



# Efficiency difference in Ga adatom incorporation in MBE growth of GaAs with As<sub>2</sub> and As<sub>4</sub> molecular beams

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## Abstract

The surface diffusion length of Ga adatom incorporation under As<sub>2</sub> and As<sub>4</sub> mixture flux was measured using microprobe-RHEED intensity oscillations in molecular beam epitaxy. The incorporation diffusion length of Ga on the (0 0 1) surface towards the [1 1 0] orientation showed a strong dependence on the As<sub>2</sub>/As<sub>4</sub> ratio in the incident beam from the cracker cell. In keeping the total number of As atoms in the beam constant, it was found that the incorporation diffusion length of Ga decreases with higher As<sub>2</sub>/As<sub>4</sub> ratio. This shows that As<sub>4</sub> molecules are partly incorporated into the GaAs epi-layer by the dissociative reaction at Ga atoms, while As<sub>2</sub> is almost completely incorporated. According to the calculation for the diffusion length of Ga, a single As<sub>4</sub> molecule decomposes to produce one As<sub>2</sub> molecule which is incorporated into the growing layer, whereas another As<sub>2</sub> molecule is lost by desorption. On the other hand, almost all As<sub>2</sub> molecules are active and adsorbed. This means that As<sub>2</sub> molecules are incorporated into GaAs epi-layer more efficiently than As<sub>4</sub> molecules. © 2000 Elsevier Science B.V. All rights reserved.

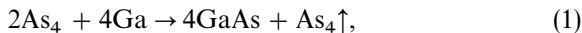
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## 1. Introduction

To control the vapor growth of III–V compounds for the fabrications of microstructures in semiconductors, understanding of the elementary process involved in the growth reaction between group III and V compounds is of fundamental importance. Arsenic-related mechanisms of GaAs

MBE growth have been studied by various groups [1–3]. A model of the chemical reactions during MBE growth of GaAs was proposed by Foxon and Joyce as follows [1,2]:



According to Eq. (1), the reaction is of the second order, and one expects the maximum As<sub>4</sub> sticking coefficient to be 0.5. On the other hand, the maximum As<sub>2</sub> sticking coefficient can be unity. The order of the chemical reaction between As<sub>4</sub> molecules and Ga atoms depends on the As<sub>4</sub> pressure.

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When the  $\text{As}_4$  pressure is low, the incorporation diffusion length of Ga is proportional to the  $-0.5$  power of the As pressure. At high  $\text{As}_4$  pressure, the incorporation diffusion length of Ga is proportional to the  $-1.0$  power [4]. This means that these reactions are of the first and the second orders, respectively, at low and high As pressure [5]. In this respect, the model proposed by Foxon and Joyce [1,2] is applicable only to the case of higher As pressure, and no model is proposed so far for the  $\text{As}_4$  decomposition at low As pressure.

This paper reports the measurement of the surface diffusion length of Ga adatom incorporation with a mixture of  $\text{As}_2$  and  $\text{As}_4$  molecular beams. The incorporation kinetics of Ga with  $\text{As}_2$  and  $\text{As}_4$  molecules at low As pressure is discussed.

## 2. Experiments

The experiment was carried out in a microprobe-RHEED/SEM MBE system. The incorporation diffusion length of Ga adatoms on the GaAs(001) substrate towards the  $[110]$  orientation was measured using microprobe-RHEED intensity oscillation [6,7]. In this experiment, inter-surface diffusion from the GaAs(011) to the GaAs(001) surface was observed. GaAs substrates were used that were oriented at  $(001) \pm 0.5^\circ$  and exhibited (110) side surface which was obtained by cleaving the (001) substrate along the  $\langle 110 \rangle$  orientation. The growth was conducted at a temperature of  $580^\circ\text{C}$  and the growth rate of GaAs was about  $0.37 \mu\text{m/h}$ . The arsenic vapor was generated by a valved cracker cell, by which various  $\text{As}_2/\text{As}_4$  ratios could be obtained by changing the cracker temperature in the range of  $600\text{--}900^\circ\text{C}$ . The observed  $\text{As}_2/\text{As}_4$  ratio was higher at  $900^\circ\text{C}$  than that at  $600^\circ\text{C}$ . Because there is no quantitative data for the  $\text{As}_2/\text{As}_4$  ratio as a function of the cracker cell temperature, the  $\text{As}_2/\text{As}_4$  ratio was calculated thermodynamically as described in the following section. In spite of the cracker temperature, the total number of As atoms in the beam was maintained constant, which can be changed by adjusting the cracker-cell main-body temperature, accordingly.

