Modelling of silicon epitaxy using silicon tetrachloride as the source

D.K. Pal[1], M.K. Kowar[1], A.N. Daw[1] and P. Roy[2]

[1]Centre for Microelectronics, Institute of Radio Physics & Electronics, University College of Science & Technology, 92 A. P. C. Road, Calcutta-700-009, India
[2]Department of Chemical Engineering, Calcutta University, India

A growth-rate model, based on chemical kinetics for vapour phase epitaxy (VPE) of silicon by decomposition of SiCl4 in a horizontal rectangular reactor at atmospheric pressure, has been developed. The model incorporates the dependence of growth rate on various physical and geometrical parameters, such as temperature, flow rate, mole fraction, position, etc. The results of simulation under appropriate conditions have been found to be in very good agreement with the experimental data available in the literature. Using these data, it has been possible to determine the values of the various rate constants involved in this model.

1. Introduction

In the early days of silicon epitaxy, researchers were interested in developing suitable models for simulating the growth of silicon in vapour phase from silane and also from SiCl4. The modelling of growth from SiCl4 was relatively more complex because of the presence of an etching mechanism that affected the growth rate, especially at high mole fraction values of SiCl4. One of the early models was the one developed by Shepherd [1], which was based on the principle of material balance for the reactor. He,

however, considered the mole fraction to be low enough such that the etching action could be neglected. Bradshaw [2] proposed a model where growth rates are limited by diffusion of reactants and their by-products across a boundary layer to an equilibrium region at the silicon surface. Although he took etching into consideration, the fit of his theoretical values with experimental ones was not quite satisfactory. Vander Putte et al. [3] calculated the growth rate using three different models, ranging from pure equilibrium to equilibrium situations involving mass transfer, diffusion and temperature gradients. The validity of the models was not, however, checked with experimental results.
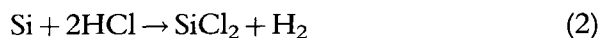
Subsequently, interest shifted to other areas of modelling, such as the positional dependence of growth [4–6], the reduction of autodoping [7–9], pattern shift and distortion [10], etc. In addition, epitaxy at low pressures engaged the attention of investigators [11, 12]. In the meantime, in view of the increasing importance

of process modelling in VLSI technology, several packages were developed for simulating the different processes involved in the fabrication of VLSI chips. Of these packages SUPREM has been the most widely used package. In this package, however, no growth rate model for epitaxy appears to have been included. In order to bridge this gap, a simple model for simulating the growth of silicon from SiH_4 was suggested by Daw et al. [13] and Pal et al. [14]. In the present paper, we have proposed a model for predicting the growth of silicon from $SiCl_4$, based upon a simplified reaction scheme. In this model, the rate of decomposition flux is calculated by using Langmuir's adsorption theory [15] and, finally, the growth rate is determined by utilizing the principle of mass balance for the fluxes. The dependence of growth rate on various process and system parameters is taken into consideration and the same is incorporated in a suitable computer program, which can be utilized for process simulation in IC technology.

In Section 2, the various relations for quantitatively simulating the process will be derived. In Section 3, a method for the determination of the various rate constants, using some growth rate data, will be described. Finally, in Section 4, the dependence of the growth rate on mole fraction and temperature, as predicted by the model developed here, will be studied and compared with the experimental results available in the literature.

2. Theory

In order to develop a model for simulating the growth rate of silicon by VPE using $SiCl_4$ as the source material, consider a simplified reaction scheme as described by the following reactions

$$SiCl_4 + 2H_2 \rightarrow Si + 4HCl \tag{1}$$

$$Si + 2HCl \rightarrow SiCl_2 + H_2 \tag{2}$$

$$SiCl_4 + Si \text{ (solid)} \rightarrow 2SiCl_2 \tag{3}$$

As is well known, the first reaction describes the deposition of Si, the second reaction the etching of Si by HCl, which is the product of the first reaction, and the third reaction an additional etching reaction that predominates, especially when the concentration of $SiCl_4$ in the gas mixture is large.

