Nitrogen surfactant effects in GaInP

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The addition of surfactant nitrogen during the growth of GaInP on (001) GaAs substrates produces significant and interesting changes in the optical and morphological properties of GaInP. In particular, multiple peaks are seen in the low temperature photoluminescence (PL) spectra of GaInP/GaInP:N heterostructures. The origin of these multiple peaks is investigated using transmission electron microscopy, energy dispersive spectroscopy, and cathodoluminescence. It is found that a discontinuous In-rich layer forms at the GaInP/GaInP:N interface leading to a $1-6$ nm thick GaInP layer that is $\approx 70\%$ In and has a PL peak energy of <1.7 eV. Cross-sectional cathodoluminescence experiments confirm the existence and composition of the interface layer. The cathodoluminescence experiments also show that the GaInP:N epilayer produces emission at a higher energy than the GaInP epilayer. Cathodoluminescence monochromatic images of surface pyramids indicate that the pyramids emit at higher energy than the surrounding GaInP:N epilayer. Atomic force microscopy of the pyramids reveals the formation of facets with angles of up to 23°. The large misorientation of the pyramids leads to GaInP material that is more disordered than the top epilayer. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1814808]

I. INTRODUCTION

Organometallic vapor phase epitaxy (OMVPE) is the preferred technique for growth of many III-V semiconducting material systems.[1] $Ga_{1-x}In_xP$ (hereafter GaInP) is an important material used in several devices, including high brightness light emitting diodes[2] and the highest efficiency triple junction solar cells.[3] These devices are almost exclusively grown via OMVPE.

GaInP is also of interest because of the CuPt microstructure that develops spontaneously during typical OMVPE growth conditions.[4,5] CuPt ordering consists of alternating {111} planes of Ga and In atoms. It results from $[\bar{1}10]$ oriented phosphorous dimers on the (2×4) reconstructed[6] (001) surface. Ordering is important and of technological interest because of the large decrease it causes in the band gap of GaInP.[7] In order to grow the complex devices that utilize GaInP, it is important to be able to control the amount of CuPt ordering. Surfactants, surface active species with low incorporation into the epilayer, are one tool that can be employed to control ordering during the growth process. They have been shown to decrease CuPt ordering in GaInP.[8] They have also been used in other material systems to decrease roughness[9,10] and improve device quality.[11] In addition, the surfactant Sb has been shown to increase In and Zn

concentration in GaAs (Ref. 12) and to alter growth facets and growth rates during lateral epitaxial overgrowth of GaN.[13]

The use of nitrogen in III-V systems is of technological importance because of the potential for 1.3 and 1.55 μm GaInAsN lasers for use in fiber optics.[14] GaNPAs is a promising material for solar cell devices on Si substrates.[15] Furthermore, the alloy, $GaInP_{1-y}N_y$ is a potentially suitable material for use in heterojunction bipolar transistors because of the possibility of a zero conduction-band offset with GaAs. This has fueled investigation of the optical properties of GaInP with $1\%-2\%$ nitrogen.[16] Nitrogen incorporation in III-V alloys is expected to be small[17] and has been shown to decrease the crystal quality of the epilayer.[18] The incorporation of nitrogen leads to an increase in nonradiative centers with a resultant decrease in the photoluminescence intensity.[19] Nitrogen has been observed to change the surface morphology of GaAs by decreasing the Ga adatom diffusion and subsequently increasing the rate of two-dimensional (2D) nucleation.[14] In AlGaP alloys grown with nitrogen, pyramids form and increase in density with increasing N content.[20] By optimizing growth conditions for nitrogen containing alloys, materials properties can be improved, but many challenges still exist.

Nitrogen has previously been investigated for use as a possible surfactant in GaInP.[21] It was shown that small amounts of N added during growth resulted in a decrease in CuPt ordering. This decrease in CuPt ordering was attributed

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to undimerized N atoms replacing P dimers on the surface, reducing the driving force for ordering. Nitrogen was also shown to impact other material properties besides ordering.

The purpose of this paper is to explain the effects of the surfactant N on the optical and morphological properties of GaInP grown by OMVPE. Dopant level incorporation of N($<2\times10^{18}$ cm^{-3}) into GaInP produces clear changes in the photoluminescence (PL) spectra. Nitrogen decreases the amount of CuPt ordering observed in GaInP and creates a thin, 1–6 nm thick, interfacial layer with different chemical composition from the GaInP:N epilayer. Pyramids are formed on the surface and the density increases with increasing partial pressure of the nitrogen precursor. We have used transmission electron microscopy and cathodoluminescence to clarify the origin of the complex PL spectra and the formation of the interfacial layer.

