1. Introduction

Immiscibility of alloy semiconductors is an intrinsic thermodynamic property of the solid phase at thermal equilibrium, giving the characteristic features in the equilibrium phase diagrams.\textsuperscript{1–5} The InGaN alloy is an example whose critical temperature for immiscibility is estimated to be somewhere at 1200 °C–1500 °C.\textsuperscript{6–8} In the metalorganic vapor phase epitaxy (MOVPE) growth process, it is usually assumed that the phase equilibrium is established at the vapor–solid interface.\textsuperscript{3,5} Then, a miscibility gap (MG), which is defined as the composition range not accessible at thermal equilibrium,\textsuperscript{1,3} should necessarily appear in the vapor–solid phase equilibrium below the critical temperature. In this regard, Refs. 8, 10–12, based on their thermodynamic calculations, claimed that the growth at around 800 °C or higher in the InGaN MOVPE will be unstable and give multi-compositions while the growth at a lower temperature, say 500 °C, will give a uniform composition corresponding to the input group-III ratio. Their calculation results have been accepted without much dispute as they generally supported the experimental results by Ref. 13 and those who followed since then.\textsuperscript{14–23} In fact, there have been many reports on the observation of phase instability or phase separation depending on the growth temperature, composition, thickness, and growth rate.\textsuperscript{14–17,19–23} The temperature range of 500 °C–800 °C, which is usually adopted for the InGaN MOVPE, must be dominated by immiscibility as it is far below the critical temperature. However, the vapor–solid phase diagrams calculated by Refs. 8, 10–12 do not show the immiscibility nature correctly, as they include unphysical cases for the equilibrium partial pressures.

With such a background, this paper presents a clear description of how the immiscibility of InGaN appears in the vapor–solid phase equilibrium and how it affects the relationship between the input group-III ratio and the solid composition in the MOVPE growth of InGaN on the basis of a thermodynamic analysis. Any extrinsic effects such as the strain effects caused by the substrates\textsuperscript{24–27} will be put aside so as to focus our discussion on the intrinsic property, i.e. immiscibility in the bulk. It is shown that the MG will definitely manifest itself in the vapor–solid equilibrium in the MOVPE growth of InGaN. Then, the experimental results of apparently uniform composition growth at low temperatures should be attributed to the non-equilibrium “freeze-out” effect of the growth species due to the slow surface kinetics.

2. Vapor–solid equilibrium of InGaN

2.1. Vapor–solid equilibrium equations

In this work, the general procedure of thermodynamic analysis closely follows the well-established manner developed by Refs. 28, 29 and extensively adopted by Refs. 8, 10–12, 30. Namely, an ideal gas is assumed for the vapor phase, and a regular solution is assumed for the solid phase. An MOVPE growth process using group-III alkyls (e.g. Ga(CH\textsubscript{3})\textsubscript{3} and In(CH\textsubscript{3})\textsubscript{3}) and NH\textsubscript{3} as the precursors is also assumed. As the group-III alkyls will be fully decomposed to release In and Ga on the growing surface, the net reaction to give In\textsubscript{x}Ga\textsubscript{1–x}N is expressed as:\textsuperscript{8,10–12}

\[
x\text{In} + (1-x)\text{Ga} + \text{NH}_3 \rightarrow \text{In}_x\text{Ga}_{1-x}\text{N} + \frac{3}{2}\text{H}_2. \quad (1)
\]

