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InGaAsN: A Novel Material for High-Efficiency Cells and Advanced Photonic Devices

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InGaAsN: A Novel Material for High-Efficiency Solar Cells and Advanced Photonic Devices

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Abstract Follows

Abstract

This report represents the completion of a 6 month Laboratory-Directed Research and Development (LDRD) program that focused on research and development of novel compound semiconductor, InGaAsN. This project sought to rapidly assess the potential of InGaAsN for improved high-efficiency photovoltaic. Due to the short time scale, the project focused on quickly investigating the range of attainable compositions and bandgaps while identifying possible material limitations for photovoltaic devices.

InGaAsN is a new semiconductor alloy system with the remarkable property that the inclusion of only 2% nitrogen reduces the bandgap by more than 30%. In order to help understand the physical origin of this extreme deviation from the typically observed nearly linear dependence of alloy properties on concentration, we have investigated the pressure dependence of the excited state energies using both experimental and theoretical methods. We report measurements of the low temperature photoluminescence energy of the material for pressures between ambient and 110 kbar. We describe a simple, density-functional-theory-based approach to calculating the pressure dependence of low lying excitation energies for low concentration alloys. The theoretically predicted pressure dependence of the bandgap is in excellent agreement with the experimental data. Based on the results of our calculations, we suggest an explanation for the strongly non-linear pressure dependence of the bandgap that, surprisingly, does not involve a nitrogen impurity band. Additionally, conduction-band mass measurements, measured by three different techniques, will be described and finally, the magnetoluminescence determined pressure coefficient for the conduction-band mass is measured.

The design, growth by metal-organic chemical vapor deposition, and processing of an $\text{In}_{0.07}\text{Ga}_{0.93}\text{As}_{0.98}\text{N}_{0.02}$ solar cell, with 1.0 eV bandgap, lattice matched to GaAs is described. The hole diffusion length in annealed, n-type InGaAsN is 0.6-0.8 μm , and solar cell internal quantum efficiencies $> 70\%$ are obtained. Optical studies indicate that defects or impurities, from doping and nitrogen incorporation, limit cell performance.

Deep level defects in MOCVD-grown, unintentionally doped *p*-type InGaAsN films lattice matched to GaAs were investigated using deep level transient spectroscopy (DLTS) measurements. As-grown *p*-InGaAsN showed broad DLTS spectra suggesting that there exists a broad distribution of defect states within the band-gap. Moreover, the trap densities exceeded 10^{15} cm^{-3} . Cross sectional transmission electron microscopy (TEM) measurements showed no evidence for threading dislocations within the TEM resolution limit of 10^7 cm^{-2} . A set of samples was annealed after growth for 1800 seconds at 650 °C to investigate the thermal stability of the traps. The DLTS spectra of the annealed samples simplified considerably, revealing three distinct hole trap levels with energy levels of 0.10 eV, 0.23 eV, and 0.48 eV above the valence band edge with trap concentrations of $3.5 \times 10^{14} \text{ cm}^{-3}$, $3.8 \times 10^{14} \text{ cm}^{-3}$, and $8.2 \times 10^{14} \text{ cm}^{-3}$, respectively. Comparison of as-grown and annealed DLTS spectra showed that post-growth annealing effectively reduced the total trap concentration by an order of magnitude across the bandgap. However, the concentration of a trap with an energy level of 0.48 eV was not affected by annealing indicating a higher thermal stability for this trap as compared with the overall distribution of shallow and deep traps.

Key Words: Photovoltaics, InGaAsN, compound semiconductor,

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I. Introduction

Increased deployment of satellites for communications and surveillance applications has led to explosive growth in the demand for high efficiency solar cells to power these platforms. Today's satellites are increasingly power hungry, since on-board power capacity directly translates to mission capability. In response to this demand, compound semiconductors have revolutionized the space photovoltaic business over the last five years by offering higher efficiency solar cells than achievable by competing technologies. Their success comes through the use of "bandgap engineering" to build multilayer structures tailored to efficiently convert photons from different bands of the solar spectrum into electricity. While this approach has led to 2- and 3-junction "tandem" solar cells with efficiencies of 22-24%, further advances have been limited by the range of bandgaps obtainable with conventional III-V compound semiconductor alloys composed of Al, Ga, In and As, P. Staff from Sandia and AFRL have identified a way to introduce small amounts of nitrogen into the group V mix to create a new class of compound semiconductors of the type InGaAsN. The small percentage of N, with a correspondingly small percentage of In added to maintain lattice matching, significantly lowers the materials bandgap, thereby opening up considerable new flexibility for bandgap engineering of new photonic devices in addition to higher-efficiency photovoltaics.

