Gas phase optical emission spectroscopy during remote plasma chemical vapour deposition of GaN and relation to the growth dynamics

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Gas phase optical emission spectroscopy during remote plasma chemical vapour deposition of GaN and relation to the growth dynamics

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Abstract
A remote plasma chemical vapour deposition (RPCVD) system for the growth of gallium nitride (GaN) thin films is investigated using optical emission spectroscopy (OES). The intensities of the various excited species in pure nitrogen as well as nitrogen/hydrogen plasmas are correlated with GaN film growth characteristics. We show a correlation between the plasma source spectrum, the downstream spectrum where trimethylgallium is introduced and the GaN film quality. In particular, we investigate the addition of hydrogen, which greatly affects the gas phase species and the GaN film characteristics. OES is demonstrated to be a valuable monitoring tool in a RPCVD system for optimization of GaN growth.

1. Introduction
Wide direct band-gap gallium nitride is a promising material for short-wavelength optoelectronic device applications such as light-emitting diodes (LEDs), laser diodes (LDs) and nitride-based solar cells [1, 2]. Gallium nitride-epitaxial films with low dislocation density are very important for improving device performance. Currently, GaN-related materials are predominantly grown on sapphire substrates on which there are large differences between the lattice constant and thermal expansion coefficient of the GaN layer and the substrate. This results in high dislocation densities in the epitaxial films, reducing device performance and yield and also adds a significant contribution to the cost of producing a device.

GaN films can be grown by several techniques, the most common of which are metal organic chemical vapour deposition (MOCVD) [3, 4] and molecular beam epitaxy [5, 6]. For GaN thin film growth with MOCVD, trimethylgallium (Ga(CH₃)₃) and NH₃ are commonly used as the respective Ga- and N-atom source gases, with film growth temperatures typically in excess of 900 °C. The requirement for high processing temperatures is two fold. Firstly, atomic nitrogen is generated via pyrolysis of ammonia. Secondly, there is a minimum temperature required to grow good quality material. Due to the high processing temperatures, the selection of substrates used commercially has been limited to sapphire and silicon carbide. MBE on the other hand can be used to grow GaN successfully at lower processing temperatures due to the absence of ammonia in the process. However, MBE is limited to smaller scale applications due to the high cost of the vacuum equipment required for the deposition process, and implementing it over larger deposition area diameters.

To expand the range of applications of GaN it is necessary to develop processes that operate at lower temperatures, with cleaner precursors and which can be applied to larger scale fabrication. Furthermore, it is important to further develop non-intrusive diagnostics such as optical emission spectroscopy (OES) to control the film growth process, and ultimately grow better quality films.

Remote plasma chemical vapour deposition (RPCVD) uses a nitrogen plasma discharge created upstream of the growth region to provide the nitrogen precursors. Excited species from the plasma flow downstream to interact with gallium precursors in the deposition chamber. The variation of process parameters such as pressure, input power and gas composition strongly influences the concentration of excited
Table 1. Competing processes during the growth of GaN. The vertical arrows indicate the loss of either N\textsubscript{2} or Ga from the film [8, 9].

<table>
<thead>
<tr>
<th>Growth reactions</th>
<th>Competition to growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Ga + N\textsubscript{2} + e\textsuperscript{−} → GaN + N\textsuperscript{*}</td>
<td>(6) GaN → Ga + \frac{1}{2}N\textsubscript{2}↑ (decomposition)</td>
</tr>
<tr>
<td>(2) Ga + N\textsubscript{2} → GaN + N\textsuperscript{*}</td>
<td>(7) Ga\textsubscript{adsorbed} → Ga↑ (desorption)</td>
</tr>
<tr>
<td>(3) Ga + N → GaN</td>
<td>(8) GaN + N → Ga + N\textsubscript{2}↑ or Ga↑ + N\textsubscript{2}↑</td>
</tr>
<tr>
<td>(4) Ga + N\textsuperscript{*} → GaN</td>
<td>(9) GaN + N\textsuperscript{*} → Ga + N\textsubscript{2}↑ or Ga↑ + N\textsubscript{2}↑</td>
</tr>
<tr>
<td>(5) Ga + N\textsuperscript{+} + e\textsuperscript{−} → GaN</td>
<td>(10) GaN + N\textsuperscript{+} + e\textsuperscript{−} → Ga + N\textsubscript{2}↑ or Ga↑ + N\textsubscript{2}↑</td>
</tr>
</tbody>
</table>

