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An Elucidation of Solid Incorporation of InGaN Grown by Metalorganic Vapor Phase Epitaxy

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We carried out a systematic study on the solid incorporation of InGaN under various growth conditions using metalorganic vapor phase epitaxy (MOVPE). The solid distribution of InGaN was found to be very sensitive to the growth temperature, and the TMGa and TMIn flow rates. Experimental results indicated that at low Ga flow rates InGaN growth is essentially governed by thermodynamic factors, whereas at high growth rate the InGaN solid concentration is determined merely by the vapor composition in the gas phase. In regard to the effect of TMIn flow rates on InGaN growth, it was found that once In droplets form on the surface, the In growth efficiency correspondingly decreases significantly, accounting for the low In solid concentration in InGaN at high TMIn flow rates.

KEYWORDS: InGaN, MOVPE, growth efficiency

Recently, group III nitrides have received much attention. The wurtzite polytypes of AlN, GaN and InN, capable of forming a continuous alloy system with a direct band gap of 1.9 eV for InN, 3.4 eV for GaN and 6.2 eV for AlN, are important materials for application to light-emitting devices operating in the red to ultraviolet wavelength range.[1)] Furthermore, their excellent physical and chemical properties, such as high thermal conductivity, high radiation hardness compared to GaAs and Si, chemical inertness to hostile environment and superior stability have also made them potentially useful for high-temperature, high power devices, as well as space applications.[2)]

Over the past several years, most studies on nitrides have been directed toward the growth of high-quality GaN films and on the study of nitride-based optoelectronic devices, and relatively few reports have been published on the subject of InGaN bulk material growth. The synthesis of InGaN over the entire composition range has already been accomplished by Osamura *et al.* in the early of 1970's using the electron beam plasma technique.[3)] However, high-quality InGaN films were not obtained until Yoshimoto, in 1991,[4)] who utilized the metalorganic vapor phase epitaxial growth technique (MOVPE) and reported for the first time, the photoluminescence spectra of InGaN films. It appears from their experimental data that it is difficult to obtain high-quality InGaN films, unless the growth is carried out at a high temperature such as 800°C. A more significant improvement was later achieved by Nakamura and Mukai,[5)] who employed the so-called "two-flow growth method" for their sample preparation and obtained a device-quality InGaN epilayer, making InGaN potential material for optoelectronic device applications.[6–8)]

Despite the significant progress being made in this field, the growth of high-quality InGaN remains a challenge. Because of the high volatility of In atoms, growth of InGaN must be carried out at temperatures below 850°C.[9)] On the other hand, when InGaN is grown at low temperatures, In droplets form densely on the surface, severely degrading the quality of the deposited film.[10,11)] Besides, it has been noted that during epitaxial growth, the In incorporation efficiency depends not only on the TMIn flow rate, but also strongly on the growth temperature,[9,12–14)] the TMGa flow rate,[14)] the growth rate[13,15)] and the V/III ratio.[15,16)] This unusual manner of growth of InGaN is rarely seen in conventional GaAs and InP material systems. Since the solid concentration in type $A_xB_{1-x}C$ is related to the mixing of group III components on the cation sublattice, the variation of In concentration in solid InGaN may be caused by a change in solid incorporation efficiency of either In or Ga during the deposition. In order to obtain a better understanding of the factors involved in InGaN MOVPE growth, we introduced the concept of growth efficiency for reagent Ga and In in this paper to investigate their individual incorporation behaviors in relation to various growth parameters. Finally, an explanation of the variation of solid incorporation in relation to the various growth parameters is also included.

InGaN films were grown on (0001) sapphire substrates using an atmospheric pressure-metalorganic vapor phase epitaxy system equipped with a horizontal quartz reactor and a RF heater. Electronic-grade trimethylgallium (TMGa, −20°C), trimethylindium (TMIn, 10°C) and high-purity ammonia (NH_3) were used as the source precursors for Ga, In and N, respectively. Resin-purified nitrogen, instead of hydrogen, was used as the main carrier gas. Immediately following chemical cleaning, the substrate was loaded into the chamber. Thereafter, it was thermal-cleaned at 1100°C for 10 min, nitridated for 5 min in ammonia ambient, and a 100Å-thick GaN buffer layer deposition was allowed to proceed at 520°C, before commencement of the InGaN epilayer growth. The thickness of resultant InGaN film was typically in the range of 0.2 to 0.4 μm. After the growth, the sample was characterized by scanning electron microscopy (SEM) in regard to the surface morphology and the film thickness. A six-ring double crystal X-ray diffractometer was used to analyze the lattice constant and solid In concentration in the InGaN epilayer, assuming that the lattice constant varied linearly with the In solid concentration.

