A DUAL EQUILIBRIUM DIFFUSION MODEL FOR EPITAXIAL GROWTH OF GALLIUM ARSENIDE LAYERS FROM THE GAS PHASE AND AN *a priori* COMPUTATION OF GROWTH RATES

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A model is proposed and quantitatively treated of epitaxial growth of gallium arsenide layers, where the rate controlling step consists in the diffusion of reactants through a stagnant gas film adhering to the substrate, and where chemical equilibria are established between the reactants in the main gas stream and at the surface of substrate. The boundary layer theory is applied to the hydrodynamic part of the model which is simplified by introducing a mean effective film thickness, and the system of Ga–As–Cl–H is reduced to six molecular species and to three chemical reactions. With this basis and using estimated values of diffusion coefficients, the growth rates of epitaxial gallium arsenide layers have been *a priori* computed in dependence on the feed rate, its composition and on temperature. The predicted three dependences are discussed from the view-point of their courses and of the significance of computed results.

In the planparallel gas flow along the substrate a velocity gradient is formed on the gas stream perpendicular to the plane of substrate, the gas velocity being usually equal to zero just at the substrate, and limiting to a constant value which is equal to the gas velocity in the main stream unaffected by the presence of the substrate. The course of this velocity profile is quantitatively treated by the boundary layer theory[1] which gives even the dependence of this profile on the distance from the leading edge of the substrate. The course of the velocity profile is continuous and asymptotic and, therefore, it is not possible to assign some final distance to this reality which would express the thickness of the boundary layer. For this reason, one proceeds here as a rule conventionally in such a way, that the thickness of the boundary layer is considered as the distance from the substrate, at which the gas velocity differs from the velocity in infinite distance for example by one per cent. This convention has been already used in the description of the epitaxial growth of the gallium arsenide[2], however, the calculated thickness of the boundary layer is not real with respect to the diameter of the reactor used. Even if we disregard the inadequacy of the this application, the arbitrariness in the selection of the thickness of the

boundary layer mentioned above remains to be the source of significant uncertainities in applications of the otherwise very progressive boundary layer theory. This theory, however, can be applied to the epitaxial growth in a quite unambiguous manner at the expense of some simplification, as it is described in the following.

It was the aim of this paper to propose a simple diffusion model which would do justice to the experimental situation in the isothermal reactor from the physical point of view and which would be quantitatively tractable.

Diffusion Model

Similarly as in other physical situations (*e.g.* with potentials of intermolecular forces), it is possible even here to substitute the real course of the velocity profile approximately by means of a rectangular function which will consist in the simplest case only of two values: a zero velocity and a maximum velocity. This most simple approximation of the real course corresponds physically to the idea of a stagnant film adhering to the substrate in which the translational gas velosity is equal zero, whereas in the region outside this film the gas is streaming at a constant velocity which is equal to the velocity at an infinite distance and, therefore, it is equal to the maximum velocity in the actual asymptotic velocity profile. The stagnant film model is frequently used in chemical engineering, however, in such a way, that the film thickness is an adjustable parameter which sometimes masks the model imperfections. The boundary layer theory, however, offers an opportunity to determine *a priori* the stagnant film thickness in the case of parallel fluid flow over a flat plate. That is to say, an opportunity is offered to identify the thickness of the stagnant film at the substrate with the so-called displacement thickness, which represents the distance[1] by which the streamlines are displaced outwards as a consequence of the formation of a boundary layer. For the displacement thickness δ, an expression follows from the boundary layer theory in the laminar region

$$\delta = 1{\cdot}7208 x Re^{-1/2} , \qquad (1)$$

where x denotes the distance from the leading edge of the substrate in the direction of the gas stream and Re represents the Reynolds number modified for the given physical situation in such a way that the linear dimension is here the distance x. Consequently the Reynolds number is obtained as

$$Re = xu\,\varrho/\mu , \qquad (2)$$

where u is the linear gas velocity at such a large distance from the substrate that its retarding effect is not felt, and ϱ and μ are the density and dynamic viscosity of the streaming gas.