Figure 1. Schematic diagram of the reactor chamber.
(This figure is in colour only in the electronic version)

species in the discharge which may play an active role in the film growth process. As shown in table 1 [7–9] there are several possible mechanisms that may promote growth or cause decomposition of GaN layers. The atomic nitrogen ion (N\textsuperscript{+}), metastable atomic nitrogen (N\textsuperscript{*}) and neutral atomic nitrogen (N) can all participate in the formation as well as the decomposition of GaN. On the other hand, molecular species (N\textsubscript{2} and N\textsubscript{2}*) contribute directly to the formation of the GaN layer and indirectly to its decomposition due to the generation of a nitrogen atom when forming GaN. Both atomic and metastable molecular nitrogen contain significantly more energy than is required for GaN formation. When atomic nitrogen is incorporated into the lattice, excess energy is released, which can drive unfavourable reactions such as Ga desorption, GaN dissociation or point defect formation. In contrast the excited nitrogen molecule can incorporate one nitrogen atom into growing GaN while the other atom desorbs, carrying away the excess energy. This scenario suggests improved growth based on the presence of N\textsubscript{2}* excited nitrogen molecules. Competition between growth, surface decomposition and adsorbed nitrogen capture might also limit the efficacy of atomic nitrogen. Such a situation would promote point defect formation, leading to poor electrical properties of the GaN film produced. A greater understanding of plasma processes involved in the creation of different nitrogen species is required in order to optimize the film growth process.

To gain a better understanding of GaN film growth mechanisms, OES is employed to correlate plasma species in the source and afterglow region with GaN film growth properties. In particular, we investigate the effect that hydrogen has on the gas chemistry and GaN film growth properties. The main aim is to obtain reliable information regarding active species (atoms, molecules and ions) via OES of a microwave nitrogen plasma. The relative concentrations of these species contribute to the film growth process in the deposition chamber.

2. Experimental setup

The research and development test reactor consists of two parts: the remote plasma source and the growth region, as shown in figure 1. At the top end of the plasma source tube, nitrogen gas is injected at flow rates \(<5\text{l min}^{-1}\) and the pressure in the system adjusted by means of a throttle control valve and pressure controller. Hydrogen can also be added to the gas flow to create a binary mixture flowing into the source tube. The other end of the source tube is coupled to the deposition chamber. Nitrogen gas is ionized in the source tube by applying microwave power at 2.45 GHz. Long-lived excited species produced in the plasma flow downstream into the growth chamber to partake in the film growth process. The total pressure in the system was maintained at 3 Torr, with a constant nitrogen flow of 650 sccm. The substrate temperature
Table 2. Competing e-impact reactions in nitrogen plasma.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>Threshold energy (eV)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $e^- + N_2 \rightarrow N_2^* + e^-$</td>
<td>6.17</td>
<td>Excitation</td>
</tr>
<tr>
<td>(2) $e^- + N_2 \rightarrow N_2(A^{1}\Sigma_u^+) + e^-$</td>
<td>6.17</td>
<td>Excitation</td>
</tr>
<tr>
<td>(3) $e^- + N_2 \rightarrow N_2(B^3\Pi_u) + e^-$</td>
<td>7.36</td>
<td>Excitation</td>
</tr>
<tr>
<td>(4) $e^- + N_2 \rightarrow N^+(S) + N^+(S) + e^-$</td>
<td>9.8</td>
<td>Dissociation</td>
</tr>
<tr>
<td>(5) $e^- + N_2 \rightarrow N^+ + N^+(S) + e^-$</td>
<td>12.14</td>
<td>Dissociative excitation</td>
</tr>
<tr>
<td>(6) $e^- + N_2 \rightarrow N^+(D) + N^+(S) + e^-$</td>
<td>12.14</td>
<td>Dissociative excitation</td>
</tr>
<tr>
<td>(7) $e^- + N_2 \rightarrow N^+(P) + N^+(S) + e^-$</td>
<td>14.34</td>
<td>Dissociative excitation</td>
</tr>
<tr>
<td>(8) $e^- + N \rightarrow N^+ + 2e^-$</td>
<td>14.55</td>
<td>Atomic ionization</td>
</tr>
<tr>
<td>(9) $e^- + N_2 \rightarrow N_2^+ + 2e^-$</td>
<td>15.58</td>
<td>Molecular ionization</td>
</tr>
<tr>
<td>(10) $e^- + N_2 \rightarrow N^+ + N^+(S) + 2e^-$</td>
<td>24.32</td>
<td>Dissociative ionization</td>
</tr>
</tbody>
</table>

