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RF plasma sources for III-nitrides growth: influence of operating conditions and device geometry on active species production and InN film properties

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The optical emission from an RF inductively coupled plasma source has been monitored at various flow rates and RF powers in the spectral range of 500–900 nm. It was found that low powers and high flow rates resulted in emission from the 1st-positive series of excited molecular nitrogen dominating the spectrum relative to atomic nitrogen. Growth of InN on GaN showed improved electrical properties when the molecular species dominated the spectrum. In contrast, growth of InN on (111) yttrium stabilised zirconia (YSZ) was found to yield films of similar electrical properties at different plasma operating conditions. Reflection high energy electron diffraction (RHEED) patterns were used to monitor the *a*-lattice constant during growth. Films grown on GaN with higher relative atomic flux were found to relax within the first several nm of growth, whereas films grown with higher molecular nitrogen species did not fully relax until approximately 50 nm of growth. These observations suggest that the active nitrogen species plays a significant role in determining how strain is accommodated during InN epitaxy.

1 Introduction

The commercialisation of the III-nitride material system has been driven largely by MOCVD growth where the active nitrogen flux is supplied using thermally cracked ammonia. At the same time great advances have been made in the plasma assisted molecular beam epitaxy (PAMBE) growth of the III-nitrides, where the nitrogen flux is typically provided by an inductively coupled plasma source. The two competing plasma sources which have been studied in detail are the radio frequency (RF) [1–3], and the electron cyclotron resonance (ECR) plasma sources [4]. The RF source has become the most common choice for PAMBE growth as films produced with this technique have been shown to have superior electrical, optical and structural properties [5, 6]. Active nitrogen species produced by both these sources typically consist of a combination of atomic nitrogen, varying series of excited molecular nitrogen and ionic forms of both species. Studying the optical emission from both sources has proved a useful tool in determining the relative composition of active species produced by the plasmas [1, 2, 7–9]; a complete description of all optical transitions involving atomic and molecular nitrogen is given by Wright et al. [10]. Typically ECR sources are found to produce a high content of 2nd-positive series excited molecular nitrogen and ionic species [4, 6, 9]. In contrast, the RF source typically consists of mainly 1st-positive series excited molecular nitrogen and atomic nitrogen [6, 8].

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Although the decision to use an RF source for nitride growth may be relatively straight forward, a number of different RF source products are available, with the Veeco UNI-Bulb and the Oxford Applied Research HD-25 among the most commonly noted. A number of groups have shown that the active nitrogen species produced by different RF sources can vary substantially and can have a profound influence on substrate nitridation effectiveness [11, 12], electrical characteristics [13], and optical properties [7]. Furthermore, studies of the optical spectra of nitrogen plasmas at different RF powers and flow rates have shown that the relative amounts of active species can change quite dramatically depending on the plasma operating conditions [8]. In this study we investigate the effect of varying the plasma operating conditions for an Oxford Applied Research HD-25 nitrogen source on the growth of InN films grown by PAMBE. The active nitrogen species are monitored by examining the spectral content of the plasma emission which is related to the electrical and structural properties of the films.

2 Experimental procedure

A Perkin–Elmer model 430 PAMBE system with a base pressure of approximately 10^{-11} Torr was used for film growth. Active nitrogen was supplied with an Oxford Applied Research HD-25 inductively coupled RF plasma source (RF-ICP). Indium and gallium elemental fluxes were supplied by standard effusion cells heated to 780 and 965 °C, respectively, which resulted in fluxes of approximately 10^{14} cm^{-2} s^{-1} for both sources as measured by a water cooled quartz crystal microbalance. (0001) sapphire substrates from Honeywell or (111) ytrium stabilised zirconia (YSZ) substrates from Danning were employed. Growth on sapphire substrates entailed nitriding for 15 min at 650 °C before a 150 nm GaN buffer layer was deposited at 650 °C; approximately 600 nm of InN was then deposited at 450 °C. Nitriding and buffer layer growth was performed with an RF power of 350 W, whereas indium nitride growth was performed using a range of RF powers (110–350 W). The nitrogen flow rate for nitriding, buffer layer and film growth remained fixed at 1.3 sccm. Indium nitride films grown on YSZ had no nitriding or buffer layer steps. The films were grown directly on the substrates at 400 °C and were approximately 600 nm thick. Growth rates for InN and GaN were ~200 nm/h. Growth was monitored in-situ by 20 kV reflection high-energy electron diffraction (RHEED). Hall effect measurements utilised an EGK-2000 0.5 T system. Optical characterisation of the plasma emission was achieved using a Jobin Yvon CCD-3000 spectrometer fitted with a 150 groove/mm grating.