Our effort consisted of both a theoretical and an experimental component. As detailed below, part of our theoretical emphasis was to develop an in-depth understanding of materials bandstructure, including bowing parameters for ternary alloys. These calculations yielded critical input parameters to further calculations of optical gain in a number of relevant III-N heterostructures. Yet another area of theoretical focus was to apply ab-initio calculations to study extended defects in III-N materials. A major focus of our experimental effort was to understand the optical properties of the III-N materials, through the use of experimental techniques such as time-resolved photoluminescence and magneto-luminescence. X-ray k-mapping was also performed on a number of III-N epilayers to gain an understanding of materials evolution, strain and cracking mechanisms in these materials. Finally, a number of experimental studies were undertaken to gain insight into how these materials respond to post-growth processing. These studies include ion implantation for the purpose of enabling p- or n-type doped materials, plasma etching to enable patterned materials for various device applications, and post-growth annealing to activate dopant species and/or more generally alter the optical or electrical properties of the materials.

II. Optical properties of InGaAsN: A new 1eV bandgap material system

A. Introduction

The quaternary alloy system, InGaAsN, is a new material system that appears to have many exciting and important device applications. Because of a large negative bowing parameter,^{1,2} the addition of small amount of nitrogen to the 1.4 eV bandgap energy GaAs system lowers the energy! With the bandgap energy of GaN $\sim$ 3.5 eV, normally, one would expect that the GaAsN alloy bandgap energy would increase with nitrogen content. Besides also lowering the bandgap energy, adding indium to GaAsN strain compensates the effect of nitrogen, resulting in a material system with bandgap energies $\sim$ 1eV and lattice matched to GaAs! The InGaAsN alloy system has been identified as a key candidate material for long wavelength laser systems³⁻⁵ and high-efficiency multi-junction solar cells.^{6,7} While light emitting diodes (LED) based on InGaAsN have not yet been reported, this could be an ideal system to provide infrared wavelength LED's. Lattice matching allows the design of optoelectronic devices without the inherent problems found in strained systems. Of prime importance is the role of the nitrogen isoelectronic atom: (1) What is the origin of the large bandgap reduction? (2) Are the states extended (band-like) or localized (impurity-like)? (3) How is the nominally light GaAs conduction-band effective mass $m_c = 0.067$ affected by the addition of nitrogen? For optimum device performance, a better understanding of the electronic properties of this type of alloy system is required.

Both first-principles⁸⁻¹⁰ and empirical¹¹⁻¹⁴ theoretical treatments for this material system have concentrated on understanding the dependence of the bandgap energy on nitrogen composition. In the first part of this paper we review previously reported¹⁵ pressure dependent photoluminescence (PL) data together with a first principles local density approximation (LDA) calculation for the band structure and its pressure dependence. It will be shown that, while it is well known that bandgap energies calculated by the LDA method are not accurate, the predicted pressure dependence of the bandgap energy is in excellent agreement with experiment. Similar observations have been reported for silicon.¹⁶ Because of this good agreement, the character of the states is accurately described and we also have confidence that this technique could be useful for understanding the properties of other low concentration alloy systems.

In the second part of the paper, we present conduction-band effective mass determinations using different three different experimental techniques: (1) Studying the bandgap energy dependence as a function of InGaAsN/GaAs quantum-well width. (2) Photoreflectance measurements of the ground state and excited state energies of an InGaAsN/GaAs quantum well for various quantum-well widths. (3) Magnetoluminescence measurements of the magnetic field dependence of the InGaAsN exciton diamagnetic shift in bulk epilayers. Additionally, the pressure dependence of the conduction band-mass has also been measured using the magnetoluminescence method.

