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Anomalous Temperature Dependence of Ge Surface Segregation in Si-MBE

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Ge surface segregation on Si(100) and Si(111) substrates during silicon molecular beam epitaxy was studied using X-ray photoelectron spectroscopy. The Ge segregation phenomena increased to maxima at around 450°C in the case of the Si(100) substrates and at around 650°C in the case of the Si(111) substrates. Segregation decreased above these temperatures. These reverse temperature dependences enable not only good crystallinity of the heteroepitaxial layer, but also abrupt heterointerface. The incorporation coefficients for Si(111) were much larger than those for Si(100), which is well explained by a model based on surface migration.

1. Introduction

There are reports on novel devices with Si-Ge heterostructures, which enable the modification of the band structures.[1,2] Since these devices utilize the band discontinuity at the Si-Ge interfaces, the abruptness of the interface is very important for obtaining high device performance. Molecular beam epitaxy (MBE) has been recognized as a powerful tool for achieving abrupt interfaces. This is because the growth temperature of MBE is sufficiently low that the effects of thermal diffusion and intermixing at the heterointerface are thought to be avoided. Recent studies, however, have shown that Ge segregates to the epitaxial surface during the MBE growth of Si/Ge/Si structures.[3] This phenomenon inhibits the formation of abrupt heterointerfaces.

To gain insight into a solution to this problem, the authors performed detailed studies on the temperature dependence of the Ge surface segregation. As a result, the authors have discovered a temperature range in which Ge surface segregation is inversely effected by increased temperature.

This paper describes these new findings on Ge surface segregation, which enables abrupt heterointerfaces with good crystallinity of the heteroepitaxial layer.

2. Experimental

The silicon MBE apparatus used was a Vacuum Generator V80 system with a base pressure of about $2x10^{-11}$ Torr. Si(100) and Si(111) substrates were precleaned by chemical treatment and a protective thin oxide layer was formed. Next, the oxide layer was sublimated at 850 °C for 20 min. to obtain a clean surface. The substrate temperature was then lowered to 700 °C and a buffer layer of 500 Å was grown to prepare a clean, smooth surface. After that, about 3 monolayers (ML) of germanium atoms were deposited on the silicon surface. Then, silicon layers with various thicknesses were overgrown on the germanium deposited surface at various substrate temperatures.

The surface concentration of Ge atoms segregated on the overgrown silicon surfaces was measured using X-ray photoelectron spectroscopy (XPS). Since the escape depth of the electrons is less than 10 Å, the XPS signals of Ge(2p) electrons observed here mainly came from the Ge atoms segregated on the Si surfaces. The XPS signal height of the Ge atoms relative to that of the Si was confirmed to be proportional to the Ge surface concentration.

3. Experimental Results

3.1 Surface segregation of Ge on Si(100) and Si(111) substrates during MBE

The segregated Ge concentration on the grown Si surfaces was measured. The results are summarized as a function of the Si thickness in Fig.1 (a) and (b) for Si(100) and Si(111) cases, respectively. The Si deposition rate was kept at 1 Å/s for the measurements. The segregated Ge concentration decreases with the Si deposition thickness. The highest temperature in the experiments was 750 °C. The desorption coefficient even at this temperature was quite low at about $3x10^{-3}$ $min.^{-1}$ Therefore, the decrease in the Ge surface concentration caused by the Si growth is due to Ge incorporation in the growing Si films and not due to thermal desorption. In the case of the Si(100) substrate, the segregation phenomenon increases as the growth temperature is increased from 150°C to 450°C, and decreases above 450°C.

