Pressure and temperature dependence of Zn incorporation in metalorganic chemical vapour deposition grown GaAs and AlGaAs using diethylzinc as precursor

P.R. Hageman a, M.H.J.M. de Croon b, X. Tang c and L.J. Giling a

a Department of Experimental Solid State Physics, RIM, Faculty of Science, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, Netherlands
b Laboratorium voor Chemische Technologie, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, Netherlands
c AMTC - Advanced Semiconductor Materials International, Rembrandtlaan 24, 3723 BJ Bilthoven, Netherlands

Received 19 October 1992; manuscript received in final form 4 December 1992

Zinc doping of MOCVD grown GaAs and AlGaAs using diethylzinc (DEZn) as precursor has been studied as a function of the zinc input mole fraction, growth temperature, aluminum fraction of the AlGaAs alloy and total reactor pressure. The experiments have been performed in two different reactors which differ in pressure and temperature distributions. We have found that the zinc incorporation follows a linear behaviour in a log-log plot of hole concentration versus zinc input mole fraction with a slope of 1 and that the incorporation of zinc is independent of the fraction Al in AlxGa1-x As up to x = 0.45. The zinc incorporation decreased with increasing growth temperature following an Arrhenius type of behaviour for both GaAs and AlGaAs. This temperature behaviour did not change when the reactor pressure was lowered. All experimental results can be explained satisfactorily by a model which takes into account that the incorporation of zinc is precluded by an adsorption−desorption equilibrium of zinc at the step of the growing crystal.

1. Introduction

Metalorganic chemical vapour deposition (MOCVD) nowadays is an important technique for growing III/V semiconductor materials. Making devices requires multi-layer structures which consist of doped and undoped layers. As a p-type dopant the elements Zn [1–4], Mg [5–7], Be [8,9], Cd [10] and C [11–13] have been employed in MOCVD. Among these elements, zinc is the one most widely used in MOCVD growth of GaAs and AlGaAs.

Although the diffusion coefficient of zinc in these III/V semiconductors is rather high [14–16], zinc is preferred by most users because the zinc precursors can be handled very easily and it has a wide doping range (10^{16}−10^{20} \text{ cm}^{-3}). The most commonly used zinc precursor in MOCVD is diethylzinc (DEZn).

In the literature, a considerable number of studies on zinc doping of GaAs have been published [1–4,12,17–24], in contrast to the relatively small amount of work on the p-type doping of AlGaAs with zinc [25]. When the hole concentration is plotted versus the input mole fraction DEZn on a log-log plot, in most cases a linear relation has been reported [1,2,19–21] with slopes varying between 0.4 and 1.4, although also non-linear relations have been obtained [2,21,22].

In contrast with the previous point, there is much more agreement when the temperature dependence is regarded of the zinc doping using DEZn. It is found that the hole concentration decreases with increasing growth temperatures [1,3,21,26] with an "apparent activation energy" which varies between −48 kcal/mol (−2.1 eV) and −76 kcal/mol (−3.3 eV). This exothermic reaction enthalpy is explained in the literature by the temperature dependence of the zinc evaporation from the crystal surface [2–4] or by the temperature dependence of the concentration of gallium vacancies [27].
In this paper we present experimental results on the zinc doping of GaAs and Al$_x$Ga$_{1-x}$As (up to $x = 0.45$) as a function of growth temperature, input mole fraction DEZn and total reactor pressure. The depletion effects of the zinc incorporation are also presented.

2. Experimental procedure

The experiments were carried out in two different reactors. The first MOCVD reactor (hereafter referred to as reactor I) was operated at atmospheric pressure [28] and was equipped with a horizontal reactor cell with a rectangular cross section. In principle it is possible to calculate the temperature gradient and mass fluxes in this reactor [28]. The second reactor (hereafter referred to as reactor II) is a commercially available, computer controlled, low pressure MOCVD reactor [29].

In both reactors the growth was performed using arsine (AsH$_3$), trimethyl gallium (TMG), trimethyl aluminium (TMA) and DEZn as p-dopant. Hydrogen, purified by a Pd-diffusion cell, was used as a carrier gas. The experimental details are given in table 1. The thicknesses of the layers, grown on (100) 2° (110) oriented GaAs substrates, were measured with an interference-contrast microscope or, if necessary, a scanning electron microscope (SEM). The samples were electrically characterized by Hall-Van der Pauw measurements (300 K) or, when specifically mentioned, using a conventional $C-V$ profiler.

