

# Modeling growth of $\text{Si}_{1-x}\text{Ge}_x$ epitaxial films from disilane and germane

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A Langmuir–Hinshelwood-type kinetic model is developed for modeling growth of silicon–germanium alloys from disilane and germane on Si substrates. Gas source molecular beam epitaxy was employed to grow  $\text{Si}_{1-x}\text{Ge}_x$  films at various germanium fractions,  $x$ , in the alloy and at different temperatures. The model correctly predicts experimentally observed and previously reported behavior; a monotonic decrease with germanium fraction at higher substrate temperatures (700 °C) and a maximum in the growth rate for lower temperatures (550 °C and 610 °C).

## I. INTRODUCTION

$\text{Si}_{1-x}\text{Ge}_x$  epitaxial layers have been grown by chemical vapor deposition in recent years.<sup>1–8</sup> These alloys are of interest because of their potential for improvement of circuit speed in conjunction with silicon technology.<sup>9</sup> Experimental observations of the growth rate and its dependence on the experimentally accessible parameters have been confusing. In the first hot wall reactor study<sup>2</sup> of the growth at 550 °C and 1 mTorr pressure, it was found that the layer growth rate increased monotonically with increasing Ge fraction,  $x$ , in the alloy up to  $x=0.2$ . The enhancement in the alloy growth rate was attributed to a lowering of the activation energy for hydrogen desorption from the surface germanium atoms when compared to pure silicon. Other investigators,<sup>4</sup> using silane and germane in an ultrahigh vacuum chemical vapor deposition (UHV-CVD) system, have observed a temperature dependent maximum in the plot of growth rate with Ge mole fraction in the temperature range 577–665 °C at pressures of close to 1 mTorr. A molecular beam study<sup>10</sup> using beams of disilane and germane at a substrate temperature of 630 °C showed a decrease in the growth rate as  $x$  increased. A growth model<sup>3</sup> based on homogeneous gas phase reactions was proposed but the authors concluded that an increase in the rate of hydrogen desorption from the alloy surface could not explain the experimental results at 625 °C.

Robbins *et al.*<sup>7</sup> studied epitaxial  $\text{Si}_{1-x}\text{Ge}_x$  alloy growth from a  $\text{H}_2\text{-SiH}_4\text{-GeH}_4$  mixture in an UHV cold wall reactor ( $\sim 0.1$  Torr pressure) at substrate temperatures of 610, 650, and 750 °C. Their results show that at 610 °C there is a distinct peak in the growth rate as a function of Ge fraction  $x$  in the alloy, and that at 750 °C the rate of growth decreases monotonically with Ge fraction  $x$ . Based on their experimental observations, Robbins *et al.* have proposed a macroscopic chemical model of the growth process. This model is qualitatively successful in predicting the temperature and the mole fraction dependencies of the

growth rate. In two recent articles Jang and Reif further explore the experimental dependence of the growth rate on temperature<sup>11</sup> and deposition pressure and gas phase hydrogen.<sup>12</sup>

In this manuscript, we present experimental data for epitaxial growth of  $\text{Si}_{1-x}\text{Ge}_x$  from  $\text{Si}_2\text{H}_6$  and  $\text{GeH}_4$  under UHV conditions. We extend the basic ideas of the Robbins *et al.* model to growth from germane and disilane and critically compare the model predictions with experimental data.