B. Experimental

The structures were grown in a vertical flow, high speed rotating disk, EMCORE GS/3200 metalorganic chemical vapor deposition (MOCVD) reactor. The $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ films were grown using trimethylindium (TMIn), trimethylgallium (TMG), 100% arsine and dimethylhydrazine (DMHy). Dimethylhydrazine was used as the nitrogen source since it has a lower disassociation temperature than ammonia and has a vapor pressure of approximately 110 torr at 18°C. Unintentionally doped InGaAsN was p-type. InGaAsN films for Hall and optical measurements were grown on semi-insulating GaAs orientated 2° off (100) towards $\langle 110 \rangle$. Lattice matched ($\Delta a / a < 8 \times 10^{-4}$) films were grown at 600°C and 60 torr using a V/III ratio of 97, a DMHy/V ratio of 0.97 and a TMIn/III ratio of 0.12. The growth rate was 10 Å/s. These conditions resulted in films with an indium mole fraction of 0.07 ± 0.005 and a nitrogen mole fraction of 0.022 ± 0.003 . The composition was determined by calibration growths of GaAsN and InGaAs along with double crystal x-ray diffraction measurements. The nitrogen composition of bulk films was also confirmed from elastic recoil detection measurements. A significant increase in photoluminescence intensity was observed from these films following a post-growth anneal. Ex-situ, post-growth anneals were carried out in a rapid thermal anneal system under nitrogen using a sacrificial GaAs wafer in close proximity to the InGaAsN sample.

The photoluminescence intensity was a maximum for samples annealed either at 700°C for 2 minutes or at 650°C for 30 minutes. Similar results have been reported by Rao et.al.¹⁷ Transmission electron microscopy measurements indicate that the samples are random and no evidence for clustering or phase separation was observed.¹⁸ The pressure was generated using a small BeCu piston-cylinder diamond anvil cell,⁸ .75-mm-diameter and 12.5-mm-height.¹⁹ Methanol, ethanol, and water in a ratio of 16:3:1 was used for the pressure medium.²⁰ The shift in the fluorescence of a small chip of ruby placed in the pressurized volume was used to calibrate the pressure at 4K with an accuracy of ± 0.5 kbar.²¹ A single 600- μm -diameter optical fiber, butted up against one of the diamonds, brought the 1 mW power 5145-nm-wavelength laser to the sample and also collected the PL signal from the sample. A beam splitter system was used to direct the PL signal to an optical monochromator. Depending on the bandgap energy, two liquid-nitrogen-cooled detectors were used to detect the PL signal. For low pressure regimes, where the bandgap energies were near or below 1 eV, a NORTH-COAST EO-817L Ge-detector was employed, while at higher pressures, a standard CCD array was used.

Photoreflectance spectra were obtained for a variety of MOCVD InGaAsN/GaAs MQW structures. For these experiments, the optical pump source was a blue LED having a 15 degree divergence angle and a peak emission wavelength of 470 nm (Nichia Chemical Industries part number NSPB 300A.). The LED was driven by a square-wave current source operating at 15 mA and 325 Hz. The sample reflectance was measured using a 10 W tungsten-halogen lamp followed by a 0.25-m grating monochromator in conjunction with an InGaAs photodiode detector and a lock-in amplifier.

C. Discussion

A typical low temperature (4K) PL spectrum for 2% nitrogen in InGaAsN lattice matched to GaAs is shown in Fig. 1. As can be seen, the 4-K bandgap energy is near 1150 meV, which is significantly less than the 4-K GaAs bandgap energy $E_g \approx 1515$ meV. The full-width-half-maximum (FWHM) PL linewidth is about 22.5 meV. As mentioned above, the PL intensity increased significantly with annealing. Other optical parameters, such as the FWHM and PL-peak energy appear to remain unaffected by our annealing process. The pressure dependence of the bandgap energy shift data, as determined from by the PL-peak energy, is shown in Fig. 2 as solid circles. The pressure data ranged between ambient and 110 kbar. The solid curve drawn through the data is discussed in the following section, however, it should be noted here that similar studies for GaAs/AlGaAs or InGaAs/GaAs quantum wells exhibit a G-X crossing near 40 kbar. For pressures greater than 40 kbar, the X-point becomes the conduction-band ground state and because of large non-radiative recombination paths at the X-point, the PL signal normally disappears.²² For the InGaAsN pressure data shown in Fig. 2, this is obviously not the case. Thus, to be able to understand the behavior of the InGaAsN system, we need information about its band structure, which will be discussed in Sec C.1. Section C.2 presents experimental measurements and estimates for 2% nitrogen InGaAsN alloy conduction-band effective mass while Sec. C.3 discusses the pressure dependence of the same conduction-band effective mass.

