

# Calculation of point defect concentrations in GaAs grown by molecular beam epitaxy

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Thermodynamic chemistry of native defects is applied to molecular beam epitaxial (MBE) growth of GaAs. Following the model of Stringfellow [J. Cryst. Growth **70**, 133 (1984)], we assume that the equilibrium is established at the solid-vapor interface. Calculated results show that the defect concentration is rather low, less than  $10^{15} \text{ cm}^{-3}$  under usual growth conditions and that MBE GaAs is less As-rich than those grown by organometallic vapor phase epitaxy or halogen transport vapor phase epitaxy.

Molecular beam epitaxy (MBE) is widely used to grow thin layers of III-V compounds. The growth process of MBE is usually regarded as a nonequilibrium process, but it has been pointed out that the thermodynamic phase equilibria should be taken into account in addition to kinetic factors. Heckingbottom discussed impurity incorporation in MBE GaAs on the basis of a thermodynamic model.<sup>1</sup> Seki *et al.* thermodynamically analyzed the MBE growth process<sup>2</sup> by extending a theoretical model of Stringfellow.<sup>3</sup> According to the results in Ref. 2, the rate of MBE growth and alloy composition of the grown solids can be predicted assuming the phase equilibrium near the solid-vapor interface. Recently, Ivanov *et al.* adopted the same thermodynamic model to predict a pressure range within which segregation of group III elements occurs.<sup>4</sup> They noted that the point defect concentrations can also be calculated thermodynamically, although they did not present numerical results.

In this study, we calculate point defect concentrations in MBE GaAs on the basis of a thermodynamic model. The method for calculating defect concentrations under the equilibrium condition was established more than thirty years ago,<sup>5</sup> but there are only several works in which the method is applied to III-V compounds.<sup>6-12</sup> In addition, it has not been fully extended to actual vapor growth processes yet. Since the thermodynamic analysis of the growth process has been well developed, we are able to extend the defect model to various growth methods. In previous studies, we calculated defect concentrations in GaAs grown by halogen transport vapor-phase epitaxy (VPE)<sup>13</sup> and by organometallic vapor-phase epitaxy (OMVPE).<sup>14</sup> The method is extended further and applied to MBE in the present study, and the results are compared with those of the previous studies.

According to the model of Stringfellow and Seki *et al.*, the solid-vapor phase equilibrium is assumed to be established near the solid-vapor interface, although the incident beam pressures differ from the equilibrium pressures.<sup>2,3</sup> The equilibrium pressures are calculated by the following equations:

$$p_{\text{Ga}} p_{\text{As}_2}^{1/2} = K_0, \quad (1)$$

$$p_{\text{As}_2}^2 p_{\text{As}_4} = K_{\text{As}}, \quad (2)$$

$$p_{\text{Ga}}^0 - p_{\text{Ga}} = 2p_{\text{As}_2}^0 + 4p_{\text{As}_2}^0 - 2p_{\text{As}_2} - 4p_{\text{As}_4}. \quad (3)$$

Here,  $p_x^0$  and  $p_x$  represent the incident and equilibrium pressures of a molecule  $X$ , respectively.  $K_0$  is the equilibrium constant of the reaction  $\text{Ga} + \frac{1}{2}\text{As}_2 = \text{GaAs}$ , and  $K_{\text{As}}$  that of the reaction  $2\text{As}_2 = \text{As}_4$ . The third condition is imposed because the grown solid is nearly stoichiometric, i.e., the same number of Ga and As atoms are lost from the incident beams. Values of the thermodynamic parameters necessary for the calculation are taken from Ref. 15.

The defect concentrations are calculated from the equilibrium pressures thus obtained. We adopt a defect model of Van Vechten and consider the following defect formation reactions:<sup>16,17</sup>



Here  $V$  is a vacancy, and  $e$  and  $h$  are an electron and a hole, respectively. Subscripts  $g$ ,  $\text{Ga}$ , and  $\text{As}$  represent a gas phase, a Ga site, and an As site, respectively. The superscripts refer to charge states.

The equilibrium condition of reaction (4), for example, is given by

$$\frac{[V_{\text{As}}^0]}{p_{\text{Ga}}} = \exp\left(-\frac{G_0(\text{Ga}) + G(V_{\text{As}}^0)}{kT}\right), \quad (10)$$

where  $[V_{\text{As}}^0]$  is the relative concentration of  $V_{\text{As}}^0$ ,  $G(V_{\text{As}}^0)$  the formation energy of  $V_{\text{As}}^0$ , and  $G_0(\text{Ga})$  the energy of incorporation of Ga from the vapor phase to a proper lattice site.  $T$  is the absolute temperature and  $k$  the Boltzmann constant. The formation energies of the defects are taken from Refs. 16 and 17.

The defect concentrations are calculated from the equilibrium conditions of reactions (4)–(9) and the charge neutrality condition.

