

# Kinetics of dopant incorporation in GaAs grown by organometallic vapor-phase epitaxy

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## Abstract

A diffusive capture reaction of dopant atoms by relevant host atoms, via the Rideal–Eley mechanism, in GaAs grown by organometallic vapor-phase epitaxy is shown to result in the dopant concentration in the crystal acquiring a dependence on  $p_{\text{Ga}}$  (which is proportional to the growth rate) in agreement with data on  $\text{S}_{\text{As}}$ ,  $\text{Zn}_{\text{Ga}}$ , and  $\text{Si}_{\text{Ga}}$  where  $p_{\text{Ga}}$  is the partial pressure of trimethylgallium in the input gas stream.

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## 1. Introduction

The gross features of dopant incorporation in crystals grown by organometallic vapor-phase epitaxy (OMVPE) are accounted for by a model developed by Stringfellow [1,2]. In a previous paper [3] some modifications to this model were suggested to specifically apply to the formation of charged defects, such as  $\text{S}_{\text{As}}^+$ ,  $\text{Zn}_{\text{Ga}}^-$ , and  $\text{Si}_{\text{Ga}}^+$  in GaAs. In the present note the model is extended further by investigating the *kinetics* of dopant incorporation. It is proposed that dopant atoms in the vapor react directly with relevant host atoms on the surface—a process known as the Rideal–Eley mechanism [2,4]. This results in the dopant concentration in the crystal acquiring a dependence on growth rate in agreement with the limited data available.

To briefly summarize the results of the model [1–3] suppose that arsine,  $\text{AsH}_3$ , and trimethylgallium (TMGa),  $\text{Ga}(\text{CH}_3)_3$ , are the source gases used for crystal growth with partial pressures of  $p_{\text{As}}$  and  $p_{\text{Ga}}$ , respectively, in the input gas stream. Also, let  $p_{\text{D}}$  be the partial pressure of the

gas containing the dopant (D) of interest in the input gas stream. Near the vapor/crystal interface the As tetramer  $\text{As}_4$  with partial pressure  $p_{\text{As}_4}^i$ , the gallium monomer with partial pressure  $p_{\text{Ga}}^i$ , and the dopant monomer D with partial pressure  $p_{\text{D}}^i$  are taken to be in equilibrium with the solid. In the solid at the interface the electron concentration is taken to have the behavior  $n \propto p_{\text{As}}^{3/4}$ . The observed dependence of the dopant concentration  $[\text{D}–\text{H}]$  in the crystal on  $p_{\text{As}}$  and  $p_{\text{D}}$  is then correctly modeled [3] for both S and Zn and approximately for Si, where H is the relevant host atom (As or Ga) that binds to the dopant atom. An observed [5,6] but previously unexplained dependence of  $[\text{D}–\text{H}]$  on  $p_{\text{Ga}}$  is the subject of the present note.

## 2. Equilibrium reactions

The constraint of stoichiometric growth of the solid is imposed by equating the net diffusive fluxes of As and Ga arriving at the growth interface from the input gas stream:

$$p_{\text{As}} - 4p_{\text{As}_4}^i \approx p_{\text{Ga}} - p_{\text{Ga}}^i \quad (1)$$

Under the conditions that (a) the  $p_{\text{As}}/p_{\text{Ga}}$  partial pressure ratio in the input gas stream is large and (b) essentially all gallium from the input gas stream is incorporated in the

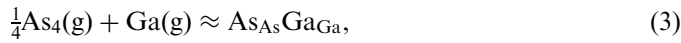
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solid it follows that:

$$p_{As} \approx 4p_{As_4}^i \quad (2)$$

In applying equilibrium thermodynamics to the growth of the crystal from the vapor it is implicitly assumed that throughout a small volume encompassing both solid and vapor all vapor molecules (e.g. Ga and  $\frac{1}{4}As_4$ ) can freely interact with all solid molecules. Crystal growth then occurs via the reaction



which, through the law of mass action, leads to

$$(p_{As_4}^i)^{1/4} p_{Ga}^i \propto 1. \quad (4)$$

Using Eq. (2) it is seen that

$$p_{Ga}^i \propto 1/p_{As}^{1/4}. \quad (5)$$

In the crystal dopant atoms bind to host atoms and the observed dopant–host concentration, [D–H], is given by the ratio of the net fluxes of D and Ga arriving at the growth interface from the input gas stream. Assuming the pyrolysis of the dopant source molecules to be complete and the diffusion of the different source molecules through the boundary layer to be identical it follows that:

$$[D-H] \approx (p_D - p_D^i)/p_{Ga}. \quad (6)$$

A useful, measurable, parameter to introduce is the effective dopant distribution coefficient

$$k_D = [D-H]p_{Ga}/p_D. \quad (7)$$

Then, if  $k_D \ll 1$ , as is the case for S, Zn, and Si treated below, it is apparent that most of the dopant is not incorporated in the crystal and so

$$p_D^i \approx p_D, \quad (8)$$

a relation that will be adopted in the following.

