
A QUANTITATIVE MODEL OF EPITAXIAL LAYERS GROWTH FROM THE GAS PHASE WITH A SIMULTANEOUS PARTICIPATION OF DIFFUSION, ADSORPTION, AND CHEMICAL REACTION

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For a quantitative description of the epitaxial growth rate of gallium arsenide, a model has been proposed including two rate controlling steps, namely one step of physical nature and the other one of chemical nature. As the step of physical nature, the diffusion of gaseous components between the gas phase and the epitaxial layer surface has been considered, and from the steps of chemical nature the adsorption of gaseous components on the epitaxial layer surface and a heterogeneous surface reaction have been taken into account. According to the kind of the chemical rate controlling step, five mechanisms have been proposed, where a one — centre model was used in all cases, *i.e.* the idea that the rate controlling step takes place under participation of one active centre. For all the mechanisms considered, the pertaining rate equations have been derived, which were confronted with the experimentally found dependences of the growth rate on partial pressures of components in the feed. The results are discussed both from the view point of plausibility of individual mechanisms and from the point of view of their applicability and of the next research direction.

This paper represents a continuation of the theoretical study¹ of kinetics of the epitaxial layer growth from the gas phase, where a diffusion kinetic model was formulated with a participation of diffusion and chemical reaction, described by a formal kinetic expression for the reaction rate which met the condition of equilibrium. In this paper, the diffusion kinetic model is extended in such a way as to include even the adsorption processes, namely both the adsorption of reactants and of gaseous products. At the same time it was necessary to abandon the formal kinetic description of the chemical reaction used previously, and to approach a more realistic conception of the surface reaction. These changes are so extensive that it appears convenient to summarize all the basic ideas of the model newly proposed.

THEORETICAL

Basic Model Ideas

Let us imagine that the whole growth process of epitaxial gallium arsenide layers takes place in the following way. The gallium compounds in the form of chlorides and the arsenic in the form of arsine together with some amount of hydrogen chloride are fed as reactants into a stream of hydrogen as a carrier gas. When passing through the high temperature zone, a homogeneous equilibrium is established in this gas mixture, which is metastable with regard to the deposition of the solid gallium arsenide. The molecular species, which are present in the equilibrium mixture, are diffusing to the surface of the substrate, where they are adsorbed on active centres, and where the chemical reaction takes place among them. At the same time, however, it is not necessary, that all the species taking part in the surface heterogeneous reaction should be in an adsorbed state. On the contrary, even the more general cases will be considered, where the activated complex will be formed with participation not only of the adsorbed reaction partners but also of particles forming it by an impact from the gas phase. In the surface reaction, the solid gallium arsenide is formed on the one hand, and on the other hand the hydrogen chloride is formed, which is released into the gas phase either directly or after a preceding desorption in cases where it is formed in an adsorbed state. In both cases the gaseous hydrogen chloride will be transported by diffusion into the main gas stream with which it will be carried away into the space outside the substrate and, finally, even outside the reactor.

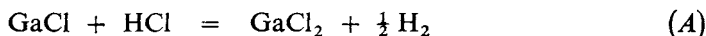
In the sequence of steps mentioned above it will be assumed in addition, that two of them are simultaneously controlling the resulting rate of the whole process, *i.e.* that there exist two rate controlling steps. Therefore it follows, that the remaining steps will take place at equilibrium. With regard to the dependence of the epitaxial growth rate of gallium arsenide on the velocity of the gas flow found by experiment, one of the rate controlling steps must be a transport process in the gas phase, in the given case the diffusion. The other rate controlling step can be either the heterogeneous chemical reaction on the substrate surface or the adsorption of some species taking part in the surface reaction.

In proposing a kinetic model of the type considered above, it is finally necessary to define the number of active centres, under the participation of which the rate controlling step of chemical nature takes place. In other steps, which take place at equilibrium, this point is irrelevant, since in these steps only the condition of equilibrium applies which is independent of the mechanism and, therefore, of the number of active centres. In the kinetics considered, the minimum number of active centres is equal to one, and in this case also the simplest model results. With regard to the present stage of development of kinetic studies, the one centre model has here been

investigated, namely in five contingent variants in accordance with the assumed mechanism, that is according to the type of the second rate controlling step.

