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Reaction models for the epitaxial growth of III–V semiconductors by chemical beam epitaxy

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A reaction model for the epitaxial growth of GaAs by chemical beam epitaxy using triethylgallium (TEG) and diatomic arsenic, based on experimental observations, is described in detail. The model includes physical effects, which have been partly or totally neglected in earlier studies, involving site-blocking effects, lateral interactions between adsorbed species involved in growth and a role for adsorbed As in inhibiting growth. Computer simulations based on the model are carried out to make comparison with the experimental observations for this growth system, and the approximations involved in making these calculations are outlined. The model is shown to provide good agreement with some of the detailed spectroscopic observations relating to CBE, as well as accounting for the overall growth kinetics observed.

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1. Introduction

The mechanism of GaAs growth using the ultra-high vacuum technique of chemical beam epitaxy (CBE) has been extensively investigated in recent years. Measurements of the dependence of CBE growth rate on substrate temperature and the flux of precursors triethylgallium (TEG) and As_2 (Kobayashi *et al.* 1987; Chiu *et al.* 1987, 1989; Martin & Whitehouse 1990) have been made, and there have been a number of surface science studies of the interactions of TEG with GaAs(100) (Murrell *et al.* 1990; Donnelly & McCaulley 1990; Pemble *et al.* 1990; Banse & Creighton 1991).

Several authors have proposed kinetic models for the CBE growth of GaAs based on these experimental observations (Murrell *et al.* 1990; Robertson *et al.* 1988; Liang & Tu 1990; Asahi *et al.* 1991). The first of these (Robertson *et al.* 1988) was published at a time when little information on the surface reactions of TEG was available. Robertson *et al.* proposed a stepwise mechanism for TEG decomposition, estimated the relative magnitudes of the kinetic parameters, and fitted these parameters to their observed GaAs growth rates. While subsequent experimental studies have apparently supported some of the assumptions of this model, in particular the physical prediction that the decline in the GaAs growth rate observed at high substrate temperature arises from desorption of an intermediate diethylgallium (DEG) species from the surface (Murrell *et al.* 1990; Donnelly & McCaulley 1990), some of Robertson's kinetic parameters have since been shown to be inconsistent with experimental results and the model also assumed that the surface coverage of all adsorbed species is negligibly small at all temperatures. This was an important

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deficiency, since later work by Murrell *et al.* which included surface site blocking effects indicated that the rate of desorption of alkyl species was the rate-limiting step controlling the GaAs growth rate at low temperatures.

Although the kinetic parameters in the model proposed by Murrell *et al.* were more consistent with surface science data on TEG decomposition than those of Robertson *et al.*, some deficiencies still remained. It has been shown in static surface science experiments that the branching ratio for TEG desorption/decomposition depends on the TEG surface coverage and this was not reproduced in the early model. At low surface coverages, nearly all the adsorbed TEG decomposes to Ga as the surface temperature is raised, while at higher initial coverages relatively more desorbs as TEG and DEG. Both previous models have shown the branching ratios controlling the extent of TEG and DEG desorption, in comparison to cracking to Ga, determine the rate of GaAs growth at high substrate temperature; accordingly, the influence of surface coverage on these reactions need to be considered in a complete model of GaAs growth. Site-blocking effects were also not properly described in the work of Murrell *et al.* Both the Robertson and the Murrell models considered the rate of decomposition of the group III species, TEG, only to be important in determining the rate of GaAs growth. However, experimental studies by Chiu *et al.* (1989) have shown that the rate of CBE growth of GaAs is also influenced by the arsenic flux: very high arsenic fluxes depress the GaAs growth rate at low growth temperatures. Two models for CBE growth which consider the effect of the group V flux have been published: that of Liang & Tu (1990) proposed that surface As_2 enhances the rate of both TEG desorption and DEG decomposition, while in the model of Asahi *et al.* (1991) for GaSb growth, excess antimony is proposed to slow the GaSb growth rate by blocking sites available for the cleavage of the first gallium–ethyl bond in adsorbed TEG. Unfortunately neither of these models were based on the reaction schemes actually indicated by the experimental data. More recently French & Foord (1992) showed that a model which takes account of the recognized shortcomings noted above could satisfactorily describe growth rates for CBE of GaAs using TEG as the precursor, including the inhibiting effect of excess Gp V species. In this paper we describe critically in detail how such a model is constructed, the approximations involved in computing predicted growth behaviour, and the success of the model in describing relevant surface spectroscopic data which forms a much more critical test than the computation of overall growth rates.

2. The model

(*a*) *Reaction Schemes for TEG and* As_2 *interactions on* GaAs *surfaces*

The reactions chosen to describe TEG decomposition on the GaAs(100) surface are listed in table 1 reactions (0) to (7). It is based on the model proposed by Murrell *et al.* (1990) from surface spectroscopic data and is similar to that of Robertson *et al.* (1988), with the exception that the desorption of organic species is modelled explicitly. The role of empty sites in the overall reaction scheme is now treated in proper detail, however, in that all reactions which increase the number of surface species are assumed to require the presence of adjacent vacant surface sites. This is one of the significant improvements in comparison to our previous work and is discussed in detail below.