3. Results and discussion

All the samples showed specular morphology, independent of the input mole fraction of DEZn, the growth temperature and the aluminum fraction of the AlGaAs epilayers. In the following sections the influence of these parameters on the incorporation of zinc will be discussed. Finally, the depletion effect of the zinc incorporation in reactor I is examined and explained.

3.1. The effect of the input mole fraction DEZn on the hole concentration

3.1.1. GaAs

For reactor I, two series of GaAs doping experiments were performed under the same growth conditions ($V/III$ 20 and $P_{reactor}$ = 1 atm, same $P_{TMG}$) except for the growth temperatures which were 680 and 705°C, respectively. In fig. 1 these
data points are shown in a log-log plot. In this plot the hole concentration is linearly dependent on the input mole fraction DEZn with a slope of 1. The difference in concentration between these two sets of experiments is solely caused by the difference in growth temperature, as will be discussed further on in this paper.

In fig. 1, data points are also given from experiments performed in reactor II at 640°C, with a V/III ratio of 125 at 20 mbar total reactor pressure. These data points also give a straight line with a slope of 1. The lower hole concentrations in this case are due to the trivial effect that at lower total pressures also all partial pressures are reduced. This effect was checked in reactor II for three pressures, i.e. 20, 100 and 1000 mbar (inset fig. 1). From this log-log plot it follows that the hole concentration increases linearly with higher total pressure with a slope quite close to 1, demonstrating that this is indeed due to the increase of the partial pressure of DEZn at increasing total reactor pressure.

From these experiments it follows that both at atmospheric and at low pressure the hole concentration increases linearly with increasing input mole fraction DEZn with slope 1 and no saturation effect is observed, which is confirmed in the literature [3].

3.1.2. AlGaAs

Similar growth and doping experiments were performed with Al\textsubscript{x}Ga\textsubscript{1-x}As with x varying between 0 and 0.45 (fig. 2). In reactor I (atmospheric pressure), Al\textsubscript{0.10}Ga\textsubscript{0.90}As was grown at a temperature of 720°C as a function of the input mole fraction DEZn. Again a linear relationship between the input mole fraction DEZn and the hole concentration is observed. The small deviation from the value 1 in the slopes of the lines in figs. 1 and 2 is entirely due to the uncertainties in layer thicknesses and hole concentrations.

At low pressure two sets of experiments were performed in reactor II. The first set was performed at 720°C for \( x_{Al} = 0.25 \), while the second set was carried out at 710°C for \( x_{Al} = 0.45 \). These points give a straight line with a slope 1 (fig. 2) for both Al fractions. The difference in hole concentration as observed between the two sets of experiments in reactor II is completely due to the 10°C difference in growth temperature. So it appears that the amount of aluminum has no direct influence on the zinc incorporation.

3.2. The effect of growth temperature on the hole concentration

In both reactors experiments were performed to investigate the influence of the growth temperature on the zinc incorporation. In these experiments the input mole fraction of DEZn and other growth parameters were kept constant, whereas the growth temperature was varied (fig. 3). For both reactors the zinc incorporation in GaAs and AlGaAs decreased for increasing temperature, as was already observed in figs. 1 and 2. The hole concentration shows an Arrhenius behaviour with a negative apparent activation energy (\( E_{\text{act}} \)) of \(-67\) kcal/mol for GaAs grown in reactor II, an activation energy of \(-90\) kcal/mol for GaAs grown in reactor I and of \(-70\) kcal/mol for Al\textsubscript{0.10}Ga\textsubscript{0.90}As grown in reactor II. From these negative values one can conclude that this \( E_{\text{act}} \) is not a activation energy but really a \( \Delta H \) from an adsorption/desorption equilibrium.
This temperature behaviour cannot be attributed solely to the evaporation of zinc, as described in refs. [3,4], because the obtained values for the apparent activation energy of the zinc incorporation process are significantly higher than the value given for the evaporation of zinc (48 kcal/mol) from the surface [2-4].

3.3. Model

In the discussion of the zinc incorporation mechanism we have to explain the experimental results as described earlier in this paper, i.e. the linear behaviour of the zinc incorporation as a function of the input mole fraction DEZn (fig. 1 and fig. 2), the dependence on the total reactor pressure (inset fig. 1) and the typical temperature dependence (fig. 3).

From equilibrium calculations [30] it is known that at the temperatures used (600-700°C), the most abundant zinc species is monoatomic zinc (Zn). As the partial pressure of Zn will be proportional to the input mole fraction of DEZn, we have

\[ P_{Zn} \propto P_{DEZn}. \]  

In this section we will use the concentration ([Zn] = \( P_{Zn}/RT \)) instead of partial pressure. We will assume that there is a steady-state situation at the surface and that in a first approximation, at the used growth conditions, the (001) surface is almost of free adsorbed species [31].

