A DIFFUSION KINETIC MODEL FOR EPITAXIAL GROWTH OF GALLIUM ARSENIDE LAYERS FROM THE GAS PHASE

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The growth model of gallium arsenide epitaxial layers has been further extended in two ways. First of all, the location of the substrate in experiments in the reactor has been taken into account, and a general relationship has been derived for dependence of the mean effective thickness of the boundary layer on the distance of the substrate from the leading edge and on the substrate size. Secondly, the effect of rate of the chemical heterogeneous reaction has been investigated in addition to the diffusion rate on the resulting growth velocity of epitaxial gallium arsenide layers. A quantitative model comprising the rates of the both partial processes has been formulated. The theoretical relationships obtained in this way have been confronted with experimental results.

A comparison of isothermic dependences found experimentally with the theoretical results obtained with the model, where the rate controlling step was the gas film diffusion[1], has shown that the theoretical values are on the average 8·8 times higher than the experimental ones, whereby the individual values of this factor were fluctuating with a mean deviation of $\pm 13\%$. This result is in a qualitative agreement with previous conclusions, namely that rates predicted for a purely diffusion model are the maximum values, *i.e.* that they represent an upper limit to which the reality can just approach. In a quantitative treatment, however, it is still necessary to take into consideration that the front boundary of the substrate in the direction of the gas flow is not usually identical with the leading edge, as it has been considered in theoretical computations previously, but that it is usually located at a certain distance downstream from the leading edge represented by the holder margin. Therefore, it seemed as necessary to solve these conditions in a quantitative manner.

Dependence of Boundary Layer Thickness on Distance from Leading Edge

For the effective thickness δ of the boundary layer, an equation has been derived previously[1] from the boundary layer theory

$$\delta = 1{\cdot}7208(\mu/G_m)^{1/2} \, . \, x^{1/2} \, , \tag{1}$$

where G_m denotes the mass velocity, μ is the dynamic viscosity of the streaming gas, and x represents the distance from the leading edge. In addition, a mean effective thickness, $\bar{\delta}$, has been considered, which has been defined according to the mean value theorem as

$$\bar{\delta} = 1/L \int_0^L \delta \, dx \, , \tag{2}$$

where L denotes the length of the substrate (*i.e.* the dimension of the substrate in direction of the gas flow). In this way a relation has been obtained

$$\bar{\delta} = 1{\cdot}1472(\mu/G_m)^{1/2} \, . \, L^{1/2} \tag{3}$$

which was used in theoretical computations.

The lower limit of the integral on the right hand side of equation (2), is, however, valid only in the case, when the leading edge of the gas is identical with the boundary of the substrate. In other cases it is necessary to define the mean effective thickness generally as

$$\bar{\delta} = 1/(L_2 - L_1) \int_{L_1}^{L_2} \delta \, dx \, , \tag{4}$$

where L_1 denotes the distance of the front boundary of the substrate (in the direction of the gas flow) from the leading edge of the gas which is formed in this case by the front boundary of the holder, and L_2 is the distance of the hinder boundary of the substrate from the leading edge. The length, L, of the substrate is given in this case by the relation

$$L = L_2 - L_1 \, . \tag{5}$$

Substituting the equation (1) into equation (4) and integrating, an expression is obtained

$$\bar{\delta} = 1{\cdot}1472(\mu/G_m)^{1/2} \, . \, (L_2^{3/2} - L_1^{3/2})/(L_2 - L_1) \tag{6}$$

which in combination with the relation (5) is transformed to

$$\bar{\delta} = 1{\cdot}1472(\mu/G_m)^{1/2} \, . \, L^{1/2}[(1 + L_1/L)^{3/2} - (L_1 - L)^{3/2}] \, . \tag{7}$$

Thus, the equation (7) expresses a general dependence of the mean effective thickness, $\bar{\delta}$, of the boundary layer on the distance, L_1, of the front boundary of the substrate

from the leading edge of the gas, and on the length dimension, L, of the substrate. From this equation, it is also evident, that if the front boundary of the substrate forms the leading edge, then $L_1 = 0$, and the equation (7) is simplified to the equation (3) as the limiting case.