Quantitative Description of One Centre Model

On the basis of an analysis of occurrence of individual species in the epitaxial growth of gallium arsenide, which has been carried out previously², the following three chemical reactions have been considered as sufficient for a quantitative description:



Under experimental conditions (A) and (B) are homogeneous gas reactions, which will take place at equilibrium in accordance with the ideas given above, so that the values of partial pressures of components, p_i , in the main stream will be given by the equations

$$\frac{p_{\text{GaCl}_2} \cdot p_{\text{H}_2}^{1/2}}{p_{\text{GaCl}} \cdot p_{\text{HCl}}} = K_A \quad (1)$$

$$\frac{p_{\text{As}_4}}{p_{\text{As}_2}^2} = K_B \quad (2)$$

together with inlet concentrations of components. The quantities K_A and K_B in equations (1) and (2) denote the equilibrium constants of reactions (A) and (B) which are functions of the temperature only. Between the main gas stream and the substrate surface, the gas film diffusion will take place, the driving force of which consists in the difference of values of the partial pressures on both sides of the film. Thus the rate of diffusion of the i -th component, $r_d(i)$, is given by the expression²

$$r_d(i) = k_G(i) \cdot (p_i - p_i^*), \quad (3)$$

where p_i^* denotes the partial pressure of the i -th component in the gas phase close at the surface of the substrate. The transport coefficient $k_G(i)$ depends on the diffusion coefficient D_i and on the mean effective thickness of the boundary layer, δ , according to the relation²

$$k_G(i) = \frac{D_i}{RT\delta} \quad (4)$$

The value of the mean effective thickness of the boundary layer, δ , is dependent on the distance of the front boundary of the substrate from the leading edge of the gas, L_1 , and on the length of the substrate, L , according to the equation¹

$$\delta = 1.1472 \left(\frac{\mu}{Gm} \right)^{1/2} \cdot L^{1/2} \left[\left(1 + \frac{L_1}{L} \right)^{3/2} - \left(\frac{L_1}{L} \right)^{3/2} \right], \quad (5)$$

where μ denotes the dynamic viscosity of the streaming gas.

The values of partial pressures, p_i^* , in the equation (3) are given on the one hand by the conditions of partial equilibria in reactions (A) and (B) in the gas phase close at the surface of the substrate which are analogical to the equations (1) and (2), thus

$$\frac{p_{\text{GaCl}}^* \cdot (p_{\text{H}_2}^*)^{1/2}}{p_{\text{GaCl}}^* \cdot p_{\text{HCl}}^*} = K_A \quad (6)$$

and

$$\frac{p_{\text{As}_4}^*}{(p_{\text{As}_2}^*)^2} = K_B, \quad (7)$$

and on the other hand by the steady state conditions which are of the following form. The first of them respects the fact, that the diffusion rate of arsenic, $r_d(\text{As})$, and of gallium, $r_d(\text{Ga})$, in all their forms has to take place in the stoichiometric ratio corresponding to the solid product, namely, that

$$r_d(\text{As}) = r_d(\text{Ga}). \quad (8)$$

The other expresses the circumstance, that the total diffusion rate of chlorine in all its forms is equal to zero, or

$$r_d(\text{Cl}) = 0. \quad (9)$$

These two conditions are accompanied by a third condition, namely, that the rates of both rate controlling steps, *i.e.* of the diffusion, r_d , and of the other step, r , must be equal, or

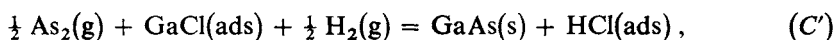
$$r_d = r. \quad (10)$$

If this condition was not fulfilled, an accumulation or a decumulation of components would take place in the vicinity of the substrate in dependence on that, which of both steps was faster, and in this way the steady state would be violated. In the equation (10), either the $r_d(\text{Ga})$ or $r_d(\text{As})$ may be substituted for the diffusion rate, r_d , as it follows from the relation (8), and for the r , it is necessary to substitute an

expression for the rate of the other rate controlling step, that is of the chemical surface reaction or of the adsorption of some component. Therefore, in what follows the rate equations are derived for five contingent mechanisms, the summary of which is contained in Table I. In all cases mentioned above, it has been taken into account, that the final product is formed in the reaction (C), and that one active centre participates in the rate controlling step, as it has been referred to.

