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# Activation Energy of $Si_{1-x}Ge_x$ Epitaxial Growth Rate Using $Si_2H_6$ and $GeH_4$

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Epitaxial growth of $Si_{1-x}Ge_x$ on Si(100) or Ge(100) substrates has been studied in the Ge fraction range of 0 to 1 by ultrahigh vacuum chemical vapor deposition (UHV-CVD) using $Si_2H_6$ and $GeH_4$ gases. The growth rates plotted in Arrhenius coordinates show that the growth rates in surface-reaction controlled regime, which correspond to $H_2$ desorption rates from $Si_{1-x}Ge_x$ surface, have the same value at 1100℃ for all Ge fractions. These activation energies decrease linearly with increasing in the Ge fractions. The activation energy dependence suggests that Si and Ge atoms on $Si_{1-x}Ge_x$ surface affect their bonds to H atoms mutually.

## 1. Introduction

$Si_{1-x}Ge_x$ alloy is one of the attractive device materials, because the band gap can be controlled with changing its Ge fraction. $Si_{1-x}Ge_x$ epitaxial films on Si substrates are expected to be applied to the base layers of high speed bipolar transistors[1]. Low temperature (below approximately 800℃) has been needed for the $Si_{1-x}Ge_x$ epitaxial growth on Si in order to suppress misfit dislocation generation[2],[3]. Ultrahigh vacuum chemical vapor deposition (UHV-CVD) has realized the heteroepitaxy with good film quality around 600℃, reducing $O_2$ and $H_2O$ partial pressures[4]-[7]. The gases with high activity such as $SiH_4$, $Si_2H_6$ and $GeH_4$ have been used for UHV-CVD.

In the low-temperature deposition regime, $Si_{1-x}Ge_x$ growth rates are thought to be limited by $H_2$ desorption from the surface[4],[7]. A dramatic acceleration in the $Si_{1-x}Ge_x$ growth rate at the low temperature has been reported with the introduction of $GeH_4$ to a deposition source gas, compared to the growth of Si alone[4]-[7]. It is speculated that Ge atoms at the growth interface serve as desorption centers which results in a lowering of the activation energy for $H_2$ desorption from the growing layer and the dramatic increase in the growth rate[4]. In particular, the reduction in the activation energy with the introduction of $GeH_4$ has been confirmed by the studies on the $Si_{1-x}Ge_x$ growth rate[7] and thermal desorption spectroscopy (TDS)[8].

However, there remain several questions; how the activation energy changes with changing Ge fraction in the wide range, and what is the role of Ge atoms in the $H_2$ desorption process? In this study, we concentrate the dependence of the $Si_{1-x}Ge_x$(100) growth rate on Ge fraction. The $Si_{1-x}Ge_x$ deposition has been performed using $Si_2H_6$ and $GeH_4$ by UHV-CVD at the Ge fractions from 0 to 1. Moreover, the activation energy in the low-temperature deposition regime has been studied. We show for the first time that the growth rates in the surface reaction controlled regime have the same value at 1100℃ for all Ge fractions and the activation energy decrease linearly with increasing Ge fraction. We present the kinetics of $H_2$ desorption from $Si_{1-x}Ge_x$ surface.

## 2. Experimental

The UHV-CVD system used in this study included a stainless steel growth chamber, a water cooled jacket and separate nozzles for process gases. A turbo-molecular pump reduced the base pressure to $1.5 \times 10^{-9}$ Torr and the gas pressure below $10^{-3}$ Torr during the growth. Si(100) substrates were precleaned with a chemical solution ($NH_4OH : H_2O_2 : H_2O = 1 : 6 : 20$) to form a protective thin $SiO_2$ layer before loading into the growth chamber. The $SiO_2$ layer on the Si surface was evaporated by a thermal process of 850℃ for 5 min. Pure $Si_2H_6$ and $GeH_4$ were used for the growth. The growth rates were estimated by the cross-sectional transmission electron microscopic (TEM) observation of $Si_{1-x}Ge_x$ alternating layers grown at various temperatures. In order to avoid misfit dislocation generation, the Si-rich and Ge-rich $Si_{1-x}Ge_x$ alloys were grown on Si(100) and Ge(100), respectively.

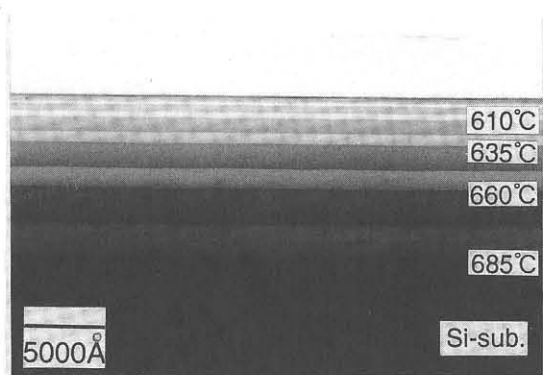Fig. 1. Cross-sectional TEM micrograph of $Si_{1-x}Ge_x$ alternating layers. Dark bands are composed of $Si_{0.9}Ge_{0.1}$ and lighter bands are $Si_{0.98}Ge_{0.02}$. These layers are grown at temperatures between 535-685°C for 180 seconds.