The kinetics of the film growth rate on the basis of the above reactions can be expressed in terms of a number of fluxes. For example, the amount of flux (F_1) of $SiCl_4$ from the bulk of the gas to the surface of the growing film can be written as

$$F_1 = H(C_{BS} - C_{ss}) \tag{4}$$

where C_{BS} is the bulk concentration of $SiCl_4$, C_{ss} is the concentration of $SiCl_4$ in the gas phase adjacent to the growing surface and H is the gas phase mass transfer coefficient of $SiCl_4$, which is defined as [16]

$$H = D / \left(\frac{\eta X}{\rho V}\right)^{1/2} \quad [0 < X \leq L]$$

where D is the diffusivity of $SiCl_4$ in H_2, ρ and η are, respectively, the density and viscosity of the carrier gas, V is the flow velocity of the gas mixture within the reactor tube and X is the coordinate of the point of study along the X-direction, i.e. along the length (L) of the reactor tube (assumed horizontal).

Let us now consider the process of decomposition of $SiCl_4$ into silicon and its subsequent deposition as single crystal layers on the substrate surface. It is known that this process takes place on the substrate surface and not in the gas phase. What happens in practice is that $SiCl_4$ molecules coming into the proximity of the substrate surface get decomposed and the silicon atoms are deposited at the available sites on the substrate surface. Obviously, the rate of decomposition of $SiCl_4$ will be proportional to the amount of $SiCl_4$ adsorbed on the surface, hence also proportional to the number of sites on the surface occupied by $SiCl_4$. Therefore, the flux

F_2, representing the rate of decomposition of $SiCl_4$ per unit surface area, can be written as

$$F_2 = K^0 S \qquad (5)$$

where S is the fraction of sites occupied on the surface and K^0 the reaction rate constant. We now proceed to determine S using Langmuir's adsorption theory [15]. We note that the rate of adsorption of $SiCl_4$ molecules on the substrate surface is proportional to the surface concentration of $SiCl_4$ (C_{ss}) and the fraction of available sites on the surface $(1 - S)$, and the rate of desorption is proportional to the fraction of occupied sites (S) on the surface. Thus, at equilibrium, one can write

$$K^* S = K^\wedge C_{ss}(1 - S) \qquad (6)$$

where K^* and $K^\wedge$ are the corresponding constants of proportionality. From eq. (6), S can be shown to be given by

$$S = \frac{K_1 C_{ss}}{1 + K_1 C_{ss}} \qquad (7)$$

where $K_1 = K^\wedge / K^*$. Substituting this expression for S in eq. (5), we have

$$F_2 = \frac{K^0 K_1 C_{ss}}{1 + K_1 C_{ss}} = \frac{K C_{ss}}{1 + K_1 C_{ss}} \qquad (8)$$

where $K(= K^0 K_1)$ is a composite constant containing the reaction rate constant (K^0) and the adsorption rate constant (K_1). Both K and K_1 will have the Arrhenius form of dependence on temperature and may be written as $K = K_0 \exp(-E/RT)$ and $K_1 = K_{10} \exp(-E_1/RT)$ where E and E_1 are the respective activation energies and K_0, K_{10} are constants.

Due to the third chemical reaction (eq. (3)) silicon is depleted by $SiCl_4$ and the amount of depletion is considered to be $K_3 C_{ss}$, where K_3 is the surface reaction rate constant of $SiCl_4$ on Si and is defined as $K_3 = K_{30} \exp(-E_3/RT)$, E_3 being the activation energy of that reaction and K_{30} a constant.

Using the steady-state condition $F_1 = F_2 + K_3 C_{ss}$ and rearranging, one obtains

$$C_{BS} = C_{ss}\left[1 + K_3/H + \frac{K/H}{1 + K_1 C_{ss}}\right] \qquad (9)$$

Equation (9) relates the concentration of $SiCl_4$ molecules on the surface to their concentration in the incoming gas stream.

The flux (F_3) relating to the formation of HCl (from the first reaction (eq. (1)) is given by

$$F_3 = 4F_2 = \frac{4K C_{ss}}{1 + K_1 C_{ss}} \qquad (10)$$

From the second reaction (eq. (2)), designating the flux relating to the depletion of HCl at the surface by F_4, we can write

$$F_4 = K_2 C_{S,HCl} \qquad (11)$$

where K_2 is the surface reaction rate constant of HCl with Si and is given by the relation $K_2 = K_{20} \exp(-E_2/RT)$, with E_2 being the activation energy of that reaction, K_{20} a constant and $C_{S,HCl}$ the concentration of HCl at the silicon surface.