Mechanism I

If only GaCl is adsorbed from the reactants, the reaction (C) may be written with more precision in the form



which complies with the fundamental requirement of the activated complex theory, namely, that the activated complex in the direct reaction is the same as the one in the reverse reaction. In this case, the activated complex contains only one active centre, which is occupied by a molecule of GaCl in the direct reaction and by a molecule of HCl in the reverse reaction. If the rate controlling step consists in the surface reaction (C'), we can express its rate, r , by an equation

$$r = k_+(p_{\text{As}_2})^{1/2} \cdot c_{\text{GaCl}} \cdot (p_{\text{H}_2}^*)^{1/2} - k_-c_{\text{HCl}}, \quad (11)$$

when the reaction orders with respect to gaseous components are equal to the stoichiometric coefficients in the reaction (C'). The remaining two steps, *i.e.* the adsorption of GaCl and the desorption of HCl will take place at equilibrium, so that their

TABLE I
Considered mechanism

Designation	Second rate controlling step	Comment
I	Surface reaction	GaCl is adsorbed
II	Surface reaction	As is adsorbed
III	Adsorption of GaCl	—
IV	Adsorption of As ₂	—
V	Desorption of HCl	—

equilibrium surface concentrations, c_{GaCl} and c_{HCl} , may be written as^{3,4}

$$c_{\text{GaCl}} = c_n K_{\text{GaCl}} p_{\text{GaCl}}^* \quad (12)$$

$$c_{\text{HCl}} = c_n K_{\text{HCl}} p_{\text{HCl}}^*, \quad (13)$$

where c_n denotes the surface concentration of unoccupied active centres, and K_{GaCl} and K_{HCl} are equilibrium adsorption constants of pertinent components. Substituting the expressions (12) and (13) into equation (11), one obtains on rearranging

$$r = k_+ K_{\text{GaCl}} c_n \left[(p_{\text{As}_2}^*)^{1/2} p_{\text{GaCl}}^* (p_{\text{H}_2}^*)^{1/2} - \frac{K_{\text{HCl}} p_{\text{HCl}}^*}{K' K_{\text{GaCl}}} \right], \quad (14)$$

where K' denotes the equilibrium constant of the surface reaction (C') which is equal to the ratio of rate constants for the direct reaction, k_+ , and the reverse reaction, k_- , or

$$K' = k_+ / k_-. \quad (15)$$

The concentration of unoccupied active centres, c_n , can be eliminated from the equation (14) by means of the balance of active centres, according to which the total number of active centres, L , is equal to the sum of the number of centres both unoccupied by molecules of GaCl and HCl, so that

$$c_n + c_{\text{GaCl}} + c_{\text{HCl}} = L. \quad (16)$$

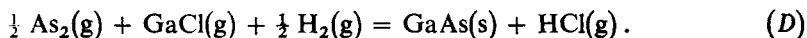
Substituting the expressions (12) and (13) into the balance (16), the concentration of unoccupied centres may be written as

$$c_n = \frac{L}{1 + K_{\text{GaCl}} p_{\text{GaCl}}^* + K_{\text{HCl}} p_{\text{HCl}}^*} \quad (17)$$

and after substitution into the relation (14) and after rearranging, the rate equation of the chemical rate controlling step is obtained

$$r = \frac{k_+ L K_{\text{GaCl}} \left[(p_{\text{As}_2}^*)^{1/2} p_{\text{GaCl}}^* (p_{\text{H}_2}^*)^{1/2} - \frac{p_{\text{HCl}}^*}{K_D} \right]}{1 + K_{\text{GaCl}} p_{\text{GaCl}}^* + K_{\text{HCl}} p_{\text{HCl}}^*}, \quad (18)$$

where K_D is the equilibrium constant of reaction (C) in the form



This equilibrium constant can be determined from known thermodynamic data of substances appearing in the reaction (D), and its relationship to other equilibrium constants is given by an expression

$$K_D = K' \frac{K_{\text{GaCl}}}{K_{\text{HCl}}} \quad (19)$$

Mechanism II

If only the As is adsorbed from the reactants, the reaction (C) assumes the form



and if this surface reaction is rate controlling, its rate r may be expressed by the equation

$$r = k_+ c_{\text{As}} p_{\text{GaCl}}^* (p_{\text{H}_2}^*)^{1/2} - k_- c_{\text{HCl}} \quad (20)$$

using the same approach as with the previous mechanism. Then the other two steps, *i.e.* the adsorption of As and HCl will take place at equilibrium. Thus the equilibrium surface concentration of HCl can be expressed immediately by the relation (13), however, with the arsenic the situation is somewhat more complicated. In accord with the equation (C''), the arsenic reacts in the form of adsorbed atoms, whereas according to previous analyses², the prevailing form of the arsenic in the gas phase are diatomic molecules As_2 . These facts may be respected by taking into account the surface dissociation of As_2 molecules. According to this idea, the molecule of As_2 is adsorbed first of an unoccupied centre n in accord with the equation