## 3. Results and discussion

### 3.1. $\text{As}_2/\text{As}_4$ ratio dependence of Ga incorporation diffusion length

Fig. 1 shows the Ga incorporation diffusion length on a GaAs(001) substrate towards the  $[110]$  orientation in MBE of GaAs as a function of the cracker cell temperature. When the cracker temperature is increased, the fraction of  $\text{As}_2$  molecules versus total As molecules increases, resulting in an increase of the  $\text{As}_2/\text{As}_4$  ratio. As seen in Fig. 1, the incorporation diffusion length of Ga decreases with increasing  $\text{As}_2/\text{As}_4$  ratio. When the cracker-cell main-body temperature is increased, the total number of As atoms in the beam increases, which reduces the incorporation diffusion length.

Fig. 2 shows the dependence of the Ga incorporation diffusion length on the  $\text{As}_2$  pressure. It is inversely proportional to the square root of the  $\text{As}_2$  pressure in the pressure range from  $1.6 \times 10^{-4}$  to  $3.0 \times 10^{-4}$  Pa. In the pressure range between  $3.0 \times 10^{-4}$  and  $5.3 \times 10^{-4}$  Pa, the Ga incorporation diffusion length is inversely proportional to the  $\text{As}_2$  pressure. Fig. 3 shows the dependence of Ga incorporation diffusion length on the  $\text{As}_4$  pressure, which reveals a similar dependence as Fig. 2. In the case of  $\text{As}_4$ , the Ga diffusion length is inversely proportional to the square root of the  $\text{As}_4$  pressure in the pressure range from  $7.0 \times 10^{-5}$  to  $1.3 \times 10^{-4}$  Pa, and it is inversely proportional to the  $\text{As}_4$  pressure in the range from  $1.3 \times 10^{-5}$  to

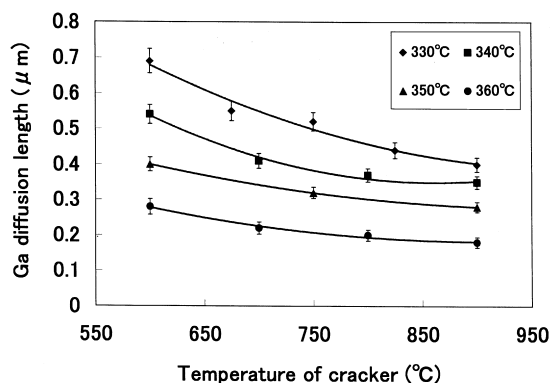


Fig. 1. Surface diffusion length of Ga incorporation  $\lambda_{\text{inc}}$  versus cracker-cell temperature for different cracker-cell main-body temperature values.

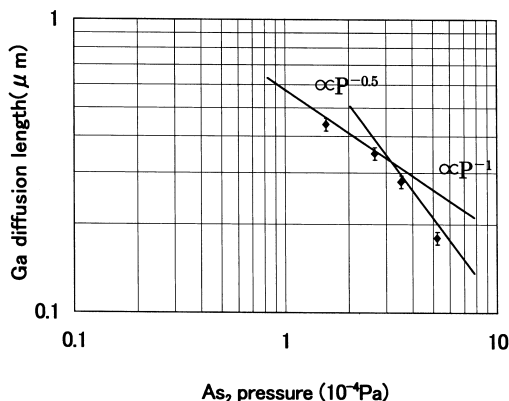


Fig. 2. Incorporation diffusion length of Ga  $\lambda_{\text{inc}}$  at a temperature of 580°C on a (0 0 1)GaAs as a function of  $\text{As}_2$  pressure.

