydrogen coverage with substrate temperature, then, which results in the observed strong temperature dependence in the segregation profiles.

4. Conclusion

We have investigated Ge surface segregation during Si-GSMBE by *in-situ* growth rate measurements using RHEED intensity oscillations. Temperature studies reveal that the Ge surface segregation can be minimized below 600°C in Si-GSMBE. This is indicative of a crucial role of surface hydrogen, leading to a more precise control of heterointerfaces. Simulated Ge segregation profiles using the two-site exchange model indicate that the "surfactant" effect of hydrogen results from the reduction of the effective Gibbs heat of segregation during growth rather than from kinetic effects.

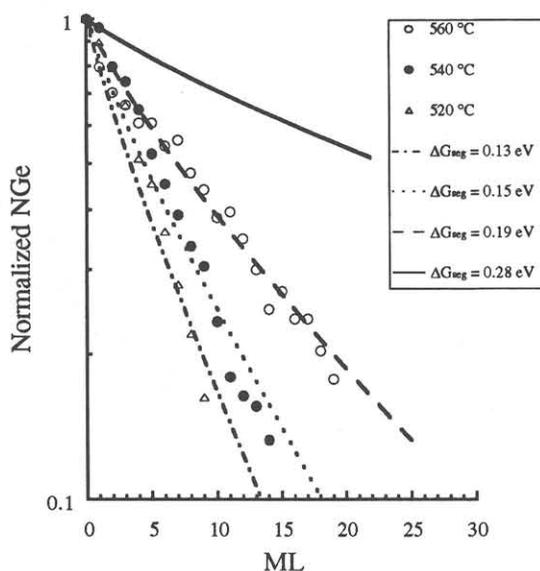


Fig. 4. Simulation results of the segregation profiles found by reducing the Gibbs heat of segregation, ΔG_{seg} : The solid line is simulated at 560°C with $\Delta G_{seg} = 0.28$ eV (corresponding to solid source MBE), the dashed line at 560°C with $\Delta G_{seg} = 0.19$ eV, the dotted line at 540°C with $\Delta G_{seg} = 0.15$ eV, and the dot-dashed line at 520°C with $\Delta G_{seg} = 0.13$ eV. $E_1 = 1.63$ eV is the same for all the profiles.

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