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Metalorganic chemical vapor deposition of InGaAsN using dilute nitrogen trifluoride

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Abstract

The metalorganic chemical vapor deposition of $In_{0.06}Ga_{0.94}As_{1-x}N_x$, with $x = 0.00$–0.02, has been examined using nitrogen trifluoride (NF_3) and tertiarybutylarsine. The solid N/V ratio increased linearly with the gas-phase N/V ratio up to a limit of 2.0% nitrogen in the film at a gas N/V = 0.35. No further increase in nitrogen content could be achieved at a growth temperature of 550 °C unless the feed rate of the group III sources was reduced. It was shown that NF_3 addition to the reactor results in a growth rate decrease of 40% with increasing NF_3 feed rate up to 3.0×10^{-4} mol/min (N/V = 0.35). Further addition of NF_3 did not affect the growth rate, but caused the surface roughness to rise rapidly from 0.1 to over 1.0 nm. Results presented in this paper indicate that the increased surface roughness may be due to fluorine etching of the adsorbed group III elements.

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1. Introduction

Dilute III–V nitrides have been the focus of much research as the addition of a small amount of nitrogen into InGaAs can dramatically reduce the semiconductor's band gap [1,2]. An InGaAsN alloy with N concentrations in the range of a few percent is of interest for producing long-wavelength photodetectors, laser diodes, and vertical-cavity surface-emitting lasers (VCSELS) on GaAs substrates [3–5]. However, incorporating greater than 1.0% nitrogen in the film is difficult, especially for alloys grown by metalorganic chemical vapor deposition (MOCVD) [6]. In this case, extremely high ratios of dimethylhydrazine (DMH) to arsine must be fed to the reactor. Furthermore, the addition of indium greatly reduces the incorporation rate of nitrogen using DMH, making it harder to control the InGaAsN composition during MOCVD [7,8]. This has led crystal growers to study other nitrogen precursors such as hydrazine [8], ammonia [9], tertiarybutylhydrazine [10,11], and nitrogen trifluoride [8,12].

NF_3 is a promising source of nitrogen for InGaAsN, since it exhibits high incorporation efficiency and is not affected by the presence of indium [8]. However, NF_3 is a strong oxidizer that presents an explosion hazard when used in the hydrogen ambient found in MOCVD reactors [13]. Moreover, the use of pure NF_3 has been found to result in a relatively narrow operating window for the InGaAsN growth process [8].

In this report, we assess the feasibility of using helium-diluted NF_3 as a nitrogen source for the MOCVD of InGaAsN. Diluting the precursor in He allows one to keep the NF_3 concentration in hydrogen below the flammability limit at the point of mixing [14]. NF_3 is found to incorporate nitrogen readily at feed rates below 3.0×10^{-4} mol/min, but at higher feed rates, increases the

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surface roughness dramatically. The results presented below suggest that this may be due to fluorine etching of the group III elements.

2. Experimental methods

Indium gallium arsenide nitride films were grown on vicinal GaAs (0 0 1) substrates in a Veeco (formerly Emcore) D125 MOCVD reactor. The reactor was maintained at 60 Torr with a total flow of 37.0 standard-liter/min ultrahigh-purity hydrogen. The H_2 was passed through a SAES Pure Gas, Inc. purifier (model PS4-MT3-H) which removed any remaining oxygen, nitrogen or carbon species to below a few parts per billion. The precursors were liquid trimethylindium (TMIn), trimethylgallium (TMGa), tertiarybutylarsine (TBAs), tertiarybutylphosphine (TBP), and 10% NF_3 diluted in helium. Two separate InGaAsN structures were grown: 500-nm InGaAsN on a 50-nm InGaP etch-stop for growth rate determination; and 120-nm InGaAsN on a GaAs buffer for structural and compositional analysis. The GaAs and InGaP layers were deposited at 650 °C, while the InGaAsN layers were grown at 550 °C. The surface temperature was monitored in real-time using the emissivity-corrected RealTemp® instrumentation available from Veeco. After growth of the InGaAsN layer, the samples were cooled to room temperature and examined by in situ X-ray photoemission spectroscopy (XPS), and ex situ high-resolution X-ray diffraction (XRD) and atomic force microscopy (AFM). For the in situ measurements, the samples were transferred from the MOCVD reactor to the ultrahigh vacuum (UHV) surface analysis system via an interface chamber that was evacuated to 1×10^{-9} Torr.