Since the HCl that is formed at the Si surface leaves the reaction tube with an excess mixture of H_2 and $SiCl_4$, the bulk concentration of HCl can be considered to be zero. However, the flux (F_5) of HCl diffusing from the Si surface to the bulk can be written as

$$F_5 = H_{HCl}(C_{S,HCl} - 0) \qquad (12)$$

where H_{HCl} is the gas phase mass transfer coefficient of HCl. Its value has been reported to be three times that of the gas phase mass transfer coefficient of $SiCl_4$ [17] and we shall use this value in our calculation.

In the steady state, using the mass balance principle, we have

$$F_5 = F_3 - F_4 \qquad (13)$$

or

$$H_{HCl} \, C_{S,HCl} = \frac{4K \, C_{ss}}{1 + K_1 C_{ss}} - K_2 \, C_{S,HCl} \qquad (14)$$

From the above equation, the expression for $C_{S,HCl}$ can be written as

$$C_{S,HCl} = \frac{1}{(H_{HCl} + K_2)} \frac{4K \, C_{ss}}{1 + K_1 C_{ss}} \qquad (15)$$

From the stoichiometries of the chemical reaction represented by eq. (2) and using eqs. (8) and (11), the silicon deposition rate F is obtained as

$$F = F_2 - \frac{1}{2} F_4 - K_3 C_{ss}$$
$$= \frac{K \, C_{ss}}{1 + K_1 C_{ss}} - \frac{1}{2} K_2 C_{S,HCl} - K_3 C_{ss} \qquad (16)$$

Substituting the value of $C_{S,HCl}$ from eq. (15) in the above equation, the expression for F becomes

$$F = \frac{K \, C_{ss}}{1 + K_1 C_{ss}} \left[1 - \frac{2K_2}{H_{HCl} + K_2} \right] - K_3 C_{ss} \qquad (17)$$

Recalling that under steady-state conditions $F_1 = F_2 + K_3 C_{ss}$, and using eqs. (4) and (8), eq. (17) can be written as

$$F = \{H(C_{BS} - C_{ss}) - K_3 C_{ss}\}$$
$$\left[1 - \frac{2K_2}{H_{HCl} + K_2} \right] - K_3 C_{ss} \qquad (18)$$

Hence the growth rate of silicon film is given by

$$G = \left[\{H(C_{BS} - C_{ss}) - K_3 C_{ss}\} \right.$$
$$\left. \left(1 - \frac{2K_2}{H_{HCl} + K_2} \right) - K_3 C_{ss} \right] \frac{1}{N} \qquad (19)$$

where N is the number of silicon atoms incorporated in a unit volume of the film. Now, C_{BS} in eq. (19) can be substituted by $N_1 M$, where M is the mole fraction of $SiCl_4$ in the mixture at the inlet end and N_1 is the molecular density of the

gas. Thus, the expression for growth rate becomes

$$G = \left[\{H(N_1 M - C_{ss}) - K_3 C_{ss}\} \right.$$
$$\left. \left(1 - \frac{2K_2}{H_{HCl} + K_2} \right) - K_3 C_{ss} \right] \frac{1}{N} \qquad (20)$$

It should be noted that in the above expression, apart from the various reaction rate constants, all of which are functions of temperature, the parameter $H \, [= D/(\eta X/\rho V)^{1/2}]$ is also a function of temperature through the terms D, η, ρ and V, as already mentioned in our earlier work [13]. In inductively heated horizontal reactors, since there is a temperature gradient normal to the surface of the substrate, the variations of the aforesaid parameters with temperature have to be appropriately taken into consideration in predicting the growth rate as a function of temperature. Also, the flow velocity inside a reactor is not uniform all over the reactor and this factor also has to be considered while developing an accurate model of growth by VPE, as has been done earlier [14].

In order to prove the validity of the above model, it is obviously necessary to compare the growth rates predicted by this model with those obtained experimentally. Now, calculation of growth rate from eq. (20) requires a knowledge of the various rate constants K, K_1, etc., besides information about the process parameters such as temperature, flow velocity, etc. Since values of the various rate constants are not readily available in the literature, we have developed a method for their determination using some relevant experimental data relating to epitaxial growth. After determining these values, the growth rate will be calculated as a function of mole fraction using eq. (20) and then compared with the experimental results available in the literature. The method of determination of rate constants referred to above is described below.

