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On low temperature kinetic effects in metal–organic vapor phase epitaxy of III–V compounds

R.A. Talalaev[a,*], E.V. Yakovlev[a], S.Yu. Karpov[a], Yu.N. Makarov[b]

[a] *Soft-Impact Ltd., P.O. Box 33, 194156 St.Petersburg, Russia*

[b] *Fluid Mechanics Institute, University of Erlangen-Nürnberg, Cauerstraße 4, D-91058 Erlangen, Germany*

Abstract

Kinetic effects limiting the growth rate in MOVPE of III–V compounds are analyzed. A general mechanism—the blocking of group III species adsorption sites by methyl radicals—is suggested and accounted for in an original model of surface chemistry, using experimental data on the decomposition of group III metal–organic precursors on III–V semiconductor surfaces. The application of the model to GaAs, GaN and InP MOVPE provides a good agreement between the predicted and measured growth rates in a wide range of growth conditions and reactor types. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Among various aspects of MOVPE modeling, such as gas flow dynamics, heat and mass transfer, and gas-phase reactions, the development of surface chemistry models still remains a critical issue. Working out a detailed kinetic model is difficult due to a large number of possible gas-phase and surface reactions, as well as the mechanisms involved. Another problem is that only a limited number of surface reaction rates could be directly measured, especially under realistic MOVPE conditions.

One of the most frequently cited detailed kinetic models of GaAs MOVPE with trimethylgallium and arsine as precursors was developed by Mountziaris and Jensen [1]. Among the large number of reactions which might, in principle, occur in the gas-phase and on the surface, they identified a reduced set that preserves key features observed in experimental studies. The model predicts quantitatively the decomposition of metal–organic precursor in a hot isothermal tube and reproduces the main tendencies observed in GaAs growth behavior in a wide range of growth temperatures. According to [1], the growth rate at low temperatures is limited by the reaction between adsorbed group III and group V species, namely, monomethylgallium and AsH, to form GaAs. Since the rate parameters of this reaction

*Corresponding author. Tel.: +7-812-554-4570; fax: +7-812-326-6194.

E-mail address: talalaev@softimpact.fi.ru (R.A. Talalaev).

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were unknown, the authors of [1] obtained them by adjusting the theoretical predictions to the available experimental data. This fact makes the model applicable to a limited range of growth conditions and necessitates a change of the kinetic parameters in order to reproduce the growth rate in another type of reactor [2]. A similar approach of lumping the model uncertainties into the pre-exponential factor and activation energy of the film growth reaction was used by Theodoropoulos et al. [3] and Mihopoulos [4] in detailed kinetic models of InP MOVPE from trimethylindium and phosphine and of GaN from trimethylgallium and ammonia, respectively. Although these models provide relatively accurate prediction of the growth rate at moderate temperatures where it is limited by mass transport of group III species to the growing surface, the description of low temperature kinetics still remains their common weak point.

The aim of the present paper is to develop an alternative model accounting for kinetic effects in MOVPE of III–V binary compounds, which does not require "tuning" for each particular set of experimental data and is able to explain the basic trends in the growth of different materials.

2. Model description

As the starting point of the model development, we consider a few facts providing useful insights into the nature of kinetic mechanisms limiting the growth rate:

- Decrease of the growth rate at low temperatures is the feature specific for growth techniques using metal–organic species as group III precursors. In conventional molecular beam epitaxy using the elemental sources of group III species, the growth rate of GaAs is limited by group III flux and is independent of the growth temperature at least down to 200°C.
- Studies of atomic layer epitaxy of GaAs [5] and InP [6] show that surfaces covered with alkyl radicals prevent further adsorption of group III metal–organic compounds.
- The GaAs surface studied by reflectance difference spectroscopy under MOVPE conditions at 400–550°C was found to be terminated by methyl groups bonded to group III atoms [7].
- A comparative analysis of experimental MOVPE growth rates versus temperature (see, e.g, [7] for GaAs, [8] for GaN, [3] for InP, and [9] for InAs) shows that the low temperature kinetics is significant in the same (400–600°C) temperature range for Ga-containing compounds, but kinetic fall-down of the InP and InAs growth rate is observed at lower temperatures.
- According to the data on trimethylgallium decomposition on GaAs [10] and GaN [11], the kinetic parameters of methyl radical desorption are very close for both materials. Although such data are unavailable for the InP surface, the results on trimethylindium decomposition on GaAs [10] show a higher rate of methyl radical desorption in this case (see Fig. 1). We attribute this difference to the formation of a thin InAs layer on top of the GaAs surface.