Figure 1. Low temperature (4K) PL spectrum for an annealed InGaAsN sample with 2% N. The FWHM = 22.5meV.

Figure 2. Experimental (dots) and theoretical (solid line) shift of the bandgap energy on pressure at 4K for 2% N in InGaAsN.

C.1 Band Structure of InGaAsN alloys

In order to model the band structure for the InGaAsN system, we used the Vienna Ab initio Simulation Package²³⁻²⁶ (VASP) to perform first-principles electronic structure calculations based on the Kohn-Sham density functional theory with plane wave basis sets, ultrasoft pseudopotentials,²⁷ and the local density approximation for the exchange-correlation functional. In construction of the pseudopotentials, the Ga 3d electrons were treated as valence electrons in order to accurately represent any effects of a near resonance with the nitrogen 2s level that has been observed in GaN.²⁸ We modeled the InGaAsN system in the experimentally relevant concentration range using a series of supercells of the zincblende GaAs structure each with a single arsenic replaced by a nitrogen. The lattice constants of the supercells were varied to simulate the effects of pressure, and for each cell, the ionic positions were relaxed using first-principles forces until the residual forces were less than 20 meV/Å. In all cases, we found that the nitrogen atom remained in the symmetric position during relaxation. In order to compare to experimental data, which is taken as a function of pressure, an ab initio calculation of the system pressure was performed. We have investigated supercells with the following stoichiometries: Ga₃₂As₃₁N, Ga₆₄As₆₃N, Ga₁₀₈As₁₀₇N, and Ga₁₂₈As₁₂₇N. These cells correspond to nitrogen concentrations of 3.13, 1.56, 0.93 and 0.78%, with the nitrogen atoms ordered in simple cubic, fcc, bcc, and simple cubic lattices respectively. In contrast, the nitrogen atoms in the experimental system are believed to be nearly randomly distributed.¹⁸ However, we found that calculated band structures of our supercells were qualitatively similar despite their differing symmetries, indicating that the nitrogen atoms interact weakly with each other at these low concentrations. Therefore, we believe that our artificially ordered supercells provide an adequate model of the near-

band-gap electronic structure of the disordered experimental system. Likewise, we have ignored the presence of In in the experimental system (except for indirect effects due to the change in lattice constant, as will be discussed below). This is justified since experimental studies of InGaAs alloys indicate that the low concentration of indium found in the experimental InGaAsN system has a small effect on the electronic properties.^{3,4}

Figure 3 shows a representative band structure for the 3.13% system. It should be noted that the band structure is plotted with respect to the Brillouin zone of a 64-atom cell. Since the nitrogen substitution breaks the symmetry of the underlying zincblende structure, there is no uniquely defined way to “unfold” the band structure into the Brillouin zone of the primitive 2-atom zincblende unit cell. The high symmetry points of the primitive GaAs cell fold into the G-point of the 64-atom cell, and therefore in the presence of a real symmetry breaking term (such as produced by nitrogen substitution), we expect interaction between the resulting levels. The valence band and the conduction band are indicated by the heavy solid line. The conduction band is well separated from the other bands throughout most of the Brillouin zone, and it is quite dispersive with a bandwidth more than 1 eV. Likewise, the bands above the conduction band show a substantial amount of dispersion, and there is no evidence of a flat impurity-like band anywhere above the conduction band. The absence of a nitrogen derived impurity-like state is supported by a decomposition of the wave-functions in terms of atomic-like orbitals, which shows that the conduction band has about 5% of its weight on the nitrogen atom, which is by far the highest fraction of any of the bands above the gap. The calculated bandgap is only 0.12 eV, while the experimental bandgap is of order 1 eV for this concentration of nitrogen. This large error in the bandgap is a well known problem of the LDA. A central result of this paper is that despite this large error in the absolute magnitude of the bandgap, the change in bandgap with lattice constant is in excellent agreement with experiment (see Fig.2).

