Impact of Gas-Phase and Surface Chemistry During InGaN MOCVD

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Motivation—With bandgaps spanning the visible spectrum, InGaN alloys now form the basis of current solid-state-lighting technology. Metalorganic chemical vapor deposition (MOCVD) is the technique used to grow epitaxial InGaN thin films for such devices. However, indium incorporation into the growing InGaN films is very inefficient, temperature sensitive, and difficult to control. While these problems are often thought to be due to the limited thermodynamic stability of InGaN, other issues such as gas-phase parasitic chemical reactions during growth may also play an important role.

Accomplishment—As an extension to our earlier *in situ* light-scattering results we have employed a thermophoretic particle capture probe, whereby nanoparticles are collected on a TEM grid just "downstream" of the heated surface. During InGaN conditions we observe a significant population of particles with diameters in the 15-40 nm range, for example see Figure 1. This general observation of size range agrees well with our previous optical measurements. The particles appear to have a nearly spherical core, but often contain one or more irregular appendages, reminiscent of earlier GaN results. Many of the larger particles have well-defined lattice planes, and detailed analysis of the d-spacings revealed the presence of metallic indium, as expected, but also hexagonal InN and cubic In_2O_3. We believe the In_2O_3 results from the oxidation of the metallic indium during the air transfer of the grids to the TEM chamber. We therefore conclude that the gas-phase nanoparticles are actually a composite of metallic indium and InN. The composite structure possibly explains one peculiar aspect of the light-scattering measurements, which had suggested the presence of non-spherical particles. In order to test the relative importance of parasitic gas-phase chemistry versus surface chemistry we have examined the residence time dependence of the InGaN MOCVD process. In an ideal rotating-disk reactor (RDR) the residence time in the boundary layer is inversely proportional to the platen spin rate ($\mathbf{\Omega}$), so increasing the spin rate will tend to quench unwanted gas-phase reactions that may be depleting the growth precursors. For AlN and GaN MOCVD conditions where gas-phase parasitic reactions are very significant, the growth rate is strongly proportional to $\mathbf{\Omega}^n$, with n = 1.5-2.5. Therefore, if the parasitic gas-phase reactions are depleting the availability of indium, we would expect the InGaN growth rate and composition to respond dramatically to changes in $\mathbf{\Omega}$. We have instead found a rather weak dependence during growth of an InGaN multi-quantum well (MQW) structure at 770°C (see Figure 2). The GaN barrier layer thickness scales as $\sim\mathbf{\Omega}^{0.42}$, which is reasonably close to the $\mathbf{\Omega}^{1/2}$ dependence expected for transport-limited growth. The InGaN QW thickness scales as $\sim\mathbf{\Omega}^{0.25}$, which is even weaker than GaN barrier thickness dependence. The indium composition (not shown) is nearly independent of spin rate. These surprising results suggest that nanoparticles may play no significant role in limiting indium incorporation during InGaN MOCVD.

Significance—Results indicate that for growth temperatures of ~800°C nearly 100% of the indium near the surface is converted into gas-phase nanoparticles and is no longer available for InGaN growth. However, MOCVD results as a function of platen spin rate suggest that the nanoparticles may only be a "downstream" consequence and therefore play only a minor role in limiting indium incorporation. We are in the process of developing a detailed MOCVD chemical reaction mechanism that will hopefully reconcile the seemingly contradictory aspects of these findings.