In this simplified diffusion model the displacement thickness δ can be accordingly identified with an effective thickness of the stagnant film which is adhering to the substrate and is immobilized so that the mass transport through this film will take place solely by means of molecular diffusion, whereas, in the region outside this film a streaming will take place at a velocity which will possess the same value and direction at all points. Further on, we will assume that in the region outside the stagnant film there will be the same composition at all points, and that a concentration gradient will exist solely across the film. Combining the expressions (*1*) and (*2*), a relation is obtained

$$\delta = 1{\cdot}7208(\mu x/G_m)^{1/2}\,, \quad (3)$$

where $G_m = u\,.\,\varrho$ and denotes the mass velocity, *i.e.* the mass of the gas passed through a unit cross-section in a unit time. According to the relation (*3*), the effective film thickness, δ, increases with the square root of the distance from the leading edge, and consequently it is a variable quantity which is a function of the position on the substrate. With respect to common experimental conditions (especially small dimensions of the substrate and accuracy of measurement), however, it is sufficient in the first approximation to consider a mean value of the thickness δ and to take it as constant along the whole substrate. Denoting the length of the substrate in the direction of gas flow as L, we arrive from the relation (*3*) according to the mean value theorem to an expression for the mean effective thickness of the gas film, $\bar{\delta}$, in the form

$$\bar{\delta} = 1{\cdot}1472(\mu/G_m)^{1/2}\,L^{1/2}\,. \quad (4)$$

It may be mentioned that the mean effective thickness is a quantity which is averaged twice: for the first time in the direction perpendicular to the substrate plane (effective value) and for the second time in the direction of the gas flow along the substrate (mean value).

Further on, a steady state will be assumed in this diffusion model. At a constant feed rate and its constant composition, concentrations will be established in the main gas stream not varying with time, and since even the composition of the formed epitaxial layer is constant, the epitaxial growth rate will be independent of time too. And with respect to the small capacity of the gas film as compared with the capacity of the epitaxial layer, it can be expected that the steady state will be established rather quickly under given conditions. Under current times of experiment (approximately hours) it is to be expected that the time for steadying the regime will be negligibly short and that the steady state approximation will be an adequate way of description. Under the steady state conditions, the diffusion rate, r_d, of the i-th component through the stagnant gas film of the thickness $\bar{\delta}$ can be expressed according to

Fick's law as

$$r_d(i) = -D_i \, . \, (\Delta c_i/\bar{\delta}) \, , \quad (5)$$

where Δc_i is the difference of concentrations of the i-th component on both sides of the stagnant film. With gases, there is a practice to deal rather with partial pressures than with concentrations, and under ideal behaviour of the gas mixture it is possible to rewrite the equation (5) into the form

$$r_d(i) = (-D_i/RT\bar{\delta}) \, . \, \Delta P_i \, . \quad (6)$$

The equation (6) may be put into a form common in chemical engineering, namely

$$r_d(i) = k_G(i) \, . \, (-\Delta P_i) \, , \quad (7)$$

where the transport coefficient of the i-th component $k_G(i)$ in the gas phase is given by the expression

$$k_G(i) = D_i/RT\bar{\delta} \, . \quad (8)$$

Accordingly, the value of the transport coefficient can be *a priori* determined from the values of diffusion coefficients D_i (either experimental or estimated ones) and from the mean effective thickness of the stagnant gas film $\bar{\delta}$ in compliance with the equation (4).

Chemical Equilibria

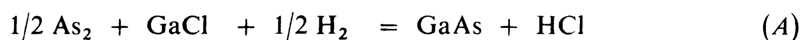
To calculate the diffusion rate according to the equation (7), it remains to determine the difference of partial pressures of the i-th component, ΔP_i. Since this paper is aimed at the case, where the rate controlling step of the whole process is the gas phase diffusion, it follows from this premise, that all other steps will take place at equilibrium. Therefore, equilibrium conditions will be established at the surface of epitaxial layer, where the equilibrium partial pressures of components, P_i^*, will exist. Since the temperature of experiment is rahter high (1 000 K and more), it is feasible to assume in the diffusion model considered that a chemical equilibrium will be established in the gas phase too, and the corresponding partial pressures of components will be denoted as P_i. The difference between this equilibrium and the equilibrium at the surface of epitaxial layer consists in that the solid phase of gallium arsenide is absent in the gas phase, although the same chemical reactions can take place here as at the surface of the substrate. From the thermodynamic point of view, the homogeneous equilibrium in the gas phase will be metastable with regard to the formation of the solid product. The assumption of the metastable equilibrium in the

gas phase appears here as a plausible one, since on forming a solid product in the gas phase, solid aggregates of the gallium arsenide would appear, which on reaching the surface would possess a significantly lowered mobility so that rather a polycrystalline product would be formed than an epitaxial monocrystal. In accord with the model proposed above, which can be called as a dual equilibrium model, the driving force of diffusion of the *i*-th component in the equation (7) will be given by the relation

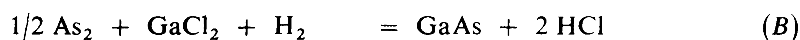
$$-\Delta P_i = -(P_i^* - P_i) = P_i - P_i^* , \qquad (9)$$

where P_i refers to the homogeneous metastable equilibrium and P_i^* to a complete heterogeneous equilibrium in the presence of the solid product phase. Here, the symbol Δ denotes the difference between the final state and the initial one, similarly as in thermodynamics.

