Ge composition in $Si_{1-x}Ge_x$ films grown from SiH_2Cl_2/GeH_4 precursors

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A simple model for the Ge composition in $Si_{1-x}Ge_x$ films grown from SiH_2Cl_2/GeH_4 precursors is developed on the basis of adsorption and desorption kinetics for the intermediate temperature range (600 °C$<T<$900 °C). For this system, the solid phase composition of Ge, x, is related to the gas phase composition ratio of the two source gases, G, by $x^2/(1-x)=\text{constant}\times G$, which contrasts with the conventional relationship, $x/(1-x)=\text{constant}\times G$, that is known for SiH_4/GeH_4 chemical vapor deposition. The proportionality constant depends not only on temperature but also on pressure. The model compares well with the experimental data in the literature. © *2000 American Institute of Physics.* [S0021-8979(00)04819-2]

I. INTRODUCTION

$Si_{1-x}Ge_x$ epitaxial layers have been extensively investigated because of their potential application to heterojunction bipolar transistors and other heterojunction devices. Much work has been carried out to clarify the kinetics of the epitaxial growth with SiH_4 and GeH_4.[1–3] For this SiH_4/GeH_4 system, it is well known that H_2 desorption is the rate-limiting step at low temperature but hydride adsorption controls the rate process at high temperature.[1,3] Although chlorosilanes are frequently used for $Si_{1-x}Ge_x$ film growth, very few studies have examined the details of kinetics of the growth with SiH_2Cl_2 and GeH_4.[4–8]

One of the major quantities of interest in the deposition is the composition of Ge in the grown film and its dependence on growth conditions. For the SiH_4/GeH_4 system, several authors found that the film composition did not change with temperature.[1,3] They attributed this behavior to weak temperature dependence of the reactive sticking coefficient ratio of silane to germane that they claim to determine the temperature dependence of the germanium content. This ratio has been found to be constant over a limited range of the germanium content x. A generally accepted relationship between the germanium fraction and the gas phase composition is[3]

$$\frac{x}{1-x}=m\frac{P_{GeH_4}}{P_{SiH_4}}, \tag{1}$$

where P_{SiH_4} and P_{GeH_4} are the partial pressures of silane and germane, respectively, and the constant m is between 2 and 5 depending on individual experiment. Equation (1) has successfully been used to describe various experimental data for the SiH_4/GeH_4 system. However, the correlation is limited to a given set of experiments. Moreover, Eq. (1) is not appropriate for the SiH_2Cl_2/GeH_4 system.

Much less is known when the silicon source gas is SiH_2Cl_2. For this SiH_2Cl_2/GeH_4 system, Ito *et al.*[4] assumed that the reaction order for SiH_2Cl_2 adsorption is twice that for GeH_4 adsorption. Their model for the germanium content in the grown film is quite satisfactory but it is not applicable to other experimental data, as was the case with the SiH_4/GeH_4 system. For a rather thorough kinetic model with SiH_2Cl_2/GeH_4 system, the reader is referred to the work of Hierlemann *et al.*[5]

When the process temperature is high enough, i.e., $T>$900 °C, the adsorption is a rate-limiting step and purely adsorption-limited growth can be observed.[9] In this case, the majority of the surface sites are free and deposition is limited by the sticking coefficient of the arriving molecules. On the other hand, if the temperature is lower than about 600 °C, the deposition is desorption limited. In this case, the desorption of H_2 and Cl_2, and HCl controls the growth rate. In the intermediate temperature range of 600–900 °C, therefore, adsorption and desorption steps are equally important and both kinetics should be considered to completely describe the deposition behavior.

In this article, we consider both adsorption and desorption kinetics and present a simple model for the Ge composition in $Si_{1-x}Ge_x$ films for the SiH_2Cl_2/GeH_4 system for the intermediate temperature range (600 °C$<T<$900 °C). The model is applicable to all chemical vapor deposition systems regardless of the microstructure of the film.