For the chemical equilibrium of the reaction, we have the two equilibrium equations,

\[
K_{\text{InN}}(T, p) = \frac{a_{\text{InN}}P_{\text{H}}^\frac{3}{2} P_{\text{NH}_3}^\frac{1}{2}}{P_{\text{Ga}}P_{\text{NH}_3}}, \quad (2)
\]

\[
K_{\text{GaN}}(T, p) = \frac{a_{\text{GaN}}P_{\text{H}}^\frac{3}{2} P_{\text{NH}_3}^\frac{1}{2}}{P_{\text{Ga}}P_{\text{NH}_3}}. \quad (3)
\]

where \(K_{\text{InN}}(T, p)\) and \(K_{\text{GaN}}(T, p)\) are the equilibrium constants (dimensionless) at the temperature \(T\) and the total pressure \(p\) for the solid components InN and GaN, respectively. The total pressure \(p\) can be replaced by any standard pressure, \(p_{\text{std}}\), usually chosen as 1 atm, as is known from the ideal-gas thermodynamics.\textsuperscript{1,2} Then, \(K_{\text{InN}}(T, p_{\text{std}})\) and \(K_{\text{GaN}}(T, p_{\text{std}})\) are dependent only on the temperature. \(P_{\text{In}}, P_{\text{Ga}}, P_{\text{H}}\) and \(P_{\text{NH}_3}\) are the equilibrium partial pressures of In, Ga, H\textsubscript{2} and NH\textsubscript{3}, respectively. \(a_{\text{InN}}\) and \(a_{\text{GaN}}\) are the activities of the solid components expressed as\textsuperscript{1–3}.
where $\alpha_{\text{InN-GaN}}$ is the interaction parameter, and $R$ is the gas constant.

The temperature dependences of $K_{\text{InN}}(T, p^{\text{std}})$ and $K_{\text{GaN}}(T, p^{\text{std}})$ were listed in Refs. 31, 32 from the literature values of the free energy of formation, $\Delta G_{\text{InN}}^0$ and $\Delta G_{\text{GaN}}^0$, at $p^{\text{std}} = 1$ atm, as $K_{\text{InN}} \equiv \exp (-\Delta G_{\text{InN}}^0/RT)$ and $K_{\text{GaN}} \equiv \exp (-\Delta G_{\text{GaN}}^0/RT)$. They are shown in Fig. 1, with the specific values at the three typical temperatures. It is noted that both $K_{\text{InN}}$ and $K_{\text{GaN}}$ very rapidly decrease over several orders of magnitude with increasing temperature and always $K_{\text{InN}} \ll K_{\text{GaN}}$, which leads to $p_\text{In} > p_\text{Ga}$, as is seen later.

### 2.2. Immiscibility inherent in the activities

It can be shown that the immiscibility is inherently prepared in the activities, Eqs. (4) and (5), through the positive interaction parameter, $\alpha_{\text{InN-GaN}}$. The estimated value of $\alpha_{\text{InN-GaN}}$ is somewhat scattered from 5.98 to 6.56 kcal mol$^{-1}$ (Ref. 13) in this work, the value of 7.00 kcal mol$^{-1}$ is adopted following Refs. 8, 10–12 for the sake of comparison of the results. Then, the critical temperature, $T_C = \alpha_{\text{InN-GaN}}/2R$, is estimated to be 1488°C.

Figure 2(a) shows the activities, $a_{\text{InN}}$ and $a_{\text{GaN}}$, as the functions of the solid composition $x$ at various temperatures between 2368 °C ($t = 1.5$) and 519 °C ($t = 0.45$), where the reduced temperature is defined as $t \equiv T/T_C$. It is seen that the activities are monotonically increasing ($a_{\text{InN}}$) or decreasing ($a_{\text{GaN}}$) functions at and above the critical temperature ($t \geq 1.0$), similar to the ideal mixtures where $\alpha_{\text{InN-GaN}} = 0$, while they have extrema (a local maximum and a local minimum) below the critical temperature ($t < 1.0$). From the conditions of the extrema, $\frac{\partial a_{\text{InN}}}{\partial x} = 0$ and $\frac{\partial a_{\text{GaN}}}{\partial x} = 0$, an equation is derived as

$$RT \ln \left( \frac{1-x}{x} \right) = \alpha_{\text{InN-GaN}}(1 - 2x),$$

which is identified as the expression for the binodals, $x_0$ and $x_2$, which define the boundaries of the stable and metastable composition ranges, as depicted in Fig. 2(b). Likewise, from the condition of the equal activities, $a_{\text{InN}} = a_{\text{GaN}}$, another equation is derived as