With the above conclusions, we suggest the following explanation of the kinetic effects in MOVPE: at low temperatures the growing surface is covered by methyl radicals originating from the decomposition of metal–organic precursors. The methyl radicals block the adsorption sites available for group III species and, therefore, limit the growth rate. Desorption of these radicals from the surface may be considered as the rate limiting stage in low temperature growth.

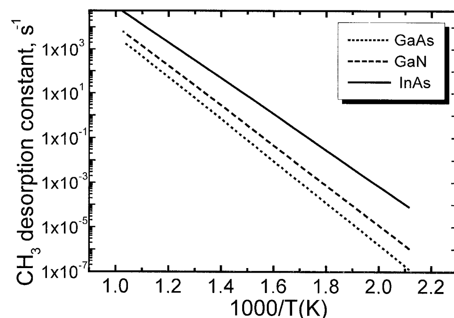

Fig. 1. CH_3 desorption constants from GaAs, GaN, and InAs surfaces. The latter is taken from experiments on TMIn decomposition on the GaAs(1 0 0) surface [10].

In order to account for this mechanism, we include it into the quasi-thermodynamic model originally suggested in Ref. [12] to describe the surface chemistry in group III nitride MOVPE. The basic advantage of the approach is the combination of kinetic and thermodynamic considerations of surface processes. In particular, the rate-limiting stage is described using an appropriate kinetic mechanism. All other processes, which are fast compared to the rate-limiting one, are assumed to occur under near-equilibrium conditions. This allows a significant reduction in the number of model parameters and avoids the fitting procedure, which is a usual way of determining unknown rate constants. We list here the basic assumptions and equations, with reference to the low-temperature kinetics of GaAs growth as an illustration which can be easily extended to the case of MOVPE of other III–V materials.

The quasi-thermodynamic approach is based on the following assumptions:

A. The atoms in the adsorption layer on the surface are nearly in equilibrium with the crystal bulk. This means that the rates of atomic incorporation into the crystal and of the crystal decomposition (occurring at the step edges) are much higher than their net difference, i.e. the growth rate.
B. Kinetic effects occurring at the adsorption/desorption stage can be accounted for by the sticking/evaporation coefficients of individual species. Generally, these coefficients are dependent on temperature and partial pressures of the species.

We suggest that the adsorption/desorption of the species can be described by the Hertz–Knudsen equations, i.e. the total atomic flux (the difference between the adsorption and desorption rates) of the ith species can be expressed as

$$J_i = \alpha_i \beta_i \left(p_i - p_i^0\right), \quad (1)$$

where α_i is the sticking coefficient accounting for the kinetic limitations of the adsorption/desorption rates, $\beta_i = (2\pi m_i kT)^{-1/2}$ is the Hertz–Knudsen factor for the ith species, m_i is the mass of the molecule, k is the Boltzmann constant, p_i is the partial pressure of the ith species near the growing surface, and p_i^0 is the equilibrium partial pressure of the ith species. The pressures p_i^0 correspond to a certain gas composition resulting in zero net adsorption rate of every species and, therefore, to the equilibrium between the gas phase and the crystal.