Since the segregated Ge concentration does not decrease exponentially as seen in the figures, at least a second order reaction, as well as a first order reaction, is necessary to describe the Ge incorporation phenomenon in silicon. The incorporation phenomenon of Ge during MBE can be described by use of the conservation relation. That is,

$$dC_s/dx = J/l - K_1 (C_s)^1 - K_2(C_s)^2 - D\, C_s/l,$$

where Cs (atoms/cm^2) is the Ge surface concentration, x (cm) is the thickness of the silicon growth layer, J (atoms/cm^2s) is the incident flux of a Ge beam, l (cm/s) is the incident flux of a Si beam, Ki (i=1,2) is the incorporation coefficient of the i-th order reaction and D (1/s) is the desorption coefficient. The second order reaction means that Ge atoms are incorporated as pairs during Si overgrowth. Under this experimental condition, J and D are 0. The calculated results that matched the experimental ones best were obtained at K_1/K_2 = 0.37, which did not change so much with growth temperature or substrate orientation. The growth temperature dependence of the first order incorporation coefficient, K_1, is presented in Fig.2. The incorporation coefficient on the Si(100) is lower than that on the Si(111), meaning that the surface segregation is greater on the Si(100). As the growth temperature increases, the incorporation coefficients decrease to the minimum at around 450 °C for the Si(100) and then increase above 450°C. At the growth temperature of 750°C, the segregation becomes quite small and is almost the same as that at 250°C. In the case of the Si(111)

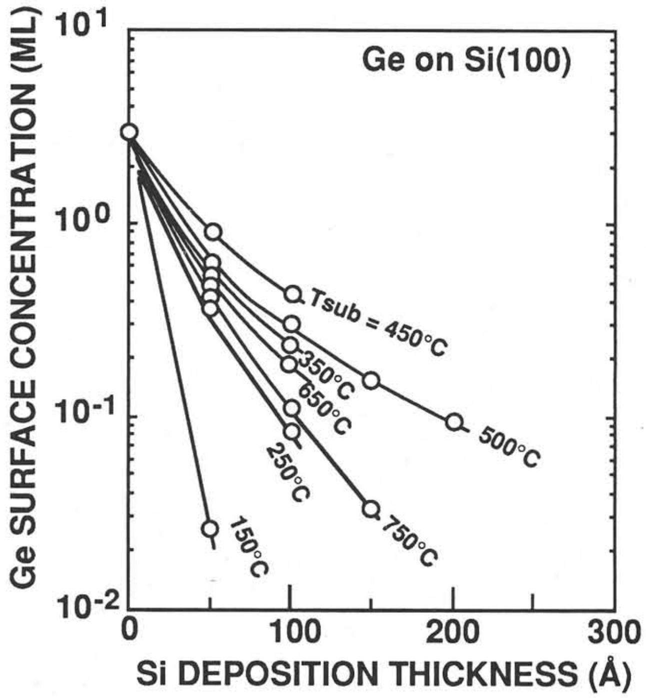

Fig.1(a) Segregated Ge concentration on Si(100) surface as a function of Si deposition thickness. Deposition rate was fixed at 1 Å/s.

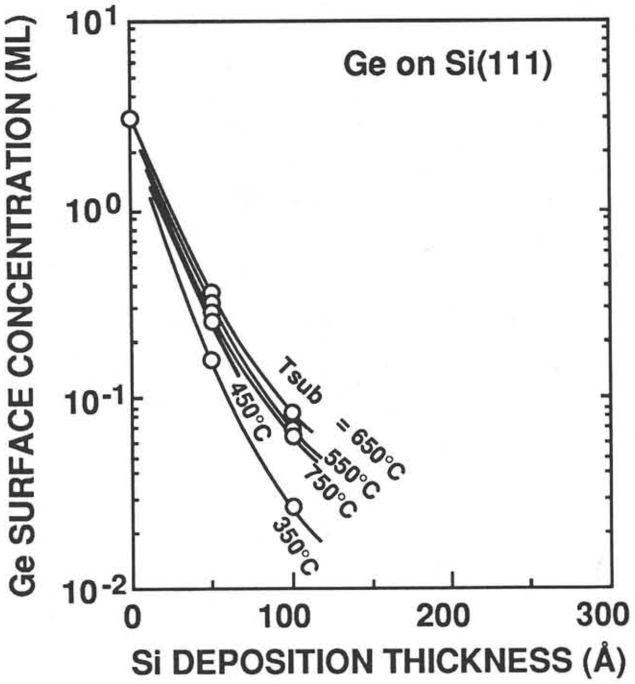

Fig.1(b) Segregated Ge concentration on Si(111) surface as a function of Si deposition thickness. Deposition rate was fixed at 1 Å/s.