$$RT \ln \left( \frac{1-x}{x} \right) = \alpha_{\text{InN-GaN}}(1 - 2x),$$

For the MOVPE growth conditions, we follow the previous work, i.e. the total pressure $p = 1$ atm, the input group-III (i.e. In + Ga) partial pressure $= 1 \times 10^{-5}$ atm, V/III = 20000, and the NH$_3$ dissociation rate = 25%. The carrier gas is assumed as an inert gas, having the role to adjust the total pressure to 1 atm, and H$_2$ is only from the dissociation of NH$_3$. The role of the byproducts of the dissociation of the group-III alkyls such as CH$_4$ is ignored. Then, the partial pressures of NH$_3$ and H$_2$ are virtually fixed at $p_{\text{NH}_3} = 0.15$ atm and $p_{\text{H}_2} = 0.075$ atm, respectively, as they are much in excess of the group-III partial pressures. The previous work has calculated the dependencies also on the V/III ratio, the NH$_3$ dissociation rate and the H$_2$ fraction in the carrier gas. However, as they do not affect the essential feature of immiscibility we discuss, we concentrate ourselves only to the temperature dependence under the fixed growth parameters given above. Then, the temperature dependences of the equilibrium partial pressures come only from $a_{\text{InN}}/K_{\text{InN}}$ and $a_{\text{GaN}}/K_{\text{GaN}}$ for $p_{\text{In}}$ and $p_{\text{Ga}}$, respectively.

Figure 3 shows the calculated equilibrium partial pressures of the vapor species involved in the growth reaction as the functions of the solid composition $x$ at the three typical temperatures, (a) 1664 °C ($t = 1.1$), (b) 1488 °C ($t = 1.0$), and (c) 784 °C ($t = 0.6$). This representation of equilibrium partial pressures in logarithmic scale is the usual way as it can show the partial pressures varying over several orders of magnitude. It is noted that $p_{\text{In}} > p_{\text{Ga}}$ and the both pressures rapidly decrease over several orders of magnitude with decreasing temperature. In Figs. 3(a) and 3(b), the equilibrium partial pressures of both In and Ga exceed the input partial pressures, and hence no growth is expected practically with the assumed growth parameters. The anomalous behavior that the equilibrium partial pressure of In (Ga) decreases (increases) for increasing $x$ in the middle composition range is barely seen in Fig. 3(c). A similar plot is presented in the previous work without any particular notice for this behavior. Another thing to be noticed is that the In vapor will condense into droplets when the partial pressure of In
The In partial pressure shown in Fig. 3(c) is the case. The linear plots of the equilibrium partial pressures of In and Ga, shown in Fig. 4, more clearly show the dependencies of $p_{\text{In}}$ and $p_{\text{Ga}}$ at each temperature. We note that the functional shapes of $p_{\text{In}}(x)$ and $p_{\text{Ga}}(x)$ are exactly identical with those of the $x$ dependences of the activities, $a_{\text{InN}}(x)$ and $a_{\text{GaN}}(x)$ in Eqs. (4) and (5), respectively. At the temperatures at and above the critical temperature ($t \geq 1.0$), there is only one-to-one correspondence between $p_{\text{In}}$ or $p_{\text{Ga}}$ and $x$. At the temperatures below the critical temperature ($t < 1.0$), we must be aware that the calculated equilibrium partial pressures are valid only for the stable compositions. Namely, the calculated partial pressures within the MG [dashed parts in Fig. 4(c)] are not stable and must be excluded. Then, the equilibrium partial pressures are fixed at those for the two end compositions of the MG (i.e. binodals) as designated by the horizontal lines across the MG in Fig. 4(c). In Fig. 4(c), the unstable region (UR) is also indicated.