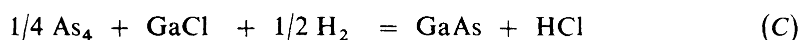
Analyzing the computation[3,4] of equilibrium compositions on forming the gallium arsenide in the system Ga–As–Cl–H, it is possible to find that from all considered species only the following reaction components are present in significant concentrations: As_2, As_4, GaCl, $GaCl_2$, HCl and hydrogen which is present in a considerable excess. Accordingly, in the formation of gallium arsenide the following reactions can play the leading part



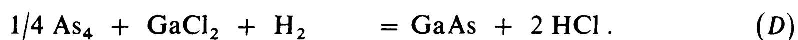
$$1/2\, As_2 + GaCl + 1/2\, H_2 = GaAs + HCl \qquad (A)$$



$$1/2\, As_2 + GaCl_2 + H_2 = GaAs + 2\, HCl \qquad (B)$$



$$1/4\, As_4 + GaCl + 1/2\, H_2 = GaAs + HCl \qquad (C)$$

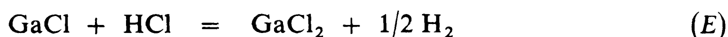


$$1/4\, As_4 + GaCl_2 + H_2 = GaAs + 2\, HCl\,. \qquad (D)$$

The four reactions listed above are not, however, independent, because a relation exists among them

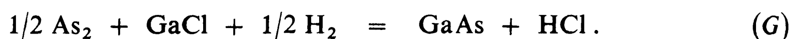
$$(A) + (D) = (B) + (C), \qquad (10)$$

so that only three of them or their three linear combinations are independent, for instance



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

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



$$1/2\, As_2 + GaCl + 1/2\, H_2 = GaAs + HCl\,. \qquad (G)$$

The last three equations were obtained in the following way

$$(E) = (A) - (B) = (C) - (D) \tag{11}$$

$$(F) = 4(C) - 4(A) = 4(D) - 4(B) \tag{12}$$

$$(G) = (A)\,. \tag{13}$$

With regard to the very small and consequently negligible concentration of the gallium arsenide in the gas phase, it is possible to determine the values of P_i by a simultaneous solution of equilibria only in two reactions (E) and (F) together with a material balance basing on the feed composition.

The determination of partial pressures P_i^* is somewhat more complex, since their values are determined not only by equilibrium conditions but also by the rates of diffusion of individual species towards to the substrate. From considerations concerning the diffusion rates, two conditions are arising. First of all, because of the assumed existence of the steady state, the diffusion of both components from which the epitaxial layer of the gallium arsenide is formed has to take place in a stoichiometric ratio. Accordingly, the total rate of diffusion of the arsenic, $r_d(\text{As})$, has to be equal to that of the gallium, $r_d(\text{Ga})$, so that

$$r_d(\text{As}) = r_d(\text{Ga})\,, \tag{14}$$

where the total rate of arsenic diffusion is given by the sum of diffusion rates of dimer and tetramer of the arsenic, and the total gallium diffusion rate is given by the sum of diffusion rates of the gallium monochloride and dichloride, as it is also evident from the reaction set of (A) to (D). With regard to the stoichiometry, the following relations are valid

$$r_d(\text{As}) = 2r_d(\text{As}_2) + 4r_d(\text{As}_4) \tag{15}$$

and

$$r_d(\text{Ga}) = r_d(\text{GaCl}) + r_d(\text{GaCl}_2)\,, \tag{16}$$

the diffusion rates of individual species on the right hand sides of equations (15) and (16) being given by the relation (7) in combination with the equations (8) and (9). The second condition concerns the element which is co-transported in reagents to the substrate, which is not, however, built-in into the epitaxial layer, so that it has to be retransported from the substrate back into the main gas stream. The chlorine is the matter which reaches the substrate in the form of gallium mono- and dichloride and passes back in the form of hydrogen chloride. If the steady state is not to be disturbed, the total diffusion rate of chlorine in all its forms has to be equal to zero