The second improvement is that we now recognize that excess surface Gp V species

Table 1. *Reaction scheme for TEG decomposition in the presence of an arsenic flux*

	reactant	product	A/s^{-1}	$E/(\text{kJ mol}^{-1})$
(0)	$\text{TEG}_{(g)}+\text{e.s.}$	$\text{TEG}_{(ads)}$	—	—
(1)	$\text{TEG}_{(ads)}$	$\text{TEG}_{(g)}+\text{e.s.}$	10^{11}	50
(2)	$\text{TEG}_{(ads)}+\text{e.s.}$	$\text{DEG}_{(ads)}+\text{Et}_{(ads)}$	10^{14}	55
(3)	$\text{DEG}_{(ads)}+\text{Et}_{(ads)}$	$\text{TEG}_{(ads)}+\text{e.s.}$	10^{11}	105
(3*a*)	$\text{DEG}_{(ads)}$	$\text{DEG}_{(g)}+\text{e.s.}$	10^{14}	165
(4)	$\text{DEG}_{(ads)}+\text{e.s.}$	$\text{Ga}+2\ \text{Et}_{(ads)}$	10^{12}	135
(5)	$\text{Et}_{(ads)}$	$\text{C}_2\text{H}_{4(g)}+\text{H}_{(ads)}$	10^{12}	147
(6)	$\text{Et}_{(ads)}+\text{H}_{(ads)}$	$\text{C}_2\text{H}_{6(g)}+2\ \text{e.s.}$	10^{14}	165
(7)	$\text{H}_{(ads)}+\text{H}_{(ads)}$	$\text{H}_{2(g)}+2\ \text{e.s.}$	10^{13}	126
(8)	$\text{As}_2(\text{g})$	As_2^*	—	—
(9)	$1/2\ \text{As}_2^*+\text{Ga}$	GaAs	—	—
(10)	$\text{As}_2^*+2\ \text{e.s.}$	$2\ \text{As}_{(ads)}$	—	—
(11)	$2\ \text{As(ads)}$	$\text{As}_2(\text{g})+2\ \text{e.s.}$	10^{11}	125
(12)	As_2^*	$\text{As}_2(\text{g})$	—	—

e.s., empty site.

can inhibit GaAs growth because of their site-blocking effects on active surface sites. To do this, it is necessary to specify a reaction scheme for the adsorption, decomposition and desorption of As_2 on the GaAs(100) surface. The most widely quoted experimental studies of the interaction of As_2 with the GaAs(100) surface are the molecular beam studies of Arthur (1974) and Foxon & Joyce (1977) who report the sticking coefficient of As_2 is zero in the absence of a gallium flux, increasing to unity in the limit where the Ga flux is twice the As_2 flux. This model, which has found widespread use in understanding the processes involved in MBE, assumes that the incoming arsenic flux first physisorbs in a precursor state denoted here as As_2^*. If a pair of Ga atoms is available, this state dissociates to form GaAs; otherwise, it desorbs. Below 600 K Foxon & Joyce found that an association reaction of two physisorbed As_2^* species leading to the desorption of As_4 is also important. However, Foxon & Joyce's finding that the sticking coefficient of As_2 is zero if Ga atoms are not available is not consistent with the occurrence of As adsorption which is well known to occur, albeit at temperatures below that normally used for growth (Schafer *et al.* 1988; Kowalczyk *et al.* 1981; Bachrach *et al.* 1981; Chiang & Spicer 1989; Wee 1990). More importantly, the GaAs(100) c(4 × 4) surface, which is stable at a range of arsenic coverages in excess of one monolayer, also consists of excess arsenic chemisorbed on an arsenic-terminated surface and *is* observed during growth in the lower temperature régime and at high V–III ratios (Deparis & Massies 1991; van der Veen *et al.* 1984; Sauvage-Simkin *et al.* 1989; Biegelsen *et al.* 1990; Neave *et al.* 1983). Clearly to satisfactorily account for this observation, the GaAs–As_2 interaction must include processes which permit the formation of chemisorbed As with a significant surface lifetime, during growth, in the absence of a surface population of Ga atoms. For the GaAs growth model presented here, the Foxon & Joyce model for the interaction of As_2 with GaAs(100) will therefore be modified to include arsenic chemisorption and desorption from an arsenic-terminated surface. The reaction scheme is depicted in reactions (8)–(12) in table 1. The Foxon & Joyce model also includes a step for As_2 desorption from the GaAs lattice, but for simplicity this was not included in the model; such processes would be expected to occur at relatively high substrate temperatures. Foxon & Joyce found that the formation and desorption of As_4 was important in the temperature range 300–500 K, where the experimental evidence discussed above suggests a full layer of chemisorbed arsenic is present (Chiang & Spicer 1989; Wee 1990). The As_4 processes, then, are probably associated with multilayers of adsorbed arsenic. The model presented here is concerned with the site-blocking effect of chemisorbed arsenic, which would not be affected by multilayer formation. Arsenic adsorption beyond one monolayer, and the As_4 formation and desorption reactions, are therefore not included in the model.

(*b*) *The model for* GaAs *growth*

It is assumed of necessity in the current reaction model that the GaAs growth surface consists of a uniform square array of surface sites on which TEG chemisorbs with a sticking probability proportional to the fractional coverage of vacant surface sites. This is an oversimplification in the sense that under most growth conditions RHEED and optical techniques would suggest that both Ga and As sites were present in a defective c(2 × 8) surface. Precursor state effects, that is the reduction in sticking probability for chemisorption with temperature which tends to occur when chemisorption takes place via the physisorbed state, which would be expected to reduce the TEG sticking probability at high temperatures are also ignored (Gasser 1985). The approximations seem successful in the case of CBE growth from TEG, since MBMS studies indicate similar decomposition kinetics on Ga- and As-terminated surfaces (Foord & Singh 1993), and precursor state effects seem to play a secondary role to the reactions within the chemisorbed phase in determining overall decomposition efficiencies. The growth rate in this model is thus controlled by two aspects: (i) the availability of surface sites, which are controlled by the presence of chemisorbed species formed by TEG decomposition and the chemisorbed As species discussed above; (ii) the branching ratios involved in TEG decomposition, which control the efficiency by which adsorbed TEG species become converted to surface Ga. The GaAs growth rate is equated to the rate at which these Ga species are produced.

(*c*) *Computational details*

Adsorption of TEG is computed by using Langmuir adsorption kinetics,

$$\text{RATE } 0 = (\text{flux of TEG}) \times (1-\theta), \tag{1}$$

with a clean surface sticking probability of unity.