From the assumption A, the following mass action law equations can be used, regarding all the species as ideal gases:

$$\prod_{i=1}^{N_c} \left(p_i^0\right)^{v_{ji}} = K_j(T), \quad j = 1 \ldots N_r. \quad (2)$$

Here N_c is the number of gaseous species contributing to the growth, N_r is the number of independent heterogeneous chemical reactions occurring on the growing surface, v_{ji} is the matrix of stoichiometric coefficients, K_j is the equilibrium constant of the jth heterogeneous reaction, calculated from standard Gibbs energies of the vapor and solid compounds involved in the reaction [13,14]. It should be noted that these reactions do not describe the actual surface reaction pathways but serve only to interrelate p_i^0. Hence, any set of independent reactions can be considered within the model.

Finally, Eqs. (1) and (2) should be supplemented by the mass balance equations corresponding to stoichiometric incorporation of Ga and As atoms into GaAs and to zero total atomic fluxes of C and H on the surface:

$$\sum_{i=1}^{N_c} f_{ki} J_i = V_g x_k / \Omega, \quad k = 1 \ldots N_\mathrm{e}. \quad (3)$$

Here N_e is the number of elemental components in the system, f_{ki} is the matrix showing how many atoms of the kth elemental component is contained in the molecule of the ith species, x_k is the vector showing how many atoms of the kth elemental component is contained in the solid phase, $\Omega_\mathrm{s} = M_s / \rho_s N_\mathrm{A}$ is the molecular volume of the crystal, M_s is the molar mass, ρ_s is the density of the crystal, N_A is the Avogadro number, and V_g is the growth rate of the crystal.

In accordance with the assumption B, appropriate expressions for the sticking coefficients α_i

should be derived. The presence of methyl radicals as the major products of TMGa decomposition on GaAs under vacuum conditions is supported by numerous experimental observations. However, the mass-spectrometric measurements of tri-methylgallium and arsine simultaneous pyrolysis products under the MOVPE conditions [15] indicate that only methane is dominant among other hydrocarbon products in the gas-phase. This species is likely to be the product of a surface reaction between methyl radicals and atomic hydrogen originating from arsine decomposition.

We assume that the desorption rate of methane molecules is controlled by the bond breaking between surface gallium and the adsorbed methyl radical and that the recombination of the methyl radical with hydrogen is a rapid process. This allows us to derive the desorption rate of CH_4 molecule in the following way: $R_{CH_4} = K^d_{CH_3}\theta_{CH_3}$, where $K^d_{CH_3}$ is the rate constant of CH_3 desorption from the GaAs surface, θ_{CH_3} is the surface coverage with methyl radicals. On the other hand, a similar quantity follows from Eq. (1): $R_{CH_4} = \alpha_{CH_4}\beta_{CH_4}P^o_{CH_4}$. From the comparison of these two expressions we get

$$K^d_{CH_3}\theta_{CH_3} = \alpha_{CH_4}\beta_{CH_4}P^o_{CH_4}. \tag{4}$$

This equation is used to relate methyl coverage with desorption rate of CH and to calculate θ_{CH_3}. Assuming that alkyl groups also prevent adsorption of methane molecules , we get the sticking coefficients

$$\alpha_{TMGa} = \alpha_{MMGa} = \alpha_{CH_4} = \alpha_{CH_3} = 1 - \theta_{CH_3}. \tag{5}$$

The sticking coefficients of all other species are assumed to be unity.

The derived set of equations can be considered as the boundary conditions relating the species fluxes to their concentrations (partial pressures) on the surface. Surface partial pressures p_i and equilibrium partial pressures p_i^0 of all the species, fraction of the surface sites covered by methyl θ_{CH_3} and growth rate can be found from the solution of Eqs. (1)–(5) coupled to mass transport calculations in the reactor volume.