## 3. Growth rate dependence on Ge fraction

Figure 1 shows one of the cross-sectional TEM images of $Si_{0.98}Ge_{0.02}/Si_{0.9}Ge_{0.1}$ alternating layers with changing growth temperatures, which were observed to estimate the growth rates. Dark bands are composed of $Si_{0.9}Ge_{0.1}$ and lighter bands are $Si_{0.98}Ge_{0.02}$, both of which are grown in the 685-535°C temperature range. Arrhenius plots of the $Si_{1-x}Ge_x$ growth rates for various Ge fractions are shown in Fig. 2. Both $Si_2H_6$ and $GeH_4$ flow rates are constant at each Ge fractions. Each curve can be divided into two parts. In the higher temperature region, the $Si_{1-x}Ge_x$ growth rate does not strongly

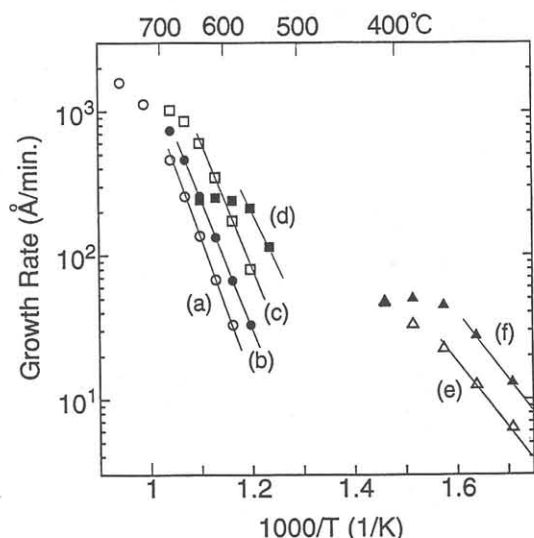depend on the growth temperature, indicating that the growth is controlled by the adsorption of $Si_2H_6$ or $GeH_4$ at the growing surface. On the other hand, in the lower temperature region, the growth rate is very sensitive to the growth temperature. In this temperature range, the $Si_{1-x}Ge_x$ growth is considered to be controlled by the $H_2$ desorption from the surface[7]. Therefore, it is a reasonable assumption that the $Si_{1-x}Ge_x$ growth rate in this deposition regime exhibits the $H_2$ desorption rate from $Si_{1-x}Ge_x$ surface.

The $H_2$ desorption rates from $Si_{1-x}Ge_x$ surface in an Arrhenius plot for various Ge fractions are shown in Fig. 3. Once $H_2$ is desorbed from Si or Ge atom, the film thickness is considered to increase by $a_x/4$ followed by $Si_2H_6$ or $GeH_4$ adsorption, where $a_x$ is the lattice constant of $Si_{1-x}Ge_x$. Therefore, the desorption rates were estimated with $Si_{1-x}Ge_x$ growth rates in the low-temperature regime. Furthermore, the desorption rates can be extended to the higher temperature region, which are shown as solid lines. It is noted that all the lines in the Arrhenius plot cross at the same point (A Point: approximately 1100°C). This reason shall be discussed further below. The reduction in the activation energies has been observed with increasing in the Ge fractions. Figure 4 shows the relationship between the Ge fractions and the activation energies. The activation energy decreased linearly with the Ge fraction increasing, indicating the activation energy of $Si_{1-x}Ge_x$ has the average value between those of Si ($E_S$) and Ge ($E_G$), which are calculated at 43 and 18 kcal/mol, respectively.



Fig. 2. Arrhenius plots of $Si_{1-x}Ge_x$ growth rates. (a), (b), (c), (d), (e), and (f) are for x=0, 0.02, 0.1, 0.4, 0.9, and 1, respectively. Each curve is divided into two parts: The growth is controlled by $Si_2H_6$ or $GeH_4$ gas adsorption in the higher temperature range, and by surface reaction in the lower temperature range.
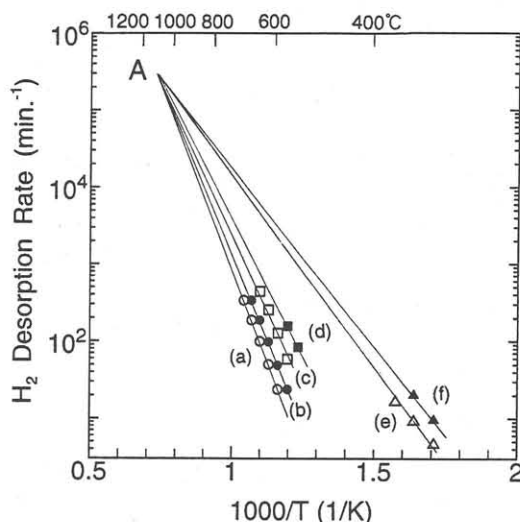