For arsenic adsorption, all of the incoming flux is assumed to chemisorb initially into a precursor state As_2^* (reaction (8), table 1). It is assumed that the sticking coefficient for arsenic incorporation is unity if there are free Ga atoms on the surface, so the rate of reaction (9) (formation of GaAs) is set equal to the rate of Ga atom formation from TEG. The remaining As_2^* is considered to chemisorb onto the surface according to the Langmuir isotherm for molecular (first-order model) or dissociative (second-order model) adsorption (reaction (10)). In the first-order process, the rate of chemisorption is thus equal to the arsenic flux (minus the rate of GaAs formation) multiplied by the coverage of empty sites, while the rate of second-order chemisorption refers to the coverage of adjacent empty sites. We compute both possibilities since little information is available at present concerning the correct choice. The rate of change of the As_2^* surface coverage is set equal to zero, so any As_2^* which does not form GaAs or chemisorb is assumed to immediately desorb (reaction (12)).

The rate of each of the elementary steps in the reaction schemes of table 1 (except those involving adsorption) are modelled by the Arrhenius expression,

$$\text{rate} = A \times (\text{coverage term}) \times \mathrm{e}^{(-E_\mathrm{a}/(RT))}, \tag{2}$$

where A is the pre-exponential factor and E_a the activation energy for the reaction. The simplest form of this expression assumes that the adsorbed species are randomly arranged on the surface and do not interact with each other; in this simplest case the activation energy does not vary with coverage and the coverage term is simply the product of the concentrations of the species involved. In addition to the adsorption of TEG and arsenic (reactions (0) and (10), table 1), the decomposition of TEG to DEG plus Et (step (2)) and of DEG to Ga plus 2 Et (step (4)) each increase the surface coverage and an empty site must be available for these reactions to proceed. The concentration of empty sites (which is simply $(1-\theta)$) is therefore explicitly included in the rate equations for these reactions.

As discussed in the introduction, the experimental data for the reaction of TEG with GaAs(100) indicate that the branching ratios for TEG recombination, DEG desorption and Ga formation vary with TEG exposure (Murrell *et al.* 1990; Donnelly & McCaulley 1990), suggesting that the activation energies of at least some of the TEG surface reactions depend on the surface coverage. This is modelled by including lateral interactions between adsorbed species using the quasi-chemical approximation (Fowler & Guggenheim 1952; Goymour & King 1973). In this model, species occupying adjacent sites on the surface repel each other with interaction energy ω. The distribution of adsorbed species is assumed to be in equilibrium, enabling the concentration of nearest neighbour pairs to be calculated. The total energy of the surface is changed by reactions which change the surface concentration, so the activation energy of any such surface reactions varies with coverage. In applying the quasi-chemical approximation to the TEG–GaAs system, a decision has to be made: should all species experience equal repulsions, or should the repulsions between some pairs of species be larger than between other pairs? Desorption from mixed layers of interacting particles has been considered in detail by Bridge & Lambert (1980); they have shown that the calculations become intractable if different repulsion energies between differing species are allowed. For TEG–GaAs, adsorbed DEG would be expected to occupy more space on the surface than the other adsorbed species (Et, H and As) so it would be reasonable to assume the most important interaction is the repulsion of adsorbed DEG species occupying adjacent sites (strictly speaking, by the same arguments TEG should also experience lateral repulsions, but the surface concentrations of TEG at growth temperatures are sufficiently small that this effect will be ignored). Pairs of DEG therefore are assigned an interaction energy ω; the interaction energy between DEG and TEG, Et H, or As, and between any other pairs of species is set to zero. Reactions (3) and (3*a*), which bring about a reduction in the number of adsorbed species on the surface have a decrease in activation energy with increased coverage; the activation energy of reaction (2), the formation of DEG + Et is assumed not to vary with coverage on the grounds that the transition state is likely to occupy a similar area on the surface as the reactants. It is assumed that for a bimolecular reaction (reactions (3), (6) and (7), and reaction (11) in the second-order arsenic model) to occur the reactants must occupy adjacent sites. Reactions which lead to an increase in total surface coverage (reactions (2) and (4)) require that the reactant (TEG or DEG) is next to an empty site. The quasi-chemical approximation enables these site-concentrations to be evaluated for the non-random site

Table 2. *Rate equations for TEG and* As_2 *decomposition*

(θ, total adsorbate coverage; θ_{OO}, concentration of near neighbour vacant site pairs; θ_{AO}, single empty sites; θ_X, concentration of X; $\omega = -10\ \mathrm{kJ\ mol^{-1}}$. ENDIS $= E_a + 0.5Z\omega(1-(1-2\theta)/(1-4\theta)(1-\theta)(1-\exp(\omega/RT)$ from the quasi-chemical approximation describes the coverage dependence of the activation.)

$$\mathrm{RATE0} = \mathrm{FLUX} \times (1-\theta)$$
$$\mathrm{RATE1} = A_1 \times \theta_{\mathrm{TEG}} \times \mathrm{e}^{-E_1/(RT))}$$
$$\mathrm{RATE2} = A_2 \times (2 \times \theta_{\mathrm{TEG}} \times (1-\theta)/(1-\theta_{\mathrm{DEG}})^2) \times \theta_{\mathrm{OO}} \times \mathrm{e}^{-E_2/(RT))}$$
$$\mathrm{RATE3} = A_3 \times \theta_{\mathrm{DEG}} \times (\theta_{\mathrm{Et}}/(1-\theta_{\mathrm{DEG}}) \times \theta_{\mathrm{AO}} \times \mathrm{e}^{-\mathrm{ENDIS},3/(RT))}$$
$$\mathrm{RATE3a} = A_{3a} \times \theta_{\mathrm{DEG}} \times \mathrm{e}^{-\mathrm{ENDIS},3a/(RT))}$$
$$\mathrm{RATE4} = A_4 \times \theta_{\mathrm{DEG}} \times ((1-\theta)/(1-\theta_{\mathrm{DEG}}) \times \theta_{\mathrm{AO}} \times \mathrm{e}^{-E_4/(RT))}$$
$$\mathrm{RATE5} = A_5 \times \theta_{\mathrm{Et}} \times \mathrm{e}^{-E_5/(RT))}$$
$$\mathrm{RATE6} = A_6 \times (2 \times \theta_{\mathrm{H}} \times \theta_{\mathrm{Et}})/(1-\theta_{\mathrm{DEG}})^2) \times \theta_{\mathrm{OO}} \times \mathrm{e}^{-E_6/(RT))}$$
$$\mathrm{RATE7} = A_7 \times (\theta_{\mathrm{H}} \times \theta_{\mathrm{H}})/(1-\theta_{\mathrm{DEG}})^2) \times \theta_{\mathrm{OO}} \times \mathrm{e}^{-E_7/(RT))}$$