In an attempt to understand the solid distribution behavior of InGaN in relation to various growth parameters, we grew several series of InGaN samples. The first series as grown at temperatures between 600 and 800°C with the flow rates of TMGa, TMIn and NH_3 maintained at 1.4 μmol/min, 0.44 μmol/min and 0.96 slpm, respectively. The high V/III ratio, of 23000, intentionally used in this series was to prevent the formation of any metal droplets, particularly In, at low growth temperatures. To investigate the dependence of InGaN solid composition on TMGa and TMIn molar flow rates, we car-

ried out an additional two sets of experiments at a growth temperature of 700°C with the NH_3 flow rate kept at 0.96 slpm. The resultant In solid concentration (X^s_{In}) as a function of growth temperature, TMGa and TMIn flow rates are illustrated in Figs. 1(a), 1(b) and 1(c), respectively. As can be seen in Fig. 1(a), the InGaN solid composition depends strongly on the growth temperature. A decrease of In concentration (X^s_{In}), from 0.31 to 0.04, is noted as the growth temperature increases from 600 to 800°C. More complex and interesting growth behaviors were observed at different TMGa and TMIn flow rates, as shown in Figs. 1(b) and 1(c). The corresponding In solid concentration was found to increase abruptly with increase in the TMGa flow rate initially, but then it dropped slowly for TMGa flow rates above 1.4 μmol/min. This result is not entirely consistent with the observations of other groups. Most of them have observed a slow increase of In solid concentration with increasing TMGa flow rate over the range studied.[14] For the dependence of InGaN growth on TMIn flow rates, a similar X^s_{In} trend was observed. The In solid concentration increased with increasing TMIn flow rate up to 1.1 μmol/min, and subsequently, with further increase in TMIn flow rate, it decreased.

Based on the above observations, it is apparent that the solid incorporation for nitride ternaries is not as straightforward as for conventional GaAs and InP material systems.[17,18] In the conventional cases, essentially all of the group III components, whether Al, Ga or In, that reach the growing interface, are incorporated. Thus, their solid composition is directly proportional to the vapor composition in the reaction chamber. On the other hand, a different growth mechanism is involved in InGaN MOVPE growth. For InGaN, the solid In concentration was found to increase initially, and subsequently decrease with increasing group III source flow rate, regardless of TMGa or TMIn flow rates. Since the composition in InGaN layer is interrelated to solid incorporation of both In and Ga atoms, the increase of X^s_{In} may be simply due to the increase of In solid incorporation or due to the decrease of Ga solid incorporation. In order to study the effect of each reactant on growth behavior during the deposition, we introduce the so-called concept of growth efficiency (μm/mol) in our study, which is defined as the ratio of growth rate (μm/min) to the input molar flow rate of individual group III elements (mol/min). Hence, the γ_{GaN} and γ_{InN} employed here denote the growth efficiencies of GaN and InN in InGaN, respectively, assuming that the overall growth rate of InGaN is a linear combination of GaN and InN growth rates. It is obvious that the growth efficiency presented here resembles to a certain extent the possibility that a reactant can enter the solid phase. Indeed, the examination of growth efficiencies of Ga and In atoms gives a much clearer picture of the solid distribution in InGaN. The corresponding GaN and InN growth efficiencies as functions of reciprocal growth temperature, TMGa and TMIn flow rates are shown in Figs. 2(a), 2(b) and 2(c), respectively.