3 Results and discussion

The optical emission in the range 500–900 nm from the plasma source was measured at RF powers ranging from 75–400 W and flow rates ranging from 0.65–1.9 sccm. The 500–900 nm spectral range is dominated by emission from the 1st-positive series of molecular nitrogen and atomic nitrogen. The rather broad term ‘active nitrogen’ can also include other series of excited molecular nitrogen and ions [10]. However, previous studies have shown that atomic nitrogen and 1st-positive series molecular nitrogen are typically the dominant species emitted from RF sources [6]. As a result, this spectral range is ideal for characterising the interplay between the two dominant active species in an RF-ICP as the plasma operating conditions change. Figure 1 shows the plasma emission spectrum at a flow rate of 1.3 sccm and RF power of 400 W (solid curve) and 110 W (dotted curve). The emission from atomic nitrogen is visible as sharp peaks located at 745, 821 and 869 nm for the 400 W measurement [6, 9]. Fine structure exists within these peaks but it is not visible in Fig. 1 due to the grating resolution. The emission from 1st-positive series molecular nitrogen appears as broader bands with the band peaks located at 540 (not visible in Fig. 1), 590, 660, 760 and 820 nm [6, 9].

As is visible in Fig. 1, the emission intensity associated with both atomic and 1st-positive series molecular nitrogen increases with increasing RF power. However, the increase of the atomic nitrogen related features is greater than that of molecular nitrogen as shown in Fig. 2, which plots the intensity of the atomic nitrogen peak at 822 nm divided by molecular nitrogen intensity at 651 nm. This trend signals that at higher RF powers the proportion of atomic nitrogen increases preferentially, while at lower RF

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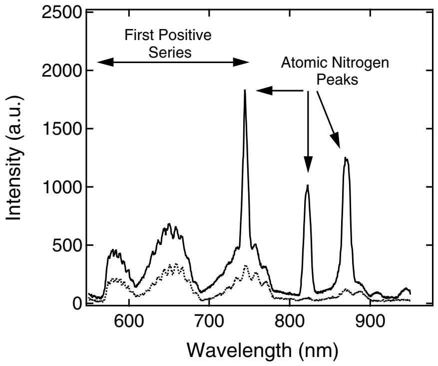

Fig. 1 Optical emission from an RF inductively coupled plasma operated at a flow rate of 1.3 sccm and RF power of 400 W (solid curve) and 110 W (dotted curve).

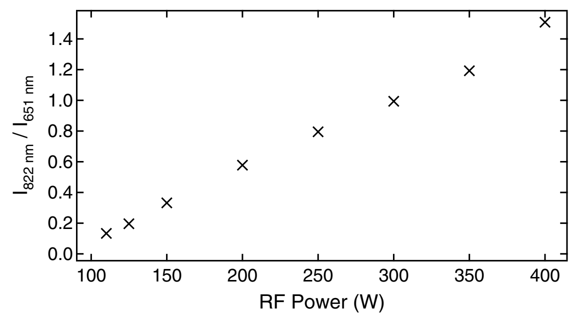

Fig. 2 Ratio of emission intensity measured at 822 nm (atomic nitrogen) and 651 nm (1st-positive series molecular nitrogen), respectively, at a constant flow rate of 1.3 sccm as a function of RF power.

powers the proportion of 1st positive series of molecular nitrogen increases. The flow rate dependence of the active nitrogen was also investigated, and it was observed that higher flow rates enhanced relative molecular nitrogen emission while at lower flow rates atomic nitrogen emission increased.