In the experiments mentioned above, the substrate of gallium arsenide had a shape of the sector of a circle with vertex angle of $90°$ and with the radius of $1 \cdot 1$ cm, and it was located 1 cm from the holder's leading edge. According to these data, the length dimension of the substrate assumes the value of $L = 0 \cdot 953$ cm and the distance from the leading edge is $L_1 = 1 \cdot 0$ cm. Substituting these values into the relation (7), an expression for the mean effective thickness is obtained in the given case as

$$\delta = 2 \cdot 0817 (\mu / G_m)^{1/2} , \tag{8}$$

whereas in the previous computations[1], the parameters assumed the values of $L = 1 \cdot 0$ and $L_1 = 0$, so that the equation for the film thickness was of the form

$$\delta = 1.1472 (\mu / G_m)^{1/2} . \tag{9}$$

By comparing the expressions (8) and (9), it follows that, in the mentioned experiments, the theoretical thickness, δ, was roughly twice as large, or more priceiselly $1 \cdot 815$ times, under otherwise identical conditions. Since the diffusion rate is indirectly proportional to this thickness, the theoretical rates in the given case are not $8 \cdot 8$ times higher than the experimental ones, but only 4 85 times. Nevertheless, even this difference exceeds the probable experimental error by orders of magnitude, and, therefore, the previously used purely diffusion model has been modified in such a way, that, in addition to the diffusion, the effect of the rate of chemical reaction on the resulting velocity of the epitaxial growth has been taken into account.

Diffusion Kinetic Model for Growth of Epitaxial Layers from Gas Phase

The hitherto used diffusion model[1] for growth of epitaxial layers stemmed from the idea that the rate controlling step of the whole process is the diffusion through a gas film adhering to the substrate, and that the driving force of diffusion is the difference of partial pressures of components on both sides of the gas film, *i.e.* from the side of the main stream and from the side of the substrate. In this model, it has been assumed, that a chemical equilibrium is established among the present components on both sides of the film, namely in the way, that in the gas phase there exists a homogeneous equilibrium solely among the gas components, whereas at the substrate, there exists a complete heterogeneous equilibrium with participation of the solid phase, in the given case of the gallium arsenide. Regarding the possibility of solid separation, the homogeneous equilibrium is a stable one. The above compari-

son of theoretical and experimental rates has shown quite distinctly, that besides the diffusion, an additional hindering factor (or factors) is present, even though the purely diffusion model does justice to the qualitative trends altogether satisfactorily. Among the additional factors, the chemical reaction must be considered in the first place, and it is also taken into consideration in the model which is proposed in the following. Since this model is in fact only a modification or a more precise elaboration of the previous model, we will focus our attention to the points, where both the models differ.

The most important difference consists in that not a single one, but two rate controlling steps will be considered, *i.e.* the diffusion and the chemical reaction. From the three chemical reactions considered previously[1]

$$GaCl + HCl = GaCl_2 + 1/2\,H_2 \qquad (A)$$

$$2\,As_2 = As_4 \qquad (B)$$

$$1/2\,As_2 + GaCl + 1/2\,H_2 = GaAs + HCl, \qquad (C)$$
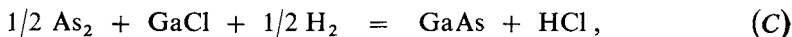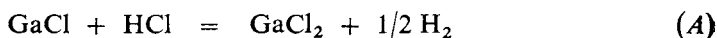
the heterogeneous reaction in which the solid gallium arsenide is formed will be considered as the joint controlling chemical step, *i.e.* the reaction (C). In addition, it will be postulated that the pertaining rate equation should be valid up to the equilibrium, *i.e.* that the equilibrium condition should be fullfilled

$$\left[p^*_{HCl}/(p^*_{As_2})^{1/2} \cdot p^*_{GaCl} \cdot (p^*_{H_2})^{1/2}\right]^a = K_c^a = K, \qquad (10)$$

where K_c is the equilibrium constant of the reaction (C) and the exponent a is a positive, for the present, a closely undertermined number. The simplest rate equation, which would be consistent with the equilibrium condition (10), is of the form

$$r = k\left[(p^*_{As_2})^{a/2} \cdot (p^*_{GaCl})^a \cdot (p^*_{H_2})^{a/2} - (1/K)(p^*_{HCl})^a\right], \qquad (11)$$

where r denotes the rate of reaction (C) and k is the pertinent rate constant. In the first approximation we can put $a = 1$, and the equation (11) may be simplified to

$$r = k\left[(p^*_{As_2})^{1/2} \cdot p^*_{GaCl} - (1/K_c) \cdot p^*_{HCl}\right], \qquad (12)$$

since the partial pressure of hydrogen is practically equal to the atmospheric pressure, and partial pressures of all the components are taken relatively to the atmospheric pressure, so that $p^*_{H_2} = 1$ (in this case the partial pressures of components are equal to their mole fractions).