Figure 2 compares experimental data to results of our theoretical model. The agreement between theory and experiment is excellent. In order to make a meaningful comparison, some nontrivial analysis of the theoretical calculations is required. The basic principle of this analysis is to treat the lattice constant and nitrogen concentration as independent variables, while the bandgap and pressure are treated as dependent variables. The dependent variables are then shifted to remove known LDA errors. In order to obtain results applicable to the 2.0% experimental nitrogen concentration, the bandgap and the pressure are linearly interpolated between the results of 128-atom (1.56% N) and 64-atom (3.13% N) supercells for each lattice constant. Then, results obtained at the experimental lattice constant of GaAs are taken as the reference (assumed to correspond to the experimental zero of pressure), and we plot the change in bandgap against the change in pressure. This procedure compensates for two well known errors of the LDA: (1) The bandgap is severely underestimated, as discussed above. (2) The lattice constant is underestimated by about 1%. The second error may seem to be insignificant compared to the errors in LDA results for some other quantities, but it corresponds to about a 20 kbar error in pressure, which is significant on an experimental scale. Since the experimental GaAs lattice constant is used, this procedure also helps to implicitly compensate for neglecting the In, which is added to the experimental system to match the lattice constant to that of GaAs.

Figure 3. First principles local density approximation calculation for 3.3% nitrogen InGaAsN alloy. The solid lines, top and bottom, are respectively the conduction and valence bands.

The approach described here could prove useful for similar systems. However, we believe that a reason for the success of our approach is that, with the exception of the largest nitrogen concentration at the largest lattice constant, all of our model systems have a positive bandgap. Previous first-principles calculations for the GaAsN system⁸⁻¹⁰ have used high nitrogen concentrations in order to obtain smaller model systems, which are computationally less demanding. At these higher concentrations, the LDA bandgap error is so severe that computed band structures do not have a bandgap. This artificial bandgap collapse leads to unphysical occupations of the electronic states (i.e. conduction-band-like states are occupied, while valence-band-like states are unoccupied), producing a significant error in the electronic charge density. In this regime of strongly negative LDA bandgaps, we are not confident that our simple LDA-based approach to computing the pressure dependence of excited state energies could be applied fruitfully.

A remarkable feature of Fig. 2 is the strongly non-linear dependence of the gap on the pressure. This is in marked contrast to the parent GaAs material and provides additional evidence, beyond the large reduction in the bandgap, that a few percent of nitrogen is producing remarkable changes in the material. In order to understand this nonlinearity, it is necessary to study additional bands above the conduction band. Figure 4 shows the theoretical pressure dependence of the G-point energies of several additional

bands treated with the same analysis that was used for the conduction band in Fig. 2. Eight energy bands of the system are shown, but these fall into five degenerate groups. The figure shows three singlet states (filled circles), a doublet (open squares), and a triplet state (open triangles).

Figure 4. Theoretical pressure dependence of the conduction-band states near the bandgap energy minimum for 2% nitrogen GaAsN alloy. There are three singlets (filled circles), a doublet (open squares), and a triplet state (open triangles).

A common origin of nonlinear behavior of energy levels as a function of a parameter (such as pressure) is band repulsion. Band repulsion results from the mixing (hybridization) of bands in the same representation of the crystal symmetry group in such a way that level crossings are replaced with non-intersecting horizontal curves separated by a gap-like region. In Fig. 4, the highest singlet on the left and the triplet on the upper right bend downward due to repulsion from higher energy bands that have been omitted from the figure in order to improve its clarity. Whether the upper two singlets cross or repel at about 80 kbar can not be determined from the limited number of points that we have calculated, but if they repel, the effect is not very strong. We have chosen to show the bands as crossing in order to aid the eye in following their relationship with the doublet and the triplet. These assignments were chosen by comparing our results for