3. Determination of rate constants

It is evident from eq. (19) that the terms $2K_2/(H_{HCl} + K_2)$ and K_3C_{ss} predict a decrease in the growth rate, the former representing etching of silicon by the HCl produced (eq. (2)) and the latter representing etching of silicon by $SiCl_4$ (eq. (3)). It is well known that the etching action represented by eq. (3) is much more predominant than that represented by eq. (2) [16]. In fact, the effect of the term involving K_2 is only to decrease the rate of growth of the epi-layer by a negligibly small amount (as will also be shown later), whereas eq. (3) ultimately leads to etching of silicon instead of growth. As such, for the sake of simplicity, we neglect the term containing K_2 in the expression for G (eq. (19)), which then takes the form

$$G = [H(C_{BS} - C_{ss}) - 2K_3C_{ss}]\frac{1}{N} \qquad (21)$$

In order to find out the value of the $SiCl_4$ concentration (i.e. mole fraction) for which the growth rate passes through zero, indicating a transition from growth to etching, we put the right-hand side of eq. (21) equal to zero and obtain

$$H(C_{BO} - C_{ss}) = 2K_3C_{ss}$$

or

$$\frac{C_{BO}}{C_{ss}} = \frac{2K_3 + H}{H} \qquad (22)$$

where C_{BO} is the value of C_{BS} when transition occurs from growth to etching. Eliminating C_{ss} between eqs. (9) and (23), we have

$$C_{BO} = \frac{(K - K_3)(2K_3 + H)}{K_1 K_3 H} \qquad (23)$$

When the mole fraction is very small, the term containing K_3 in eq. (21) can obviously be neglected. The rate of change of growth rate with $SiCl_4$ concentration in this region can then be written as

$$\frac{dG}{dC_{BS}}\bigg|_1 = H\left(1 - \frac{dC_{ss}}{dC_{BS}}\right)\frac{1}{N} \qquad (24)$$

where $dG/dC_{BS}|_1$ signifies the value of dG/dC_{BS} at very low values of C_{BS}. Again, for very large values of C_{BS}, when the etching action is predominant, the term H in eq. (21) can be neglected and we can write

$$\frac{dG}{dC_{BS}}\bigg|_2 = -2K_3\frac{dC_{ss}}{dC_{BS}}\frac{1}{N} \qquad (25)$$

where $dG/dC_{BS}|_2$ signifies the value of dG/dC_{BS} at very high values of C_{BS}.

Now from eq. (9), differentiating C_{ss} with respect to C_{BS}, we obtain

$$\frac{dC_{ss}}{dC_{BS}} = \frac{KC_{ss}}{KC_{BS} - K_1H\{C_{BS} - (1 + K_3/H)C_{ss}\}} \qquad (26)$$

From eqs. (23)–(26), assuming H to be known, the three constants K, K_1 and K_3 can be evaluated in the following manner.

It is to be noted that the term dC_{ss}/dC_{BS} in eqs. (24), (25) and (26) corresponds to different values of the bulk concentration (C_{BS}) of $SiCl_4$. However, although from eq. (9) the parameter dC_{BS}/dC_{ss} seems to be a function of the surface concentration of $SiCl_4$ molecules, this dependence is indeed quite small and, to a first approximation, the term dC_{BS}/dC_{ss} can be considered to be constant. Using this argument, we can eliminate the term dC_{ss}/dC_{BS} between eqs. (24) and (25) and write

$$K_3 = \frac{1}{2}\left[\frac{-HN\dfrac{dG}{dC_{BS}}\bigg|_2}{H - N\dfrac{dG}{dC_{BS}}\bigg|_1}\right] \qquad (27)$$

Now, at extremely low values of C_{BS}, the expression for growth rate may be approximately written as

$$G = H(C_{BS} - C_{ss})\frac{1}{N} \qquad (28)$$

From eq. (28), the value of C_{ss} is obtained if G is measured for a given value of C_{BS}. Substituting these values of C_{BS} and C_{ss} in eq. (26) and determining dC_{ss}/dC_{BS} from eq. (24), the value of K_1/K is obtained. Finally, using this value of K_1/K, and of K_3 determined earlier from eq. (27), the values of K and K_1 are separately obtained with the help of eq. (23).