The remaining ideas are identical with those in the previous purely diffusion model, so that the quantitative description of the proposed diffusion kinetic models will be given by the following relations. In the gas phase, there exists a homogeneous equilibrium in the reactions (A) and (B) at the given temperature which is described by the equations

$$p_{GaCl} \cdot p_{H_2}^{1/2}/(p_{GaCl} \cdot p_{HCl}) = K_A \tag{13}$$

$$p_{As_4}/p_{As_2}^2 = K_B \,, \tag{14}$$

where the equilibrium constants K_A and K_B are functions of the temperature only, and the values of the partial pressures, p_i, of components are determined by their inlet concentrations in addition to the equations (13) and (14). On the opposite side of the gas film at the substrate, where all three reactions (A), (B), and (C) can take place, there exists only a partial equilibrium, namely in the reactions (A) and (B) which is determined by analogous equations

$$p_{GaCl_2}^* \cdot \left(p_{H_2}^*\right)^{1/2}/p_{GaCl}^* \cdot p_{HCl}^* = K_A \tag{15}$$

and

$$p_{As_4}^*/\left(p_{As_2}\right)^2 = K_B \,, \tag{16}$$

whereas the course of the reaction (C) will be described by the rate equation (12). Partial pressures, p_i^*, of components appearing in the equations (12), (15), and (16) are denoted here by small letters, as to differentiate the values, P_i^*, in the total equilibrium in the purely diffusion model. In addition to the equations given above, they are determined by the steady state conditions, the assumption of which is equally justified as previously[1]. Two of the steady state conditions are of the same form, *i.e.* that the diffusion rate of arsenic, r_d (As), and of gallium, r_d (Ga), (in all the species) must take place in a stoichiometric ratio, or

$$r_d \,(As) = r_d \,(Ga) \,, \tag{17}$$

and further on, that the total diffusion rate of chlorine in all its forms is equal to zero thus

$$r_d \,(Cl) = 0 \,. \tag{18}$$

Besides the above two conditions, still a third one is added in this diffusion kinetic model, namely, that the rates of the both rate controlling steps, diffusion and chemical reaction, must be equal, or

$$r_d \,(Ga) = r \,. \tag{19}$$

That is to say, if this condition would not be fulfilled, an accumulation or decumulation of components would take place at the substrate according to that, which of both rate controlling steps would be faster, and in this way the steady state would be violated. The driving force of individual components consists here in the difference of their partial pressures, p_i and p_i^*, so that the diffusion rate of the i-th component is given by the expression[1]

$$r_d(i) = k_G(i) \cdot (p_i - p_i^*), \qquad (20)$$

where the transport coefficients $k_G(i)$ are dependent on diffusion coefficients D_i and on the mean effective thickness of the boundary layer δ according to the relation[1]

$$k_G(i) = (D_i/RT) \delta. \qquad (21)$$

Consequently, the diffusion kinetic model is completely described by a set of equations from (12) up to (21), and from a mathematical point of view, this description differs from the previous purely diffusion model[1] in that it contains one adjustable parameter, *i.e.* the rate constant k, whereas the previous model contained no such parameter. This fact is leading to a different procedure in comparing the model with experiments, as it will be shown in the following.

Comparison of Diffusion Kinetic Model with Experiments

With regard to the mentioned existence of the parameter k, the value of which cannot be predicted, it is possible to proceed in confronting the model with experiments in two ways. Either we can compute the value of k for individual experiments by means of the mentioned set of equations and of the rate found experimentally, and appreciate the adequacy of the model according to the behaviour of parameter k obtained under various conditions, or we can compute the theoretical courses of reaction rates with given values of the parameter k and appreciate the model by comparing the theoretical dependences with the corresponding ones found experimentally. Both procedures will be illustrated on available experimental data[2].

The last named procedure is suitable for isothermic dependences when the rate parameter k remains constant, and especially for dependences on the concentrations of components. These courses have been computed theoretically for values of rate constants in the range from $1.4 \cdot 10^{-4}$ up to $2.8 \cdot 10^{-4}$, and are represented in figures 1, 2, and 3. As it is evident, the experimental values of growth rates are situated in the network of theoretical courses given by the mentioned range of the rate constant, and the observed rates exhibit the same trends as the computed courses. From the quantitative point of view, however, it is possible to detect some systematic deviations, namely the following ones. In the dependence of the epitaxial growth rate on the arsine concentration in the feed, demonstrated in the Fig. 1, the experi-

mental points are not situated on a curve corresponding to a single value of the rate constant, but with the increasing arsine concentration, the corresponding value of the rate constant increases to twofold in the given range. An opposite trend of deviations is exhibited in the dependence of growth rates on the gallium concentration, represented in the Fig. 2, where with the increasing gallium concentration the corresponding value of the rate constant decreases roughly to one half, Evidently, both trends of deviations are practically compensated in the growth rate dependence on the feed composition with equal concentrations of arsine and gallium, as it is seen from the Fig. 3. That is to say in this case, the rate constant with a value of $1\cdot8 \cdot 10^{-4}$ reproduces the observed course with an accuracy of about 10%, *i.e.* practically within the limits of experimental errors.