so that the following is valid

$$r_d(Cl) = r_d(GaCl) + 2r_d(GaCl_2) + r_d(HCl) = 0\,, \qquad (17)$$

where the individual diffusion rates are expressed analogously as above. The values of partial pressures, P_i^*, of the components of As_2, As_4, GaCl, $GaCl_2$, and HCl are then determined by equilibrium conditions of three reactions (*E*), (*F*), and (*G*) together with the diffusion conditions (*14*) to (*17*) in combination with the equations (7) to (9) and with the values of partial pressures P_i, the determination of which has been discussed above. The equilibrium condition of chemical reactions (*E*) to (*G*) have been used in the form

$$K_E = P^*(GaCl_2)/P^*(GaCl)\,.\,P^*(HCl)\,, \qquad (18)$$

$$K_F = P^*(As_4)/[P^*(As_2)]^2\,, \qquad (19)$$

$$K_G = P^*(HCl)/[P^*(As_2)]^{1/2}\,.\,P^*(GaCl)\,. \qquad (20)$$

In these expressions, the partial pressures of hydrogen and of gallium arsenide are included in the equilibrium constants. The partial pressure of hydrogen practically does not change in consequence of the great excess in which it is present in the reaction mixture, and the partial pressure of gallium arsenide remains practically constant owing to the presence of the solid phase.

Rate of Epitaxial Growth of Gallium Arsenide

The diffusion model described above has been brought to the stage of quantitative treatment which permits to calculate the rate of epitaxial growth. This rate, v, can be expressed by means of the reaction rate, r, by the relation[5]

$$v = M_P\,.\,\nu_P\,.\,r/\varrho_P\,, \qquad (21)$$

where M_P, ν_P, and ϱ_P are the molecular mass, stoichiometric coefficient, and density of the solid product forming the epitaxial layer. The reaction rate of the surface reaction, r, is here referred to the unit area of the epitaxial layer, and it is expressed by means of the reaction extent in agreement with the contemporary convention. The product of $\nu_P\,.\,r$ denotes the rate of product formation in molar units, that means in the same units by which the diffusion rate is usually expressed. In the steady state, the diffusion rate of reactants, r_d, is equal to the rate of the surface reaction, so that

$$r_P = \nu_P\,.\,r\,. \qquad (22)$$

As a reactant, either the arsenic or the gallium can be selected in the given case. If the diffusion rate is expressed by means of gallium, an expression is obtained for the rate of epitaxial growth in the following form on combining the equations (*21*), (*22*), and (*16*)

$$v = (M_{GaAs}/\varrho_{GaAs}) \left[r_P(GaCl) + r_P(GaCl_2) \right] , \tag{23}$$

where the diffusion rates of gallium mono- and dichloride are given by the relation of the type (*7*) in combination with equations (*8*) and (*9*).

The physical parameters that have been used for calculations according to the equation (*23*) are given in the following. For the density of the gallium arsenide, the value of $\varrho_{GaAs} = 5{\cdot}317 \text{ g cm}^{-3}$ has been taken[6]. To calculate the diffusion coefficients of individual species in a polycomponent gas mixture, it is possible to use the relation[7]

$$D_i = \left[(1 - N_i) / \sum_{k \neq i} N_k \right] D_{ik} , \tag{24}$$

where N_i and N_k are mole fractions and D_{ik} is the diffusion coefficient in the partial binary system *i–k*. Since the hydrogen as a carrier gas is present in a great excess in the considered reaction mixture, the mole fractions of all other components assume negligible values as compared to the practically unit value for hydrogen, and the relation (*24*) degenerates to