Growth rates were determined by etching the InGaAsN up to the InGaP layer with an ammonium hydroxide/hydrogen peroxide/water solution in a 1:1:20 ratio, and then measuring the thickness of the film with a Dektak 8 profilometer. Core level photoemission spectra of the In 3d, Ga 2p, As 3d, and N 1s lines were collected using a PHI 3057 XPS spectrometer, with magnesium K_α X-rays ($h\nu = 1253.6$ eV). All spectra were taken in small area mode with a 7° acceptance angle and 23.5 eV pass energy. The take-off angle with respect to the surface normal was 25°. The surface composition was determined from the integrated intensity of the In 3d, Ga 2p, As 3d, and N 1s photoemission peaks, dividing by their sensitivity factors, 4.36, 3.72, 0.68 and 0.48, respectively. The N/V (In/III) ratio was obtained by dividing the N (In) atom% by the total group V (group III) atom%. The XRD measurements were made on a Bede D^3 high-resolution diffractometer using Cu K_α X-rays. Atomic force micrographs were obtained on a Quesant 250 microscopy system in tapping mode. Film compositions were determined from room temperature photoluminescence (PL) and XRD using Vegard's law and Moon's method [15] in conjunction with bowing parameters available from Ferhat [16].

3. Results

3.1. MOCVD growth

Shown in Fig. 1 is the gas phase versus solid N/V ratios for InGaAsN films deposited at 550 °C on GaAs. Data from Kurtz et al. [8] have been included for reference. The films were grown at 3.4 μm/h. A slightly higher gas phase N/V ratio was required to achieve the same solid composition as Kurtz obtained due to the better cracking efficiency of the TBAs used in the present work. The half-filled circle corresponds to a growth rate of 2.7 μm/h, whereas the filled circle corresponds to 2.3 μm/h. A linear relationship is observed between the solid N/V ratio and the gas N/V ratio up to 2.0% in the solid. Beyond this value, the solid N/V ratio could not be increased by raising the gas N/V ratio further. Instead one had to simultaneously raise the gas N/V ratio and lower the feed rate of the group III sources (i.e., the half-filled and filled circles).

Shown in Fig. 2 is the InGaAsN lattice mismatch relative to GaAs measured by XRD as a function of the TMGa and NF_3 feed rates. All films in this figure have an indium content of 5.8±0.2%. At a TMGa feed rate of 1.4×10^{-4} mol/min, the epilayer peak shifts closer to the lattice matched condition with increasing NF_3 feed rate up to 3.0×10^{-4} mol/min. However, above this value, the epilayer remains 0.1% mismatched independent of the NF_3 feed rate. Improved lattice matching due to higher nitrogen incorporation was accomplished only when the TMGa and TMIn feed rates were decreased, while keeping the NF_3 feed rate at 2.7×10^{-4} mol/min (cf. triangle and open box in Fig. 2).