II. MODEL AND COMPARISON WITH EXPERIMENTS

From the gas phase, molecular species of SiH_2Cl_2 and GeH_4 can adsorb onto the surface in two ways. The species can adsorb in its original or in decomposed form, i.e., $SiCl_2$ and GeH_2. Both cases should be considered to completely describe the film growth. According to computational chemistry calculations[10,11] and experiments,[12] the most probable decomposition pathways of SiH_2Cl_2 and GeH_4 are $SiH_2Cl_2 \rightarrow SiCl_2+H_2$ and $GeH_4 \rightarrow GeH_2+H_2$, respectively. Therefore, we can write the reaction scheme as

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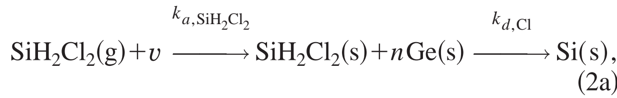
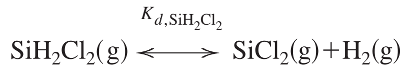
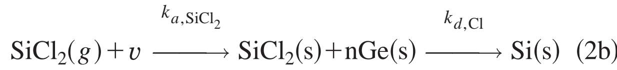


$$SiH_2Cl_2(g)+v \xrightarrow{k_{a,SiH_2Cl_2}} SiH_2Cl_2(s)+n\text{Ge}(s) \xrightarrow{k_{d,Cl}} Si(s), \quad (2a)$$

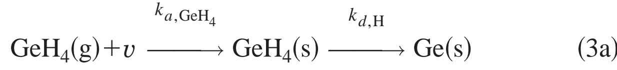


$$SiH_2Cl_2(g) \overset{K_{d,SiH_2Cl_2}}{\longleftrightarrow} SiCl_2(g)+H_2(g)$$

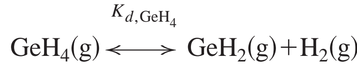


$$SiCl_2(g)+v \xrightarrow{k_{a,SiCl_2}} SiCl_2(s)+n\text{Ge}(s) \xrightarrow{k_{d,Cl}} Si(s) \quad (2b)$$

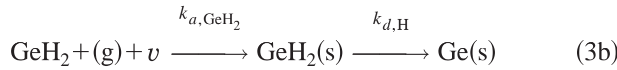
for dichlorosilane and



$$GeH_4(g)+v \xrightarrow{k_{a,GeH_4}} GeH_4(s) \xrightarrow{k_{d,H}} Ge(s) \quad (3a)$$



$$GeH_4(g) \overset{K_{d,GeH_4}}{\longleftrightarrow} GeH_2(g)+H_2(g)$$



$$GeH_2+(g)+v \xrightarrow{k_{a,GeH_2}} GeH_2(s) \xrightarrow{k_{d,H}} Ge(s) \quad (3b)$$

for germane, where v is the vacant site on the surface. We assume in Eqs. (2) and (3) that H_2 and HCl adsorption is negligible compared with that for Si and Ge adspecies. There are two possible ways for an adsorbed Cl atom on a Si atom to desorb from the surface. One is the direct desorption by breaking bond with Si and the other is the desorption from a Ge atom by migrating to the neighboring Ge site due to the high activation barrier involved in desorbing directly from the Si atom.[13] These are competing processes and the mediation of Ge in Cl desorption in reactions (2a) and (2b) can be viewed as an additional pathway to direct desorption from Si. In this light, n may be allowed to take values between 0 and 1, which reflects the extent to which the Cl desorption contributes through migrating to neighboring Ge site.

The Ge composition in the film is given by

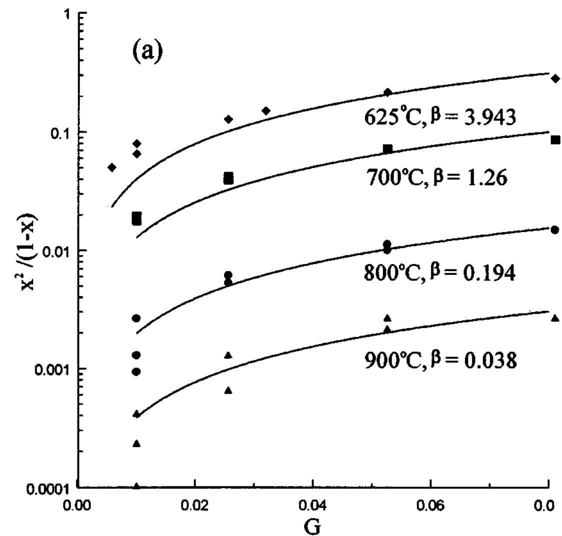
$$x=\frac{R(\text{Ge})}{R(\text{Si})+R(\text{Ge})}, \quad (4)$$