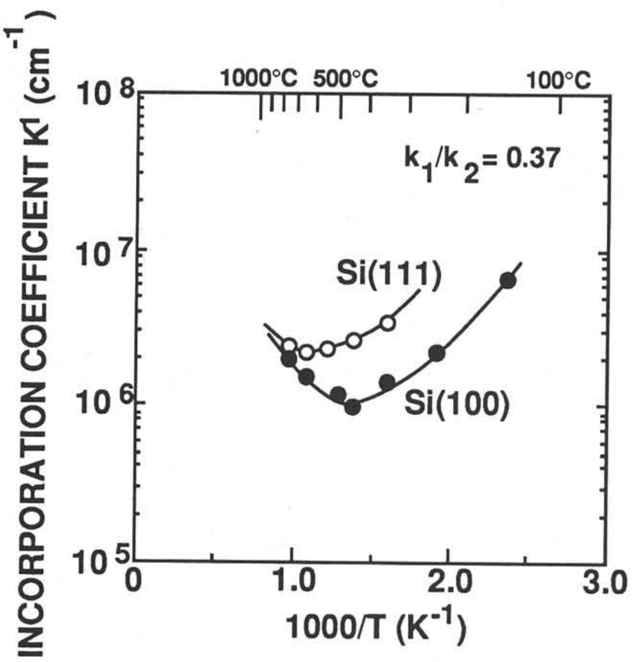

Fig.2 Incorporation Coefficients of the first order reaction as a function of growth temperature.

substrate, the incorporation phenomenon has its minimum at around 650°C. It should be pointed out that this behavior for Si(100) and Si(111) cannot be explained using a simple thermal activation process.

In order to confirm the reverse temperature dependence, Ge profiles after Si overgrowth were measured using secondary ion mass spectrometry (SIMS). As shown in Fig.3, the Ge peak of the sample prepared on a Si(100) substrate at 650°C is about 1.5 times larger than the one for 450°C. Moreover, the tail of the Ge signal of the former sample is much smaller than that of the latter one.

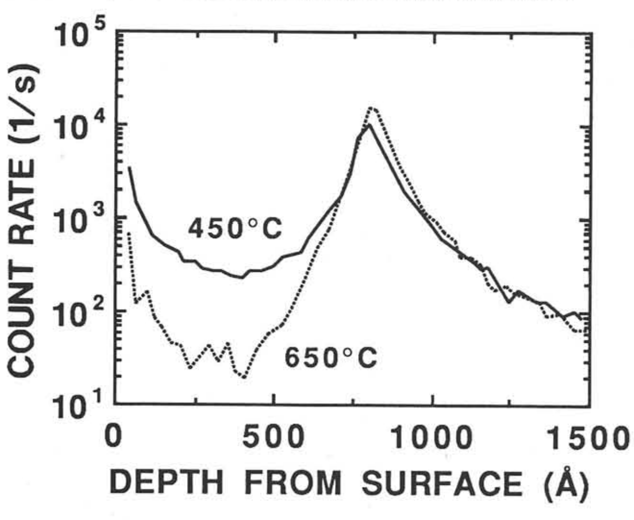

Fig.3 Depth profiles of Ge atoms in samples prepared at 450°C and 650°C, as measured by SIMS.