first-order As_2

$$\mathrm{RATE8} = \mathrm{FLUXAs}$$
$$\mathrm{RATE9} = \text{rate of Ga deposition} = \mathrm{RATE4}$$
$$\mathrm{RATE10} = (\mathrm{RATE8} - \tfrac{1}{2}\,\mathrm{RATE9}) \times (1-\theta)$$
$$\mathrm{RATE11} = A_{11} \times \theta_{\mathrm{As}} \times \mathrm{e}^{-E_{11}/(RT))}$$
$$\mathrm{RATE12} = \mathrm{RATE8} - \tfrac{1}{2}\,\mathrm{RATE9} - \mathrm{RATE10}$$

second-order As_2

$$\mathrm{RATE8} = \mathrm{FLUXAs}$$
$$\mathrm{RATE9} = \text{rate of Ga deposition} = \mathrm{RATE4}$$
$$\mathrm{RATE10} = (\mathrm{RATE8} - \tfrac{1}{2}\,\mathrm{RATE9}) \times ((1-\theta)/(1-\theta_{\mathrm{DEG}}))^2 \times \theta_{\mathrm{OO}}$$
$$\mathrm{RATE11} = A_{11} \times (\theta_{\mathrm{As}}/(1-\theta_{\mathrm{DEG}}))^2 \times \theta_{\mathrm{OO}} \times \mathrm{e}^{-E_{11}/(RT))}$$
$$\mathrm{RATE12} = \mathrm{RATE8} - \tfrac{1}{2}\,\mathrm{RATE9} - \mathrm{RATE10}$$

Table 3. *Rate equations for TEG decomposition*

$$\begin{aligned}
\mathrm{d}\theta_{\mathrm{TEG}}/\mathrm{d}t &= \mathrm{RATE0} - \mathrm{RATE1} - \mathrm{RATE2} + \mathrm{RATE3} \\
\mathrm{d}\theta_{\mathrm{DEG}}/\mathrm{d}t &= \mathrm{RATE2} - \mathrm{RATE3} - \mathrm{RATE3}a - \mathrm{RATE4} \\
\mathrm{d}\theta_{\mathrm{Ga}}/\mathrm{d}t &= \mathrm{RATE4} \\
\mathrm{d}\theta_{\mathrm{Et}}/\mathrm{d}t &= \mathrm{RATE2} - \mathrm{RATE3} + 2\mathrm{RATE4} - \mathrm{RATE5} - \mathrm{RATE6} \\
\mathrm{d}\theta_{\mathrm{H}}/\mathrm{d}t &= \mathrm{RATE5} - \mathrm{RATE6} - 2\mathrm{RATE7} \\
\mathrm{d}\theta_{\mathrm{As}}/\mathrm{d}t &= 2\mathrm{RATE10} - 2\mathrm{RATE11} \\
\mathrm{d}\theta^*_{\mathrm{As}}/\mathrm{d}t &= \mathrm{RATE8} - \tfrac{1}{2}\,\mathrm{RATE9} - \mathrm{RATE10} - \mathrm{RATE12} \\
&= 0 \\
\text{GaAs growth rate} &= \mathrm{RATE9}
\end{aligned}$$

distributions which arise when lateral interactions are included. With the coverage dependence of the coverage term and activation energy thus specified, it is now possible to express the rate of each reaction (table 2).

(*d*) *Simulation of TPD spectra and* GaAs *growth rates*

The rate of change of the concentration of each surface species are described by a set of coupled differential equations as given in table 3. These coupled differential equations were solved numerically by the NAG subroutine D02EBF which calculated the surface concentrations as a function of time.

TPD spectra are calculated by noting that under the experimental conditions used the desorption signal measured by the mass spectrometer is simply proportional to the desorption rate (King 1975). A temperature ramp β was specified so that the temperature T in the rate equations varied with time. The TPD spectra were then given by the equations in table 4. To generate the TPD spectra the initial condition

Table 4. *Equations for TPD simulation*

$\mathrm{TPD(TEG)} = 1/\beta\ \mathrm{RATE1}$
$\mathrm{TPD(DEG)} = 1/\beta\ \mathrm{RATE3}a$
$\mathrm{TPD(C_2H_4)} = 1/\beta\ \mathrm{RATE5}$
$\mathrm{TPD(C_2H_6)} = 1/\beta\ \mathrm{RATE6}$
$\mathrm{TPD(H_2)} = 1/\beta\ \mathrm{RATE7}$
$\mathrm{TPD(As_2)} = 1/\beta\ \mathrm{RATE11}$

was specified that a given fraction of a monolayer (ML) of TEG or arsenic was present on the surface in the chemisorbed state. The flux of incoming species was set to zero.