Fig. 3. Arrhenius plots of $H_2$ desorption rates from $Si_{1-x}Ge_x$ surfaces. The desorption rates are shown as solid lines, which were estimated by $Si_{1-x}Ge_x$ growth rates in the low temperature range, and extended to higher temperature. (a), (b), (c), (d), (e), and (f) are for x=0, 0.02, 0.1, 0.4, 0.9, and 1, respectively.

From above results, the $H_2$ desorption rate from $Si_{1-x}Ge_x$ surface $(DR_x)$ can be given as a function of the Ge fraction (X) by the following equations:

$$DR_x = DR_0 exp(-E_x(1/RT - 1/RT_0)), \quad (1)$$
$$E_x = E_S - (E_S - E_G)X, \quad (2)$$

where $DR_0$ is the desorption rate at A point $(3 \times 10^5$ min.$^{-1})$, $E_x$ is the activation energy of the desorption rate from $Si_{1-x}Ge_x$, R is the gas constant, T is the absolute temperature, $T_0$ is the absolute temperature at A point (1373K). Using these formulas, the $H_2$ desorption rate can be estimated at any Ge fraction and at any growth temperature.
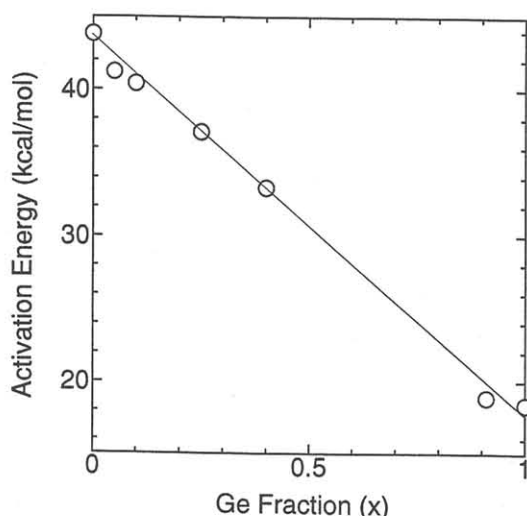


Fig. 4. Relationship between Ge fraction and activation energy of $H_2$ desorption rate from $Si_{1-x}Ge_x$ surface.

## 4. Kinetics of $H_2$ desorption

The result that the activation energy of $H_2$ desorption from $Si_{1-x}Ge_x$ has the average value disagrees with the model[4] that the surface Ge atoms act as a $H_2$ desorption center. This model requires the same activation energy from $Si_{1-x}Ge_x$ as that from Ge. Another model can be derived from this result that the surface Si and Ge atoms affect their bonds to H atoms mutually. Since surface Ge atoms are expected to weaken the Si-H bonds, and surface Si atoms are expected to strengthen Ge-H bonds, Si and Ge atoms on $Si_{1-x}Ge_x$ surface are thought to have the same activation energy. This is the reason that $Si_{1-x}Ge_x$ has the average activation energy between Si and Ge surfaces. This continuous reduction in the activation energy agrees the TDS study, where it is confirmed that the $H_2$ desorption peak continues to shift to lower temperature with increasing in Ge fraction[8]. The reason that all the desorption rates are quite equal at 1100℃ can be explained as follows.

The desorption rates from the Si and Ge atoms on $Si_{1-x}Ge_x$ surface are also expected to have the same value, which is the medium between those from Si and Ge surfaces. Since the $H_2$ desorption rates from Si and Ge surfaces are equal at 1100℃, and the desorption rate from $Si_{1-x}Ge_x$ has the medium value between them, the desorption rate from $Si_{1-x}Ge_x$ must be the same value at 1100℃ at any Ge fraction.

## 5. Conclusions

$Si_{1-x}Ge_x$ (100) growth rate in the surface-reaction controlled regime, which corresponds to $H_2$ desorption rate from $Si_{1-x}Ge_x$ surface, and its activation energy were investigated in the Ge fraction range of 0 to 1. The $Si_{1-x}Ge_x$ epitaxial growth was performed using $Si_2H_6$ and $GeH_4$ gases by UHV-CVD. The $H_2$ desorption rates are quite equal to one another at 1100℃ for all the Ge fractions. The activation energy from $Si_{1-x}Ge_x$ decreases linearly with increasing in the Ge fraction. From these results, the $H_2$ desorption rate is successfully formulated as a function of the Ge fraction. The activation energy dependence on the Ge fraction suggests that Si and Ge atoms on $Si_{1-x}Ge_x$ surface affect their bonds to H atoms mutually.

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