was 750 °C and the trimethylgallium (TMG) flow was 22 sccm. The substrates used in this study are GaN/sapphire templates, with a film thickness of 3–4 µm. It should be noted that in this study, we intend to gain insight into the effect of hydrogen on the film growth process and its influence on the morphology of GaN films, moving from 3D columnar growth to 2D lateral growth.

The total gas pressure in the system is maintained at a constant value for all experiments. Plasma source gases (N$_2$/H$_2$ or (N$_2$ + H$_2$) admix) are introduced at the top of the source tube and flow through the source tube where they undergo excitation. Longer lived excited nitrogen species are transported into the deposition chamber where they interact with TMG introduced through a downstream dispersal grid. The gas flow is directed towards the substrate position where mixing and interactions with the excited species extracted from the plasma source occur. Under certain conditions the interaction of excited nitrogen species with TMG produces a violet glow in the downstream region due to gas phase reactions.

The radiation emitted from the remote plasma source and the downstream growth region just above the substrate position were collected via a UV-grade quartz fibre optic and transmitted to a low-noise Ocean Optics spectrometer (QE65000, 200–1000 nm). The background was subtracted prior to all measurements and data analysis. The source spectra were obtained for an integration time of 100 ms. Due to the weak emission just above the substrate position, the downstream spectra were obtained for an integration time of 10 s and average of 4. It is important to note that the microwave operates in a pulsed mode (duty cycle ~20%). Hence, the optical emission that is measured is averaged so one would expect higher intensities in the ‘on’ period.

3. Results

3.1. Remote plasma source

The optical emission spectrum from the plasma source region provides insight into the plasma dynamics and excited species that are produced and which may take part in the film growth process. The principal atomic, molecular and ionic nitrogen species generated in the microwave plasma by electron impact collisions are listed in table 2. Figure 2 shows the optical emission spectrum for (a) a pure nitrogen plasma and (b) nitrogen plasma with 20 sccm of hydrogen at a process pressure of 3 Torr. The spectrum shows the dominant emission peaks from the plasma in the range 450–1000 nm. The first-positive series of molecular transitions is clearly observed in all of the spectra [16]. The first-positive system

$$N_2(B^3\Pi_u) \rightarrow N_2(A^{1}\Sigma_u^+) + h\nu$$

appears as six bands of regularly spaced emission peaks in the visible and near-infrared (IR) spectral regions. Due to the transmission properties of the plasma source tube, we were
unable to observe any spectral emission below 450 nm. The atomic septet lines $3p^3P \to 3s^3P$ are observed around 822 nm with excitation energy of 11.84 eV.