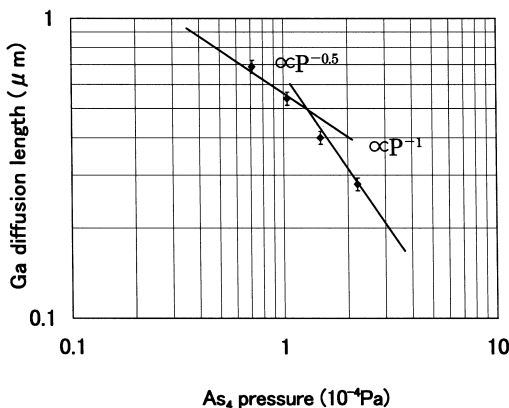


Fig. 3. Incorporation diffusion length  $\lambda_{\text{inc}}$  versus  $P_{\text{As}_4}$  at a temperature of 580°C on (0 0 1)GaAs.

$2.3 \times 10^{-4}$  Pa. For both  $\text{As}_2$  and  $\text{As}_4$ , the reactions are of the first order at low arsenic pressure and of the second order at high arsenic pressure.

### 3.2. Thermodynamic calculation of the $\text{As}_2/\text{As}_4$ ratio

As mentioned in the previous section, no measured values of  $\text{As}_2/\text{As}_4$  ratio as a function of cracker temperature are available in literature. Hence, we calculated the ratio thermodynamically.

The following equilibrium was assumed to be established in the cracker cell.



The equilibrium constant of Eq. (1) is given as [8],

$$K = \frac{P_{\text{As}_4}}{P_{\text{As}_2}^2} = 15.4 \times 10^2 - 18.1 \times 10^5/T - 57.2 \ln T, \quad (4)$$

where the pressures are given in Pa. Since the cracker-cell main-body temperature is kept constant, the total number of supplied As atoms emitted is constant. This yields the relation between the total number of supplied As atoms and the arsenic pressures, which can be written as

$$N_{\text{As}} = \frac{4P_{\text{As}_4}}{RT} + \frac{2P_{\text{As}_2}}{RT}. \quad (5)$$

With Eqs. (4) and (5), the  $\text{As}_2/\text{As}_4$  ratio, or the pressure of  $\text{As}_4$ ,  $\text{As}_2$  and their mixture can be calculated. Fig. 4 shows the percentage of  $\text{As}_2$  and  $\text{As}_4$  molecules in the flux. The composition of the arsenic beam changes dramatically as a function of the cracker-cell temperature. At a temperature of 900°C, the beam is nearly entirely dominated by  $\text{As}_2$  molecules, whereas  $\text{As}_4$  is the dominant species at a cracker-cell temperature of 600°C.

### 3.3. The growth kinetics of GaAs MBE

At high  $\text{As}_4$  pressure, the chemical reaction between  $\text{As}_4$  and Ga is of the second order. In this case, a pair of  $\text{As}_4$  molecules which are in the precursor state produces two active  $\text{As}_2$  molecules and one desorbing  $\text{As}_4$  molecule. The two active  $\text{As}_2$  molecules are incorporated into the GaAs layer [1,2]. At low  $\text{As}_4$  pressure, the chemical reaction of  $\text{As}_4$  and Ga is of the first order, as demonstrated in the experiments discussed above. The detailed chemical reaction between  $\text{As}_4$  and Ga requires further investigation.

It is shown in Figs. 2 and 3 that the incorporation diffusion length of Ga is inversely proportional to the square root of the  $\text{As}_4$  pressure in the pressure range of  $P_{\text{As}_4} = 1.6 \times 10^{-4} \sim 3.0 \times 10^{-4}$  Pa and to the square root of the pressure of  $\text{As}_2$  in the pressure range of  $P_{\text{As}_2} = 7.0 \times 10^{-5} \sim 1.3 \times 10^{-4}$  Pa, respectively. The growth reactions with both  $\text{As}_4$  molecules and  $\text{As}_2$  molecules are of the first order.