3. Application to MOVPE of III–V compounds

To demonstrate the model workability, we apply it to MOVPE of GaAs in a vertical rotating-disk reactor and of GaN and InP in horizontal tube reactors. Since our study is focused on the role of the low-temperature kinetics in the growth process, we use a simplified treatment of species transport to the substrate. For a horizontal reactor we use the boundary layer approximation proposed in Ref. [16] and modified in Ref. [12] according to the quasi-thermodynamic surface chemistry model. In the case of MOVPE in a vertical rotating-disk reactor the transport processes are considered in terms of the 1D approach [17] suggested for the gas flow between an infinite-radius, porous, non-rotating disk and an infinite-radius, non-porous, heated, rotating disk on which the substrate is placed.

3.1. *MOVPE of GaAs from TMGa and AsH_3*

The proposed model of surface chemistry coupled with the simulation of flow dynamics, heat transfer and mass transport is applied to predict the GaAs growth rate in the vertical rotating-disk reactor described in Ref. [7]. Tri-methylgallium gas-phase decomposition via loss of two methyl radicals is taken into account [18]. The set of gaseous species includes TMGa and AsH_3 as the gallium and arsenic precursors, H_2 as the carrier gas, As_2 and As_4 as the products of heterogeneous arsine decomposition, MMGa as the product of TMGa pyrolysis, as well as CH_3 and CH_4 hydrocarbons. The kinetic constant of methyl radical desorption from GaAs surface is borrowed from Ref. [10] and has a pre-exponential factor of $10^{13}\,s^{-1}$ and an activation energy of 43 kcal/mole.

The GaAs growth rate predicted by the model in a wide range of substrate temperatures and TMGa inlet partial pressures is shown in Fig. 2. One can see that under the growth conditions of interest growth rate is sub-linearly dependent on the TMGa supply and is highly temperature-activated, indicating that the kinetic effects play a key role in the deposition process. The surface coverage with methyl radicals is significant, resulting in a strong

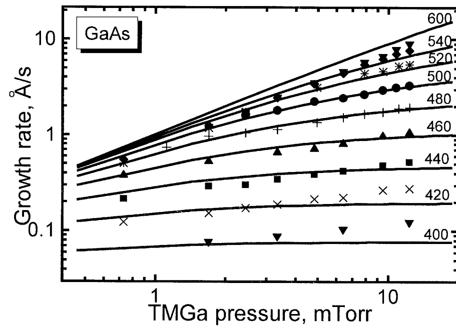

Fig. 2. GaAs growth rate in a vertical rotating-disk reactor as a function of TMGa partial pressure for various growth temperatures (from 400°C to 600°C). Lines represent theoretical predictions, symbols are the experimental data from Ref. [7].

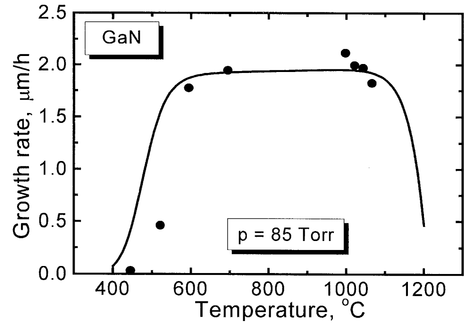

Fig. 3. GaN growth rate in a horizontal reactor versus growth temperature. Line is the theoretical prediction, points are the experimental data from Ref. [8]. The operating pressure is 85 Torr.

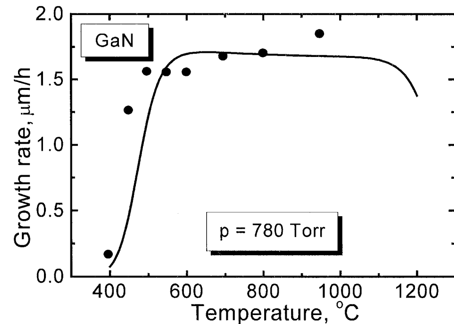

Fig. 4. GaN growth rate in a horizontal reactor versus growth temperature. Line is the theoretical prediction, points are the experimental data from Ref. [8]. The operating pressure is 780 Torr.

site-blocking effect for group III species. The comparison between theoretical and experimental [7] data shows an excellent agreement without any fitting.