In the second step, a dissociation takes place under participation of another free centre according to the equation



The equilibrium conditions in both these steps may be written as³

$$c_{\text{As}_2} = c_n K_E p_{\text{As}_2}^* \quad (21)$$

and

$$\frac{c_{\text{As}}^2}{c_{\text{As}_2} \cdot c_n} = K_F, \quad (22)$$

where K_E denotes the equilibrium adsorption constant of diatomic molecules As_2 and K_F is the equilibrium constant of the surface dissociation (F). Combining the equations (21) and (22) and rearranging, an expression for the surface concentration of adsorbed arsenic atoms, c_{As} , is obtained in the form

$$c_{As} = c_n (K'_{As_2})^{1/2} \cdot (p_{As_2}^*)^{1/2}, \quad (23)$$

where the quantity K'_{As_2} may be denoted as the equilibrium adsorption constant of arsenic with dissociation, since it is equal to the product of equilibrium constants of both steps, *i.e.* of the adsorption (E) and of the surface dissociation (F)

$$K'_{As_2} = K_E \cdot K_F. \quad (24)$$

Substituting the expressions (23) and (13) into the equation (20), a relation is obtained after an arrangement

$$r = k_+ (K_{As_2})^{1/2} c_n \left[(p_{As_2}^*)^{1/2} p_{GaCl}^* (p_{H_2}^*)^{1/2} - \frac{K_{HCl} p_{HCl}^*}{K' (K'_{As_2})^{1/2}} \right], \quad (25)$$

where K' denotes the equilibrium constant of the surface reaction (C''), which is even here equal to the ratio of rate constants, analogously as in the relation (15). In a similar way as in the previous case, the concentration of unoccupied centres can be eliminated by means of the balance of active centres, which assumes here the form

$$c_n + c_{As} + c_{As_2} + c_{HCl} = L. \quad (26)$$

If the equilibrium constant of the surface dissociation (F) is much greater than the equilibrium constant of adsorption (E), the concentration c_{As_2} is negligible as compared with the concentration c_{As} , and the balance (26) is simplified to

$$c_n + c_{As} + c_{HCl} = L. \quad (27)$$

The concentration of unoccupied centres can be expressed by substituting the expressions (23) and (13) into the balance (27) as

$$c_n = \frac{L}{1 + (K'_{As_2})^{1/2} \cdot (p_{As_2}^*)^{1/2} + K_{HCl} p_{HCl}^*} \quad (28)$$

and substituting the relation (28) into the equation (25), a rate equation for the

mechanism II is obtained in the form

$$r = \frac{k_+ L (K'_{As_2})^{1/2} \left[(p_{As_2}^*)^{1/2} \cdot p_{GaCl}^* \cdot (p_{H_2}^*)^{1/2} - \frac{p_{HCl}}{K_D} \right]}{1 + (K'_{As_2})^{1/2} \cdot (p_{As_2}^*)^{1/2} + K_{HCl} p_{HCl}^*}, \quad (29)$$

where the K_D is the equilibrium constant of the reaction (D) which is related to other equilibrium constants by

$$K_D = K' \frac{(K'_{As_2})^{1/2}}{K_{HCl}}. \quad (30)$$

Mechanism III

In the case that the rate controlling step is the adsorption of the GaCl, the overall rate r is equal to the rate of adsorption of the GaCl, for which the following is valid³,

$$r = r_{GaCl} = k_{GaCl} \left(p_{GaCl}^* \cdot c_n - \frac{c_{GaCl}}{K_{GaCl}} \right), \quad (31)$$

if the adsorption of the GaCl takes place on one centre, *i.e.* in the case of molecular adsorption. The surface concentration of adsorbed molecules, c_{GaCl} , may be expressed from the condition of equilibrium of the surface reaction (C') as

$$c_{GaCl} = \frac{1}{K'} \frac{c_{HCl}}{(p_{As_2}^*)^{1/2} \cdot (p_{H_2}^*)^{1/2}}, \quad (32)$$

where the surface concentration of hydrogen chloride is obtained from the condition of equilibrium in the adsorption of HCl, *i.e.* from the equation (13), so that we obtain after substitution

$$c_{GaCl} = c_n \frac{K_{HCl}}{K'} \cdot \frac{p_{HCl}^*}{(p_{As_2}^*)^{1/2} (p_{H_2}^*)^{1/2}}. \quad (33)$$