On the basis of the three given concentration dependences, it is possible to regard the agreement of the diffusion kinetic model with experiments as a semiquantitative one. Nevertheless, the systematic character of deviations, which is evident from the Fig. 1 and 2, indicates with a sufficient distinctness the presence of an additional step in addition to the chemical reaction and diffusion.

In comparing the growth rate dependence on temperature with experiments, the other procedure has been selected, where the values of rate constants at distinct
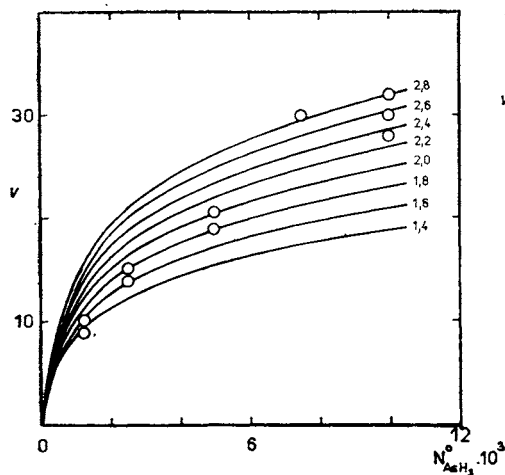

FIG. 1

Dependence of epitaxial growth rate v (μm h^{-1}) of GaAs on arsine concentration in feed; ——— theoretical curves computed for values of rate constants appended to curves ($k \cdot 10^4$); ○ experimental values
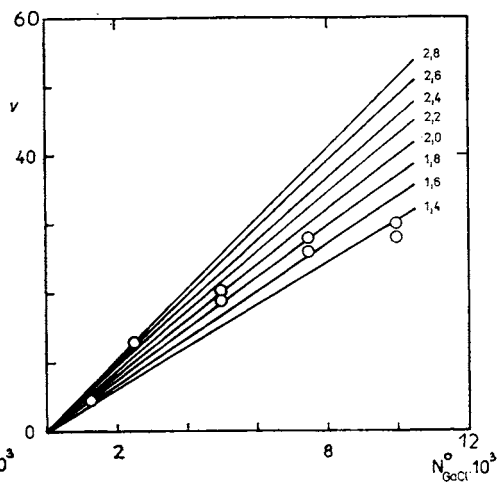
FIG. 2

Dependence of epitaxial growth rate v (μm h^{-1}) of GaAs on gallium concentration in feed; ——— theoretical curves computed for values of rate constants appended to curves ($k \cdot 10^4$); ○ experimental values

temperatures have been computed by means of the given set of equations and of the rates found experimentally. The temperature dependence of the rate constant com-
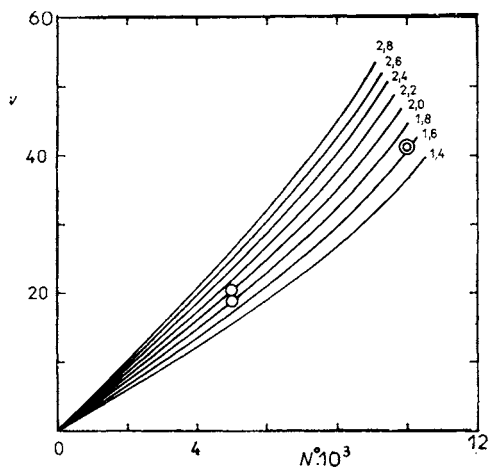