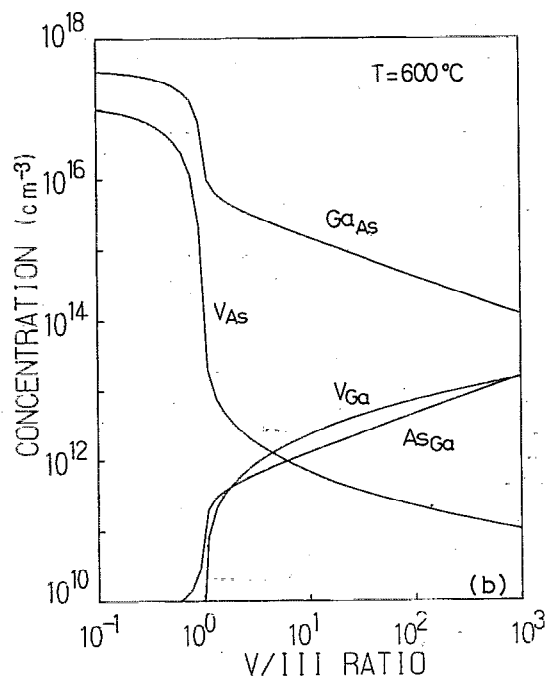
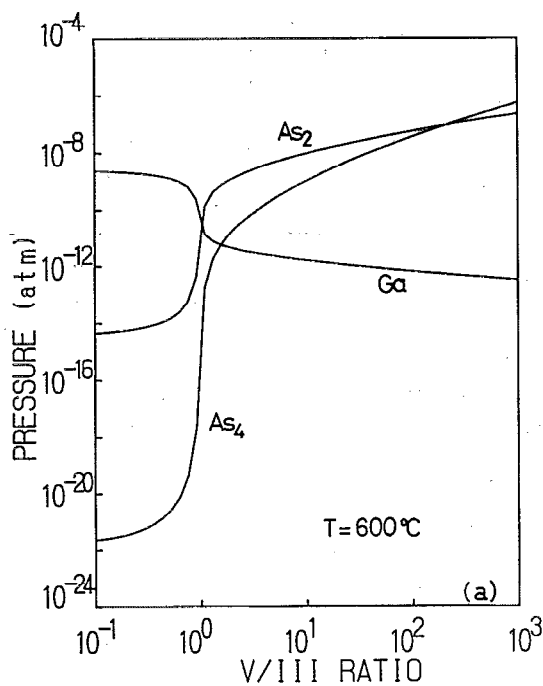


FIG. 1. The equilibrium partial pressures (a) and the defect concentrations (b) for GaAs at 600 °C. The incident Ga pressure is  $2 \times 10^{-6}$  Torr.

In the following, the calculation results are given as a function of  $R$ , the V/III ratio of the incident beams, which is given by  $R = (2p_{\text{As}_2}^0 + 4p_{\text{As}_4}^0)/p_{\text{Ga}}^0$ .

Figure 1 shows calculation results of the equilibrium pressures (a) and the defect concentrations (b) at 600 °C. The incident Ga pressure is  $2 \times 10^{-6}$  Torr ( $2.63 \times 10^{-9}$  atm), which corresponds to a incident flux of  $2.7 \times 10^{14}$  atoms/cm<sup>2</sup> s or a growth rate of 0.5  $\mu\text{m/h}$  under the As-rich condition, according to the Hertz-Knudsen equation. At 600 °C, a Ga-rich liquid phase is formed when  $p_{\text{Ga}}$  exceeds  $6 \times 10^{-11}$  atm, although we neglect the formation of

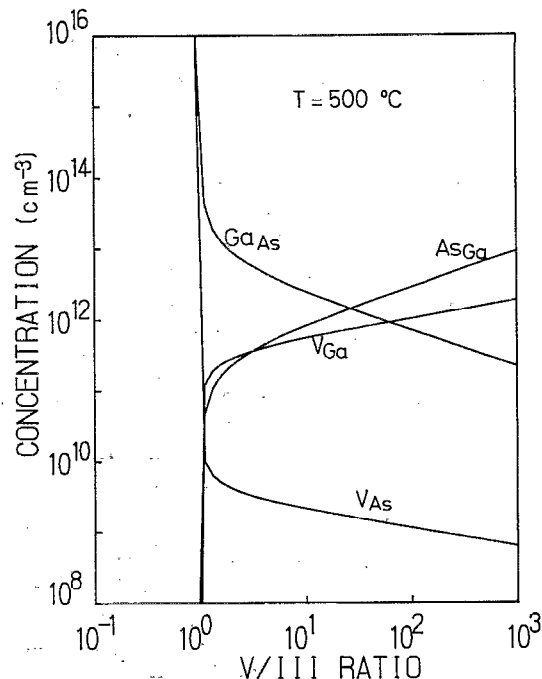


FIG. 2. The defect concentrations for GaAs at 500 °C. The incident Ga pressure is  $2 \times 10^{-6}$  Torr.

the liquid phase in the calculation. For  $R < 1$ , the calculated  $p_{\text{Ga}}$  exceeds the critical value, and thus the grown GaAs is actually in equilibrium with the Ga-rich liquid and not with the vapor phase. Therefore, our calculation is not valid for  $R < 1$ . In fact,  $R$  is larger than unity in usual growth conditions.