3.2 Surface segregation dependence on Si deposition rate

Since it is thought that surface segregation is due to surface migration as we reported previously,[4] surface segregation is expected to be suppressed when Si atoms are deposited much faster than the Ge surface atoms migrate. The dependence of the Ge segregation phenomenon on the Si deposition rate at 500°C is shown in Fig.4. The increase in the deposition rate causes a decrease in the segregated Ge concentration.

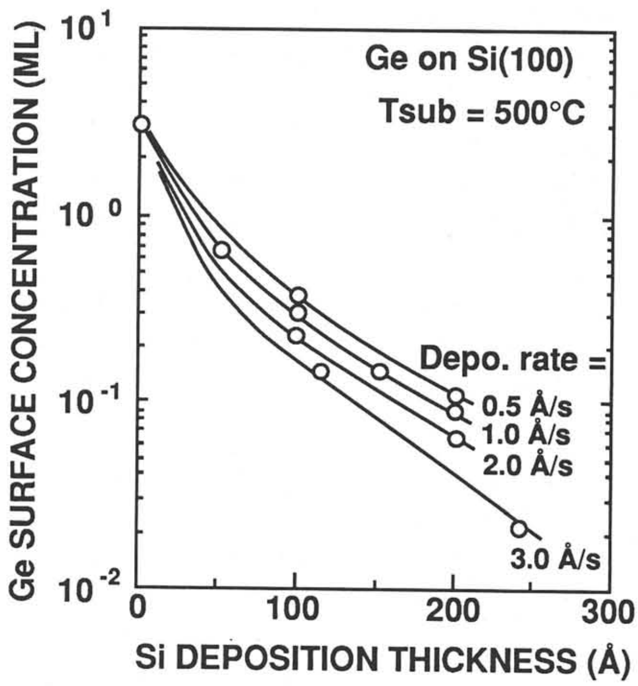

Fig.4 Dependence of Ge surface segregation on Si deposition rate.

4. Discussion

The incorporation coefficient of Ge on Si(100) is lower than that for Ge on Si(111), as shown in Fig.3. The authors have proposed a model based on surface migration concerning dopant surface segregation.[4] That is, the segregation of atoms is caused by the atoms climbing over surface steps formed by silicon deposition, and the probability of the atoms climbing over the surface steps is larger with greater surface migration. It is well known that MBE growth takes place on Si(100) at lower temperatures than on Si(111), implying that surface migration is larger on Si(100) than on Si(111). This is thought to be the reason larger segregation was observed for Si(100). The model also predicts that the segregation phenomenon depends on the Si deposition rate. That is, when Si atoms are deposited before Ge atoms climb over surface steps, the phenomenon is thought to be suppressed. This prediction agrees with the experimental results.

As the growth temperature is decreased below around 450°C, the segregation decreases. A heterostructure prepared by low-temperature growth, however, is not suitable for device application due to the deterioration of the crystallinity. On the other hand, high-temperature growth above around 600°C provides the good crystallinity, as is known well. Besides, the new finding of the reverse temperature dependence of Ge surface segregation enables a reduction in the segregation above 600°C, as discovered in the present experiments. When the growth temperature is higher than 800°C, however, the desorption coefficient is larger than $1x10^{-2}$ min. and a significant amount of Ge atoms sublimate during the MBE process. Thus, thermal desorption creates the limits of the temperature range for obtaining an abrupt heterointerface with good crystallinity.

The mechanism that explains the peak in the surface segregation phenomenon is not yet known . Detailed analysis is now under way.

5. Summary

Ge surface segregation on Si(100) and Si(111) substrates during MBE was studied using X-ray photoelectron spectroscopy. Temperature ranges above 450°C for Si(100) substrates and above 650°C for Si(111) substrates were found in which Ge surface segregation decreased with increased temperature. This new finding enables heterostructures with abrupt interface and good crystallinity.

The substrate orientation dependence of Ge surface segregation is explained by a model based on surface migration. The model is supported by the results of the influence of the Si deposition rate on the Ge segregation.

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