Under these conditions the zinc incorporation can be described by the rate of adsorption, desorption and incorporation of the Zn species at the surface:

\[ \frac{k_a C}{y=0} - \frac{k_d \Theta_{Zn}}{\text{adsorption}} - \frac{N_s \Theta_{Zn}}{N_{Av} \tau} \text{desorption} = 0, \]

\[ \text{incorporation} \]  

in which \( k_a \) is the constant for adsorption of monoatomic zinc on GaAs or AlGaAs (cm s\(^{-1}\)), \( k_d \) is the rate constant for desorption of monoatomic zinc from GaAs or AlGaAs (mol cm\(^{-2}\) s\(^{-1}\)), \( C \big|_{y=0} \) is the concentration of monoatomic zinc in the gas phase at the height of the surface (mol cm\(^{-3}\)) (\( C \big|_{y=0} = (P_{DEZn} \big|_{y=0})/(RT y_0) \)), \( \Theta_{Zn} \) is the Zn coverage of the surface (dimensionless), \( N_s \) is the number of adsorption sites (cm\(^{-2}\)), \( N_{Av} \) is Avogadro's number (mol\(^{-1}\)), and \( \tau \) is the time needed for the growth of 1 monolayer of GaAs or AlGaAs (s).

Eq. (2) is very general, i.e. it can also be used for the adsorption, desorption and incorporation taking place at a step instead of a surface process. In this last case only the number of adsorption sites, \( N_s \), and the time needed to incorporate the adsorbed species, \( \tau \), have to be redefined. It appears, however, that these two numbers fortunately decrease proportionally to each other. So the same expression will hold when the process takes place entirely at the step.

The time needed for the growth of a monolayer of III/V semiconductor (\( \tau \)) is given by:

\[ \tau = \frac{d \rho_{(III/V)}}{M_{(III/V)} r_{(III/V)}}, \]  

in which \( d \) is the thickness of a monolayer of GaAs or AlGaAs (cm), \( \rho_{(III/V)} \) is the density of GaAs or AlGaAs (g cm\(^{-3}\)), \( M_{(III/V)} \) is the molecular weight of GaAs or AlGaAs (g mol\(^{-1}\)) and \( r_{(III/V)} \) is the growth rate of GaAs or AlGaAs (mol cm\(^{-2}\) s\(^{-1}\)).
From eq. (2) one can derive the zinc coverage of the surface:

$$\Theta_{Zn} = \frac{k_a C_{y=0}}{k_d + N_s/N_{Av} \tau} = \frac{(k_a/k_d) C_{y=0}}{1 + N_s/N_{Av} \tau k_d}. \quad (4)$$

The deposition rate of zinc can be expressed as:

$$r_{dep,Zn} = \frac{N_s \Theta_{Zn}}{N_{Av} \tau} (\text{mol cm}^{-2} \text{ s}^{-1}). \quad (5)$$

With eq. (3) and eq. (4) this results in:

$$r_{dep,Zn} = \frac{N_s k_a C_{y=0}}{N_{Av} k_d \tau (1 + N_s/N_{Av} \tau k_d)}. \quad (6)$$

For eq. (6) two extremes can be distinguished.

The first situation, case A, is valid when:

$$\frac{N_s}{N_{Av} \tau k_d} \ll 1, \quad \text{so} \quad r_{dep,Zn} = \frac{N_s k_a}{N_{Av} k_d \tau} C_{y=0}. \quad (7)$$

Eq. (7) can be written as follows:

$$N_s \Theta_{Zn} \ll k_d \Theta_{Zn},$$

so that it becomes clear that in case A the incorporation of zinc is much slower than the desorption of zinc from the step or from the GaAs surface. This implies that the Zn coverage, \(\Theta_{Zn}\), is determined by the adsorption–desorption equilibrium.

The second situation, case B, is valid when:

$$\frac{N_s}{N_{Av} \tau k_d} \gg 1, \quad \text{so} \quad r_{dep,Zn} = k_a C_{y=0}. \quad (8)$$

Case B (eq. (8)) represents the situation at which every zinc species that arrives at the III/V surface will stick to the step and be incorporated. However, this situation describes a pure kinetic adsorption reaction for which the activation energy of \(k_a\) will always exhibit a zero or a positive activation energy, i.e. the hole concentration will increase when the growth temperature is increased. This is in complete disagreement with the experimental results and with the literature data [1,3,21,26]. Therefore only case A will be worked out in more detail.