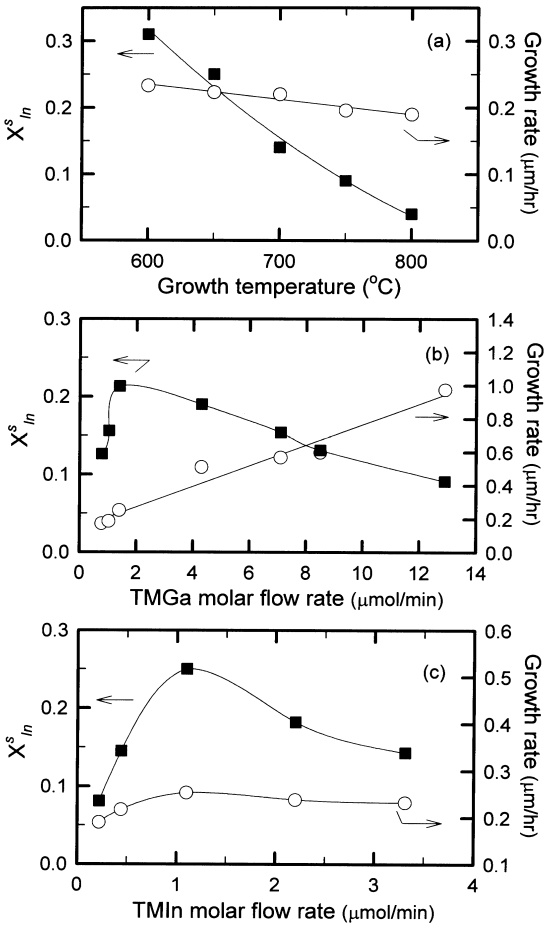

Fig. 1. The In solid concentration (X^s_{In}) and the growth rate of InGaN epilayers as functions of (a) growth temperature, (b) TMGa flow rate and (c) TMIn flow rate, respectively.

It is commonly known that MOVPE growth is, in general, subdivided into low-temperature kinetically-limited, mid-temperature mass-transport-controlled and high-temperature growth regimes. As can be seen from Fig. 2(a), the growths of GaN and InN in InGaN from 600 to 800°C are proceeding under different regimes. While the growth of GaN is mass-transport-controlled, InN growth is already in the high-temperature region. Since the effect of Ga incorporation efficiency on growth temperature remains nearly unchanged here, the decrease of In concentration in the solid is apparently the result of a decrease in the InN growth efficiency, due possibly to the increasing In desorption rate at high growth temperatures.[9] An Arrhenius fit gives an activation energy of $\sim$20.7 kcal/mol for the declining In growth efficiency. Moreover, it can be noticed that the presence of TMIn flow has a dramatic effect on the incorporation of Ga. Without TMIn flow, the Ga growth efficiency in the GaN binary growth is roughly $\sim$2800 μm/mol; as the In reactant is added, the Ga growth efficiency decreases significantly to a value of $\sim$2000 μm/mol, regardless of the growth temperature being used.

In regard to the dependence of In solid concentration on TMGa flow rate, as mentioned earlier, a very interesting X^s_{In} (see Fig. 1(b)) curve feature is presented. Based on the observations of the growth of GaAs and InP materials, one would expect a linear decrease of X^s_{In} with an increase in TMGa flow rate for InGaN under a fixed TMIn flux growth condition. However, this was not the case. From the limited information provided in Fig. 1(b), it seems difficult to have a simple explanation for describing such an anomalous In solid incorporation behavior in relation to TMGa flow. In contrast, using the concept of γ_{GaN} and γ_{InN} in this study, more plausible results can be obtained. As shown in Fig. 2(b), a large increase in γ_{InN}, together with a sharp decrease in γ_{GaN}, is observed at

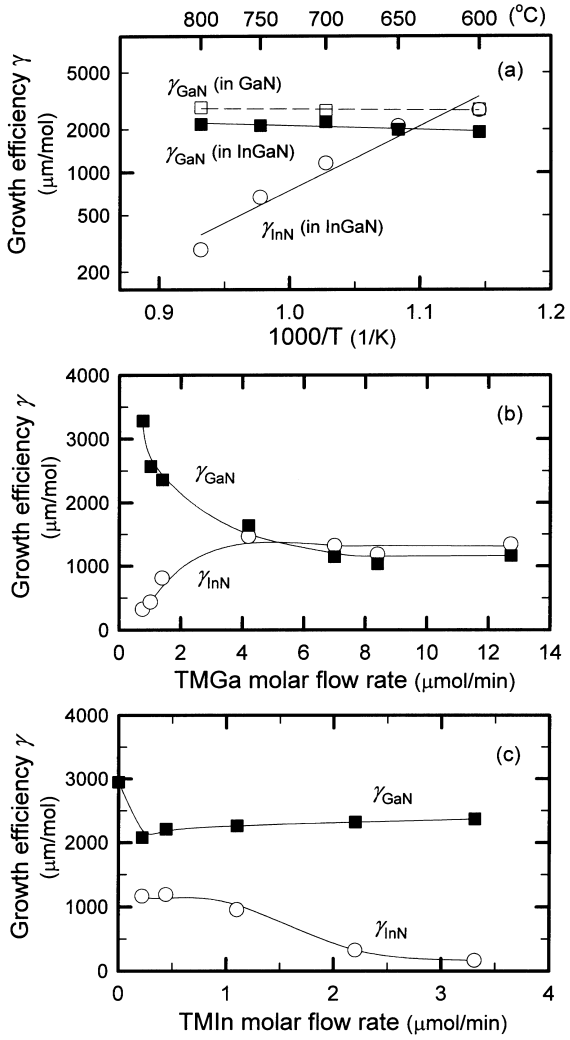

Fig. 2. The individual growth efficiencies of GaN(γ_{GaN}) and InN(γ_{InN}) in ternary InGaN as functions of (a) reciprocal growth temperature, (b) TMGa flow rate and (c) TMIn flow rate, respectively. For comparison, the growth efficiency of binary GaN is also included.