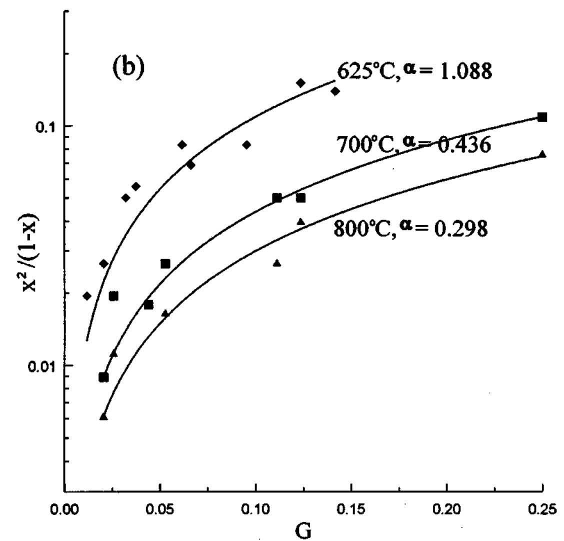
where R(Si) and R(Ge) are the growth rates of Si and Ge sites, respectively. Based on the kinetic steps of Eqs. (2) and (3) and the fact that the Ge on the surface mediates the Cl desorption from the adsorbed Si, R(Si), and R(Ge) can be derived to give

$$R(\text{Si})=(k_{a,SiH_2Cl_2}k_{d,Cl}+mK_{d,SiH_2Cl_2}k_{a,SiCl_2}k_{d,Cl}/[H_2]) \times(1-\phi)P_{SiH_2Cl_2}[\text{Ge}]^n, \quad (5)$$

$$R(\text{Ge})=(k_{a,GeH_4}k_{d,H}+m'K_{d,GeH_4}k_{a,GeH_2}k_{d,H}/[H_2]) \times(1-\phi)P_{GeH_4}, \quad (6)$$

where $1-\phi$ is the total concentration of the vacant sites, m and m' ($0<m,m'<1$) are the fractional contributions of decomposition-mediated adsorption for Si and Ge, respectively, and [Ge] is the composition of Ge in films, which is x. As the Cl desorption occurs through two pathways, $k_{d,Cl}$ can be given by





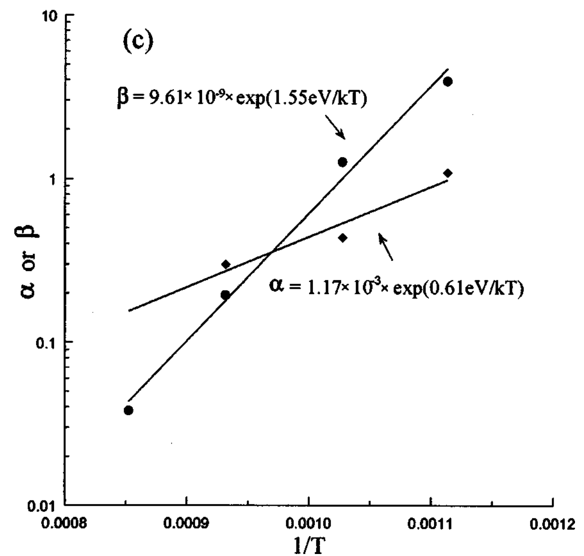


FIG. 1. Best fitting parameters of α and β are chosen at each temperature for (a) high ($P>200$ Torr) and (b) low ($P<20$ Torr) deposition pressure assuming $n=1$. Arrhenius plots for the activation energies are given in (c).

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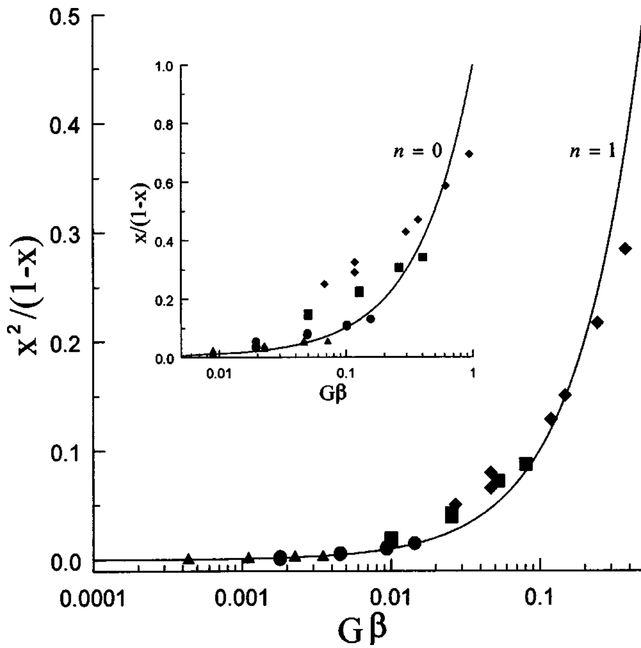