From the balance of active centres, which in this case assumes the form of the equation (16), an expression for the concentration of unoccupied centres is obtained after substituting the relations (13) and (32)

$$c_n = \frac{L}{1 + \frac{K_{HCl}}{K'} \frac{p_{HCl}^*}{(p_{As_2}^*)^{1/2} (p_{H_2}^*)^{1/2}} + K_{HCl} p_{HCl}^*}, \quad (34)$$

so that combining the equations (31), (33), (34), (13) and rearranging, a relation for the reaction rate is obtained in final form

$$r = \frac{k_{\text{GaCl}} + L \left[p_{\text{GaCl}}^* - \frac{p_{\text{HCl}}^*}{K_D (p_{\text{As}_2}^*)^{1/2} (p_{\text{H}_2}^*)^{1/2}} \right]}{1 + K_{\text{GaCl}} \frac{p_{\text{HCl}}^*}{K_D (p_{\text{As}_2}^*)^{1/2} (p_{\text{H}_2}^*)^{1/2}} + K_{\text{HCl}} p_{\text{HCl}}^*}. \quad (35)$$

The K_D in this rate equation denotes the equilibrium constant of the reaction (D) which is connected to the other constants through the relation (19).

Mechanism IV

In this mechanism, the rate controlling step is the adsorption of the arsenic, and analogously as with the mechanism II, we will start even here from the idea, that the arsenic is first adsorbed in the form of diatomic molecules As_2 which dissociate in the next step under participation of another free centre into adsorbed atoms of the arsenic. This idea may be consequently recorded by the equations (E) and (F). In contrast to the mechanism II, the rate controlling step is here the adsorption (E) and both the surface reaction (F) and the chemical reaction (C'') will take place at equilibrium, whereas, in the mechanism II, both the steps (E) and (F) have been considered as the equilibrium ones, since the rate controlling step was the chemical reaction. The desorption of the hydrogen chloride takes place at equilibrium in both cases. Consequently, the overall rate r will be equal to the adsorption rate of the arsenic (E), for which the following equation may be written³

$$r = r_{\text{As}_2} = k_{\text{As}_2} \left(p_{\text{As}_2}^* c_n - \frac{c_{\text{As}_2}}{K_E} \right). \quad (36)$$

The surface concentration of adsorbed molecules of the arsenic, c_{As_2} , will be given by the condition of equilibrium in the surface dissociation (F)

$$c_{\text{As}_2} = \frac{c_{\text{As}}^2}{K_F c_n}, \quad (37)$$

where the concentration of adsorbed arsenic atoms, c_{As} , can be expressed from the condition of equilibrium in the surface reaction according to the equation (C'') as

$$c_{\text{As}} = \frac{c_{\text{HCl}}}{K' p_{\text{GaCl}} (p_{\text{H}_2})^{1/2}}. \quad (38)$$

Finally, the surface concentration of the hydrogen chloride, c_{HCl} , appearing in the expression (38), is given by the condition of equilibrium in desorption of the HCl, *i.e.* by the equation (13). Combining the equations (36), (37), (38), (13), a rate equation is obtained in the form

$$r = k_{\text{As}^+} \cdot c_n \left[p_{\text{As}_2} - \frac{K_{\text{HCl}}^2}{K_E \cdot K_F \cdot (K')^2} \frac{(p_{\text{HCl}}^*)^2}{(p_{\text{GaCl}}^*)^2 \cdot p_{\text{H}_2}^*} \right], \quad (39)$$

where the concentration of unoccupied centres, c_n , can be expressed from the balance of active centres

$$c_n + c_{\text{As}} + c_{\text{As}_2} + c_{\text{HCl}} = L, \quad (40)$$

from which a relation is obtained on combining with the equations (38), (37), and (13)

$$c_n = \frac{L}{1 + \frac{K_{\text{HCl}}}{K'} \frac{p_{\text{HCl}}^*}{p_{\text{GaCl}}^* (p_{\text{H}_2}^*)^{1/2}} + \frac{K_{\text{HCl}}^2}{(K')^2 K_F} \frac{(p_{\text{HCl}}^*)^2}{(p_{\text{GaCl}}^*)^2 \cdot p_{\text{H}_2}^*} + K_{\text{HCl}} p_{\text{HCl}}^*}. \quad (41)$$