Growth rates and surface coverages can be calculated by specifying incident TEG and As_2 fluxes and solving the rate equations as a function of time at a fixed temperature. Once equilibrium conditions are reached, the temperature is increased by 10 K and the new surface concentrations calculated. The growth rate curve for GaAs is given by the equilibrium deposition rate of Ga (reaction (4)) as a function of temperature. The kinetic parameters chosen for each elementary step are listed in table 1. The desorption activation energies and pre-exponential for As_2 desorption (reaction (10)) were chosen to simulate experimental TPD spectra for chemisorbed arsenic (Wee 1990) (see next section). The most important criterion used in the determination of the kinetic parameters for TEG decomposition was that they simulate satisfactorily the TPD and other experimental data of Murrell *et al.* The kinetic parameters of Robertson *et al.* and Murrell *et al.* were taken as a starting point. The desorption energy and pre-exponential for H_2 desorption (reaction (7)) was determined from TPD spectra recorded following exposure of GaAs(100) to atomic hydrogen; the rate of reaction (5) (C_2H_4 desorption) was determined from the TPD following exposure of GaAs(100) to TEG, and the rate of reaction (6) was chosen so that the branching ratios for C_2H_4 and C_2H_6 desorption approximated those seen experimentally. The kinetic parameters for TEG (reaction (1)) and DEG (reaction (3*a*)) desorption were also derived from their TPD signals. Only a fraction of the original TEG on the surface was allowed to desorb, otherwise, contrary to experiment, no Ga would be deposited at the end of a TPD cycle. This was accomplished by adjusting the kinetic parameters for TEG (reaction (2)) and DEG (reaction (4)) decomposition so that small desorption peaks were seen, but the majority of the TEG and DEG decomposed before it desorbed. The interaction energy ω was set by a process of trial and error. A value of $-10\ \mathrm{kJ\ mol^{-1}}$ was found to reproduce the broad TEG desorption feature without allowing excess TEG desorption; this repulsion energy is within the range quoted for other systems (e.g. H_2 on W(110), $\omega = -6\ \mathrm{kJ\ mol^{-1}}$ (King 1975); CO on W, $\omega = -20\ \mathrm{kJ\ mol^{-1}}$ (Goymour & King 1973)).

3. Simulation results

Previously we have shown briefly that a physical model based on the surface chemical processes discussed above can satisfactorily describe growth rate data in CBE (French & Foord 1992). In this section we investigate whether the model and parameters selected can satisfactorily describe more detailed experimental data relating to CBE. Figure 1 shows the calculated surface coverages as a function of temperature in a TPD experiment in which 0.5 ML of TEG is adsorbed on the model surface at low temperatures and the associated thermal desorption spectra are shown in figure 2. A small amount of TEG desorbs at low temperatures before the adlayer

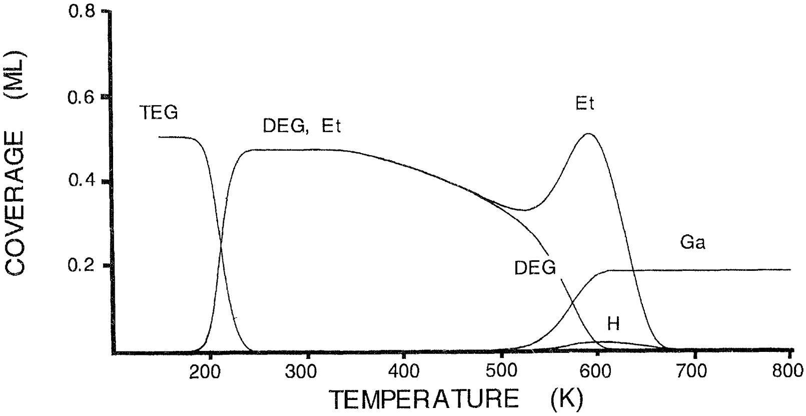

Figure 1. Calculated surface coverage during a TPD sweep ($\beta = 17$ K s^{-1}) for an initial TEG coverage of 0.5 ML.

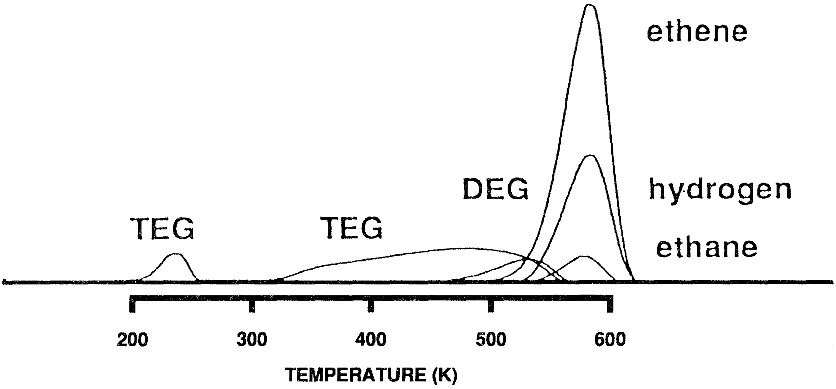

Figure 2. Calculated TPD spectrum for initial TEG coverage of 0.5 ML and heating rate β of 17 K s^{-1}.

dissociates to form Et and DEG. The surface concentrations of DEG and Et then decrease with temperature due to the recombination (reaction (3)) and desorption (reaction (1)) of TEG but their concentrations remain equal until 500 K, where DEG desorption ((3*a*), 0.058 ML) and decomposition of DEG to Et plus Ga (reaction (4)) become important, increasing the Et coverage and decreasing that of DEG. A small amount of hydrogen is also seen at this temperature from β-elimination of ethene. At the end of the TPD desorption sweep 0.183 ML of Ga (i.e. just over a quarter of the Ga initially present as TEG) has been deposited on the surface, which is otherwise free from adsorbates. This reproduces the experimental finding that up to 75 % of the saturated coverage of TEG desorbs as the temperature is raised, and that the Ga remaining on the surface is in metallic form with no other adsorbates present. A good description of the thermal desorption spectra of the saturated surface is given by this data. In figure 3 the calculated desorption peaks (recombined TEG, DEG and C_2H_4) for different initial coverages of TEG are presented. The TEG desorption (figure 3*a*) is seen to broaden to lower temperature with increasing coverage, corresponding to the experimental behaviour, while the DEG desorption temperature (figure 3*b*) remains constant at 575 K. As observed experimentally, the calculated C_2H_4