## II. EXPERIMENT

The experiments were conducted in a two-chamber RIBER 32 gas source molecular beam epitaxy system with a vacuum load lock.<sup>13</sup> The background pressure was in the  $10^{-9}$  Torr range. The  $\text{Si}_2\text{H}_6$  flow rate was fixed at 7 sccm. The  $\text{GeH}_4$  flow rate was varied between 0.5 and 3 sccm. The system pressure during growth was observed to be between  $1 \times 10^{-5}$  and  $5 \times 10^{-5}$  Torr depending on the  $\text{GeH}_4$  flow rate. The substrates used were B-doped Si(100). The grown  $\text{Si}_{1-x}\text{Ge}_x$  alloy compositions were determined using double crystal x-ray diffractometry. The average growth rates were obtained from measuring thickness using selective epitaxy with an  $\text{SiO}_2$  mask. For some layers, a weight change method was also adopted to characterize the thickness.<sup>10</sup> Details regarding the apparatus and measurement techniques have already been published.<sup>13</sup>

## III. DEVELOPMENT OF THE MODEL

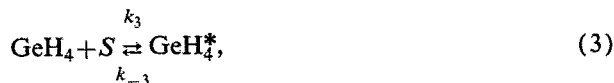
The heterogeneous growth model discussed here can essentially be represented by the following set of equations.

Disilane adsorption and decomposition:



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Germane adsorption and decomposition:



Hydrogen adsorption and desorption:



In these equations asterisked species are activated complexes and "S" represents a vacant surface site. If we make the simplifying assumption that at steady state the concentration of the surface intermediates (the "starred" species) is constant, we have the following for the concentration of the reactive surface intermediates: From Eqs. (1) and (2), we get

$$[\text{SiH}_3^*]^2 = k_1 P_{\text{Si}_2\text{H}_6} C_v^2 / (k_{-1} + k_2), \quad (6)$$

where  $C_v$  is the concentration of vacant sites on the surface and is given by

$$C_v = C_t - (C_{\text{SiH}_3^*} + C_{\text{GeH}_4^*} + C_{\text{H}^*}). \quad (7)$$

In Eq. (7),  $C_t$  is the total surface site concentration. Rearranging,

$$C_v = C_t(1 - \theta_S - \theta_G - \theta_H), \quad (8)$$

where  $\theta_S (= C_{\text{SiH}_3^*}/C_t)$  is the fractional surface coverage by  $\text{SiH}_3^*$ , and  $\theta_G$  and  $\theta_H$  are similarly defined for the other reactive surface species  $\text{GeH}_4^*$  and  $\text{H}^*$ .<sup>14</sup> Rewriting Eq. (6) in terms of the fractional surface coverages, we have

$$[\text{SiH}_3^*]^2 = [k_1 / (k_{-1} + k_2)] P_{\text{Si}_2\text{H}_6} \times [C_t^2 (1 - \theta_S - \theta_G - \theta_H)^2], \quad (9)$$

or dividing both sides by  $C_t^2$  we get

$$\theta_S^2 = [k_1 / (k_{-1} + k_2)] P_{\text{Si}_2\text{H}_6} (1 - \theta_S - \theta_G - \theta_H)^2. \quad (10)$$

Using a similar procedure, one obtains equations for the fractional surface coverage of hydrogen and  $\text{GeH}_4^*$  to be

$$\theta_G = [k_3 / (k_{-3} + k_4)] P_{\text{GeH}_4} (1 - \theta_S - \theta_G - \theta_H), \quad (11)$$

$$\theta_H^2 = (k_5 / k_{-5}) P_{\text{H}_2} (1 - \theta_S - \theta_G - \theta_H)^2. \quad (12)$$

Simultaneous solution of Eqs. (10), (11), and (12) gives, for the silicon and germanium deposition rates,

$$R_{\text{Si}} = k_2 A (1 + A + B + C), \quad (13)$$

$$R_{\text{Ge}} = k_4 B / (1 + A + B + C), \quad (14)$$

where the three constants  $A$ ,  $B$ ,  $C$  are a combination of the partial pressure and the rate constants of the individual steps as given below:

$$A = [k_1 / (k_{-1} + k_2)]^{1/2} (P_{\text{Si}_2\text{H}_6})^{1/2}, \quad (15)$$

$$B = [k_3 / (k_{-3} + k_4)] P_{\text{GeH}_4}, \quad (16)$$

$$C = (k_5 / k_{-5})^{1/2} (P_{\text{H}_2})^{1/2}. \quad (17)$$

The total growth rate is assumed to be a linear sum of the individual growth rates for silicon and germanium. Adding Eqs. (13) and (14) gives us<sup>15</sup>