The epilayer growth rate was found to decrease with increasing NF_3 feed rate to the reactor. Shown in Fig. 3 is

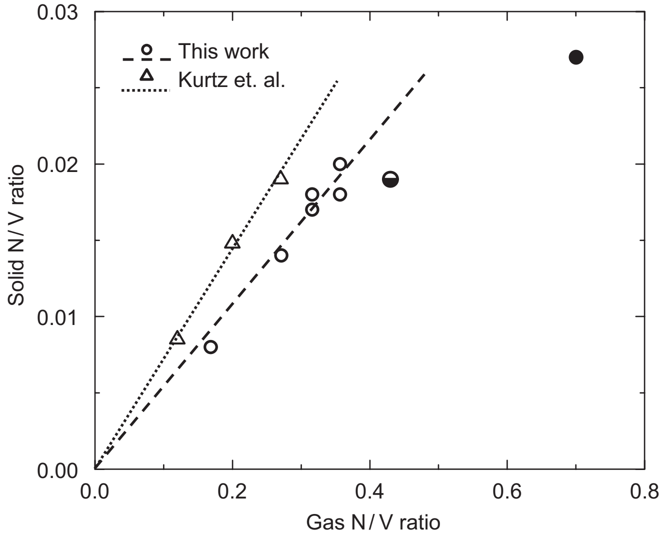

Fig. 1. Gas phase to solid N/V ratios for InGaAsN films deposited at 550 °C, including data from Kurtz et al. [8]. The TMGa flow rate for open circles was 1.4×10^{-4} mol/min, half-filled circle was 1.0×10^{-4} mol/min, and filled circle was 8.8×10^{-5} mol/min.

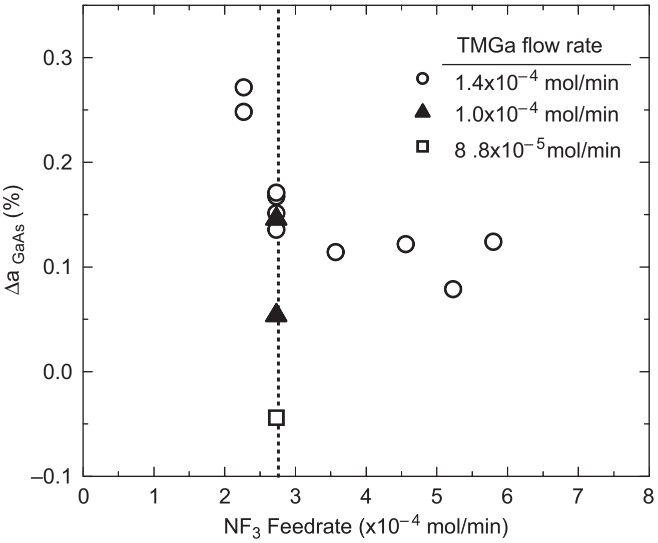

Fig. 2. Lattice mismatch of InGaAsN relative to GaAs as a function of NF_3 feed rate. The gas phase TMGa/TMIn ratio was 28.0 for all TMGa flows listed in the legend.

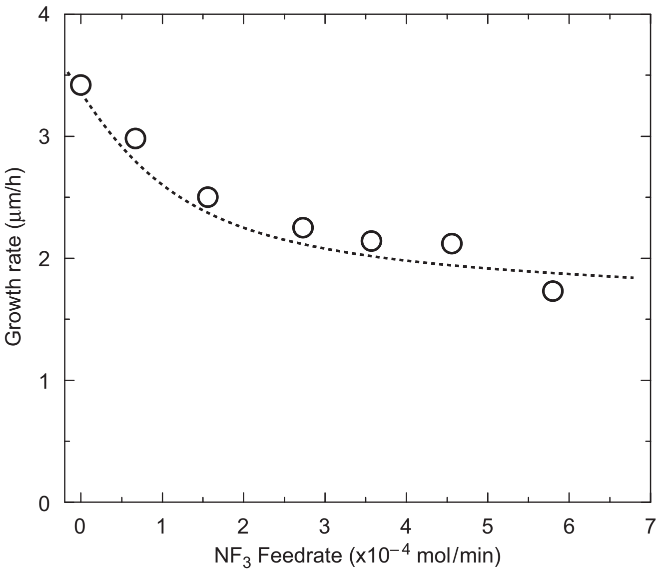

Fig. 3. Growth rate of InGaAsN films as a function of NF_3 feed rate.