### 2.4. Equilibrium-partial-pressure isotherms

When the equilibrium partial pressures calculated by Eqs. (8) and (9) are plotted in a $p_{\text{In}}$ versus $p_{\text{Ga}}$ diagram at a fixed temperature, an equilibrium-partial-pressure isotherm (like a liquidus isotherm in a liquid–solid equilibrium phase diagram) is obtained as shown in Figs. 5(a)–5(d) for the typical temperatures. The corresponding solid compositions from $x = 0$ to $x = 1$ are found on the isothermal curves as designated. When $T < T_C$ ($t < 1$), as shown in Fig. 5(c) ($T = 1136^\circ \text{C}$, $t = 0.8$) and 5(d) ($T = 784^\circ \text{C}$, $t = 0.6$), the spinodals and binodals can be very clearly identified as the cusps and a crossing point, respectively. For $T = 1136^\circ \text{C}$, the spinodals are found at $x = 0.28$ and $0.72$, and the binodals are found at $x = 0.145$ and $0.855$, as calculated from Eqs. (6) and (7), respectively. For $T = 784^\circ \text{C}$, the spinodals are found at $x = 0.185$ and $0.815$, and the binodals are found at $x = 0.046$ and $0.954$. It is seen that the equilibrium (stable) composition $x$ will jump discontinuously between the two binodal compositions.
when the partial pressures change along the isothermal curve.

Another observation from Fig. 5 is that $\frac{d^2p_{\text{Ga}}}{dp_{\text{In}}^2} > 0$ for the stable and metastable compositions where the local stability is maintained, while $\frac{d^2p_{\text{Ga}}}{dp_{\text{In}}^2} < 0$ for the unstable compositions. In fact, it can be shown from Eqs. (4), (5), (8) and (9) that

$$\frac{d^2p_{\text{Ga}}}{dp_{\text{In}}^2} = C(T) \frac{\exp[-(x^2 - 4x + 2)\alpha_{\text{InN-GaN}}/RT]}{2x(1-x)\alpha_{\text{InN-GaN}} - RT},$$

where

$$C(T) \equiv \frac{2K_{\text{InN}}^2\alpha_{\text{InN-GaN}}^2}{K_{\text{GaN}}} \frac{p_{\text{In}}}{p_{\text{Ga}}^2} > 0,$$

which is independent of $x$ and an always positive quantity. The singularity of the right-hand side of Eq. (10) gives the cusps at the spinodal compositions. On the other hand, $\frac{d^2p_{\text{Ga}}}{dp_{\text{In}}^2} < 0$ holds for the entire composition range as is known from:

$$\frac{d^2p_{\text{Ga}}}{dp_{\text{In}}^2} = -\frac{K_{\text{InN}}(T)}{K_{\text{GaN}}(T)} \frac{\exp[(2x - 1)\alpha_{\text{InN-GaN}}/RT]}{RT} < 0.$$  

3. Input group-III ratio dependence of the solid composition

For the practical MOVPE growth of In$_x$Ga$_{1-x}$N, the solid versus vapor relationship is conveniently represented by the $x$ versus input In/(In + Ga) ratio relations $^{3,8,10-12,28-30}$ When the partial pressures of the input In and Ga (supplied by e.g. (CH$_3$)$_3$In and (CH$_3$)$_3$Ga) are denoted by $p_{\text{In}}^0$ and $p_{\text{Ga}}^0$, respectively, the input In/(In + Ga) ratio $R$ is given by $^{3,8,10-12,28-30}$
The right-hand side bars show the unstable region and the MG at 800 °C. 800 °C gives an average composition of 

\[ x = \frac{m_1 x_{b1} + m_2 x_{b2}}{m_1 + m_2}, \tag{17} \]

which satisfies the lever rule,

\[ m_2 = \frac{x - x_{b1}}{x_{b2} - x}, \tag{18} \]

where \( m_1 \) and \( m_2 \) are the masses grown with the binodal compositions \( x_{b1} \) and \( x_{b2} \), respectively. The (S-shaped) dashed-curves between the binodal compositions at the corresponding temperatures are unphysical (not stable) solutions, and therefore must be excluded from the diagram.