various nitrogen concentrations with results for pure GaAs with the appropriately folded Brillouin zone. This comparison also allows useful, but non-rigorous, assignments of the low energy GaAsN bands at the G-point to special points of the primitive 2-atom GaAs Brillouin zone that are folded into the G-point. For the bands shown in Fig. 4, we propose the following assignments: (1) The bottom singlet corresponds to the G-point of the fundamental cell. (2) The second singlet on the left hand side (the third singlet on the right) plus the triplet correspond to a split quartet formed from the 4 L-points $(1\ 1\ 1)$, $(1\ -1\ -1)$, $(-1\ 1\ -1)$, and $(-1\ -1\ 1)$. (3) The remaining singlet plus the doublet correspond to a split triplet consisting of the three X-points (100), (010), and (001). In regions of band repulsion, for example, the character of different bands becomes mixed, and thus these assignments should not be taken too literally. However, we feel that they provide useful labels and help in interpreting the data.

With one exception, all of the bands within a few eV of the gap are observed to regain the degeneracies of pure GaAs to within of a few hundredths of an eV by the time our largest cell (0.78% N concentration) is reached. The exception is the L-derived singlet, which remains split off from the triplet by about 0.1 eV. This suggests that this singlet may evolve into the impurity state observed at very low nitrogen concentrations.^{29,30} However, as mentioned above, this state does not act like an impurity state at the technologically interesting concentrations around 2%. Furthermore, the L-derived singlet rises faster than the conduction band throughout the studied pressure range, and we do not see the upward curvature that would be expected if it was repelled by the conduction band. Therefore, we believe that repulsion between the L-derived singlet and the conduction band contributes at most a small amount to the nonlinearity of the conduction band. In contrast, Fig. 4 demonstrates almost textbook repulsion between the X-derived singlet and the conduction band at pressures over 100 kbar, and it is likely that this repulsion continues to lower pressures, even though the effect is obscured by the additional repulsion between the X-derived singlet and a higher state. Based on these observations, we propose that repulsion from the X-derived singlet is the chief cause of the experimentally observed nonlinear dependence of the bandgap on pressure. Based on the above, we conclude that the nonlinear dependence of the bandgap on pressure does not result from localized nitrogen states. Finally, we note that our results are consistent with recent reflectance measurements which show some of the predicted higher energy states.^{31,32}

C.2 Conduction-band mass for InGaAsN alloys

There are three convenient methods of using optical measurements for masses, and they are: (1) Study the change in luminescence energy in quantum well structures as a function of the quantum-well width. (2) Measure the quantum well energies by photoreflectance measurements as a function of quantum-well width. (3) Measure exciton diamagnetic shifts as a function of magnetic field. A fourth experimental method, low-temperature measurement of far-infrared cyclotron resonance from n-type samples was attempted, but because of the low transport mobility ($\sim 400\text{ cm}^2/\text{V}\cdot\text{sec}$), we not able to observe any cyclotron resonance. However, the question regarding the effect of on the conduction-band mass, if any, from adding a small amount of nitrogen to GaAs will now be addressed.

Figure 5. Luminescence energy versus quantum wells width L for InGaAsN/GaAs single quantum wells at 4K. The smooth curve drawn through the data is provided an aid to the eye.

A series of nominally 2% nitrogen InGaAsN/GaAs quantum wells were grown as previously described in Sec. B. The widths were estimated from growth rate calibrations. The PL measurements were made at 4K and the resulting dependence of the bandgap energy on the quantum-well width is shown in Fig. 5. The quantum well widths varied between 50 and 200 Å, and as can be seen in Fig. 5, the luminescence energy increases with decreasing quantum well width, the anticipated result. We are interested in comparing the InGaAsN and GaAs masses and thus for purposes of this paper, we will analyze the quantum well data in a simple manner assuming infinite barrier heights. Because all of the mass measurements presented here are only to serve as an illustration of the effect of nitrogen in GaAs, we feel that these simple assumptions are warranted. With the infinite barrier approximation, the luminescence energy is given by

$$E(n) = \frac{\pi^2 \hbar^2 n^2}{2ma^2} = \frac{37600}{m^* L^2}, \quad (L \text{ in } \text{\AA}) \quad (1)$$