Substituting this expression into the equation (39) and rearranging, a rate equation is obtained in the form

$$r = \frac{k_{\text{As}_2^+} \cdot L \left[p_{\text{As}_2} - \frac{(p_{\text{HCl}}^*)^2}{K_D^2 (p_{\text{GaCl}}^*)^2 \cdot p_{\text{H}_2}^*} \right]}{1 + \frac{(K_E K_F)^{1/2}}{K_D} \frac{p_{\text{HCl}}^*}{p_{\text{GaCl}}^* (p_{\text{H}_2}^*)^{1/2}} + \frac{K_E}{K_D^2} \frac{(p_{\text{HCl}}^*)^2}{(p_{\text{GaCl}}^*)^2 \cdot p_{\text{H}_2}^*} + K_{\text{HCl}} p_{\text{HCl}}^*}, \quad (42)$$

where the equilibrium constant, K_D , of the heterogeneous reaction (D) is given by the relation

$$K_D = \frac{K'}{K_{\text{HCl}}} (K_E \cdot K_F)^{1/2} = \frac{K'}{K_{\text{HCl}}} (K'_{\text{As}_2})^{1/2}, \quad (43)$$

if the equation (24) is applied. If the equilibrium constant of the surface dissociation (F) much exceeds that one of the adsorption, K_{As_2} , the third term in the denominator of the equation (42) will be negligible as compared with the second term, and the rate equation (42) is simplified to

$$r = \frac{k_{\text{As}_2^+} \cdot L \left[p_{\text{As}_2} - \frac{(p_{\text{HCl}}^*)^2}{K_D^2 \cdot (p_{\text{GaCl}}^*)^2 \cdot p_{\text{H}_2}^*} \right]}{1 + \frac{(K'_{\text{As}_2})^{1/2}}{K_D} \cdot \frac{p_{\text{HCl}}^*}{p_{\text{GaCl}}^* \cdot (p_{\text{H}_2}^*)^{1/2}} + K_{\text{HCl}} p_{\text{HCl}}^*}. \quad (44)$$

Mechanism V

The rate controlling step in this mechanism is the desorption of hydrogen chloride, so that the resulting rate of the process, r , will be equal to the desorption rate of hydrogen chloride, r_{HCl} , for which the following relation may be written³

$$r = r_{\text{HCl}} = k_{\text{HCl}} \left(\frac{c_{\text{HCl}}}{K_{\text{HCl}}} - p_{\text{HCl}}^* \cdot c_n \right). \quad (45)$$

This expression differs from the rate equation for adsorption only in the sign, since the difference between adsorption and desorption consists solely in the direction in which this process takes place. The other steps will take place at equilibrium, and in this way a relation is obtained for equilibrium in the surface reaction (C')

$$c_{\text{HCl}} = K' (p_{\text{As}_2}^*)^{1/2} \cdot (p_{\text{H}_2}^*)^{1/2} \cdot c_{\text{GaCl}}, \quad (46)$$

where the surface concentration, c_{GaCl} , can be expressed from the condition of equilibrium in the adsorption of GaCl as

$$c_{\text{GaCl}} = c_n K_{\text{GaCl}} p_{\text{GaCl}}^*. \quad (47)$$

Combining the three last relations, a rate equation is obtained in the form

$$r = k_{\text{HCl}} \cdot c_n \left[K' \frac{K_{\text{GaCl}}}{K_{\text{HCl}}} (p_{\text{As}_2}^*)^{1/2} p_{\text{GaCl}}^* (p_{\text{H}_2}^*)^{1/2} - p_{\text{HCl}}^* \right], \quad (48)$$

where the concentration of unoccupied centres follows from the balance of active centres

$$c_n + c_{\text{GaCl}} + c_{\text{HCl}} = L \quad (49)$$

by using the relations (46) and (47)

$$c_n = \frac{L}{1 + K_{\text{GaCl}} p_{\text{GaCl}}^* + K' K_{\text{GaCl}} (p_{\text{As}_2}^*)^{1/2} \cdot p_{\text{GaCl}}^* \cdot (p_{\text{H}_2}^*)^{1/2}}. \quad (50)$$