The introduction of a small admixture of hydrogen to the discharge changes the spectrum in several ways. This is highlighted by a change in the spectral emission (see figure 2). The atomic $H_\alpha$ line at 656 nm is now observed indicating dissociation of the hydrogen molecule. There is also a decrease in the intensity of the nitrogen bands. The upstream spectrum shows that the intensity of the first-positive system of nitrogen and the intensity of the atomic nitrogen line at 822 nm decreases significantly when a hydrogen flow of 20 sccm is added (figure 2). However, the decrease is not linear (figure 3). Initially there is a rapid decrease in the nitrogen intensities up to 20 sccm and then the rate of decrease slows. With a hydrogen flow of between 10 and 20 sccm, there is a deviation of the decrease in atomic nitrogen intensity from that of the molecular nitrogen intensity. The data sets then rejoin above 20 sccm of hydrogen. In the plasma gas phase several mechanisms may be occurring resulting in this deviation. In particular, hydrogen is most probably capturing nitrogen producing NH$_x$ species \(x \geq 1\). These can then flow into the growth region and contribute to the surface reactions occurring on the substrate. Figure 3 also shows the $H_\alpha$ line at 656 nm to increase rapidly up to 20 sccm and then to slow.

### 3.2. Downstream

The spectrum obtained close to the substrate table for a pure nitrogen plasma (figure 4) indicates that the first-positive band of molecular nitrogen is detected. However, the emission is extremely weak, and it is not possible to say from this spectrum whether atomic nitrogen is also present. Importantly, the strong first negative transition for molecular nitrogen ions at 391 nm is not detected, indicating little residual ionization downstream. The presence of energetic molecular ions close to the surface can degrade film quality through ion bombardment.

Although the formation reaction of GaN has an energy of only 1.9 eV and therefore all active nitrogen species, atomic or molecular, with an energy above this threshold value may lead to the growth of GaN, it has been suggested that the best species for growing GaN is the metastable molecular nitrogen state $A \Sigma_g^+$ which has an energy of 6.2 eV above the ground state \([8–10]\). This is due to two main factors: (i) the species have a long radiative decay time (~2.4–3.3 s) \([11]\) and therefore survive long enough to travel from the plasma source to the downstream growth region, and (ii) metastable molecular nitrogen brings to the surface two nitrogen atoms, allowing one atom to carry away any excess energy. However, metastable species are extremely difficult to detect due to their low intensity levels. Hughes \textit{et al} \([12]\) showed that the best quality films and highest deposition rates were grown when the plasma emission spectrum contained an intense first-positive system, a weak second positive system \((C^3 \Pi_u – B^3 \Pi_g)\) and a complete lack of the first negative system due to excited nitrogen ions. These spectral observations are consistent with a high population of the $B^3 \Pi_g$ state, and therefore the $A^3 \Sigma_u^+$ as well, and the absence of molecular ions.

On introducing TMG to the system, and with gas phase decomposition of TMG, the spectrum downstream changes significantly (figure 5(a)) while that of the upstream remains the same. For a pure nitrogen plasma, two atomic gallium lines are observed downstream, as well as CN bands. All features in the spectrum are observed to increase with increasing TMG flow. The CN molecular band emission observed in the downstream region is the CN violet \((B^2 \Sigma – X^2 \Sigma)\) and CN red system \((A^2 \Pi – X^2 \Sigma)\). This observation indicates the presence of carbon-containing impurities within the deposition chamber that result in forming excited CN radicals. The gallium lines correspond to the resonance transitions of GaI at 403.3 nm \((5s^2 S_{1/2} – 4p^2 P_{1/2})\) and 417.0 nm \((5s^2 S_{1/2} – 4p^2 P_{3/2})\), as illustrated in the partial energy level diagram shown in figure 6 \([13]\). It is interesting to note that we do not observe any spectral emission from the 639/641 nm lines \((6p–5s)\) that terminate on the $5s^2 S_{1/2}$ level. Unfortunately due to a glass lens we were not able to detect emission from the UV lines.
at 287/294 nm (4d–4p) in this experimental study. A recent experimental study of a gallium-based RF excited lamp [14] showed that 287/294 nm and 403/417 nm emission constituted ∼20% and 50%, respectively, of the total spectral output of that light source. Currently our results suggest that Ga atoms in the downstream region are selectively excited into the 5s–2S1/2 levels by collisions with excited nitrogen species, most likely the long-lived N∗(2P) metastables (see figure 6), via the slightly exothermic reaction:

\[ \text{N}^*(2P) + \text{Ga} \rightarrow \text{Ga}^*(5s^2S_{1/2}) + \text{N} + \Delta E \ (\sim 0.5 \text{ eV}) \]

and thereafter decay radiatively:

\[ \text{Ga}^*(5s^2S_{1/2}) \rightarrow \text{Ga} + h\nu \ (403/417 \text{ nm}) \]

thus producing the observed violet glow.

The effect that hydrogen has on the spectrum both upstream and downstream is significant. Hydrogen plasma is known as a cleaning source for substrates and decomposes CC bonds, making it suitable for eliminating carbon from the substrate [15]. The addition of hydrogen will therefore have a significant effect on the downstream spectrum where the TMG is introduced. As shown in figure 5(b) the hydrogen scavenges carbon and also nitrogen in the gas phase above the substrate so that the CN band system disappears. Also hydrogen removes the presence of the CN violet band at 387 nm. This is an important observation, as hydrogen will assist in removing carbon impurities that may be incorporated into the GaN sample. The features at 567.1 and 569.8 nm correspond to the \( a^3\Pi_1 \rightarrow \Sigma^+ \) band of the GaH molecule [16, 17]. The precise origin of GaH in the system is at present unclear. It is a relatively stable molecule with a binding energy of ∼2.8 eV, and may assist GaN film growth as it has been used as an alternative Gallium source to TMG for film growth [18]. Production of GaH at the wafer via Ga (surface) +1/2H2 \( \Rightarrow \) GaH is thought to occur only at relatively high substrate temperatures >900 °C [19]. A possibility is that GaH results from hydrogen etching of the GaN layer.

Downstream of the plasma source, the excited gallium lines at 403 and 417 nm follow a similar trend to the nitrogen species in the source by decreasing strongly for hydrogen flow rates up to 20 sccm and then becoming more constant with increased hydrogen flow (figure 7).

Figure 8 shows the ratio of the normalized intensities versus hydrogen flow for excited gallium at 417 nm to atomic nitrogen upstream in the plasma source (crosses), excited gallium to molecular nitrogen in the plasma source (pluses) and atomic nitrogen to molecular nitrogen in the plasma source (open circles). There is a clear deviation from unity for hydrogen flows between 5 and 20 sccm. While the ratio of atomic nitrogen to molecular nitrogen decreases, indicative of more excited molecular nitrogen, the ratio of gallium to the excited nitrogen species increases. This shows that there is a relative increase in gallium emission compared with the excited nitrogen species. There may be a number of reasons for this. For example, the formation of NH may lead to less excited atomic nitrogen to excite gallium into the 5s^2S_{1/2} levels. Also hydrogen may lead to the decomposition of GaN with the formation of free ammonia and adsorbed gallium.

3.3. GaN growth

The effect that hydrogen has on the GaN layer growth has been reported in previous studies [7–9, 20–22]. Figure 9 shows the plane view and cross-section SEM images displaying surface morphology characteristics for (a) pure nitrogen plasma, (b) nitrogen plasma with 20 sccm hydrogen flow and (c) nitrogen plasma with 50 sccm hydrogen flow. Figure 9(a), with no hydrogen added to the plasma gas mixture, displays a polycrystalline GaN layer, with discrete nano-columns forming, orientated strongly in the c-plane. With the addition of 20 sccm of hydrogen to the plasma gas mixture, the morphology changes with lateral coalescence of the nano-columns.