The incorporation diffusion length of Ga adatoms can be calculated theoretically for the beam composed of an  $\text{As}_2$  and  $\text{As}_4$  mixture. If we

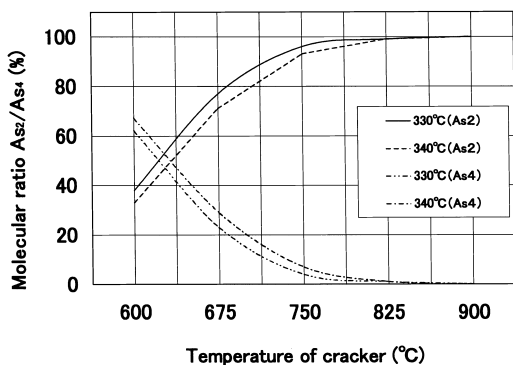


Fig. 4. Thermodynamically calculated percentage of  $\text{As}_2$  and  $\text{As}_4$  molecules in the beam.

assume that the  $\text{As}_2$  molecules are the smallest arsenic species in the first-order growth reaction [1,2], the incorporation lifetime can be written as [5]

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{As}_2}} + \frac{1}{\tau_{\text{As}_4}} = C(R_{\text{As}_2} N_{\text{As}_2} + \alpha R_{\text{As}_4} N_{\text{As}_4}), \quad (6)$$

where  $\tau$ ,  $\tau_{\text{As}_2}$ ,  $\tau_{\text{As}_4}$ ,  $N_{\text{As}_2}$  and  $N_{\text{As}_4}$  denote the incorporation lifetime of Ga with the flux of an  $\text{As}_2$  and  $\text{As}_4$  mixture, the incorporation lifetime of Ga with the  $\text{As}_2$  flux only, the incorporation lifetime of Ga with the  $\text{As}_4$  flux only, the surface density of  $\text{As}_2$  ad molecules and that of  $\text{As}_4$  ad molecules, respectively. The parameter  $\alpha$  is the average number of active  $\text{As}_2$  molecules generated by one  $\text{As}_4$  molecule.  $R_{\text{As}_2}$  and  $R_{\text{As}_4}$  are the correction factors to take the re-evaporation effect of the arsenic molecules into account. Arriving  $\text{As}_2$  and  $\text{As}_4$  molecules stay and migrate on the growing surface before they incorporate Ga at kink sites or re-evaporate. If the re-evaporation of  $\text{As}_2$  and  $\text{As}_4$  molecules occurs more frequently than the incorporation process, the values of  $N_{\text{As}_2}$  and  $N_{\text{As}_4}$  will be reduced and a smaller number for  $R_{\text{As}_2}$  and  $R_{\text{As}_4}$  has to be assumed. The diffusion length of Ga is given by

$$\lambda_{\text{inc}} = \sqrt{D_s \tau} \quad (7)$$

where  $D_s$  is the surface diffusion coefficient of Ga on the GaAs substrate surface. With Eqs. (6) and (7), one deduces the following expression for the diffusion length:

$$\lambda_{\text{inc}} = C'(R_{\text{As}_2} N_{\text{As}_2} + \alpha R_{\text{As}_4} N_{\text{As}_4})^{-0.5}, \quad (8)$$

where  $C'$  is a constant.

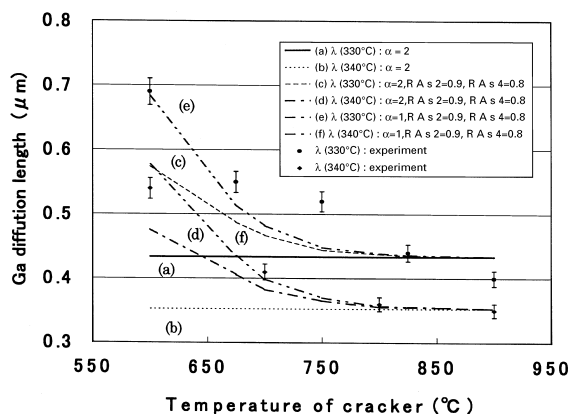


Fig. 5. Experiment and theoretical incorporation diffusion length  $\lambda_{\text{inc}}$  as a function of cracker temperature. (a) and (b): without re-evaporation;  $\text{As}_4$  supplies two active  $\text{As}_2$  molecules for the growth. (c) and (d): with re-evaporation,  $\text{As}_4$  molecule generates two active  $\text{As}_2$  molecules. (e) and (f): with re-evaporation,  $\text{As}_4$  supplies one active  $\text{As}_2$  molecule and one desorbing  $\text{As}_2$  molecule. The cracker-cell main-body temperature of (a), (c) and (e) is 330°C and that of the rest is 340°C.