II. EXPERIMENT

GaInP:N epilayers were grown in an infrared heated, horizontal flow, atmospheric pressure OMVPE reactor on singular [nominally (001)] and vicinal (3°B misoriented) GaAs substrates at a growth temperature of 620 °C. The nitrogen precursor was 1,1 dimethylhydrazine (DMHy). Details of the epitaxial growth have been previously described.[21] Double layer structures, nominally lattice matched to GaAs, were grown consisting of a 300 nm thick GaInP layer followed by a 500 nm thick GaInP:N layer. The DMHy/III ratio was varied from 0 to 60.

Samples were characterized by photoluminescence spectroscopy (PL), cathodoluminescence spectroscopy (CL), transmission electron microscopy (TEM), and atomic force microscopy (AFM). PL experiments were performed at 17 K with excitation by the 514.5 nm line of an Ar$^+$ laser at 10 mW incident intensity. The collected beam was dispersed through a Koken-Kogyo SG-500 monochromator with entrance and exit slits set at 110 μm and detected with a Hamamatsu R636-10 photomultiplier tube.

TEM was performed using a JEM 2010 instrument operated at 200 kV. For TEM experiments, two orthogonal [110] cross-section specimens were prepared using standard procedures. Dark field images were used to examine the GaInP/GaInP:N interface. Energy dispersive x-ray spectroscopy (EDS) was used in conjunction with TEM to characterize the In and N concentrations at the interfacial region.

Plan view and cross-section CL experiments were performed at liquid helium temperature using a commercial system in a scanning electron microscope. The accelerating voltage was either 5 keV or 20 keV and the electron beam current was 400 pA. For each sample, wavelength mapping was done based on the observed CL spectra.

AFM measurements were used to study pyramid formation on the surface using a Digital Instruments dimension 3000 system in tapping mode with 5 nm radius, etched Si tips.

III. RESULTS AND DISCUSSION

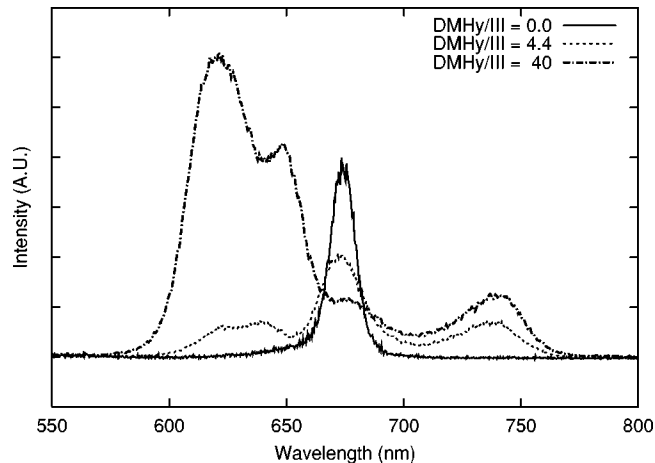It was previously reported that nitrogen is not significantly incorporated into GaInP, yet even for small concen-

FIG. 1. Normalized 17 K PL spectra from samples grown with several DMHy/III ratios.

trations CuPt ordering was reduced.[21] PL spectra for samples with varying DMHy/III ratios are shown in Fig. 1. The addition of DMHy during growth and the incorporation of small amounts of N($<2\times10^{18}$ cm^{-3}) into GaInP result in observable changes in the PL spectra. Moderately ordered GaInP (DMHy/III=0) is seen to emit at 674 nm (1.84 eV). This peak is seen in the spectra from all of the double layer structures at approximately the same wavelength and is from the 300 nm thick, ordered GaInP layer grown first in each sample. The emergence of a long wavelength peak and the appearance of peaks with shorter wavelengths than the ordered GaInP layer are direct consequences of adding DMHy during growth. The addition of N into bulk GaInP is expected to decrease the band gap;[16] however, the small amount incorporated into GaInP for this study would only lower the band gap by $\approx$2 meV. This is much smaller than the observed shift in PL for the GaInP:N layer.