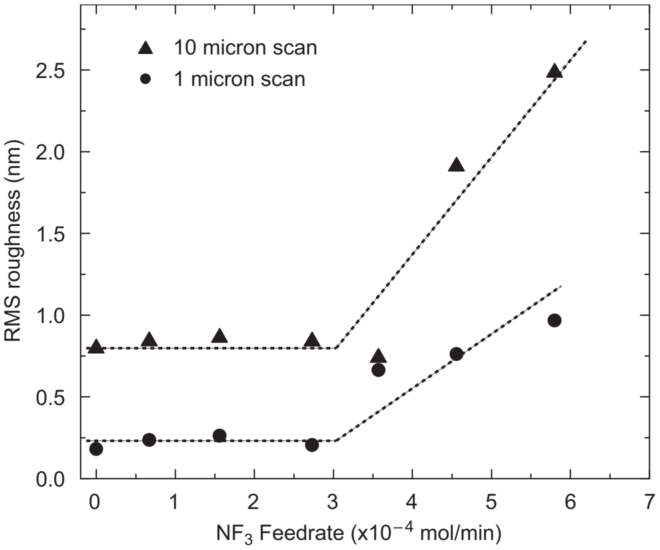

Fig. 4. Root-mean-square roughness as a function of NF_3 feed rate for 1×1 and $10 \times 10\,\mu m^2$ areas of the film surface. Films were grown at a TMGa feed rate of 1.4×10^{-4} mol/min.

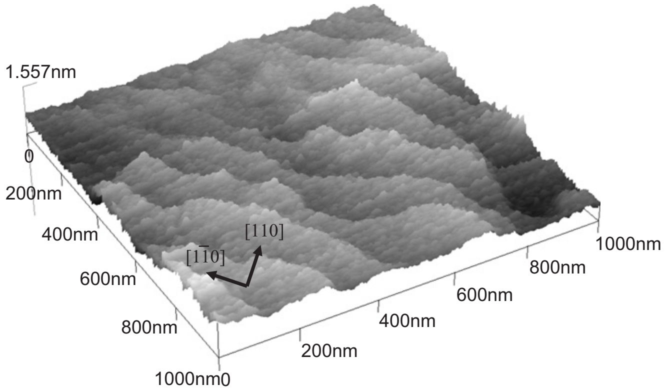

Fig. 5. AFM image of the surface of an InGaAsN film grown at TMGa and NF_3 feed rates of 1.4×10^{-4} and 2.7×10^{-4} mol/min, respectively. Image size: $1.0 \times 1.0\,\mu m^2$.

the growth rate as a function of the NF_3 flow rate at a constant TMGa flow rate of 1.4×10^{-4} mol/min. The data points were produced from a series of measurements made on at least three samples grown at each condition. Upon addition of NF_3 to the reactor, the growth rate drops quickly then levels off at about 2.0 μm/h with increasing NF_3 flow rate. At the stage where the growth rate levels off, $\sim 3.0 \times 10^{-4}$ mol/min NF_3, an abrupt increase in the surface roughness of the film is observed. Shown in Fig. 4 is the measured root-mean-square (RMS) roughness on 1- and 10-micron areas as a function of the NF_3 feed rate. The surface remains atomically flat with an average roughness of 0.2 nm (0.8 nm) over 1.0 (10.0) μm^2 for NF_3 flows up to 3.0×10^{-4} mol/min. Increasing the NF_3 flow to 6.0×10^{-4} mol/min causes the surface roughness to jump from 0.2 to 1.0 nm over 1.0 μm^2. A similar increase is observed for the AFM measurement at 10.0 μm^2.

A three-dimensional AFM image of a 120-nm-thick InGaAsN film grown at an NF_3 feed rate of 2.7×10^{-4} mol/min and 550 °C is presented in Fig. 5. Atomically smooth terraces are observed with a terrace height of 0.3 nm. Conversely, when one increases the NF_3 feed to the reactor to 3.6×10^{-4} mol/min, the surface roughens from 0.2 to 0.7 nm over an area of 1.0 μm^2. One might think that this is due to strain induced by the higher nitrogen content in the film. However, because the film is under compression, the incorporation of additional nitrogen into the film should reduce the total strain. Therefore, we surmise that the increased roughness originates from a chemical process at the surface.