From a combination of eq. (3) and eq. (7) it follows that the expression for the deposition rate of zinc can be formulated as:

$$r_{dep,Zn} = \frac{N_s k_a M_{(III/V)} r_{(III/V)}}{N_{Av} k_d \tau} C_{y=0} \quad (\text{mol cm}^{-2} \text{ s}^{-1}). \quad (9)$$

The hole concentration \((N_{Zn})\), as measured with the Hall–Van der Pauw method, is defined as:

$$N_{Zn} = \frac{N_s}{N_{Av}} r_{dep,Zn} \frac{p_{(III/V)}}{M_{(III/V)}} (\text{cm}^{-3}). \quad (10)$$

Here we have assumed that all the incorporated zinc has been built in on a substitutional site and is electrically active. This would not be true if the experiments were performed in the saturation range [3], which is not the case in our experiments, see figs. 1 and 2.

Rewriting eq. (10) in combination with eq. (9) gives the simple general description for the hole concentration in GaAs and AlGaAs for the situation (case A) that the adsorption–desorption equilibrium of the zinc species on the GaAs (or AlGaAs) surface or step determines the zinc incorporation rate:

$$N_{Zn} = \frac{N_s}{d} \frac{k_a}{k_d} C_{y=0}. \quad (11)$$

The following conclusions can be drawn from this equation. The first point to be mentioned is that the resulting hole concentration will depend linearly on the concentration of zinc species in the gas phase at the height of the surface \((C_{y=0})\), i.e. it also will depend linearly on the concentration of zinc species in the bulk gas phase, and so is linearly dependent on the input mole fraction \(DE_{Zn}\). This is consistent with the experimental results as presented in figs. 1 and 2. The second point is that the incorporation will not depend on the aluminum fraction in the Al\(_x\)Ga\(_{1-x}\)As alloy. This indeed is experimentally observed up to \(x = 0.45\) as is shown in figs. 1 and 2. So the adsorption–desorption equilibrium is not influenced by the \(x\) fraction.

The pressure dependence of the zinc incorporation (see inset of fig. 1) can be explained also. In lowering the total reactor pressure, the partial
pressure of DEZn is also lowered and with it the concentration of the zinc species at the surface \((C_{y=0})\). This explains the lower zinc incorporation at the lower pressures as compared to that of the experiments performed at 1 atm.

The temperature behaviour of zinc doping with DEZn is now easy to explain. It is entirely determined by the temperature behaviour of the ratio \(k_a/k_d\), which is equal to the equilibrium constant \(K\) for the adsorption/desorption of Zn. This constant \(K\) can be expressed as \(K = e^{\Delta H_0}/RT\) where \(\Delta H_0\) is determined by the heat of adsorption. The observed mean apparent activation energy \((E_{act})\) of the zinc incorporation, both for GaAs and AlGaAs, is \(-75\) kcal/mol. According to the model this negative value for the activation energy corresponds entirely to the adsorption enthalpy for the process of adsorbing Zn atoms on the surface or step of GaAs or AlGaAs.

The question remains whether this adsorption enthalpy is due to the adsorption on the surface or to the step. The observed value for the adsorption enthalpy of Zn on an As-stabilized GaAs surface seems to be quite high for a normal adsorption process where one bond is formed. The highest values found in the literature are \(-65.2\) kcal/mol for an As–H bond and \(-56.5\) kcal/mol for an As–C bond [31]. No specific values for the As–Zn bond could be found, but the As–Zn bond strength certainly is not that strong. However, when it is assumed that the adsorption of Zn takes place at a step, a double bond will be formed. For the desorption of Zn now two bonds have to be broken, which requires twice as much energy. This means that the value for a single Zn–As bond strength will be \(37.5\) kcal/mol, which seems to be a quite acceptable value. Therefore, in our opinion, the observed temperature behaviour of the zinc incorporation is explained by the adsorption–desorption behaviour of zinc at the step on the growing crystal.

### 3.4. Depletion effects

Although in the literature no depletion effects have been reported for the incorporation of zinc, we did observe in the top-cooled atmospheric pressure reactor a significant depletion effect. In order to study this process in more detail, we performed some specific depletion experiments in reactor I. Due to the special design of this reactor [28] (long susceptor, top-cooled reactor cell, fully developed temperature and flow profiles), the growth of GaAs and AlGaAs in this reactor can be modelled rather easily and with reasonable precision [32–34]. It must be mentioned that when undoped (or silicon doped) GaAs or AlGaAs is grown in this reactor (I), only an arsenic deposit is found at the top of the reactor due to its relatively low temperature (300 K). But when the doping experiments with DEZn are performed, a zinc containing deposit is found at the top of the reactor which is due to the strong adsorption of zinc. This deposition is responsible for the depletion of zinc. This effect is not observed in reactor II because, in this reactor, the top of the cell is not cooled and therefore the top of the reactor cell is much higher in temperature.