The 740 nm peak (1.68 eV) has been attributed to a thin In-rich interfacial region that forms at the GaInP/GaInP:N interface.[21] High resolution TEM of the interface is seen in Fig. 2. An interfacial layer is, indeed, observed. The layer is not continuous but fluctuates across the sample with thicknesses varying from a few atomic layers to about 6 nm. A
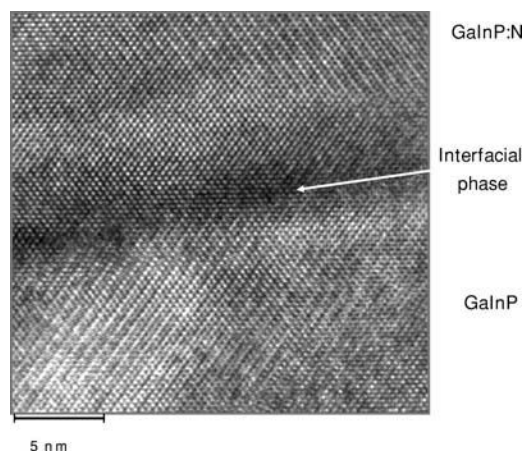

FIG. 2. High resolution TEM micrograph showing the In-rich interface that forms between GaInP and GaInP:N layers.
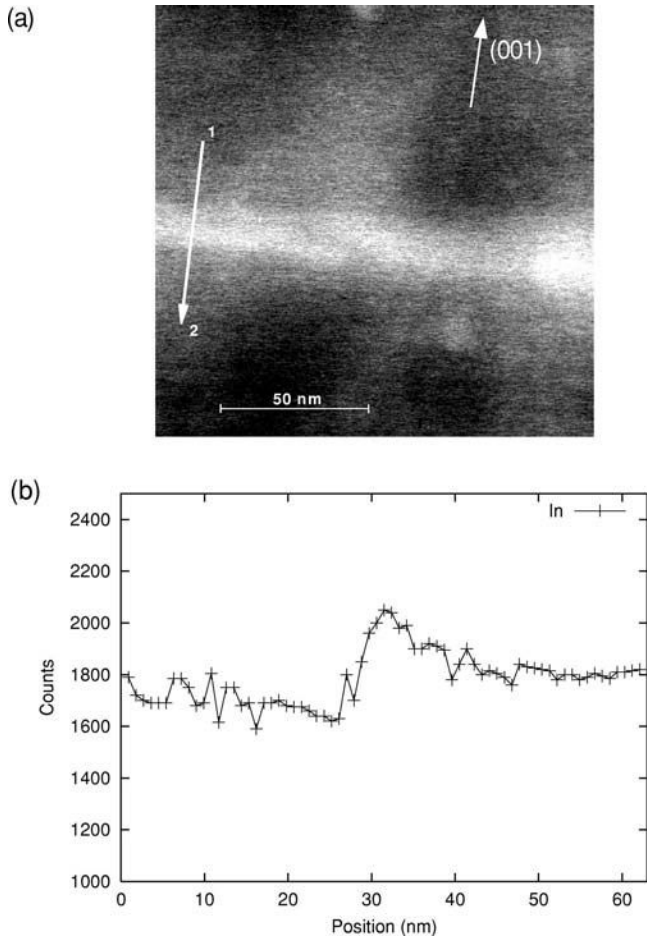
FIG. 3. TEM (a) and EDS (b) of the interfacial layer formed between the GaInP and GaInP:N layer. EDS shows that the In content is increased by 25% at the interface.

FIG. 4. PL and CL spectra from singular samples grown with DMHy/III =40. The CL spectra were taken over a 120×120 μm^2 area. 20 keV CL closely matches the PL and helps explain the origin of the multiple peaks.

transmission electron micrograph and an EDS scan taken across the interface are shown in Fig. 3. The bright region in Fig. 3(a) corresponds to an In-rich layer. EDS data in Fig. 3(b) indicate that the In content is increased through the interfacial layer. Similar EDS scans for nitrogen were unable to detect the presence of any nitrogen indicating that N is below the detectability limit for EDS. The 740 nm peak from PL experiments corresponds to a composition of $\approx 70\%$ indium (compared to 49% for lattice matched material). This agrees with the 25% increase in the In concentration seen in the EDS data to within the experimental limits.