low TMGa fluxes. Both the γ_{GaN} and γ_{InN} tend to saturate at about the same value at high growth rates. The variations in γ_{GaN} and γ_{InN} in this figure clearly show that the increase of In solid concentration at low Ga flow rates is not due to the increase of In growth efficiency alone, but largely from the sharp decrease of Ga growth efficiency in InGaN growth.

At very low TMGa flow rates, the thermodynamics is believed to predominate the InGaN growth. From the thermodynamic point of view, the GaN binary is more stable than the InN binary. The corresponding desorption rate for Ga atoms on the surface is much lower than that for In atoms.[14] Thus, the Ga atom has a high probability of being incorporated into the growing interface. This explains why Ga growth efficiency is much higher than In growth efficiency at low TMGa flow rates.

As the TMGa flow rate is further increased, the thermodynamic factor becomes less important and can be taken less advantage by the Ga species. In this situation, a steric hindrance effect starts to influence the Ga solid incorporation. The bonded species inhibit further adsorption of Ga species on those sites, which cause a decrease of Ga growth efficiency in InGaN growth. Aside from the steric hindrance effect, the other likely explanation is that since the growth rate is so low ($<$0.18 μm/h) in the low Ga flow rate region, we believe that the surface coverage of its species during the deposition may also have strong influences on the Ga solid incorporation, similar to the manner of growth during atomic layer epitaxy.[19,20] That is, when the average alkyl surface coverage is low, nearly all the group III atoms impinging on the surface can be incorporated into the surface; as the growth rate is increased, the corresponding surface coverage is increased or even saturated and the solid incorporation efficiency reduces accordingly. This could at least partially account for the decrease of Ga growth efficiency at higher Ga flow rates, observed in our InGaN study.

There is no doubt that the above-mentioned phenomena could also have a similar effect on the deposition of In atoms. However, we believe that the change of In desorption rate plays a more important role in determining the In incorporation efficiency. Note that the solid incorporation is directly related to the desorption rate of reactants, the less the desorption rate the higher the incorporation efficiency that can be obtained during the deposition. Because of the high desorption rate of In, it is known that In growth efficiency is relatively low in the very low growth rate region, and as the growth rate increases the desorption rate of In adsorbate is significantly reduced due to faster coverage of the next layer, and consequently a higher In incorporation efficiency can be obtained.[14]

On the other hand, when more than sufficient TMGa was introduced, resulting in a high growth rate, the Ga and In atoms randomly arriving do not have the time to redistribute themselves; they react chemically with the N atom bonds dangling nearby on the surface before being covered by the next layer. The unreacted physisorbed surface species, will generally be rejected from the surface under the arranged stoichiometry growth condition. Consequently, in the high growth rate region, both the group III components, either Ga or In atoms, exhibit nearly identical incorporation probability and approximately the same saturation value in growth efficiency results. For growth under this condition, the InGaN solid composition is determined virtually by the vapor composition in the reactor.

As far as the effects of the TMIn flow rate on InGaN solid composition are concerned, despite a similar growth influence on X_{In}^{s} being observed, of both TMGa and TMIn flow rates (Figs. 1(b) and 1(c)), their growth efficiencies are different. As can be seen from Fig. 2(c), unlike an exponential-like decrease of γ_{GaN} on Ga flow rate, the Ga growth efficiency in this case decreases suddenly when TMIn reactant is added the reactor; thereafter, it returns gradually and reaches a constant of $\sim$2300 μm/mol at high flow rates. The sharp decrease of Ga growth efficiency with the addition of TMIn was also observed previously in our studies on InGaN growth under different growth temperatures (Fig. 2(a)). This phenomenon may be related to the high-temperature parasitic reaction between TMGa and TMIn. However, the reason for the saturation of Ga growth efficiency at high TMIn flow rates is still unclear, and further investigations are needed.