The samples for the investigation of the depletion effect of the zinc incorporation were grown under standard conditions. Experiments were performed for \(Al_{0.1}Ga_{0.9}As\) and GaAs. The substrates were placed on the susceptor at positions from 2 to 18 cm away from the beginning of the susceptor (\(x\)-coordinate). The heating starts at the beginning of the susceptor at \(x = 0\).

In fig. 4 the hole concentration in a semi-log plot is given versus the position on the susceptor for the two materials. It is evident from this figure that, in this top-cooled reactor, the zinc incorporation exhibits a depletion effect for both GaAs and \(Al_{0.1}Ga_{0.9}As\). The depletion effect is, in both cases, about equally strong. In the figure theoretical fits are also shown, which will be discussed below.

The depletion will be modelled as follows. Because of the zinc deposition on the top of the cell at \(y = h\), we take as a boundary condition for the calculation that the concentration of Zn in the reactor at the top of the cell is zero, so \(C_{y=h} = 0\) (\(h\) is the height of the reactor). This implies that all the Zn species that arrive will completely stick at the cold part of the reactor (top). As without top-cooling no zinc depletion is
observed, we can conclude that only a very small amount of the input mole fraction $DEZn$ is incorporated in the lattice. This implies that the change in the zinc concentration at the growing surface is almost zero, i.e. the boundary condition for the zinc concentration at the growing surface is $dC/dy |_{y=0} = 0$. Working along the lines described in ref. [28], one obtains for the concentration of zinc species at the surface:

$$C |_{y=0} = \frac{4C_{Zn}}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{2n-1}$$

$$\times \exp \left( -\frac{(2n-1)^2 \pi^2 D_{Zn} X}{4 \nu h^2} \right), \quad (12)$$

in which $C_{Zn}$ is the input concentration $DEZn$, $D_{Zn}$ is the binary diffusion coefficient of zinc species in $H_2$, $x$ is the horizontal coordinate in the reactor and $\nu$ is the mean gas velocity in the direction of the flow.

When this solution for $C |_{y=0}$ is substituted in eq. (11), one arrives at the following equation for the hole concentration:

$$N_{Zn} = \frac{k_{a}}{k_{d}} \frac{N_{S}}{d} \frac{4C_{Zn}}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n-1}}{2n-1}$$

$$\times \exp \left( -\frac{(2n-1)^2 \pi^2 D_{Zn} X}{4 \nu h^2} \right). \quad (13)$$

Based on eq. (13), two calculations have been performed for the zinc incorporation, where the diffusion constant of monoatomic zinc has been calculated according to ref. [35]. These calculations are presented in fig. 4. As one can see, the theoretical lines are in good agreement with the experimental results demonstrating that the observed depletion of Zn during the growth of GaAs is indeed caused by the deposition of zinc at the cooled top of the reactor. From the parameter fit, we obtained a value for $K = k_{a}/k_{d}$ of $\approx 3.2 \times 10^{7}$ mol cm$^{-3}$. This is a realistic value. We can check this by calculating the zinc coverage of the surface ($\Theta_{Zn}$) at the used growth conditions with the aid of this $K$ value. This results in a zinc coverage of about $2.3 \times 10^{-3}$ under these experimental conditions, which corresponds well with the obtained hole concentrations.

4. Conclusions

Zinc doping experiments have been performed in two different reactors, one operating at atmospheric pressure and the other at low pressure. In contrast to the previous published results on the zinc incorporation rate, we have found that the results were reactor independent. From an analysis of the results, it follows that the incorporation of zinc can be explained by an adsorption/desorption equilibrium at the step followed by incorporation in the growing crystal. In addition depletion experiments were performed which showed that a depletion of zinc can be induced when the top of the reactor is water-cooled.
Acknowledgments

The authors would like to thank S.W. Kortbooyer and W.P.J.H. Jacobs for their assistance in growing some of the samples. The authors are greatly indebted to G.J. Bauhuis for performing the electrical characterization of the samples. This work was financed by NOVEM, project No. 41.220-003.1, and the “Stichting voor de Technische Wetenschappen” (STW) with financial support from the “Nederlandse Organisatie voor Wetenschappelijk Onderzoek” (NWO).

References