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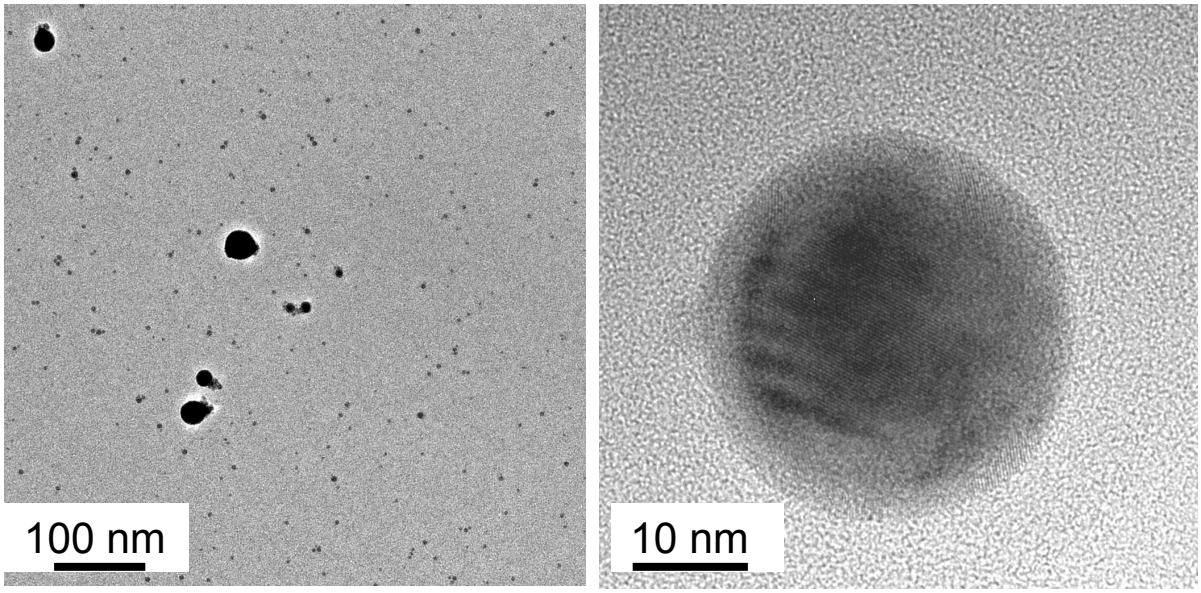

Figure 1. TEM of nanoparticles captured during InGaN conditions at 800°C

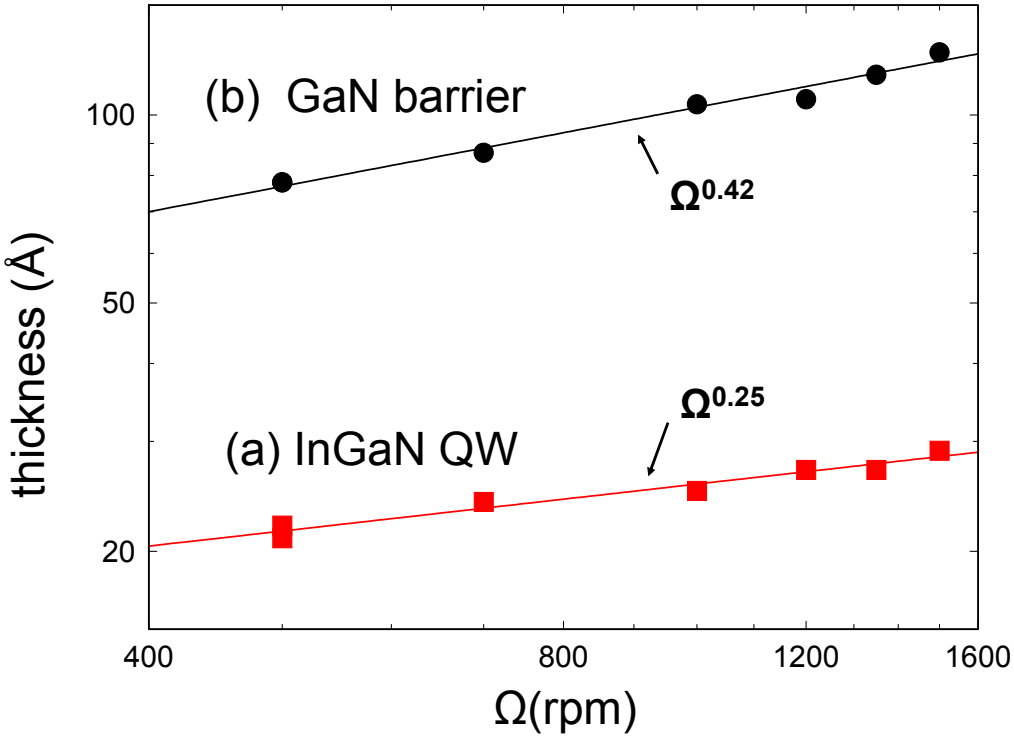

Figure 2. RDR spin rate dependence of InGaN QW thickness (curve-a) and GaN barrier layer thickness (curve-b) during MQW growth at 770°C.