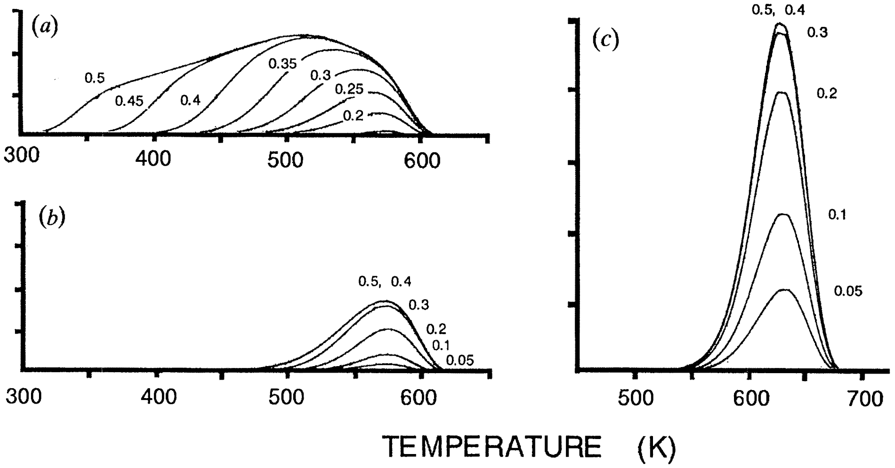

Figure 3. TPD spectra calculate for the indicated initial coverages of TEG: (*a*) TEG desorption (reaction (1)) following recombination from adsorbed DEG and Et (reaction (3)); (*b*) DEG desorption (reaction (3*a*); (*c*) C_2H_4 desorption (reaction (5)).

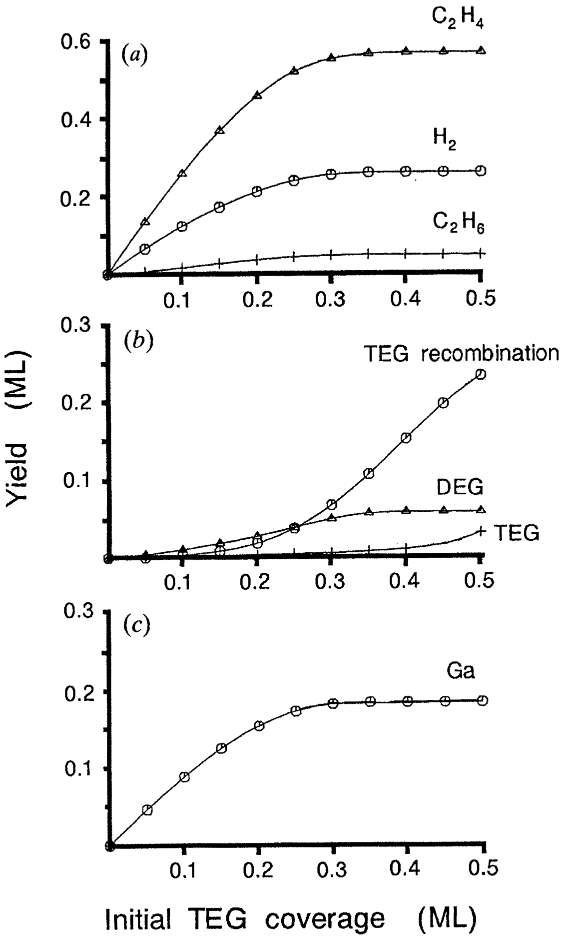

Figure 4. Calculate TPD yields as a function of initial TEG coverage: (*a*) organic species (C_2H_4, C_2H_6, H_2); (*b*) TEG and DEG; (*c*) amount of Ga deposited.

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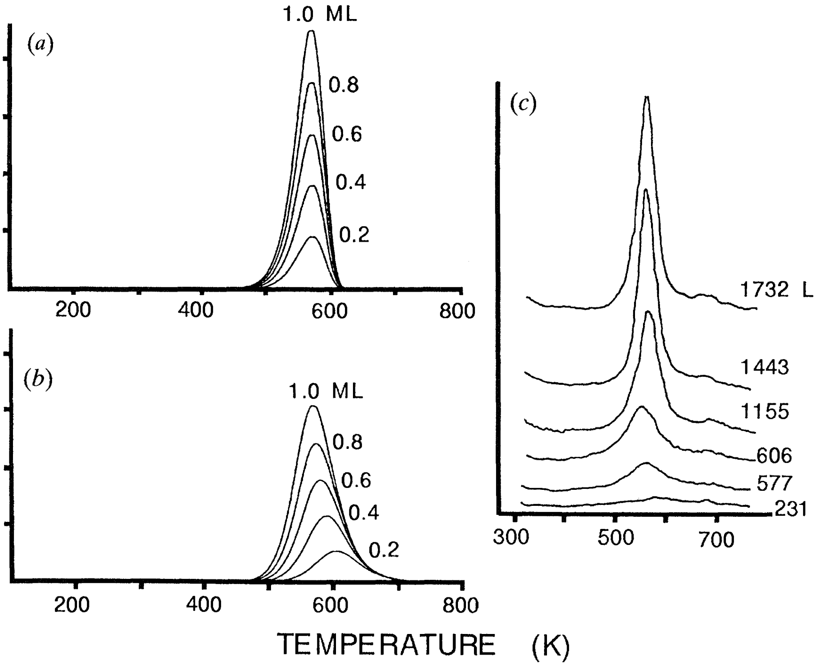

Figure 5. TPD of As_2 (a) calculated using (a) first-order, (b) second-order desorption program; (c) experimental following indicated exposures of cracked phenylarsine to GaAs(100) at 300 K (from Wee 1990). The initial surface coverages of chemisorbed arsenic used for the calculations are indicated.