The mechanism for formation of the interfacial layer is not well understood; however, similar interfacial regions are observed in InGaAs (Ref. 22) and InGaSb.[23] Both of these material systems exhibit In surface segregation. The cause is still under discussion,[24] but is thought to occur from In atoms in a buried layer switching with surface atoms and then remaining on the surface. As growth continues, an In-rich layer forms initially. Then a fraction of the In on the surface exchanges at the growth front until a steady state is reached and In concentration becomes uniform at ≈ 0.49. The interfacial layer in GaInP:N is seen most strongly in samples grown with an interrupt of growth between layers. After growth of the GaInP layer, growth was stopped by switching the group III precursors out of the growth chamber. The P source re-
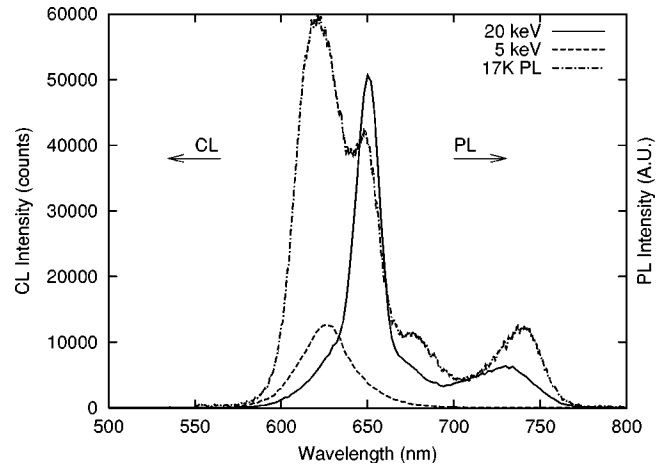
mained flowing through the chamber and DMHy was switched into the chamber for 3 min before growth resumed. During these 3 min, N on the surface is postulated to have caused In atoms to segregate to the surface due to the much weaker In–N bonds as compared with Ga–N bonds. Once growth of the GaInP:N layer commenced, In atoms would float on the surface during growth of a few monolayers, resulting in the In-rich layer before steady state is reached.

The emergence of two peaks at shorter wavelength than for ordered GaInP has proven more difficult to understand. PL and CL experiments were done to gain insight into the effects of N on the growth of GaInP. Figure 4 shows PL and CL spectra for samples grown with DMHy/III=40. The CL spectra were acquired over a 120×120 μm^2 area. By varying the accelerating voltage in the CL experiments (and thus the penetration depth of the electron beam) we can probe the separate layers. Understanding the penetration depth of both PL and CL experiments is important in order to properly interpret the observed spectra. PL excited at 514.5 nm is expected to have a shallow penetration depth of ≈ 100 nm (Ref. 25) at an incidence angle of 30°. The CL penetration depth depends on the accelerating voltage. In GaAs, the expected penetration depth for 5 keV electrons is 245 nm. For 20 keV the penetration depth would be over 2400 nm.[26] GaInP would be expected to be similar.

For CL at 5 keV, where the penetration depth is only ≈ 245 nm, only one peak at 625 nm is observed in the CL spectrum. It matches the dominant, high energy peak observed in PL. Clearly, the 625 nm peak in PL and CL originates from a near surface region. As the accelerating voltage is increased to 20 keV (penetration depth >2400 nm) the CL spectrum exhibits additional peaks. Since the penetration depth is now greater than the combined epilayer thicknesses, peaks corresponding to all of the several layers should be observed. While evidence of the 625 nm peak seen in the 5 keV spectrum is still present at 20 keV (high energy shoulder), an intense peak at 650 nm is the dominant feature in the 20 keV spectrum. A low energy shoulder at 674 nm corresponds to the PL peak at the same wavelength. This is from the, buried 300 nm thick ordered GaInP epilayer. Peaks at
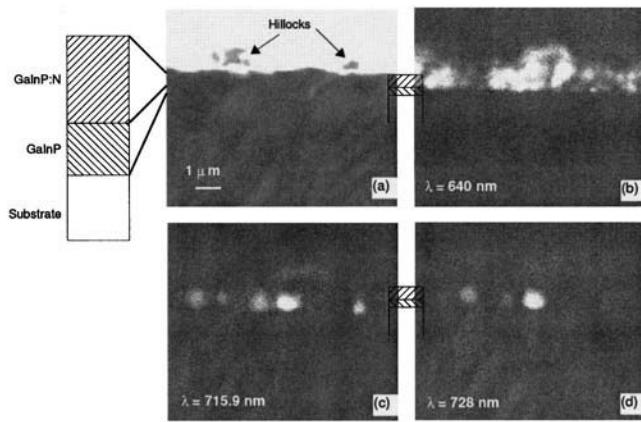
FIG. 5. Cross-sectional CL of GaInP:N/GaInP with DMHy/III=40. (a) SEM image and monochromatic CL images at (b) 640 nm, (c) 715.9 nm, and (d) 728 nm. Note the expanded scale schematically showing the layer structure on the left. The 640 nm emission clearly comes from the top 500 nm of the sample which corresponds to the GaInP:N epilayer.