As expected,  $\text{Ga}_{\text{As}}$  and  $V_{\text{As}}$  decrease and  $\text{As}_{\text{Ga}}$  and  $V_{\text{Ga}}$  increase, i.e., the solid becomes more As-rich with increasing  $R$ . However, the most dominant defect is  $\text{Ga}_{\text{As}}$  in the whole range of  $R$ . This means that the grown GaAs is Ga-rich even if the vapor phase is As-rich ( $R > 1$ ). This is mainly because arsenic is much more volatile than Ga.

Figure 2 shows defect concentrations for a substrate temperature of 500 °C. The other conditions are the same as for Fig. 1. Again, the results for  $R < 1$  are not regarded as the equilibrium values. For  $R > 30$ , the  $\text{As}_{\text{Ga}}$  concentration becomes larger than the  $\text{Ga}_{\text{As}}$  concentration, i.e., the GaAs is As-rich. At a lower temperature, the evaporation of arsenic is suppressed and thus the solid phase becomes more As-rich under a certain arsenic pressure. However, the growth temperature is usually higher than 500 °C, and  $R$  is often smaller than 30. Thus, MBE GaAs is expected to be Ga-rich in most cases, according to the present calculation.

The nominally undoped MBE GaAs is generally  $p$ -type, and the hole concentration at room temperature is about  $10^{14} \text{ cm}^{-3}$ .<sup>18</sup> The calculated concentration of  $\text{Ga}_{\text{As}}$ , an acceptor, is comparable to or larger than the reported hole concentration. However, the  $\text{Ga}_{\text{As}}$  has a rather large ionization energy and will be neutral at room temperature. Thus, the residual carrier in MBE GaAs would be due to impurities such as carbon.

According to our previous results, GaAs is As-rich or

close to stoichiometry under the conventional growth conditions of OMVPE and halogen-transport VPE.<sup>13,14</sup> The present calculation is based on the same defect model, and the results show that MBE GaAs is usually Ga-rich. Since the defect formation energy is not accurately known, there is uncertainty in the absolute values of the calculated defect concentrations. Hence, it is not conclusive that the MBE GaAs is Ga-rich. However, we can draw a qualitative conclusion that the MBE GaAs is more Ga-rich than VPE GaAs. This is mainly because the arsenic vapor pressure is low in MBE; MBE is carried out in ultrahigh vacuum, and thus the As pressure is not as high as in VPE. The net evaporation rate of arsenic from the solid and thus the solid composition are determined by the absolute value of the arsenic pressure rather than by the V/III ratio. Therefore, MBE GaAs can be Ga-rich even when  $R \gg 1$ .

Defect EL2, which is related to excess As, is observed in OMVPE and halogen-transport VPE GaAs.<sup>19-21</sup> On the other hand, EL2 is generally absent in MBE GaAs. This fact indicates that MBE GaAs is less As-rich than VPE GaAs and thus is consistent with the above conclusion.

Interstitials are neglected in the defect model of Van Vechten. Baraff and Schuler predicted from a theoretical calculation that the interstitials are not dominant in both Ga-rich and As-rich GaAs.<sup>22</sup> However, Hurle claimed that the As interstitial ( $As_i$ ) is dominant in As-rich GaAs.<sup>8</sup> If the formation energy of  $As_i$  is comparable to the vacancy formation energy as supposed by Hurle,  $As_i$  will become one of the dominant defects when the growth temperature is low ( $\sim 500^\circ\text{C}$ ) and the V/III ratio is large ( $> 30$ ). However, GaAs is Ga-rich and thus  $As_i$  is not dominant under usual growth conditions, according to the present results.  $As_i$  might be formed for kinetic reasons, e.g., by incomplete decomposition of  $As_4$ . This type of defect formation cannot be discussed in the present thermodynamic model.

Foxon *et al.* measured the  $As_2/As_4$  ratio of desorbing flux from GaAs in the presence of the  $As_4$  beam.<sup>23</sup> The ratio increases with temperature in accordance with the prediction of the thermodynamic analysis, but the ratio is smaller than the thermodynamically expected one. They also discussed the surface reaction of GaAs MBE in detail and concluded that there is a difference in the kinetics between the growth with the  $As_4$  beam and that with the  $As_2$  beam.<sup>24</sup> Thus, although the thermodynamic analysis can explain some aspects of the growth, the equilibrium does not seem rigorously established in the interface re-

gion. This means that the results of the present calculation would not be accurate. However, as described above, our analysis can qualitatively explain some properties of MBE GaAs. Moreover, if the defect formation energy is accurately known, the present calculation can be used to examine to what extent the equilibrium is established: the agreement of the calculated defect concentrations with measured ones would indicate the equilibrium near the interface, and the disagreement indicates nonequilibrium. Thus, the present calculation should be developed further to clarify the growth mechanism of MBE.

In conclusion, point defect concentrations in MBE grown GaAs have been calculated thermodynamically. It has been assumed that the equilibrium is established at the solid-vapor interface. Calculated results show that MBE GaAs is less As-rich than those grown by OMVPE or halogen transport VPE. The limitation of the thermodynamic model has been discussed on the basis of reported experimental data.

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