where $n = 1, 2, \dots$ is the quantum number of the state, m^* is the conduction-band effective mass, and L is the quantum well width. Also assumed here is that the InGaAsN/GaAs quantum-well valence-band effective mass is much heavier than the conduction-band mass, and hence the conduction-band mass and not the reduced mass as expressed in Eq. 1. Because the valence-band offset between 2% nitrogen in InGaAsN and GaAs is believed to be small and only due to the offset from the 7% indium content,^{3,4} it is reasonable to assume that quantum confinement has not caused a large splitting between the “pinned” heavy-hole and light-hole valence bands, thereby leading to a “heavy” valence-band mass. Figure 6 shows the dependence of the luminescence energy as a function of L^{-2} for the data shown in Fig. 5, and as can be seen, a straight line can be drawn through the data. From the slope of the line shown in Fig. 6 and with $n = 1$ in Eq. 1, we derive $mc \sim 0.2$. Possible sources of error in this analysis are the experimental quantum-well widths which are difficult to monitor or control during growth. However, the conduction-band effective mass for GaAs is 0.067 and thus, as in the case of the bandgap energy, we see that the addition of a small amount of nitrogen to GaAs has caused large changes to the 2% nitrogen InGaAsN conduction-band mass.

As mentioned earlier, we have also performed room temperature photoreflectance measurements on the similar structures to those used for the luminescence energy versus quantum-well-width studies. Figure 7 shows photoreflectance spectra for 50, 80, 100 and 200-Å-wide quantum wells. The solid lines are “fitted” theoretical photoreflectance line shapes to the data. The vertical lines are the critical point energies (i.e., quantum well energies) for each spectrum as calculated by the theoretical line shape fit. The difference energy dE from the quantum well states shown in Fig. 7, as vertical lines, gives $dE \sim 120$ meV. We again make the assumption that this energy difference is due entirely to the conduction-band states. With infinite barrier heights, we can arrive at a qualitative estimate for the conduction-band mass from Eq. 1, with the result $mc \sim 0.14$, a mass twice as large as that found for GaAs! However, the two measurements of mass are in reasonable agreement with each other and both lead to the conclusion that the conduction-band mass in InGaAsN is two to three times heavier than found for GaAs.

The last experimental method for an optical determination of the conduction-band mass involves measurements of the exciton diamagnetic shift as a function of magnetic field for 2% nitrogen InGaAsN alloys lattice matched to GaAs. The magnetoexciton diamagnetic shift dependence on magnetic field for ambient pressure is shown as closed circles in Fig. 8. The diamagnetic shifts for varying InGaAsN conduction-band mass mc between 0.067 and 0.5 are also indicated in the figure. The theoretical diamagnetic shifts were calculated by the variational approach as described by Greene and Bajaj.^{33,34} For the diamagnetic shift calculation presented here, we adapted our quantum-well computer codes³⁵ which were used to quantify the diamagnetic shift studies in (411)A-oriented GaAs/AlGaAs quantum wells. We account for the 3D (bulk) excitons in InGaAsN by setting the InGaAsN quantum-well width to greater than 200 nm. The trial wavefunctions for the exciton center-of-mass coordinate system are expressed in terms of a Gaussian basis set with the magnetic field perpendicular to the growth direction, i.e., the exciton orbits are in the plane of a 200-nm-wide InGaAsN/GaAs quantum well. The exciton binding energies are calculated for finite values of the height of the 7% indium InGaAsN-GaAs potential barrier. The envelope function method is also employed to account for the finite quantum-well width and height. Besides the low temperature bulk GaAs bandgap

energy, the magnetic field strength, and the quantum-well width, some of the relevant physical parameters include: (1) Conduction and valence-band offsets between InGaAsN quantum well and the GaAs barriers. (2) The Luttinger parameters γ_1 and γ_2 for both the InGaAsN quantum well and GaAs barriers. (3) Conduction and valence-band mass values for the InGaAsN quantum well and GaAs barrier. (4) Low frequency dielectric constants ϵ_0 for the quantum well and barrier materials. For these calculations, GaAs values for all parameters except the conduction-band mass were used not only for the GaAs barrier, but also for the InGaAsN quantum well. For the present stage of understanding the electronic properties of InGaAsN alloys, these assumptions are reasonable. As can be seen in Fig. 8, a best fit diamagnetic shift dependence on magnetic field occurs for an InGaAsN conduction-band effective mass $m_c \sim 0.13$, which is in excellent agreement with the two previous optical determinations presented in this paper of the energy versus quantum-well width studies which gave $m_c \sim 0.2$ and the analysis of the quantum-well states of the photoreflectance data which yielded $m_c \sim 0.14$.