716 nm and 728 nm are also observed. It is clearly seen that the 4 K CL spectrum at 20 keV closely matches what is observed in 17 K PL measurements.

Cross-sectional CL results shown in Fig. 5 give definitive evidence of where the PL peaks originate. Figure 5(b) shows the monochromatic CL image taken at 640 nm. The emission is seen to come entirely from the top 500 nm of the sample corresponding to the GaInP:N layer. Clearly, this layer is the source of the 650 nm peak seen in both CL and PL experiments. This is a direct confirmation that the presence of N acts to produce a less ordered layer than for GaInP grown without N. However, the decrease in disorder resulting from growth with N was previously overestimated[21] due to the complex nature of the PL spectra.

CL also confirms the existence of a discontinuous interfacial layer at the GaInP/GaInP:N interface. CL images were taken at both 715.9 nm [Fig. 5(c)] and 728 nm [Fig. 5(d)]. The circular pattern observed at these wavelengths results from the discontinuous nature of the In-rich interfacial layer. The spread in wavelength indicates that the In content varies in this layer. The radius of the spots is determined by the interaction volume of the electron beam and the minority carrier diffusion length in GaInP.

The origin of the three longer wavelength peaks seen in PL is also straightforward to understand after examining Figs. 4 and 5. The GaInP:N epilayer is obviously the source of the 650 nm peak in PL, and the layer at the interface between GaInP and GaInP:N is the source of the long wavelength peaks. The buried, ordered GaInP layer is responsible for the 670 nm peak.

The fourth PL peak at 625 nm (1.98 eV) still requires explanation. Figure 4 indicates that some region of the sample is emitting at 625 nm, but the location was not clearly identified in the cross-section experiment. Figure 6(b) shows the CL spectrum from a 20×20 μm^2 region of the surface surrounding a pyramid. Pyramids are formed even at low partial pressures of DMHy and increase in density with increasing DMHy partial pressure. At a DMHy/III ratio of 40, the pyramid surface density is greater than 5
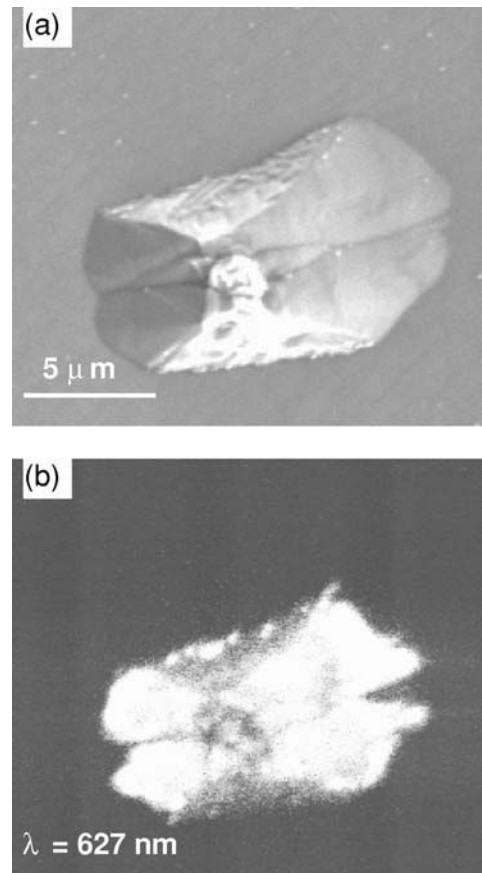

FIG. 6. SEM and 5 keV CL plan view image of a pyramid on the surface of GaInP:N with DMHy/III=40. (a) SEM micrograph, and (b) monochromatic CL image at 627 nm. The long axis of the pyramid is oriented in the [110] direction.

$\times 10^6$ cm^{-2}. CL wavelength mapping of the pyramid region clearly shows that the pyramid emits at a shorter wavelength than the epilayer [Fig. 6(b)]. Thus, the pyramids are the source for the 625 nm PL peak. Pyramids have been seen in the growth of several N containing systems including AlGaPN (Ref. 20) and are likely caused by an increase in lattice defects formed with the incorporation of N. These defects then provide a mechanism for 2D nucleation and growth of the pyramids.

