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The influence of the group V/III molar precursor ratio on the structural properties of InGaN layers grown by HPCVD

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The influence of the group V/III molar precursor ratio on the surface morphological and electrical properties of $In_{0.65}Ga_{0.35}N$ epilayers has been investigated. The layers studied have been grown by high-pressure chemical vapor deposition, a growth technique that utilizes the reactor pressure as an additional processing parameter. The surface morphology analysis revealed that with the increasing V/III molar precursor ratio, the surface morphology degrades with increasing surface roughness and decreasing average grain areas. The free carrier concentration in the $In_{0.65}Ga_{0.35}N$ epilayers increased with the increased group V/III molar precursor ratios in the 700–3000 range.

1 Introduction The ternary $In_{1-x}Ga_xN$ alloy system is being explored for advanced optoelectronics [1] and high-efficient photovoltaic [2–4] applications. Devices based on indium-rich and gallium-rich $In_{1-x}Ga_xN$ heterostructures have the potential to operate in a wide spectral range from UV ($E_g^{GaN} = 3.4$ eV) to NIR ($E_g^{InN} = 0.7$eV [5, 6]). However, the growth of $In_{1-x}Ga_xN$ alloys is challenging due to the low thermal disassociation temperature of InN compared to that of GaN, as well as the high lattice mismatch between the two binaries.

The high n-type background doping levels observed in most InN layers have been partially attributed to interstitial hydrogen atoms by the theoretical [7] and the experimental studies [8–10]. Ruffenach et al. [10] showed that the thermal annealing of InN layers at 550 °C under NH_3 atmosphere resulted in an increased free carrier concentration, a process which was reversible. In order to study the influence of the group V/III molar precursor ratio on the surface morphological, structural, and electrical properties of $In_{0.65}Ga_{0.35}N$ epilayers grown by high-pressure chemical vapor deposition (HPCVD), a set of epilayers with different group V/III molar precursor ratios ranging from 700 to 3000 was grown and analyzed. The surface morphology and free carrier concentration of the epilayers have been studied by atomic force microscopy (AFM) and infrared reflectance spectroscopy (IRS). The HPCVD growth technique [11] is explored in order to assess the stabilization of alloys with large differences in the partial pressures at higher processing temperatures. This is especially important for the InN–GaN ternary alloy system, where the different partial pressures lead to significant differences in growth temperatures between the two binaries.

2 Experimental details The $In_{1-x}Ga_xN$ layers investigated were grown by HPCVD on ~5 μm thick GaN/c-plane sapphire templates. Active indium, gallium, and nitrogen fragments were supplied to the growth surface via trimethylindium (TMI), trimethylgallium (TMG), and ammonia (NH_3) precursors, respectively. As schematically illustrated in Fig. 1, the precursors were temporally embedded in a nitrogen carrier gas stream, such that the total flow and pressure remained constant at any given time. The ammonia and (TMI, TMG) injection times were 1.5 and 0.8 s, respectively, with pulse separations between TMI/TMG–ammonia and ammonia–TMI/TMG set to 1.4 and 2.3 s, respectively. The $In_{0.65}Ga_{0.35}N$ epilayers were grown at a

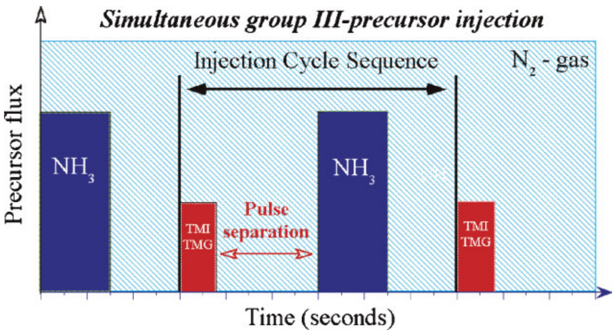

Figure 1 (online color at: www.pss-a.com) The injection sequence for the pulsed injection.

temperature of 1150 K, a reactor pressure of 15 bar, a main gas carrier flow (N_2) of 12 slm (standard liters per minute), and a growth time of 3 h. For the series presented here, all parameters were kept constant, while V/III molar precursor ratio was varied between 700 and 3000. The surface morphology of the layers was analyzed by AFM using a 'XE 100 Park' system in non-contact mode. The AFM tips used in the AFM experiments had a resonance frequency of 300 kHz and a spring constant of 45 N/m.