FIG. 2. Comparison of Eq. (10) (solid curve) with the literature data for SiH_2Cl_2 high pressure chemical vapor deposition: ♦: 625 °C, ■: 700 °C, ●: 800 °C, and ▲: 900 °C. Data points are from Refs. 15 (625 °C); 16, 17 (700–900 °C); and 18 (625–900 °C). Inset shows the best-fit result of the conventional model.

$$k_{d,\mathrm{Cl}}=(1-n)k_{d,\mathrm{Cl}}(\mathrm{Si})+nk_{d,\mathrm{Cl}}(\mathrm{Ge}), \tag{7}$$

where $k_{d,\mathrm{Cl}}(\mathrm{Si})$ is the rate constant for Cl desorption from Si site and $k_{d,\mathrm{Cl}}(\mathrm{Ge})$ is for Cl desorption from Ge site.

It is cumbersome to use the above rate expressions for each set of experiments due to many fitting parameters. Instead, we investigate two limiting cases for low and high deposition pressures.

First, in the low pressure regime where the pressure is smaller than about 10 Torr, gas-phase chemistry is insignificant such that a considerable amount of molecular species of SiH_2Cl_2 and GeH_4 adsorb onto the surface without decomposition due to the long mean free path.[10,11,14] In this case, m and m' should be close to zero. Therefore, insertion of Eqs. (5) and (6) into Eq. (4) and rearrangement gives

$$\frac{x^{n+1}}{1-x}=\alpha G, \tag{8}$$

where G is the gas phase composition ratio $(=P_{\mathrm{GeH}_4}/P_{\mathrm{SiH}_2\mathrm{Cl}_2})$ and α is defined as

$$\alpha\equiv\frac{k_{a,\mathrm{GeH}_4}k_{d,\mathrm{H}}}{k_{a,\mathrm{SiH}_2\mathrm{Cl}_2}k_{d,\mathrm{Cl}}}. \tag{9}$$

The value of α may be different for different reactor geometry, source-gas composition, surface condition, and so on.

When the pressure is relatively high, i.e., higher than about 100 Torr, source gases should decompose by collision due to very short mean free path.[10,11] In this case, decomposed species adsorb on the surface so that m and m' should be close to unity. In this high pressure regime, therefore, we have

$$\frac{x^{n+1}}{1-x}=\beta G, \tag{10}$$

where β is defined as

$$\beta\equiv\frac{K_{d,\mathrm{GeH}_4}k_{a,\mathrm{GeH}_2}k_{d,\mathrm{H}}}{K_{d,\mathrm{SiH}_2\mathrm{Cl}_2}k_{a,\mathrm{SiCl}_2}k_{d,\mathrm{Cl}}}. \tag{11}$$

Some data available in the literature involving SiH_2Cl_2 and GeH_4[6,15–21] have been analyzed to test Eqs. (8) and (10). The best-fit parameters α and β have been chosen at each temperature assuming $n=1$ and an Arrhenius plot has been made using these values at various temperatures to determine the activation energy. Physically, an n value of unity means that one Ge atom is involved for the Cl desorption and every Cl atom should migrate to the neighboring Ge site to desorb. This is quite an overestimation and n may lie between 0 and 1. It is possible to adjust the value of n to fit the individual experiment. Figure 1 shows the procedure taken to obtain α and β as a function of temperature and pressure. To find the region where the predominant adspecies is $SiCl_2$, lower pressure data have been successively added in the analysis with the result that the data for the pressure higher than 200 Torr can well be represented by

$$\beta=9.61\times10^{-9}\exp(1.55\,\mathrm{eV}/kT),\quad P>200\ \mathrm{Torr}. \tag{12}$$

The calculated values based on Eqs. (10) and (12) are compared with the experimental data[15–18] in Fig. 2. Also shown in the inset of the figure is the representation by the conventional relationship, for which $n=0$, i.e., no Ge involvement in Cl desorption. It is clear from the figure that the conventional relationship does not represent the data well. Although there is some deviation for the lowest temperature data (highest $G\beta$), the comparison shows a very good correlation for $n=1$.