3.2. Annealing in NF_3

In order to gain more insight into the processes occurring at the surface of InGaAsN films during growth, NF_3 vacuum annealing studies were carried out. Duplicates of the film used to produce the image in Fig. 5 were grown and transferred to the UHV system through an interface chamber with a base pressure of 1×10^{-9} Torr without exposure to air. They were then annealed for 20 min each at 180, 310, 420, 510 and 530 °C in 1×10^{-6} Torr NF_3. Confirmation of NF_3-induced roughening of the InGaAsN surface is shown in Fig. 6. The NF_3 treatment caused the surface to become severely pitted, with a pit density of $1.85 \times 10^{8}\,cm^{-2}$. These features are elongated in the [1 1 0] direction and have an average width and depth of 40.0 by 1.0 nm, respectively.

The InGaAsN samples were examined in situ by X-ray photoemission spectroscopy prior to AFM characterization. Shown in Table 1 are the surface atomic compositions, N/V and In/III ratios, and RMS roughness recorded for the freshly grown (Fig. 5), NF_3-annealed (Fig. 6), and a vacuum-annealed control sample. After the InGaAsN film was annealed in NF_3 at 530 °C, the ratio of the indium to group III concentration increased by about threefold. This may be compared to the sample annealed in vacuum, where the In/III ratio remained constant. At the same time, there is no significant change in the N/V ratio in either of the annealed samples. The concentration of fluorine measured by XPS is below the detection limit for the as-grown and vacuum-annealed samples and is 2.0% after annealing in NF_3. The ex situ AFM measured RMS roughness increases more noticeably when annealed in NF_3 compared to in vacuum, increasing the surface roughness of the as-grown film from 0.18 to 0.33 and 0.21 nm, respectively.

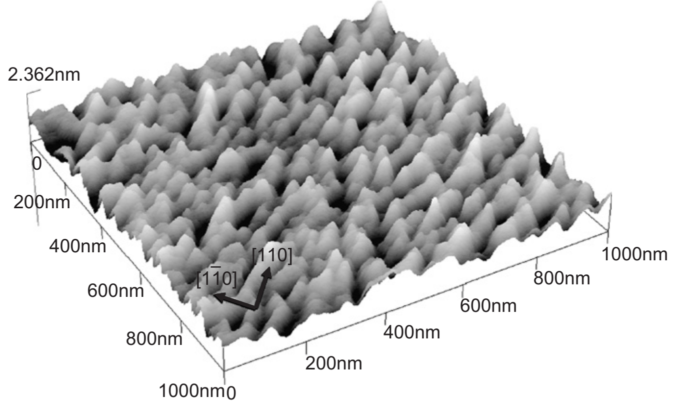

Fig. 6. AFM image of the surface in Fig. 5 after exposure to 1.0×10^{-6} Torr of NF_3 at 180–510 °C. Image size: $1.0 \times 1.0\,\mu m^2$.

X-ray diffraction and PL measurements revealed that changes in the bulk composition of the film occurred after annealing the sample in 1×10^{-6} Torr of NF_3 at 530 °C [17]. It was found that annealing for 1 h caused the bulk nitrogen to increase a lot, from 1.1 to 1.7 mol%, whereas the bulk indium increased slightly, from 5.5 to 5.7 mol%. These findings will be detailed in a separate report [17].