A series of four ~600 nm thick indium nitride films were grown on (0001) sapphire substrates with ~150 nm gallium nitride buffer layers at RF powers of 110, 150, 250, and 350 W, respectively. The nitrogen flow rate for these films was 1.3 sccm, which corresponded to a chamber pressure of 1×10^{-5} Torr. It was found that the plasma would self-extinguish if the power was reduced below 110 W at this flow rate. All four films exhibited streaky RHEED patterns throughout growth and a flat surface morphology as determined by AFM, with rms roughness less than 5 nm.

Hall effect measurements were made on the InN films grown with varying active nitrogen species composition (varying RF power) to determine trends in the electrical attributes of the films. Carrier concentration and Hall mobility measurements were all single field and no attempt was made to correct for nonhomogeneity. As such, the results represent an average of the various layers which exist within the film. It has been established that InN suffers from substantial electron accumulation at the surface, and possibly the substrate-film interface [14]. Variable field Hall effect measurements have been investigated by others as a means of separating the various layers, where it was found that the surface layer typically has a much lower mobility than the bulk [15]. However, the single field measurement is still meaningful and can be used to show changes in film carrier concentrations. The proviso is that it is not known if the changes have occurred in the bulk, the surface layer or both. Figure 3 shows the carrier concentrations

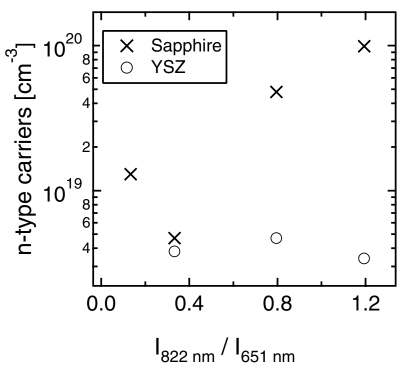

Fig. 3 Carrier concentrations of InN films grown on (0001)Sapphire/(0001)GaN and (111)YSZ as a function of active species generated by the plasma. Emission intensity is monitored at 822 nm (atomic nitrogen) and 651 nm (1st-positive series molecular nitrogen) at various RF powers and a constant flow rate of 1.3 sccm.

for films as a function of the active nitrogen species as determined in Fig. 2. Clearly the films where the dominant active nitrogen species is molecular have lower n-type carrier concentrations. The Hall mobility of these films was found to correlate strongly with the carrier concentration, as has been observed by other groups studying indium nitride [16, 17], with a maximum Hall mobility of 377 $cm^2 V^{-1} s^{-1}$ achieved for the film grown at 150 W. It is noted that for films of this carrier concentration other groups have reported a substantially higher single field Hall mobility [16–18]. The source of this discrepancy is not fully understood, but it is suspected that the non-optimised GaN buffer layer used here may be introducing higher levels of threading dislocations. Consequently the higher level of dislocations, although being electrically neutral, can be acting as scattering sites and reduce carrier mobility.

As the RF power is reduced, the ratio of active molecular nitrogen to atomic nitrogen increases but the total amount of active nitrogen also decreases. This can result in the effective III/V flux ratio increasing as the plasma power is reduced, and may complicate interpretation of Fig. 3. The III/V flux ratio is known to have a profound influence on GaN quality [19, 20], although this has not been established as definitively for indium nitride growth. Despite the reduction in active nitrogen flux with RF power we observed that the growth rate of the indium nitride films was constant throughout this set of experiments. This suggests that indium flux is the limiting factor on growth rate in this regime. Little is known about the relative lifetimes of indium and nitrogen species on the film surface, and estimating active nitrogen flux is a questionable exercise. Although we can qualitatively relate the optical emission from a plasma to the active species, quantitative calculations involve many uncertainties. However, from the apparent independence of the growth rate from the active nitrogen flux, we can speculate that the flux of active nitrogen may be much greater than that of indium. This would result in much of the active nitrogen leaving the surface before it has an opportunity to participate in growth. Hence the reduction in active nitrogen is mainly reducing the active nitrogen desorbing from the film surface, and not reducing the amount of nitrogen taking part in growth.