$$R_{\text{tot}} = (k_2 A + k_4 B) / (1 + A + B + C). \quad (18)$$

We can further expand  $k_{-5}$  as a product of a preexponential constant and a term depending on the energy of activation difference for hydrogen desorption from silicon and germanium,

$$k_{-5} = \nu \{ [(1-x) \exp(-E_{\text{SiH}}/kT) + x \exp(-E_{\text{GeH}}/kT)] \}. \quad (19)$$

In the above equation,  $\nu$  is the preexponential factor, estimated to be of the order of  $8 \times 10^{11}$  reciprocal seconds.  $E_{\text{SiH}}$  is the activation energy of hydrogen desorption from the silicon surface and has been estimated to be of the order of 197 kJ/mol.  $E_{\text{GeH}}$  is the corresponding value for germanium and is estimated as 157 kJ/mol.<sup>16</sup>  $x$  is simply the fraction of germanium on the surface. The ratio of germanium to silicon in the deposited solid is equal to the ratio of their rates of deposition,

$$k_4 B / k_2 A = x / (1-x). \quad (20)$$

Using Eq. (20) to substitute for  $k_4 B$  in Eq. (18), we have, for the total rate of deposition

$$R(x) = \frac{1}{m_1(1-x) + m_2(1-x) / \sqrt{k_{-5} + m_3 x}}, \quad (21)$$

where  $m_1$ ,  $m_2$ ,  $m_3$  are constants containing combinations of  $k_1$ ,  $k_{-1}$ ,  $k_2$ ,  $k_3$ ,  $k_4$ ,  $k_5$ , and the partial pressures of hydrogen and disilane.

The majority of the temperature dependence of Eq. (21) is contained only in  $k_{-5}$ , the hydrogen desorption rate constant. The mole fraction dependence is somewhat more complex, but Eq. (21) naturally predicts a maximum in the rate of growth as a function of germanium mole fraction. Equation (21) can be compared to Eq. (22) derived from Jang and Reif<sup>11</sup> and Robbins *et al.*<sup>7</sup> [who had to introduce a scaling factor of the type  $1/(1+m_3x)$  to force the growth rate to decrease with increasing mole fraction of Ge in the alloy],

$$R(x) = \frac{m' k_{-5}(x)}{(1-x) [m_2' + \sqrt{k_{-5}(x)}]^2 (1+m_3'x)}. \quad (22)$$

#### IV. RESULTS AND DISCUSSION

In order to apply the simple model kinetics developed above, one needs to establish the validity of some of the assumptions made above. One of the more important assumptions is to use the surface mole fraction of Ge rather than the gas phase mole fraction. Figure 1 shows the linear relationship between the  $\text{GeH}_4$  flow rate and percentage Ge incorporation at 610 °C. This linear relationship implies that we can use the gas phase mole fraction in place of the surface mole fraction interchangeably.

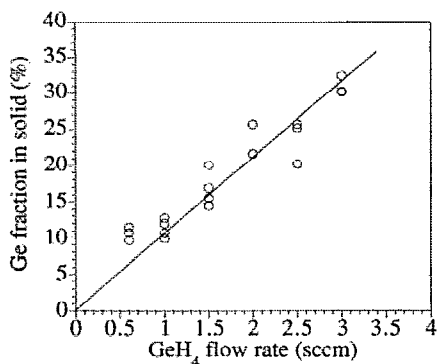


FIG. 1. Ge fraction in the Si-Ge alloy as a function of  $\text{GeH}_4$  flow rate (at  $610^\circ\text{C}$ ).