The literature data not included in Fig. 2 are those for the pressure lower than 20 Torr. The same analysis as in the above gives

$$\alpha=1.17\times10^{-3}\exp(0.61\,\mathrm{eV}/kT),\quad P<20\,\mathrm{Torr}. \tag{13}$$

The same type of comparison as in Fig. 2 is shown in Fig. 3 for the low pressure data,[6,15,19–21] where Eqs. (8) and (13) have been used for the calculated values. The comparison is also satisfactory although it is not as good for the lowest temperature data.

In the high pressure region where the main adspecies is $SiCl_2$, the activation energy of the decomposition reaction should largely be responsible for the energetic of β. The activation energy of dichlorosilane is reported to be 3.33 eV[10] and that of germane is 2.32 eV.[11] Therefore, the energy difference due to the decomposition reactions included in β is 1.01 eV. Since the adsorption energy difference is about 0.1 eV[4] and the desorption energy different between $k_{d,\mathrm{Cl}}(\mathrm{Ge})$ and $k_{d,\mathrm{H}}(\mathrm{Ge})$ is about 0.48 eV,[13] the combined value of 1.59 eV is obtained. This value is very similar to the (1.55 eV) determined for the high pressure region [Eq. (12)].

Similarly, the overall activation energy difference of α (0.61 eV) determined for the low pressure region is very close to 0.58 eV, which is the combined value of adsorption energy difference and desorption energy difference.

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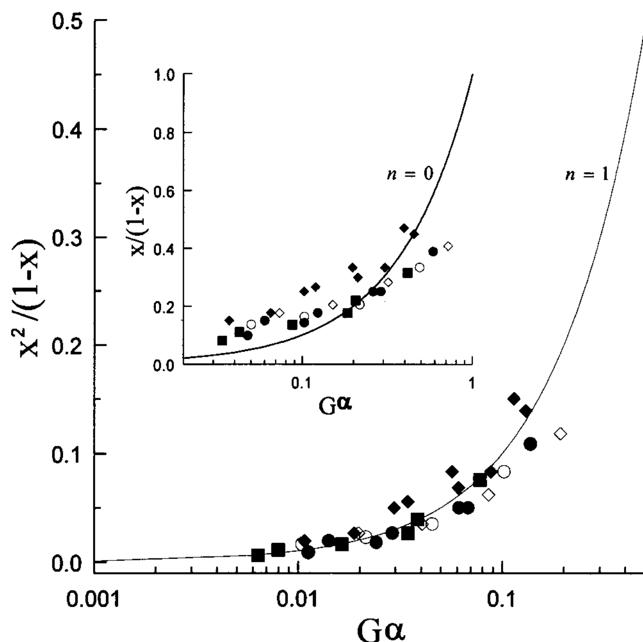

FIG. 3. Comparison of Eq. (8) (solid curve) with the literature data for SiH_2Cl_2 low pressure chemical vapor deposition: ◆: 625 °C, ◇: 650 °C, ●: 700 °C, ○: 750 °C, ■: 800 °C. Data points are from Refs. 6 (625 °C); 15 (625 °C); 19 (650–800 °C); and 20–21 (625, 700–800 °C). Inset shows the best-fit result of the conventional model.

In our model, we only consider the data for 600 °C$<T<$900 °C to justify our analysis. Otherwise, the model no longer takes hold and desorption-limited kinetics should be considered. In fact, the data for low temperature ($T\leqslant$600 °C) cannot be represented well by the model. As much less is known for the desorption kinetics of the SiH_2Cl_2/GeH_4 system and it depends heavily on the specific deposition condition, further study is needed to develop a general model for this lower temperature region. The data obtained for $T>$900 °C can be described by the conventional adsorption-limited model.

III. CONCLUDING REMARK

In summary, we have shown that simple adsorption and desorption kinetics together with Ge mediation of Cl desorption from the surface yield a relationship for Ge composition for SiH_2Cl_2/GeH_4 system, covering 600 °C$<T<$900 °C and full pressure range. The model is very simple and easily applicable to most experiments.

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