FIG. 3

Dependence of epitaxial growth rate v ($\mu m\ h^{-1}$) of GaAs on feed composition $N^0 = N^0_{GaCl} = N^0_{AsH_3}$; ———— theoretical curves computed for values of rate constants appended to curves ($k . 10^4$); $\bigcirc$ experimental values
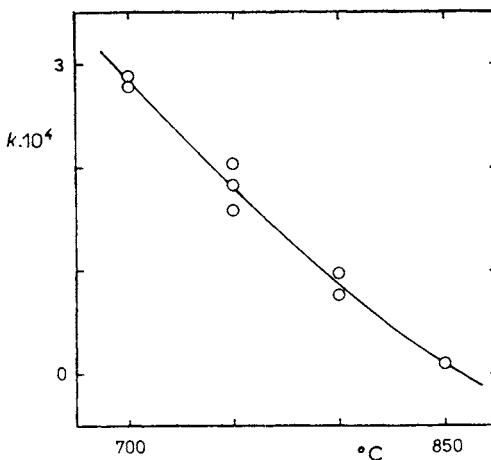
FIG. 4

Dependence of rate constant of heterogeneous reaction on temperature; $\bigcirc$ experimental values, ———— smoothed curve
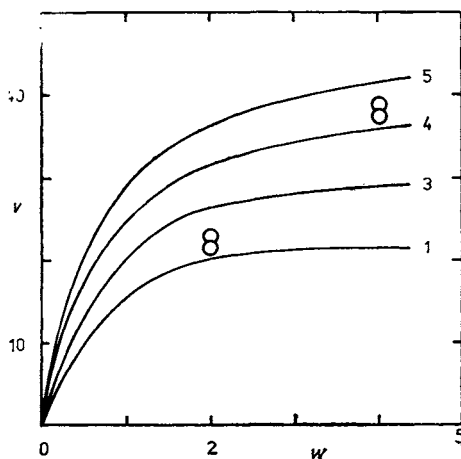

FIG. 5

Dependence of rate v ($\mu m\ h^{-1}$) of epitaxial growth of GaAs on feed rate w ($dm^3\ H_2\ min^{-1}$); ———— theoretical curves computed for values of rate constants appended to curves ($k . 10^4$); $\bigcirc$ experimental values

puted in this way is demonstrated in the Fig. 4, from which a qualitatively important fact follows at a first glance. Namely, the rate constant does not increase with temperature, as it could be expected from both the Arrhenius equation and the theory of absolute reaction rates, but it decreases monotonously. This startling fact can be interpreted in such a way that the computed rate constant is not a true rate constant, but that it is an effective rate constant which includes parameters of an additional step or steps. The corresponding effective or apparent energy of activation can be consequently affected by thermal effects of the additional steps, so that in principle it can assume even the negative values, as it is the case. In this way, the dependence on temperature confirms the hypothesis of the existence of an additional step which has been formulated above in consideration of the concentration dependence. Such an additional step may consist for instance in the adsorption of gaseous components on the surface of the solid.

Finaly, the last dependence of growth rates on the feed rate has been compared with experiment by means of both procedures. At feed rates of two and four litres per minute, the calculated value of the rate constant amounted to $2 \cdot 3 \cdot 10^{-4}$ and $4 \cdot 4 \cdot 10^{-4}$ and the theoretical courses of this dependence are given together with the experimental values in the Fig. 5. From both procedures it follows that in the given range the rate constant increases twice, although theoretically it should not be changed at all. It is possible to explain this discrepancy in such way, that the values of transport coefficients k_G increased with the feed rate faster than it corresponds to a laminar regime (*i.e.* with a square root of the feed rate), namely in consequence of turbulences, the origin of which is due to the location of the substrate in the reactor. The importance of the effect of hydrodynamic regime on the epitaxial growth is also evident from the fact, that in all the concentration dependences (Fig. 1, 2, and 3), the computed value of the rate constant ranges from $1 \cdot 4 \cdot 10^{-4}$ up to $2 \cdot 8 \cdot 10^{-4}$, however, in changing the hydrodynamic regime, this value exceeds the mentioned range and attains a value of $4 \cdot 4 \cdot 10^{-4}$.

It is necessary to add a comment to the above comparison of the proposed diffusion kinetic model with experiments. Namely, we have to bear in mind, that theoretical values have been used in computing the transport coefficients, so that the entire quantitative description includes only one adjustable parameter, *i.e.* the rate constant of the heterogeneous reaction, whereas, two adjustable parameters are met in published models of comparable complexity[3].

All computed results are contained in the graphs, where the units used for expressing the rate constant are mole, second, cm^2 and the relative pressure is referred to the atmospheric pressure.

It can be concluded that the proposed diffusion kinetic model for the growth of epitaxial layers of the gallium arsenide from the gas phase comports with experimental results in a semiquantitative manner with a precision of $1 : 2$. To increase the precision of this model, it will be necessary to take into account the effect of chemi-

sorption on the growth rate of epitaxial layers, which represents the second step of chemical nature in the overall mechanism.

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