When hydrogen flow was further increased to 50 sccm, keeping the total flow through the plasma source constant, the surface morphology changes again possibly due to etching by hydrogen (figure 9(c)) and the formation of nano-columns is seen again in the cross-section. The exact mechanism for this change in surface morphology is not known.

In the presence of hydrogen, atomic nitrogen can be efficiently captured, perhaps by forming surface adsorbed
Figure 6. Partial energy level diagram for low-lying atomic Ga, atomic/molecular nitrogen species, atomic/molecular hydrogen species and key spectral emission lines/bands.

Figure 7. The intensity dependence on hydrogen flow for excited gallium at 403 nm (crosses) and at 417 nm (open circles).

Figure 8. The ratio of the normalized intensities versus hydrogen flow for excited gallium at 417 nm to atomic nitrogen (crosses), excited gallium at 417 nm to molecular nitrogen (plus) and atomic nitrogen to molecular nitrogen (open circles).

species similar to those occurring during MOCVD growth with ammonia. This results in a decrease of excited nitrogen as shown by the optical emission measurements. However, the presence of hydrogen may increase the amount of active N species, through the formation of NH$_x$, available for GaN growth. In this scenario, H does not affect the growth by bonding directly to the GaN surface, but rather, it modifies the gas phase kinetics and/or the surface adsorbed species. Myers et al [8] provided an alternative explanation for the effect of hydrogen in rf-MBE whereby hydrogen is incorporated into the GaN layer. For N-polarity growth, a bulk-terminated surface would have a nitrogen-dangling bond making the surface prone to decomposition through attack by atomic nitrogen. With the addition of atomic hydrogen to the system, the surface can become passivated by hydrogen attached to the dangling bond creating N–H, preventing the enhanced decomposition by atomic nitrogen. On the one hand, for the R&D system, the addition of hydrogen may stabilize the growing surface for low flows on hydrogen. On the other hand the addition of hydrogen may lead to the decomposition of the surface, promoting Ga desorption or etching of the GaN layer.

To determine the impact of hydrogen on the optical properties of the GaN layers, the PL intensities were measured. As can be seen in figure 10 there is a peak in the intensity. However, the intensity of the yellow band emission decreases, perhaps due to fewer impurities in the carbon layer.

4. Conclusions

The effect of hydrogen on the optical properties and morphologies of gallium nitride thin films grown using the remote plasma chemical vapour deposition process was investigated. In situ diagnostics via optical emission spectroscopy of the microwave plasma source and the downstream region in the deposition chamber was carried out and correlated with film growth properties. It has been shown that the addition of a small amount of hydrogen to
Figure 9. (Top) The plane view and (bottom) cross-section SEM images displaying surface morphology characteristics for (a) pure nitrogen plasma, (b) nitrogen plasma with 20 sccm hydrogen flow and (c) nitrogen plasma with 50 sccm hydrogen flow.

Figure 10. A plot of the PL intensity peak (asterisk) and the broadband peak (circles) for various hydrogen flows.

the plasma gas mixture reduces the concentration of carbon-containing species in the deposition chamber, as evidenced by the reduction in intensity of CN band emission with the addition of 20 sccm hydrogen to the plasma gas flow. It has also been shown that the presence of hydrogen in the plasma gas stream influences surface morphology of the films. Scanning electron microscopy analysis of gallium nitride films shows that for 20 sccm of hydrogen in the plasma gas flow, a coalesced film is produced. By contrast, for no hydrogen present in the plasma gas flow, polycrystalline films exhibit a nano-columnar structure, strongly orientated in the c-plane. For a hydrogen flow of 50 sccm, surface morphology changes again, possibly due to etching at the surface of the film. A similar trend is observed for PL intensities, with the maximum PL peak intensity corresponding to a hydrogen flow of 20 sccm.

Acknowledgments

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References