desorption (figure 3c) first appears at very low coverages and does not change temperature with increasing coverage. Figure 4 plots the calculated desorption yields of C_2H_4, H_2, and C_2H_6 (figure 4a), DEG and chemisorbed and recombined TEG (figure 4b) and the amount of Ga deposited (figure 4c) as a function of initial TEG coverage. The calculation successfully models the experimental finding that Ga deposition and hydrocarbon desorption are the predominant processes at low TEG exposures. At higher exposures, these processes saturate and the relative desorption yields of DEG and TEG increase. It can thus be seen that the selected reaction scheme and kinetic parameters for the model of TEG decomposition are consistent with the experimental TPD data. Inclusion of lateral interactions between adsorbed DEG species has given a good description of the broad TEG desorption peak and the change in Ga deposition/$GaEt_x$ desorption branching ratios observed experimentally.

Figure 5 compares the predicted thermal desorption spectra of As_2, calculated using first-order (figure 5a) and second-order (figure 5b) desorption kinetics, with experimental data recorded following exposure of GaAs(100) (4 × 1) to cracked phenylarsine (As_2). The parameters chosen ($A_{11} = 10^{11}$, $E_{11} = 125\ \text{kJ mol}^{-1}$) give a good agreement for the desorption peak temperature with experiment. Below 580 K, the coverage of chemisorbed arsenic is one monolayer, corresponding to a chemisorbed arsenic surface observed experimentally, while above 600 K the surface has no chemisorbed arsenic present, but is still assumed to be arsenic-terminated. As expected, the desorption peak temperature remains constant with increasing initial arsenic coverage in the first-order model, and decreases with coverage in the second-order model. Both models give a reasonable description of the experimental results.

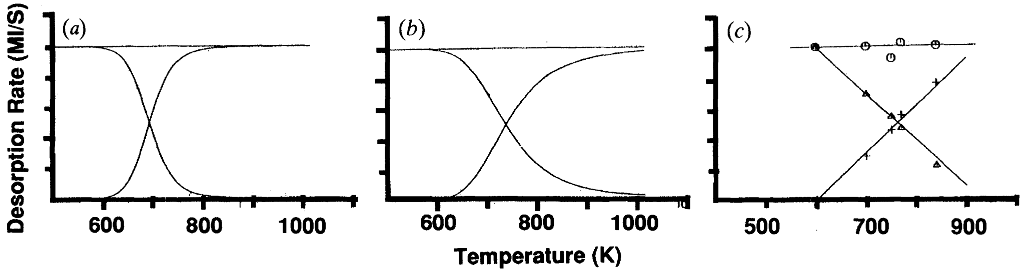

Figure 6. (*a*), (*b*) Calculated (As_2 flux = 1.0 ML s^{-1}) and (*c*) experimental results for a molecular beam of As_2 in the absence of a Ga flux. (*a*), (*b*) The reflected and desorbed As_2 fluxes and their total. (*c*) The total desorbing As_2 flux (circles), the modulated desorbing As_2 flux with the incident beam modulated (triangles), and the sticking coefficient of As_2 (crosses) (replotted from Foxon & Joyce 1977).

The arsenic chemisorption models chosen must also give a reasonable description of the molecular beam results of Foxon & Joyce (1977). Both the first and second order models predict appreciable concentrations of chemisorbed arsenic on the surface between 600 and 800 K, with the coverage in this temperature region increasing with arsenic flux. While the temperature at which the coverage equals one half monolayer is the same for a given flux for both models, the transition from near unity to near zero coverage occurs over a much narrow temperature range for the first-order than the second-order model. The relationship between the model and the molecular beam data of Foxon & Joyce is shown in figure 6. The reflected beam of unincorporated As_2, the rate of As_2 desorption and the total flux of As_2 from the surface are plotted for the first (6*a*) and second (6*b*) order models for an As_2 flux of 1.0 ML s^{-1}, with no Ga or TEG flux. Foxon & Joyce's results for a molecular beam of As_2 in the absence of a gallium flux are shown in figure 6*c*. In both the model and experiment, the total desorbing As_2 flux is constant and equal to the incoming flux. Foxon & Joyce found that this consisted of a modulated and demodulated beam whose proportions varied with temperature, and attributed the demodulated portion to desorption of As_2 from the GaAs lattice, freeing Ga sites which immediately reform GaAs with the incoming As_2 flux. The model also shows two contributions to the desorbing arsenic flux, that of arsenic reflected from the surface without chemisorption, which would show modulated behaviour if the incoming flux were modulated, and desorption of chemisorbed arsenic, which would be demodulated if the lifetime of the chemisorbed state were longer than the modulation period. The reflected beam is most important at low temperatures, where the surface coverage of chemisorbed arsenic is close to one and no further chemisorption can occur, while chemisorption of arsenic followed by As_2 desorption predominates at higher temperatures.

Simulated TPD spectra are shown in figure 7 for co-adsorbed layers of As and TEG. It is interesting to compare such spectra with the data in figure 2 for TEG adsorption in the absence of As; the significant difference is that much more of the TEG desorbs in the low temperature peak because of the site-blocking influence of As. Again this matches well the experimental result (Foord *et al.* 1992). In summary then the elements of the model involving As also fit in well with observed experimental data.

Previous studies have particularly identified the role of ethyl groups in inhibiting low temperature growth. The present work enables the relative roles of alkyl Vs

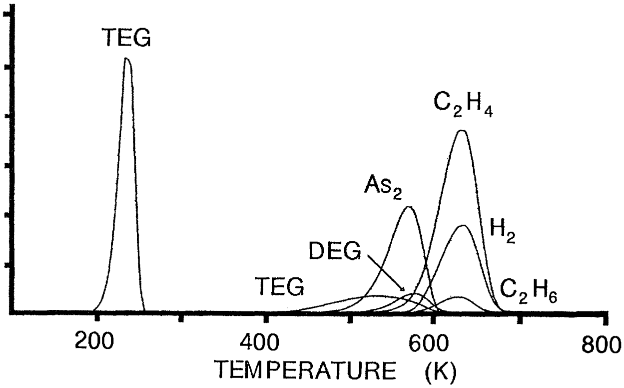

Figure 7. TPD spectrum calculated for initial coverage of 0.5 ML TEG and 0.5 ML As.