In previous modeling [1–3] all reactions between atoms were treated as being in equilibrium thereby ignoring kinetics. Nevertheless, the basic view was that these reactions actually take place on the crystal surface—a process known as the Langmuir–Hinshelwood mechanism [2,4]. This is appropriate [2] for the crystal growth reaction of As and Ga. However, for dopant incorporation it is proposed that the reaction between a dopant atom in the vapor and a host atom on the surface is a diffusive capture reaction—known as the Rideal–Eley mechanism—that proceeds for a time determined by the crystal growth rate. The result, shown below, is that previous expressions for dopant concentrations in the crystal are modified by the inclusion of an additional factor  $p_{Ga}^{1/2}$  for [S] and [Zn] and  $p_{Ga}^{-1/2}$  for [Si].

### 3. Rate coefficient for dopant–host interaction

In implementing the Rideal–Eley mechanism it is noted that the diffusive flux of Ga through the boundary layer towards the surface is proportional to  $p_{Ga}$  so that the time,

$\tau$ , for a monomolecular layer of crystal to grow has the dependence  $\tau \propto 1/p_{Ga}$ . This must also be the time during which a host atom (Ga or As) is available to bond with a dopant atom. Treating the interaction between dopant atom and relevant host atom as a diffusive capture reaction [7] the following model is suggested. Take the crystal and the vapor to occupy the half-spaces  $x < 0$  and  $x > 0$ , respectively, with the crystal surface in the plane  $x = 0$ . Suppose that a relevant host atom (H) suddenly appears on the crystal surface at time  $t = 0$  and that at this time the concentration of dopant atoms in the vapor is constant at  $N_D$ . Dopant atoms in a narrow channel leading to the host atom will then diffuse towards the latter which acts as a sink for the former. Thus, the time-dependent local concentration of dopant atoms in the channel,  $n_D(x, t)$ , is found by solving the diffusion equation

$$\frac{\partial n_D}{\partial t} = D_f \frac{\partial^2 n_D}{\partial x^2}, \quad (9)$$

where  $D_f$  is the diffusion coefficient of dopant atoms towards the crystal surface. Eq. (9) is subject to the initial and boundary conditions

$$n_D(x, 0) = n_D(\lambda, t) = N_D, \quad n_D(0, t) = 0. \quad (10)$$

The distance  $\lambda$  will be taken to be the thickness of the boundary layer in the vapor; however, it will not appear in the final expressions derived below.

The solution to Eqs. (9) and (10) is readily found to be

$$n_D(x, t) = \sum_{m=1}^{\infty} \frac{2N_D}{m\pi} \sin \frac{m\pi x}{\lambda} e^{-m^2 t/T_d} + N_D \frac{x}{\lambda}, \quad (11)$$

where  $T_d \equiv \lambda^2/\pi^2 D_f$  is on the order of the time required for a dopant atom to diffuse through the distance  $\lambda$ .

Consequently, the diffusive flux of dopant atoms at  $x = 0$  is

$$\begin{aligned} j(0, t) &= -D_f \left. \frac{\partial n_D}{\partial x} \right|_{x=0} \\ &= -D_f \frac{N_D}{\lambda} \left[ 1 + 2 \sum_{m=1}^{\infty} e^{-m^2 t/T_d} \right] \\ &= -D_f \frac{N_D}{\lambda} \theta_3 \left( 0, i \frac{t}{\pi T_d} \right) \\ &= -D_f \frac{N_D}{\lambda} \left( \frac{\pi T_d}{t} \right)^{1/2} \theta_3 \left( 0, i \frac{\pi T_d}{t} \right), \end{aligned} \quad (12)$$

where  $\theta_3$  is a theta function [8] and its properties have been used in obtaining the last result in Eq. (12).

The rate coefficient for the interaction of dopant atom and host atom is given by

$$r(t) = -\frac{\sigma}{N_D} j(0, t) \approx \frac{\sigma D_f}{\lambda} \left( \frac{\pi T_d}{t} \right)^{1/2} = \sigma \left( \frac{D_f}{\pi t} \right)^{1/2}, \quad (13)$$

valid within a few percent for  $t < 2T_d$ , where  $\sigma$  is an effective capture cross section presented by the host atom.

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