$$D_i = D_{iH_2} . \tag{25}$$

Accordingly, it is possible to substitute the diffusion coefficient of the *i*-th component in the polycomponent mixture, D_i, by the binary diffusion coefficient of this component in its binary mixture with hydrogen, D_{iH_2}, in a very good approximation. The binary coefficients of five components (As_2, As_4, GaCl, $GaCl_2$, HCl) in the mixture with hydrogen have been calculated according to a semiempirical relation of Fuller and coworkers[7], the necessary molar volumes of components being calculated additively from atomic volumes except hydrogen, where the value recommended by Fuller and coworkers has been used, *i.e.* $V(H) = 2{\cdot}0 \text{ cm}^3 \text{ mol}^{-1}$. The atomic volume for arsenic is not stated by Fuller, and for that reason the Le Bas volume[7], $V(As) = 30{\cdot}5 \text{ cm}^3 \text{ mol}^{-1}$, has been used. The Le Bas volumes are used in combination with Gilliland equation which is similar to Fuller's relation and is in fact its precursor[7]. Since the necessary value for gallium is lacking, we have estimated the atomic volume of gallium as $V(Ga) = 28{\cdot}0 \text{ cm}^3 \text{ mol}^{-1}$, considering the molar volumes of chlorides and elements in the pertinent region of the periodic system. The diffusion coefficients determined in this way have been used both in calculations of partial pressures P_i by means of equations (*14*) to (*17*) and in computations of epitaxial growth rates according to the equation (*23*) in combination with relations (*7*) and (*8*).

To calculate the mean effective thickness of the stagnant film according to the equation (*4*), the viscosity of the gaseous reaction mixture should be used. The viscosity of a gas mixture depends on its molar composition[7], and since in the considered case the mole fractions of all components are negligibly small in comparison with hydrogen and the viscosities of various gases are not greatly different, it is possible to approximate very well the viscosity of the mixture by the viscosity of the hydrogen alone. We have found that the experimental data on viscosity of the hydrogen[8] in the temperature range from 0° to 800°C can be reproduced with an excellent precision (average deviation $\pm 0.3\%$) by an empirical relation in the form

$$\mu = 2.000 \cdot 10^{-6} \cdot T^{2/3}, \quad (26)$$

where μ is the dynamic viscosity in CGS units and T is the temperature in kelvins. For that reason, the values calculated according to the relation (*26*) have been substituted into the equation (*4*).

In contrast to the viscosity, it is not possible to approximate the mass rate of the streaming gas mixture G_m by the rate of the hydrogen alone since the molecular masses of individual components differ one from another by up to two orders of magnitude, and such an approximation would lead to errors amounting some tens per cent. Therefore, the values of G_m have been computed for every gas composition separately, considering the reactor diameter as 4 cm and the length of the substrate L in the equation (*4*) as 1 cm.

By the procedure described and by means of the values given above, the epitaxial growth rate of gallium arsenide has been computed in dependence on the flow rate, on the composition of the feed and on temperature. The resulting dependences are demonstrated in Figs 1, 2, and 3, where the symbol N denotes the mole fraction.

DISCUSSION

The computed dependence of the epitaxial growth rate of gallium arsenide on the feed rate is of parabolic shape, as it is evident from the Fig. 1, which is caused by the fact that the transport coefficient, k_G, is directly proportional to the square root of the gas flow rate. This dependence follows from substituting the relation (*4*) into the equation (*8*).

With the dependence of the growth rate on composition, it is seen from the Fig. 2, that the computed course is somewhat steeper than the linear one, although the driving forces of diffusion (*i.e.* the differences of equilibrium partial pressures) of both gallium forms are almost linear functions of the partial pressure of gallium chloride in the range considered. This steeper course results from an increase of the value of the transport coefficient (about 30%) which is raised in consequence of the increase of the mass flow rates which increases owing to the enhancement of partial

pressures of components which have a mass significantly greater than the carrier gas hydrogen has.

In the temperature dependence demonstrated in Fig. 3, it is noteworthy that the computed growth rate decreases with increasing temperature in the range considered, although the values of transport coefficients of both gallium forms moderately in-

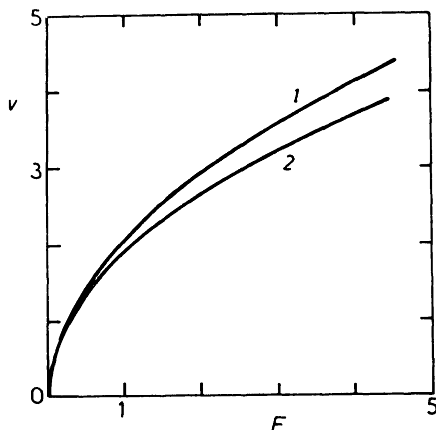


FIG. 1

Dependence of Epitaxial Growth Rate of GaAs Feed Rate F. *1* $N_{HCl} = 2{\cdot}6 \cdot 10^{-4}$, 2 $N_{HCl} = 1{\cdot}3 \cdot 10^{-3}$