Concerning the In growth efficiency in noted Fig. 2(c), a high γ_{InN}, of $\sim$1200 μm/mol, can be maintained at low TMIn flow rates. This value is reduced to 200–300 μm/mol when the TMIn flow rate is $>$2.2 μmol/min. Since in this region,

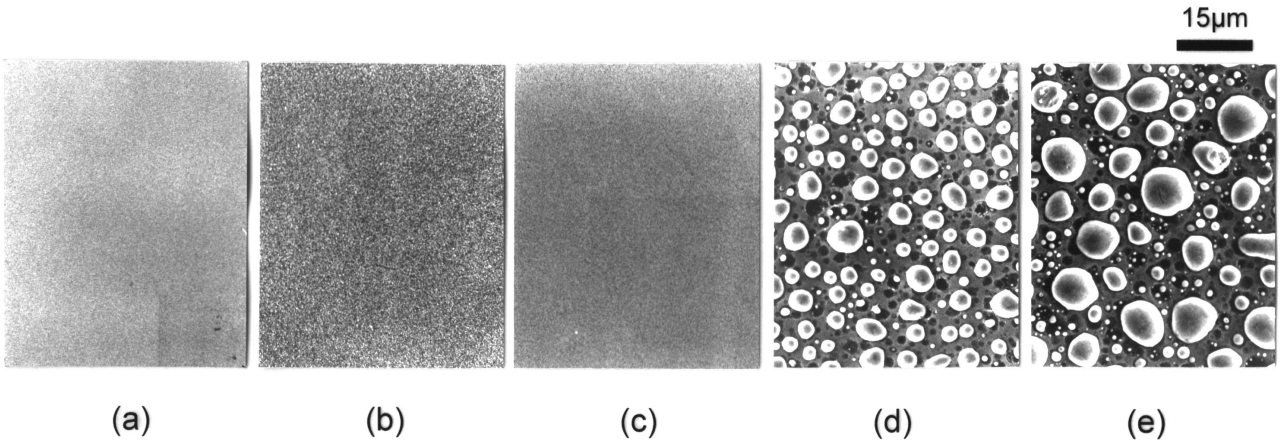

Fig. 3. The surface morphologies of InGaN films grown at the TMIn flow rates of (a) 0.22, (b) 0.44, (c) 1.1, (d) 2.2 and (e) 3.3 μmol/min, respectively.

the total growth rate of InGaN (Fig. 1(c)) is nearly constant, it is certain that the growth rate effect, as mentioned above, is not the major factor responsible for the decrease of In growth efficiency at high TMIn flow rates. If this were the case, we would have observed an increase in In solid concentration, accompanied by a constant In growth efficiency with increasing TMIn flow rates. After repeated examination of the TMIn-flow-rate-dependent samples by SEM, we conclude that the reduction of γ_{InN} is originally a result of the formation of In droplets on the surfaces. As shown in Fig. 3, when the TMIn flow rate exceeds 2.2 μmol/min, the InGaN layer is covered by numerous In droplets, the sizes of which increase when TMIn flow rate is further increased. In regard to the In growth efficiency in Fig. 2(c), one can notice that once In droplets are formed on the surface, the possibility of entry of In into the solid decreases remarkably. Therefore, to obtain an InGaN layer with high In solid concentration, special attention must be paid to avoid the formation of In droplets.

In summary, we have carried out a systematic study on the solid incorporation of InGaN under various growth conditions using metalorganic vapor phase epitaxy. Experimental results indicated that the solid composition in InGaN depends strongly on the growth parameters such as the growth temperature, and the TMGa and TMIn flow rates. Due to the high volatility of InN, a decrease of In solid concentration of InGaN was observed with an activation of $\sim$20.7 kcal/mol. Additional interesting results were observed in relation to the TMGa flow rate. It is believed that the effect of thermodynamic factors predominates on growth at low growth rates, whereas the growth rate factor becomes important, resulting in approximately the same incorporation probability for both Ga and In atoms at high TMGa flow rates. In regard to the dependence on the TMIn flow rate, it was noted that the addition of TMIn results in an immediate decrease of Ga growth efficiency. When more TMIn is introduced, the Ga growth efficiency tends to achieve a saturation value. On the other hand, a gradual decrease of In growth efficiency was observed on the TMIn flow rate. Experimental data indicated that when the In droplets formed on the surface, the In growth efficiency reduced significantly by a factor of four or more, causing a decrease of In solid concentration at high TMIn flow rates. Therefore, to obtain InGaN layers with a high In solid concentration, one must pay special attention during the deposition to avoid the formation of In droplets on the surface.

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