4. Results and discussion

From the above discussion, it is obvious that a set of experimental data of the growth rate for various values of the mole fraction would be needed for determining the various rate constants referred to above. We have utilized the experimental results of Theuerer [18] and Steinmaier [19] for this purpose. Theuerer's data were obtained at a reactor temperature of 1543 K and those of Steinmaier at a temperature of 1423 K. From Fig. 4 of Theuerer's paper, depicting the growth rate as a function of mole fraction, the following values were derived:

(i) $dG/dC_{BS}|_1$ [at low concentration] $= 2.623 \times 10^{-23}$ cm^{4}s^{-1}.

(ii) $dG/dC_{BS}|_2$ [at high concentration (etching region)] $= -2.561 \times 10^{-23}$ cm^{4}s^{-1}.

(iii) The value of bulk concentration C_{BS} at which growth ends and etching begins $= 1.335 \times 10^{18}$ cm^{-3}.

Using the above values and following the procedure described in the preceding section, the values of the rate constants were obtained as follows: $K = 5.465$ cm s^{-1}; $K_1 = 5.546 \times 10^{-18}$ cm^3; and $K_3 = 0.692$ cm s^{-1}.

Similarly, using Steinmaier's data as reported in Fig. 5 of Bradshaw [2], the values of the rate constants at $T = 1423$ K were obtained as follows: $K = 3.1846$ cm s^{-1}; $K_1 = 4.095 \times 10^{-18}$ cm^3; and $K_3 = 0.372$ cm s^{-1}.

From the above two sets of data of rate constants and noting that these constants follow the Arrhenius type of dependence, the corresponding activation energies and constants of reaction were obtained as follows: $K_0 = 2950.94$ cm s^{-1}, $E = 18.910$ kcal mole^{-1}; $K_{10} = 1.899 \times 10^{-16}$ cm^3, $E_1 = 10.620$ kcal mole^{-1}; $K_{30} = 952.058$ cm s^{-1}, $E_3 = 21.721$ kcal mole^{-1}.