The substitution of the expression (50) into the relation (48) yields on rearranging the rate equation in the final form as

$$r = \frac{k_{\text{HCl}} \cdot L \cdot K_{\text{D}} \left[(p_{\text{As}_2}^*)^{1/2} \cdot p_{\text{GaCl}}^* \cdot (p_{\text{H}_2}^*)^{1/2} - \frac{p_{\text{HCl}}^*}{K_{\text{D}}} \right]}{1 + K_{\text{GaCl}} p_{\text{GaCl}}^* + K_{\text{HCl}} K_{\text{D}} \cdot (p_{\text{As}_2}^*)^{1/2} \cdot p_{\text{GaCl}}^* \cdot (p_{\text{H}_2}^*)^{1/2}}, \quad (51)$$

where the equilibrium constant K_D of the heterogeneous reaction (D) is given by the relation

$$K_D = K' \cdot \frac{K_{\text{GaCl}}}{K_{\text{HCl}}} \quad (52)$$

The above proposed one centre model of the epitaxial growth of gallium arsenide with participation of diffusion, chemical reaction, and adsorption of components is quantitatively described by equations (1) to (10), to which one of the rate equations (18), (29), (35), (44), or (51) is attached alternatively. The last named rate equations express five mechanisms, where an additional rate controlling step (in addition to the diffusion) is the surface reaction or adsorption of some of the reactants

TABLE II
Rate equations in one centre growth model of the GaAs

Mechanism	Rate equation	k
I	$r = \frac{k \left[(p_{\text{As}_2}^*)^{1/2} p_{\text{GaCl}}^* - \frac{p_{\text{HCl}}^*}{K_D} \right]}{1 + K_{\text{GaCl}} p_{\text{GaCl}}^* + K_{\text{HCl}} p_{\text{HCl}}^*}$	$k_+ \cdot L K_{\text{GaCl}}$
II	$r = \frac{k \left[(p_{\text{As}_2}^*)^{1/2} p_{\text{GaCl}}^* - \frac{p_{\text{HCl}}^*}{K_D} \right]}{1 + (K'_{\text{As}_2})^{1/2} (p_{\text{As}_2}^*)^{1/2} + K_{\text{HCl}} p_{\text{HCl}}^*}$	$k_+ \cdot L K'_{\text{As}_2}$
III	$r = \frac{k \left[p_{\text{GaCl}}^* - \frac{p_{\text{HCl}}^*}{K_D (p_{\text{As}_2}^*)^{1/2}} \right]}{1 + K_{\text{GaCl}} \frac{p_{\text{HCl}}^*}{K_D (p_{\text{As}_2}^*)^{1/2}} + K_{\text{HCl}} p_{\text{HCl}}^*}$	$k_{\text{GaCl}+} \cdot L$
IV	$r = \frac{k \left[p_{\text{As}_2}^* - \left(\frac{p_{\text{HCl}}^*}{K_D p_{\text{HCl}}^*} \right)^2 \right]}{1 + (K'_{\text{As}_2})^{1/2} \frac{p_{\text{HCl}}^*}{K_D p_{\text{GaCl}}^*} + K_{\text{HCl}} p_{\text{HCl}}^*}$	$k_{\text{As}_2+} \cdot L$
V	$r = \frac{k \left[(p_{\text{As}_2}^*)^{1/2} \cdot p_{\text{GaCl}}^* - \frac{p_{\text{HCl}}^*}{K_D} \right]}{1 + K_{\text{GaCl}} \cdot p_{\text{GaCl}}^* + K_{\text{HCl}} K_D (p_{\text{As}_2}^*)^{1/2} p_{\text{GaCl}}^*}$	$k_{\text{HCl}+} L K_D$

or products. The survey of rate equations is given in the Table II, where the partial pressure of hydrogen is not contained, since its value is practically equal to one. That is to say, the partial pressures of components in these equations are referred relatively to the atmospheric pressure, the concentrations of other components except hydrogen being negligibly small. In addition, the effective rate constants are appearing in Table II, the signification of which in individual cases is given in the last column. The equilibrium constant, K_D , refers to the heterogeneous reaction according to the equation (D). The five variants of the one centre model have been compared with the experimental data given in the previous paper¹.