For IR reflectance, a Perkin–Elmer 2000 system was used. The experiments were carried out at room temperature in the energy range of 0.062–0.744 eV in near normal incidence geometry. The plasma frequency and free carrier concentration of $In_{0.65}Ga_{0.35}N$ layers were obtained by fitting the simulated IR spectra to the experimental spectra. The simulated spectra were constructed by using optical transfer matrices and a four-layer stack model consisting of sapphire substrate, an i-GaN layer, a p-GaN interface layer, and an InGaN layer from bottom to top. The InGaN dielectric function employed in these calculations is based on coupled contributions from plasma oscillations by classical Drude model and phonons by Lorentzian type oscillator model [12, 13]. The dielectric function for the sapphire substrate was calculated by using Sellmeier equation [14]. The effective electron mass used for the InGaN layer calculations was 0.15 m_0 [15].

3 Results and discussion Figure 2a–d shows representative 2 μm × 2μm AFM images of the $In_{0.65}Ga_{0.35}N$ layers grown with group V/III molar precursor ratios of 700, 1000, 2000, and 3000, respectively.

The statistical analyses for the surface roughness, average grain area, grain size distribution, and surface void fraction as function of the V/III molar precursor ratio are summarized in Table 1. The results show that the surface roughness increases with the increasing V/III molar precursor ratio, indicating a degradation of surface quality. The decrease in the average grain area with increased V/III molar precursor ratio suggests an increase in extended defects for higher V/III molar precursor ratios. The increased group V/III molar precursor ratio resulted in decreased amount of surface voids.

The IR reflectance spectra obtained for the $In_{0.65}Ga_{0.35}N$ epilayers grown with group V/III molar precursor ratios ranging from 700 to 3000 are depicted in Fig. 3.

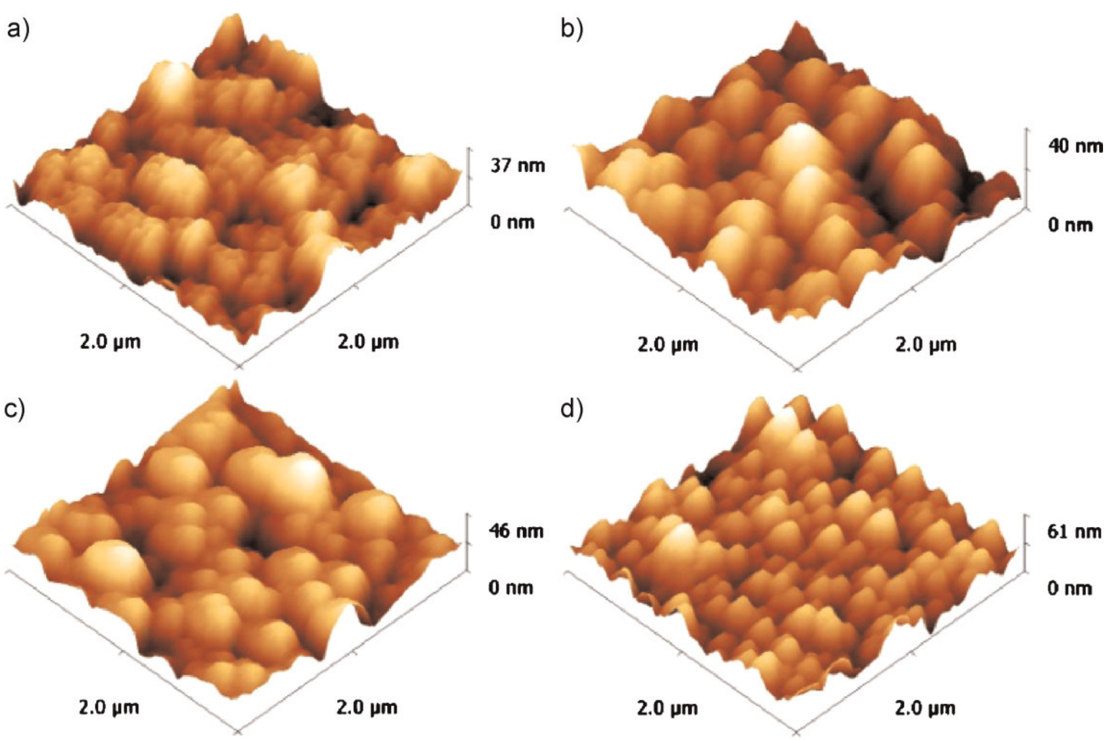

Figure 2 (online color at: www.pss-a.com) (a–d) 2 μm × 2 μm AFM images for $In_{0.65}Ga_{0.35}N$ epilayers deposited on GaN/sapphire (0001) templates. The layers were grown with group V/III molar precursor ratios of (a) 700, (b) 1000, (c) 2000, and (d) 3000.