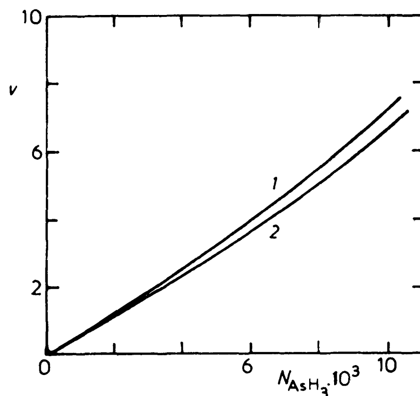


FIG. 2

Dependence of Epitaxial Growth Rate of GaAs on Feed Composition. *1* 5% HCl, 2 25% HCl; both values are refered to chlorides; $N_{AsH_3} = N_{GaCl}$

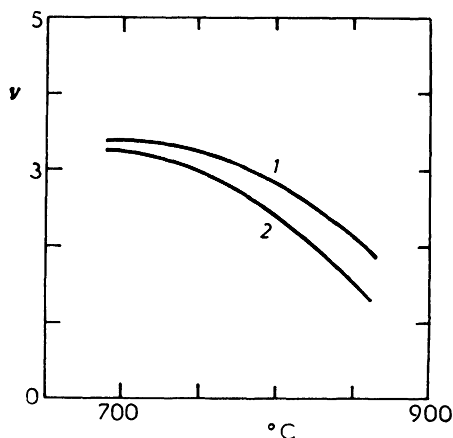


FIG. 3

Dependence of Epitaxial Growth Rate of GaAs on Temperature. *1* $N_{HCl} = 2{\cdot}6 \cdot 10^{-4}$, *2* $N_{HCl} = 1{\cdot}2 \cdot 10^{-3}$

crease (about 6%) in this interval. The decrease of the growth rate is due to the reduction of the difference of equilibrium partial pressures of components ($P_i - P_i^*$) with the temperature increase, the decrease of driving forces being significantly greater than the increase of the rate parameter, so that resulting effect is the reduction of the growth rate. Thus, in the temperature range studied, the temperature dependence of equilibrium dominates over the temperature dependence of the process kinetics.

An increase of the hydrogen chloride concentration in the feed has the same effect in all the dependences studied, *i.e.* it reduces the growth rate. This retarding effect can be explained in the following way. With increasing hydrogen chloride concentration, the fraction of gallium in the form of dichloride increases in accordance with the mass action law at equilibrium in the reaction (*E*). The dichloride as a greater molecule has a lower diffusion coefficient than the monochloride (about 17%) and, therefore, the gallium transport rate as a whole is reduced. Further on, in the formation of the gallium arsenide, the hydrogen chloride represents a gaseous by-product, as it is evident from the reaction (*A*) to (*D*), so that by increasing its concentration the equilibrium is shifted to the opposite direction. And finally, according to the computations, the gallium dichloride exhibits a peculiarity in that it has an inversed concentration gradient, so that its concentration near the substrate is higher than that in the main gas stream under all conditions studied. That means that gallium in the form of dichloride is transported from the substrate back into the main gas stream. Since all these three partial effects act in the same direction, the final effects act in the same direction, the final effect will be generally a resultant of their superposition. However, an analysis of the proportions of individual contributions does not seem indispensable, since the resulting effect is not large.

In appreciating the significance of results stated in this paper, it is necessary to realize that the computations carried out do not rest even partially upon the growth rate found experimentally. That is to say, they do not include a single adjustable parameter but they have been carried out *ab initio*, *i.e.* on the basis of a model conception only. From this point of view, it is necessary to appraise all the results stated above not as correlations but as predictions, concerning both the trends investigated and the absolute values of growth rates. In the accessible literature, such an approach appears to be without precedent up to the present time. If the dual equilibrium diffusion model proposed here represents an adequate description of the real course in the growth of epitaxial layers of the gallium arsenide, it can be expected that the predicted results will be in agreement with experiment, if the rate controlling step will be only the gas film diffusion. In cases, where the rate of chemical reaction or of other processes will partake in the growth, the course will be hindered by other factors, and the resulting rate will be lower. Therefore, the growth rates computed here should be the maximum ones, and from this point of view it is necessary to think them as an upper limit to which the reality can approach.

Even the experiments[9] carried out under conditions considered in this paper are in agreement with the above conclusion since they show the epitaxial growth rates of gallium arsenide which are several times lower than the maximum possible values stated here. The experimentally found dependences of growth rates on the feed rate, its composition, and on the temperature exhibit, however, qualitatively the same courses that were predicted in this paper. A more detailed analysis will be contained in the next paper.

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