The data obtained from CL experiments helped to explain the origin of the multiple peaks seen in PL. However, the 5 keV CL spectrum in Fig. 4 would be expected to show both a peak from the pyramids and from the top epilayer, but only one peak is observed. A peak from the GaInP:N layer is not fully resolved in the 5 keV spectrum, but a long wavelength shoulder that corresponds to the GaInP:N is observed in the spectrum. The pyramid density was very high for this sample and the emission from the pyramids dominates the spectrum at 5 keV because of the shallow penetration depth. Since the PL penetration is also shallow, and because of the high surface density of pyramids, a significant contribution should be observed in the PL spectrum as well. This is clearly seen in Fig. 1. The peak at 625 nm does not vary in wavelength with N, but does increase in intensity. The increase in PL peak intensity at 625 nm is due to the increased
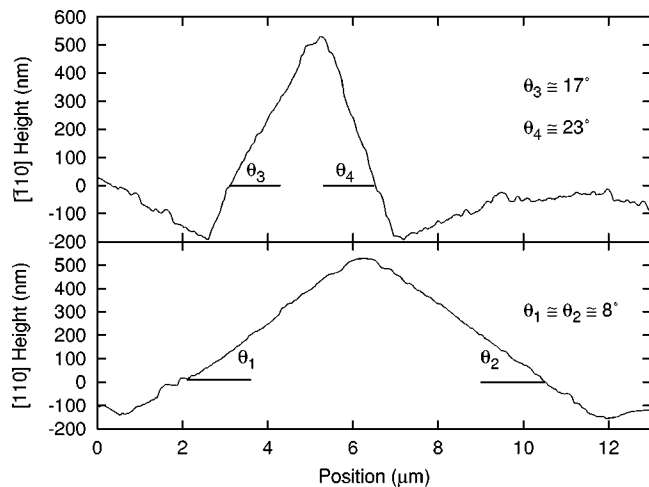
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FIG. 7. AFM cross sections of a pyramid formed with DMHy/III=40. [110] cross section indicates the facets are the same and about 8°. The [$\bar{1}$10] cross section shows asymmetry in the facets and much steeper angles than for [110].

density of pyramids in samples grown with larger DMHy/III ratios. At 20 keV, the penetration depth is sufficiently deep to allow the several layers to be seen.

Two possible explanations have been considered for why the pyramids emit at higher energies than the epilayers. First, the pyramids may be compositionally different from the epilayer. In this case the pyramids would have to be Ga-rich compared to the epilayer. Second, the pyramids could be highly disordered GaInP. No data exist to show that the pyramids are Ga rich, but compelling AFM data indicate the pyramids may indeed be disordered GaInP.

Figure 7 shows AFM cross-section data on a pyramid taken in both the [110] and the [$\bar{1}$10] directions. The long axis of the pyramid in Fig. 6 is in the [110] direction. AFM indicates the [110] direction has symmetric facets with angles of 8°. The [$\bar{1}$10] direction exhibits much steeper angles and is asymmetric. The asymmetry is most likely due to the substrate being misoriented by 3° in [110] direction. This would give a 6° difference for oppositely oriented facets, which is what is observed in the AFM scans. The effect of misorientation on ordering in GaInP has previously been studied.[27] It was shown that the maximum amount of CuPt ordering occurs on substrates misoriented by 3° in the *B* direction and decreases for larger misorientations. At 8° the sample would be significantly less ordered than for 3°, and for angles greater than 15° little ordering would be expected. Murata *et al.*[27] argued that at large angles, surface plateaus are short and step edges inhibit [$\bar{1}$10] P dimer formation. The pyramids therefore are very likely highly disordered GaInP, resulting in emission at shorter wavelength than for the top epilayer.

IV. CONCLUSIONS

The surfactant nitrogen has been used in the growth of GaInP to modify the amount of CuPt ordering. It is found that N does, indeed, disorder the epilayer. Nitrogen also promotes pyramid growth on the surface. The high angle pyra-

midal facets cause the GaInP to be highly disordered, resulting in an emission energy of ≈2.0 eV, higher than for the surrounding epilayer.

An In-rich interfacial layer is formed between the GaInP and GaInP:N layers. EDS of the interface reveals that the layer is In rich, in agreement with the 1.7 eV peak observed in PL and CL experiments. The mechanism behind the formation of this interfacial layer is not fully understood. It may result from In segregating to the surface when DMHy is introduced into the system during the growth interruption between epilayers. The surface concentration of In is increased and when growth commences the In atoms are incorporated into the first few nanometers of the epilayer until a steady state growth condition is achieved.

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