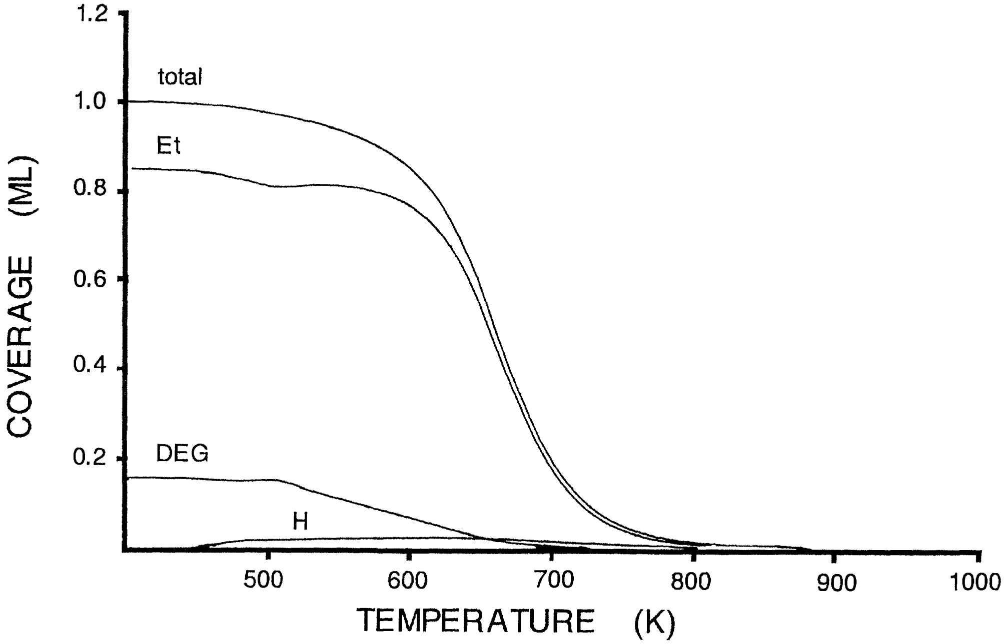

Figure 8. Calculated surface coverage as a function of temperature during GaAs growth, for a TEG flux of 1.04 ML s^{-1} with a 1 : 1 As flux.

arsenic site-blocking effects to be assessed and predicted site-coverage behaviour during CBE growth conditions calculated from the model are shown in figures 8 and 9. In the absence of excess As, TEG decomposition products block surface sites up to the threshold growth temperature. In the presence of excess As, no chemisorption of TEG is possible below about 500 K, and the alkyl site-blocking only becomes important at significantly higher temperatures.

4. Conclusion

The detailed arguments, approximations and computational details involved in developing a model describing surface chemical processes for CBE growth of GaAs using arsenic dimers and TEG have been outlined. The model represents a significant

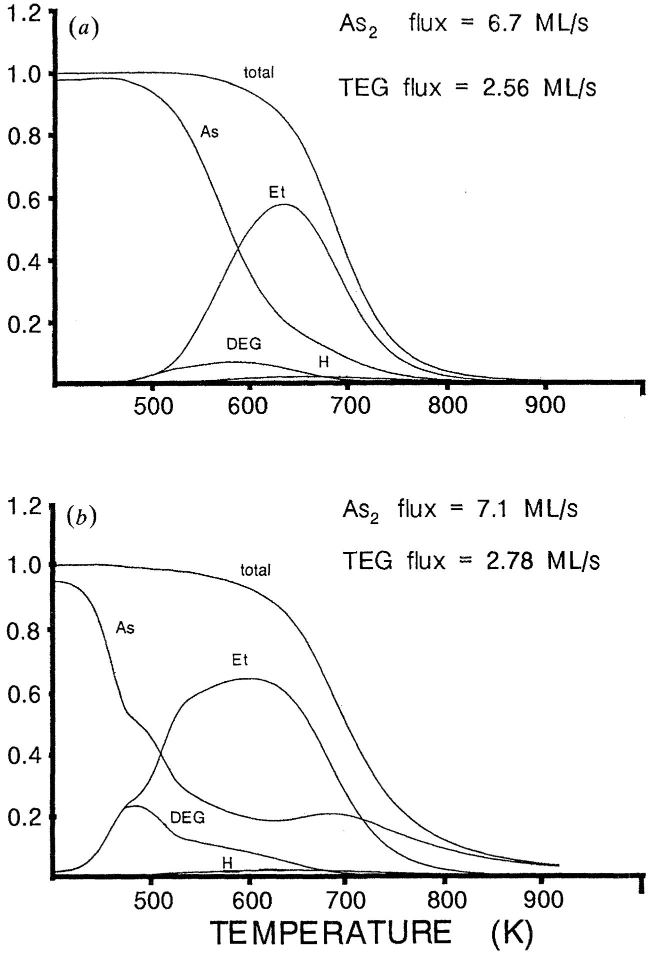

Figure 9. Coverage of adsorbed species (fractional occupancy of surface sites) during growth as a function of substrate temperature calculated using the (*a*) first-order and (*b*) second-order model and the fluxes indicated.

improvement on earlier reaction schemes in that it now treats in detail the site-blocking effects, lateral interactions and influence of Gp V species, which play an important role in CBE growth as indicated by experimental data. We have demonstrated in this paper that the same reaction scheme and kinetic parameters can successfully describe the available growth rate data as well as more detailed measurements on the surface processes involved in CBE.

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