Using the values of rate constants thus determined and substituting the same in eq. (21), the values of the growth rate were calculated as a function of mole fraction and compared with experimental results. In order to provide better fit between theory and experiment, the rate constant K_2, instead of being neglected, was assumed to be of the form $K_2 = K_{20} \exp(-E_2/RT)$, the values of K_{20} and E_2 being selected by the method of trial and error so as to give a better fit between theoretical values, as predicted by eq. (20) and experiment. The values of K_{20} and E_2 thus selected were 39.3886 cm s^{-1} and 17.490 kcal mole^{-1}. The values of growth rate, as obtained from eq. (20) using the above values of K_{20} and E_2, are plotted in Fig. 1 at $T = 1543$ K, $T = 1523$ K and $T = 1423$ K. The corresponding experimental values, as reported by Theuerer [18], Bylander [20] and Steinmaier [19], are indicated by □, × and ◇ respectively in this figure. Satisfactory agreement between theory and experiment is clearly observed. It may be noted that the difference between the rates of growth, as predicted by eqs. (20) and (21), is quite small. In fact, in the low mole fraction region, the two sets of values are identical, which is expected since, in this region, the parameter H is the dominant factor in determining the growth rate. At higher values of mole fraction, the values of G as predicted by eq. (21) (where $K_2 = 0$) are understandably a little higher since neglect of K_2 implies neglecting the etching reaction represented by eq. (2). The almost negligible difference between the two sets of values justifies our earlier assumption that the etching action repre-
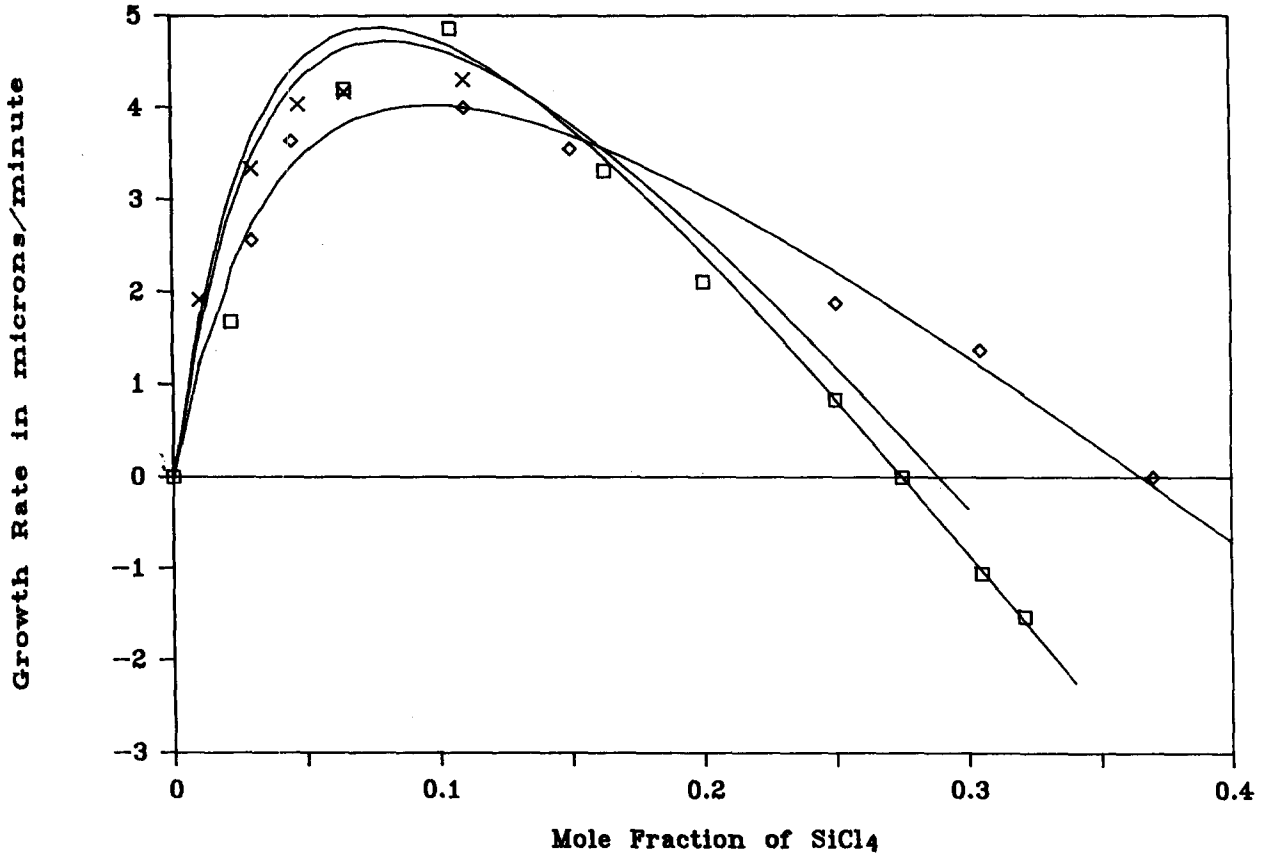
Fig. 1. Growth rate as a function of the mole fraction of $SiCl_4$ in H_2 for different temperatures. — Calculated, □ Theuerer (1543 K), × Bylander (1523 K) and ◇ Steinmaier (1423 K).

sented by eq. (2) is not a predominant one and the term containing K_2 in eq. (20) can therefore be neglected.

As already mentioned, the values of the reaction constants are not readily available in the literature. The method outlined above, however, enables us to determine these values from the growth rate versus mole fraction data at any two temperatures. Once these values are known, one can use them in the expression for the growth rate, to predict the growth rate at any temperature.

Referring to eq. (23), it is seen that the value of C_{BO} increases as K_3 decreases. Since K_3 decrea-

ses with a lowering of temperature, it follows that C_{BO} would increase with a lowering of temperature, which is corroborated from Fig. 1.

In order to obtain a higher growth rate for the same value of mole fraction, it is obvious from eq. (24) that either H should be higher or dC_{ss}/dC_{BS} should be smaller. Referring to eq. (26), it follows that a lower value of K_1/K will give a smaller value of dC_{ss}/dC_{BS}. If K_1 is small, S (eq. (7)) would also be small and consequently the probability of growth would be large. On the other hand, if K, which is proportional to the reaction rate constant K^0, is large, the growth rate would obviously be larger.

Acknowledgement

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