Also as part of this study, three ~600 nm thick indium nitride films were grown on (111) YSZ at RF powers of 150, 250 and 350 W, respectively. YSZ has a lattice mismatch of 2.5% with unrotated indium nitride as opposed to 11% for gallium nitride and has been used to grow indium nitride films with relatively low carrier concentrations [21]. Hall effect measurements revealed that films grown on YSZ were relatively insensitive to active nitrogen species as shown in Fig. 3.

Ng et al. have observed that indium nitride relaxes fully within the first several bilayers of growth as measured by RHEED spacing; the plasma operating conditions were not mentioned in this study [22]. Specht et al. have also studied strained InN layers (although not the strain evolution as growth progresses); variation in the *a*-plane lattice constant was attributed to preferential defect incorporation in the basal plane [23]. We have studied the RHEED spacing throughout growth to determine how the active nitrogen species influences the strain relaxation in indium nitride. Figure 4 shows the *a*-plane lattice constant during growth for an indium nitride film grown on gallium nitride with an RF power of 350 W (high atomic nitrogen content). The profile in this case is typical for all films we have examined

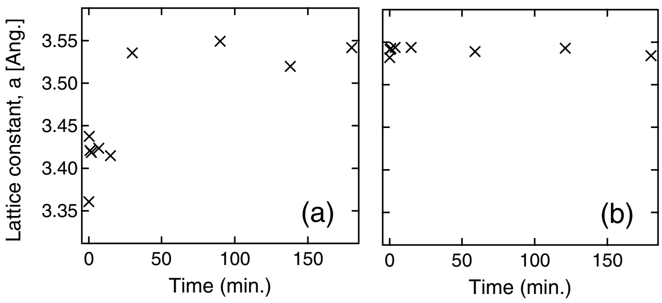

Fig. 4 InN *a*-plane lattice constant during InN growth on (0001)GaN/(0001)Sapphire with different active nitrogen species ratios: (a) low atomic nitrogen content, (b) high atomic nitrogen content.

grown with RF powers of 250 and 350 W on gallium nitride. The lattice relaxes to that of bulk indium nitride within the first 30 s of growth (1 nm), in agreement with the measurements of Ng et al. [22].

Figure 4 shows the *a*-plane lattice spacing of an indium nitride film grown on gallium nitride with an RF power of 150 W (high active molecular nitrogen content). A similar profile is observed for films grown at an RF power of 110 W. Interestingly, in this case the lattice takes far longer to relax to that of bulk indium nitride, and does not achieve this until a film thickness near 50 nm is reached. There is also evidence that the relaxation takes place in discrete steps after ~30 s and ~20 min. Measurements of the *a*-plane lattice constant on YSZ revealed that the lattice seemed to relax immediately at all RF powers, but the much lower mismatch and noise in the measurement make interpretation difficult.

These observations further reinforce the role of the active nitrogen species in influencing strain accommodation in indium nitride. The active nitrogen species appears to be having a profound influence on the formation of strain accommodating defects. The gradual incorporation of these defects (for which misfit dislocations are a prime candidate) seems to result in improved electrical characteristics. It is common practice to operate RF-ICPs in the 200–350 W range, but these results show that significant gains in indium nitride electrical properties may be possible if lower power operation is considered.

4 Conclusions

Active nitrogen species produced by an Oxford Applied Research HD-25 inductively coupled RF plasma source has been monitored by observing the plasma emission spectra in the range 500–900 nm. It was observed that at low flow rates and high RF powers atomic nitrogen dominated the spectra while at higher flow rates and lower RF powers 1st-positive series excited molecular nitrogen dominated the spectrum. Indium nitride films were grown in both regimes on (0001)GaN buffers and it was found that lower carrier concentrations and improved Hall mobilities could be achieved by growing in the regime where 1st-positive series molecular nitrogen dominated the spectrum. Electrical properties of films grown on (111) YSZ showed no dependence on active nitrogen flux composition. Monitoring the *a*-plane lattice constant during growth showed that films grown on gallium nitride with mainly excited molecular nitrogen relaxed over the first 50 nm growth. Contrastingly, films grown with higher proportions of atomic nitrogen relaxed over the first 1 nm of film growth. These results show that the active nitrogen species used for indium nitride growth can have a profound influence on how strain is accommodated within the films.

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