4. Discussion

The incorporation efficiency of nitrogen into InGaAsN using helium-diluted nitrogen trifluoride and tertiarybutylarsine is comparable to that obtained by MOCVD with pure NF_3 and AsH_3 [8]. In the former case, a slightly higher N/V ratio in the feed is needed to achieve the same solid composition [8]. As can be seen in Fig. 1, the N/V ratio in the film increases linearly with the N/V ratio in the feed up to a value of 0.02. After that, further increases in the NF_3 feed ratio have no effect on the solid composition (cf. Fig. 2). At a growth temperature of 550 °C, we were only able to raise the nitrogen in the alloy further by decreasing the feed rate of TMGa and TMIn to the reactor.

The shift of the XRD peak towards GaAs at lower TMGa flow rates in Fig. 2 is attributed to increased nitrogen incorporation. A similar shift may be expected if indium incorporation were to decrease. However, we expect the In incorporation rate into the solid to be unaffected by the presence of NF_3 during growth. An InGaAs calibration run was performed for the standard growth rate of 3.4 μm/h. The XRD-measured In concentration for the InGaAs sample was identical to that estimated for the InGaAsN samples from the XRD and PL data. This is in agreement with Kurtz and coworkers [8], who have shown by secondary ion mass spectroscopy (SIMS) and electron probe microanalysis that the addition of nitrogen using NF_3 does not change the amount of indium incorporated. PL measurements made on selected samples show a decrease in band gap that is consistent with nitrogen incorporation at a constant group III composition. For example, InGaAsN band gaps of 1.253, 1.250 and 1.211 were recorded for a lattice mismatch to GaAs of 0.17%, 0.14% and –0.04%, respectively.

The results obtained in this study suggest that etching of the group III elements occurs on the film surface that

Table 1
Surface composition in atomic % for the as-grown and annealed InGaAsN films determined by X-ray photoemission

Annealing ambient	In	Ga	As	N	F	N/V	In/III	RMS roughness (nm)
As-grown	2.3±0.5	29.7±1.6	57.5±2.1	9.8±1.4	0.0	0.15±0.03	0.07±0.01	0.18
NF_3	9.0±0.5	31.3±1.6	48.2±2.1	9.5±1.4	2.0±0.5	0.16±0.03	0.22±0.01	0.33
Vacuum	2.3±0.5	36.7±1.6	51.0±2.1	10.3±1.4	0.0	0.17±0.03	0.06±0.01	0.21

competes with InGaAsN film growth. In particular, it can be seen in Fig. 3 that the growth rate declines from 3.5 to 2.0 μm/h as the NF_3 feed rate rises from 0.0 to 3.0×10^{-4} mol/min. At higher NF_3 feed rates, the growth rate remains constant, but as shown in Fig. 4, there is an abrupt increase in the surface roughness. Further evidence for fluorine etching of adsorbed Ga and In is obtained upon annealing the InGaAsN film in 1.0×10^{-6} Torr of NF_3 at 530 °C. The AFM image in Fig. 6 reveals that the surface has become severely pitted with an increase in roughness from 0.18 to 0.33 nm. The same anneal conducted in vacuum conditions resulted in an increase from 0.18 to 0.21 nm. We suspect that the interaction of the fluorine with the adsorbed group III elements decreases their diffusion length, leading to 3-D nucleation and island growth, instead of incorporation at step edges as they sweep across the surface. It may be that the etch rates of adsorbed Ga and In with fluorine are similar, such that their incorporation rates into the film are relatively unaffected.

Nonetheless, gas-phase reactions between NF_3 and the group III metalorganic precursors cannot be ruled out, and can explain the observed drop in the film growth rate. Moreover, increased nitrogen incorporation from annealing in NF_3 may increase local strain, resulting in phase separation and the observed undulations on the film surface as detailed in a separate report [17]. Clearly, more detailed studies of dilute nitride growth using NF_3 must be carried out to fully elucidate the growth rate decrease and the possibility of fluorine-induced etching.

In conclusion, NF_3 is an efficient source for incorporating up to 2.0% nitrogen into InGaAsN films grown by MOCVD. Beyond 2.0% nitrogen, it is difficult to achieve lattice matching to GaAs.

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