One of the fundamental problems with any kinetic model is the determination of the elementary step rate constants. We are confronted with a similar difficulty. There is no independent means of determining the rate constants individually or in combination [as they appear in Eq. (21)]. The only option is to try to fit the experimental data to the equation obtained by the model and to determine the parameters. Figure 2 shows how Eq. (21) fits the data. Specifically, our model predicts a maximum in the growth rate as a function of Ge fraction and temperature without resorting to any incorporation of a scaling factor. Exclusion of the pure silicon growth rate data in curve fitting was seen to produce a maximum in the growth rate curve at about  $x=0.15$  for the lower range of temperatures considered. The experimental data do not have the adequate resolution, but the maximum in growth rate seems to be reached  $\sim 0.1-0.15$  Ge fraction in  $\text{SiH}_4$  and  $\text{GeH}_4$  systems<sup>7,11,12</sup> as well as in our system in which we are using  $\text{Si}_2\text{H}_6$  in place of  $\text{SiH}_4$ . As can be seen from Fig. 2, the model predicts very well for nonzero germanium contents. In fact, if this fit is extrapolated to the  $x=0$  point (not shown), the prediction is well within the error limits for the pure silicon data. Our absolute growth rates are comparable to those observed by Jang and Reif<sup>11</sup> and Robbins *et al.*<sup>7</sup> using silane and germane. While Robbins *et al.*<sup>7</sup> never superimposed their calculated growth rates onto

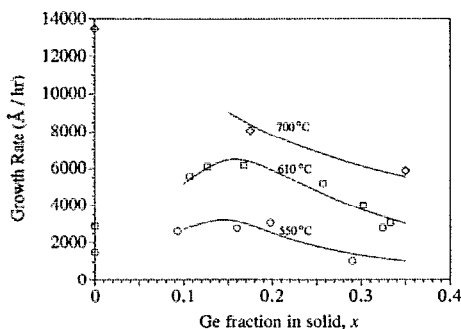


FIG. 2. Growth rate of the Si-Ge alloy as a function of Ge composition for different substrate temperatures. The symbols represent raw data and the solid lines are the respective model curve fits.

their experimental data, it is clear that the agreement in their case is poorer.

One of the interesting observations we have, after performing curve fits to determine the constants  $m_1, m_2, m_3$  is, that within the error bars of the data, the constant  $m_1$  is zero. Since  $m_1$  is a function of the rate constants of disilane adsorption and decomposition reactions, this fact explains the almost identical behavior observed with disilane (this work) and silane (Jang and Reif; Robbins *et al.*).

While our model is more realistic and does not need a scaling term, we have nevertheless made several oversimplifications in order to arrive at an algebraically tractable final growth rate expression with three unknown parameters. Our major simplification is contained in Eqs. (3) and (4), the germane adsorption and decomposition reactions. We assumed both reactions to proceed on single surface sites. The alternative, using a dual site mechanism, did not give a closed form simple growth rate equation and was abandoned. The scatter in the data as compared to the model predictions is partly due to the simplified mechanism employed. A comprehensive sequence of steps would lead to a more accurate description of the observed data, but it would also involve a larger number of unknown rate constants. Further experimentation is hence essential to explore the kinetic behavior of this system to arrive at an optimum mechanism.

In summary, a model has been developed to describe growth rate behavior of a Si-Ge alloy based on the apparent kinetics of the system. It predicts qualitatively, experimental observations at a range of temperatures. It can thus be fruitfully employed to arrive at optimum growth conditions provided the pressures involved are low enough to assume a surface reaction limited regime. However, this simplified heterogeneous growth model still does not provide an accurate description of the processes taking place. It is well known in catalysis that models of this type are not applicable if all the surface sites are not identical or if there is reactant segregation on the catalyst surface. Further kinetics studies will have to be conducted to identify the participating species. Monte Carlo based surface reaction models have proved much better in predicting complex surface phenomena. The advantage of the Monte Carlo approach is its mathematical simplicity and the enormous amount of microscopic insight it provides in understanding surface phenomena. We hope to report on Monte Carlo simulations of Si-Ge growth in the near future.

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