4. Discussion

In the present calculation of the vapor–solid phase equilibrium, the calculated partial pressures in the MG are replaced by the fixed values for the binodal compositions at the designated temperature. In other words, the partial pressures of In and Ga can never rise above those for the binodals at thermal equilibrium. This is quite a similar situation with the well-known Maxwell construction of the van der Waals isotherms in the pressure versus volume diagram for real gases, where the liquid and vapor coexist at a fixed (saturated) vapor pressure. A uniform solid composition is either unstable or metastable for the compositions in the MG, as the total (vapor + solid) free energy is not at the global minimum but at either a local maximum or only a local minimum for the unstable or the metastable compositions, respectively. The essential difference of the present calculations from those by Refs. 8,10–12 lies just in this point. They do not exclude the unphysically higher partial pressures calculated for the solid compositions in the MG. This shortcoming is carried over to their diagrams of the solid composition \( x \) versus input In/(In + Ga) ratio \( R \) relations, where the S-shaped curves (the dashed curves in Fig. 6 in the present paper) appear at high temperatures. From the multivalued-functional behavior of the \( R \) dependence of \( x \), they noted, “The deposition of compounds with various solid compositions is expected for a given input ratio of the group-III metalorganic source.” This view immediately leads to a quite unreasonable result that Ga-containing materials are grown from the group-III supply without Ga at higher temperatures where the S-shaped curve is cut by the vertical axis at \( R = 1 \). In the present treatment, the S-shaped portion is replaced by a straight line which gives a weighted average of the binodal compositions for a given \( R \), as described in Sect. 3.
Also as noted in Sect. 3, the maximum temperature for the growth is restricted by the input In partial pressure which the equilibrium In partial pressure must not exceed to keep the driving force for growth. For much higher temperature growth, such as to reduce the dislocation density or enhance the In content in the film, pressurized-reactor MOVPE which allows higher input In partial pressures may be effectively adopted.\textsuperscript{26,37,38}

It should be emphasized that a uniform composition is never an equilibrium state in the MG. However, in MOVPE, as well as in molecular beam epitaxy, the growth generally proceeds in far from equilibrium so that the grown films are not in the equilibrium state all through the growth. Then, it is quite plausible that the weight-averaged composition corresponding to a group-III flux ratio is frozen out to give a uniform composition without rendering a noticeable phase separation into the binodal compositions. In fact, the phase instability or phase separation have been observed depending on the growth temperature, composition, thickness, and growth rate.\textsuperscript{14–17,19–23} In particular, at lower growth temperatures where the surface kinetics is slow enough, the apparently uniform compositions observed will be a result of the non-equilibrium “freeze-out” effect.

In the practical epitaxial growth on a substrate, the strain effect due to the lattice mismatch between the epitaxial layer and the substrate will also substantially affect the solid phase equilibrium. Moreover, the spinodals and the binodals are clearly embedded in the activities through the positive interaction effect due to the lattice mismatch between the epitaxial layer and the substrate will also substantially affect the solid phase equilibrium.\textsuperscript{14–17,19–23} Also as noted in Sect. 3, the maximum temperature for the growth on a substrate that the strain-free cases. This issue is not within the focus of this paper, as the author wishes to emphasize the essential features of the vapor–solid relationship involved in the MOVPE growth of InGaN.

5. Conclusions
A MG definitely appears in the vapor–solid phase equilibrium of InGaN below the critical temperature. It is inherently embedded in the activities through the positive interaction parameter. The equilibrium partial pressures are fixed at those for the binodal compositions across the MG below the critical temperature. The spinodals and the binodals are clearly identified as the cusps and the crossing point of an isotherm in the In versus Ga partial-pressure diagram. A MG is represented by a straight line at a given composition in the solid composition versus input group-III ratio diagram for the InGaN MOVPE. The straight line across the MG gives a weighted average of the binodal compositions for a given input group-III ratio, and by no means indicates the growth of uniform compositions. The apparently uniform compositions observed in the low-temperature growth should be interpreted as a non-equilibrium “freeze-out” effect.

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