Table 1 Summary of the results obtained from AFM analysis of $In_{0.65}Ga_{0.35}N$ layers grown with different V/III molar ratios.

V/III molar ratio	700	1000	2000	3000
surface roughness (nm)	6.9	7.3	7.9	8.7
average grain area (10^{-2} μm^2)	7.3	6.9	3.5	1.8
standard deviation of grain size distribution (10^{-2} μm^2)	9.5	9.3	4.9	2.4
surface void fraction (%)	37	42	36	32

Table 2 Summary of the results obtained from IR reflectance for $In_{0.65}Ga_{0.35}N$ layers grown with different V/III molar ratios.

V/III molar ratio	700	1000	2000	3000
plasma frequency (cm^{-1})	800	550	1050	1150
free carrier concentration (10^{18} cm^{-3})	7	5.5	8.5	25
high frequency dielectric constant ε_∞	4.8	4.7	4.8	6.0

The IR reflectance spectra show a clear shift of the plasma frequency with increasing group V/III molar precursor ratio. The estimated free carrier concentrations from the IR simulation analyses are depicted in the inset of the figure. The analysis shows an increase in the free carrier concentration with increasing group V/III molar precursor ratio from 700 to 3000, a tendency that might be related to the increased hydrogen concentration at the growth surface, with potential incorporation in the layers as reported for InN [7–10]. A further potential contribution to the increased free carrier concentration with higher V/III molar precursor ratio (see Table 1) might be the decreased average grain area, since a higher concentration of grain boundaries may induce a higher density of edge-type threading dislocations that may contribute to a higher n-type doping as observed in MOCVD grown InN layers [16]. The best fitting parameters obtained from simulations of the experimental IR spectra are summarized in Table 2.

The increase in the dielectric function ε_∞ with increasing V/III molar precursor ratio suggests the formation of a denser layer for higher group V/III molar ratios. According to Bruggeman's effective medium approximation [17], the inclusion of void components lowers the dielectric constant ε. As depicted in Table 1, a decrease in surface void fraction is observed with increasing group V/III molar precursor ratio. Assuming that the void component is completely related to the surface morphology, a direct correlation between effective dielectric constant ε_∞ and surface void fraction is observed. Further studies in a wider range of V/III molar precursor ratios are needed to improve the material quality in this composition regime.

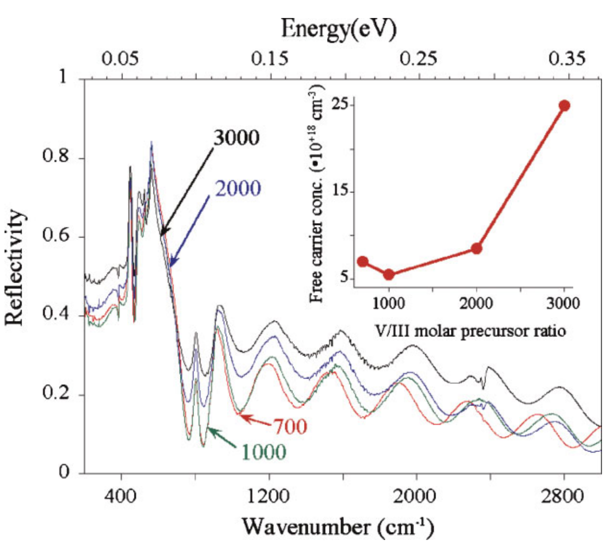

Figure 3 (online color at: www.pss-a.com) IR reflectance spectra of $In_{0.65}Ga_{0.35}N$ layers grown with different group V/III molar ratios varying between 700 and 3000. Inset plot shows free carrier concentration estimate as a function of the group V/III molar precursor ratio.

4 Conclusion

The influence of the group V/III molar precursor ratio on the surface morphological and electrical properties of the $In_{0.65}Ga_{0.35}N$ epilayers was studied. An increased group V/III molar precursor ratio from 700 to 3000 resulted in a higher free carrier concentration with a higher surface roughness, a smaller average grain area, and a denser layer. The increase in the free carrier concentration is thought to be due to the higher hydrogen concentration at the growth surface, related to the increased amount of ammonia in the gas phase and/or increased amount of grain boundaries.

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