3.2. MOVPE of GaN from TMGa and NH_3

MOVPE of gallium nitride in a horizontal tube reactor was studied with reference to the growth conditions reported in Ref. [8]. The set of species includes TMGa and NH_3 as the gallium and nitrogen precursors, H_2 as the carrier gas, Ga and N_2 as products of thermal decomposition of GaN, as well as CH_3 and CH_4 hydrocarbons. The kinetic constant of methyl radical desorption from GaN surface borrowed from Ref. [11] has a pre-exponential factor of $10^{13}\,s^{-1}$ and an activation energy of 41 kcal/mole.

The growth rate as a function of substrate temperature predicted for the reactor pressures 85 and 780 Torr is plotted in Figs. 3 and 4, respectively. Similar to GaAs, the low temperature growth rate is limited by the adsorption site blocking. This effect becomes less pronounced at higher temperatures due to enhanced desorption of the hydrocarbon species. Thus, starting from about 600°C, the growth rate becomes limited by the mass transport of TMGa to the growth surface. In this case it is almost independent of temperature. Further increase of the temperature results in an intensive desorption of gallium and a subsequent drastic reduction in the growth rate. A fairly good agreement is observed between the model predictions and the experimental data [8] in a wide range of operating parameters.

3.3. MOVPE of InP from TMIn and PH_3

Finally, the model was applied to analyze the MOVPE of indium phosphide in a horizontal reactor. The growth conditions and the reactor dimensions are borrowed from Ref. [3]. The set of species includes TMIn and PH_3 as the indium and phosphorus precursors, H_2 as the carrier gas, P_2 and P_4 as the products of heterogeneous phosphine decomposition, as well as CH_3 and CH_4 hydrocarbons.

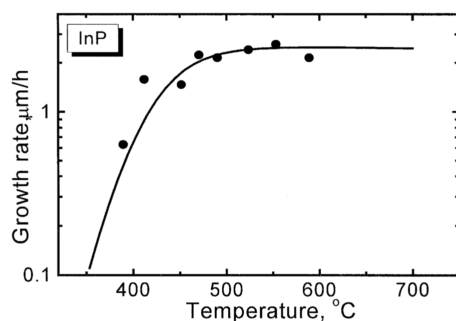

Fig. 5. InP growth rate in a horizontal reactor versus growth temperature. Line is the theoretical prediction, points are the experimental data from Ref. [3].

Since no information on the kinetics of methyl radicals from the InP surface is available in the literature, we use the data obtained from the studies of trimethylindium decomposition on the GaAs surface [10]. The authors report on the pre-exponential factor of $10^{13}\,s^{-1}$ and the range of activation energies from 33 to 43 kcal/mole for the methyl radical desorption constant. The average value of 38 kcal/mole is used in our simulations.

The temperature dependence of the InP growth rate is shown in Fig. 5. The behavior similar to that of GaAs and GaN is observed with the exception that the transition from the kinetically limited to mass transport limited conditions occurs at much lower temperatures, compared to the gallium compounds. This fact is a direct consequence of different strengths of the methyl group bonds with Ga and In surface atoms. The comparison of the model predictions with the experimental data from Ref. [3] again indicates a good agreement.

4. Conclusions

In this paper, we have made an attempt to identify general nature of low-temperature growth kinetics in MOVPE of III–V compound semiconductors. A comparative analysis of the deposition of different materials and the specific features of different growth techniques allows us to suggest a unified mechanism responsible for the low temperature kinetic effects. This mechanism is accounted for in the original model of surface chemistry, which is based on the combined kinetic and thermodynamic description of surface processes and requires the use of thermochemical data for the gaseous species in the reactor and of growing solid, as well as the knowledge of the kinetic constant of methyl radical desorption from the surface. The latter can be extracted from independent experiments. The application of the model to the MOVPE of GaAs, GaN and InP has shown a quantitative agreement between the theoretical and experimental growth rates for a wide range of growth conditions and reactor types without fitting any of the parameters.

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