If all of the supplied arsenic molecules are used for the growth of GaAs regardless of the kind of As molecule, the incorporation diffusion length of Ga should not depend on the  $\text{As}_2/\text{As}_4$  ratio, because the total number of As atoms in the beam is kept constant. Curves (a) and (b) in Fig. 5 show the values of  $\lambda_{\text{inc}}$  corresponding to this case, which is calculated with  $R_{\text{As}_2} = 1$  and  $R_{\text{As}_4} = 1$  for cracker-cell main-body temperatures of 330 and 340°C, respectively. Experimental results clearly demonstrate that the incorporation diffusion length changes when the  $\text{As}_2/\text{As}_4$  ratio is modified. To understand the reason why the incorporation diffusion length changes with  $\text{As}_2/\text{As}_4$  ratio, we varied the values of  $\alpha$ ,  $R_{\text{As}_2}$  and  $R_{\text{As}_4}$ . First, we employed the values of  $R_{\text{As}_2} = 0.9$  and  $R_{\text{As}_4} = 0.8$  at 580°C according to the experiments by Stok et al. [9] with a value of  $\alpha = 2$ . By this approach, we assume that  $\text{As}_4$  generates two  $\text{As}_2$  molecules and we take the re-evaporation of  $\text{As}_2$  and  $\text{As}_4$  into account. The value of  $\lambda_{\text{inc}}$  calculated with Eq. (8) yields curves (c) and (d) for cracker-cell main-body temperatures of 330 and 340°C, respectively. Although the agreement between the calculation and the experiment has been improved there are still large discrepancies visible.

In the next set of calculations, we chose the value of  $\alpha = 1$ , which means that the number of  $\text{As}_2$  molecules used to incorporate Ga during the decomposition of  $\text{As}_4$  is unity. Using the same values for  $R_{\text{As}_2}$  and  $R_{\text{As}_4}$  as in the previous calculation, values for  $\lambda_{\text{inc}}$  that are computed are displayed in (e) and (f) of Fig. 5 for the cracker-cell main-body temperatures of 330 and 340°C, respectively. In these calculations a very good agreement between calculation and experimental values is observed. This means that the portion of  $\text{As}_2$  molecules generated by the chemical reaction of  $\text{As}_4$  molecules with Ga is incorporated into the GaAs epi-layer. The other portion of  $\text{As}_2$  molecules desorb. On the other hand, almost all  $\text{As}_2$  molecules are active and are incorporated into the GaAs epi-layer.

Hence, in summary, the reaction kinetics of As molecules in the range of the first order reaction can be given as



and



All  $\text{As}_2$  molecules arriving on the growing surface are active and incorporate Ga at a kink site. On the other hand,  $\text{As}_4$  molecules decompose at kink sites into two  $\text{As}_2$  molecules. One molecule incorporates Ga at the same kink site and the other molecule re-evaporates and is lost. Hence, the sticking coefficient of  $\text{As}_2$  is unity, whereas the sticking coefficient of  $\text{As}_4$  is 0.5, even in the range of the first-order reaction. This means that  $\text{As}_2$  molecules incorporate Ga into the growing GaAs epi-layer more efficiently than  $\text{As}_4$  molecules.

#### 4. Summary

The  $\text{As}_2/\text{As}_4$  ratio dependence of the Ga incorporation diffusion length was studied by microprobe-RHEED/SEM MBE keeping the total number of As atoms in the flux constant. When the  $\text{As}_2/\text{As}_4$  ratio increases, the Ga incorporation diffusion length is decreased. This means  $\text{As}_2$  is the active species to fix Ga at a kink site of the

step more efficiently than  $\text{As}_4$ . It was found that the chemical reaction of Ga and  $\text{As}_4$  or Ga and  $\text{As}_2$  is of the first order at low As pressure but of the second order at high As pressure.

By comparing the experimental data and thermodynamical equilibrium calculations it is concluded that one incident  $\text{As}_4$  molecule produces one active  $\text{As}_2$  molecule which incorporates Ga into the growing GaAs epi-layer and one re-evaporating  $\text{As}_2$  molecule which is lost from the surface. On the other hand, almost all  $\text{As}_2$  molecules incorporate Ga into the GaAs epi-layer. Hence, it is concluded that  $\text{As}_2$  molecules incorporate Ga into the growing GaAs epi-layer more efficiently than  $\text{As}_4$  molecules.

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