RESULTS

The comparison has been carried out with isothermic dependences of the rate of epitaxial growth on partial pressures of components by using linearized form of rate equations given in Table II. The most probable values of both rate and equilibrium constants, appearing in these equations, have been determined by the method of least squares from all experimental data at 750°C. By means of constants, determined in this way, the growth rates have been back calculated, and the deviations of computed values from experimental ones have been determined. The level of reproduction of individual model variants may be appreciated according to the sum of squared deviations between the calculated and experimental growth rates, or more clearly according to the mean quadratic deviations, which may be compared with the accuracy of experiments themselves. The survey of results of computations is contained in Table III. The thermodynamic equilibrium constant, K_D , amounted to 148.1 in all cases considered, and the parameters characterizing the diffusion rate were of the same values as previously².

DISCUSSION

From the five one centre mechanisms considered, the mechanism I reproduces the experimental data best, as it is evident from Table III, where the additional rate controlling step (in addition to the diffusion) is the surface reaction and at the same

TABLE III
Survey of computed results

Mechanism	I	II	III	IV	V
Mean quadratic deviation ($\mu\text{m}/\text{h}$)	1.6	2.9	3.1	3.3	3.3

time the gallium monochloride is reacting in an adsorbed state, whereas, the arsenic and hydrogen participate in the formation of the activated complex from the gas phase. The mentioned mechanism reproduces the measured growth rates with a precision of $1.6 \mu\text{m/h}$ (this corresponds roughly to seven per cent), which approximates very well the accuracy of the experimental data themselves, which has been estimated to $1.3 \mu\text{m/h}$ as an average error of measurement. It is necessary to add, that a more accurate *a posteriori* determination of the experimental error was hindered by a relatively low number of experimental data.

Further on, this mechanism explains even the surprising dependence of the rate constant on temperature, discussed in the previous paper¹, at least qualitatively. According to the Table II, the effective rate constant is equal to the product of the rate constant of surface reaction and of the equilibrium adsorption constant of the gallium monochloride. The last named equilibrium constant decreases with temperature, since adsorption is an exothermic process, and the mentioned decrease can exceed the increase of the rate constant of surface reaction with temperature. To verify this interpretation in a quantitative way, it is necessary to know the dependences of the growth rate on partial pressures at different temperatures, however, the existing set contains the temperature dependence only at a constant feed composition, so that it does not allow an evaluation of the temperature dependences of rate and equilibrium adsorption constants.

The "optimum" mechanism I possesses in addition to the mentioned positive features even a shortcoming, which consists in that the computed equilibrium adsorption constant of hydrogen chloride has a negative value. Such a situation usually represents a reason for eliminating the mechanism in question, however, in the given case it is necessary to take into consideration the following circumstances. The partial pressure of hydrogen chloride at the substrate has the minimum values from all components appearing in the surface reaction, and in addition, the range in which the p_{HCl}^* varies, is very narrow in comparison with the partial pressures of arsenic or of gallium. This situation results from the fact, that in experiments, the partial pressure of hydrogen chloride in the feed has been kept at a constant value, and the slight changes of the p_{HCl}^* at the substrate are due to the variations of partial pressures of other components resulting from the interconnection of rates and equilibria in the whole system. These factors are the cause, that the accuracy of determining the value of equilibrium adsorption constant of hydrogen chloride is very low, so that owing to a compensation in the numerical treatment, a negative value of the constant can result, even if the mechanism in question is real. Such a situation is to be expected especially in cases, where the number of experimental data is relatively low with respect to their accuracy. From the reasons given above, it is necessary to consider the relevance of the occurrence of negative value of the equilibrium adsorption constant of hydrogen chloride with some reserve. Nevertheless, it remains a fact that this constant has a negative value in all one centre mechanisms and, therefore,

a quantitative investigation of mechanisms with a higher number of centres (such as two centre mechanism or higher) appears as adequate.

In general, the results contained in this study may be appraised in the following way. From the five proposed variants of the one centre model, that mechanism was shown to be most suitable, in which the surface reaction is the rate controlling step and at the same time the adsorption of gallium monochloride and of hydrogen chloride takes place at equilibrium. The incorporation of the adsorption into the previous diffusion-kinetic model¹ proved to be convenient, because even in this simplest approximation, the accuracy of reproduction of the experimental data increased significantly, *i.e.* from the original accuracy at a semiquantitative level of 1 : 2 up to a value approaching the accuracy of experimental data themselves, *i.e.* below 10%. At the same time, a necessity arised to improve the proposed model by introducing higher centre mechanisms with the aim to reach a higher physical plausibility.

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