Figure 6. Luminescence energy versus the square of the inverse quantum well width, i.e., L^{-2} for InGaAsN/GaAs single quantum wells at 4K. The straight line fitted to the data, yields an estimate for the conduction-band effective mass, $m_c \sim 0.2$.

Figure 7. Photoreflectance spectra for four InGaAsN/GaAs quantum well structures. The quantum-well widths are indicated in the figure. The solid lines are "fitted" theoretical photoreflectance line shapes to the data. The vertical lines are the critical point energies (i.e., quantum well energies) for each spectrum as calculated by the theoretical line shape fit. As an aid to the eye, the spectra have been offset from each other.

Figure 8. Ambient-pressure exciton diamagnetic shift as a function of magnetic field at 2K for 2% nitrogen InGaAsN alloy. The closed circles are the experimental points. The curves, labeled $m_c = 0.67$ to 0.50 are calculated diamagnetic shifts as a function of mass. The estimated ambient pressure InGaAsN conduction-band effective mass m_c is about 0.13.

C.3 Pressure dependence of the InGaAsN conduction-band effective mass

As mentioned in the experimental section, pressure dependent magnetoluminescence measurements were performed in the pressure range of ambient to 110 kbar and magnetic fields up to 30 tesla. The diamagnetic shift data can be readily analyzed for pressures less than 40 kbar. For higher pressures, the accuracy of the technique fails because of linewidth broadening by the non-hydrostatic component of the pressure medium and also because of an large increase of the conduction-band mass as discussed below. Also, other broadening mechanisms include possible differences to the GaAs elastic constants with the addition of 2% nitrogen. If the elastic constant differences between GaAs and InGaAsN are significant, the application of pressure (including hydrostatic pressure) will lead to anisotropic strain in the InGaAsN epilayer and hence large PL linewidths.

Figure 9 shows the magnetic field dependence of the exciton diamagnetic shift at 38 kbar and $T = 2\text{K}$. As is the case with Fig 8, the filled circles are the data points and the curves are calculated shifts as a function of mass. It is apparent from the figure that the conduction-band effective mass is nearly 0.2 in contrast to the $m_c \sim 0.13$ found from the ambient pressure data. This large increase to the mass for 2% nitrogen in GaAs is surprising. Recently, we have reported³⁶ mass measurements as a function of pressure in In_{0.2}Ga_{0.8}As/GaAs strained-single-quantum wells and, found that the conduction-band mass ranged from ~ 0.07 to ~ 0.085 for pressures between ambient and 36 kbar in a linear manner. This result for InGaAs/GaAs agrees with expectations³⁶ based on simple $k \cdot p$ theory. The large variation and nonlinear behavior of the conduction-band mass for InGaAsN may not be that surprising in light of all of the other mysteries associated with substituting nitrogen for arsenic in GaAs. Figure 10 shows the variation of the effective mass for pressures between ambient and 38 kbar. The smooth curve provides an aid to the eye.

Because of our success in using the LDA calculation to quantify the change in the bandgap energy with pressure (Fig. 2), we performed preliminary LDA calculations for the pressure dependence of the conduction-band mass. But to date, our results are inconclusive and hence will not be discussed here. We can, however, make some qualitative statements by examining the LDA results shown in Fig. 4. As discussed earlier, the band repulsion between the G-like and X-like bands at high pressure indicate that strong G-X mixing is occurring. Because the mass of the six-fold degenerate X-point in GaAs is heavy ($m_{Xt} = 1.2$ & $m_{Xl} = 0.27$), we expect that the G-X mixing will cause a corresponding increase to the G-like conduction-band mass by the heavy X-like mass. Part of the LDA mass calculation will require information about the X-like as well as the L-like masses. In the future, an obvious goal of our LDA calculations will be to replicate the curve shown in Fig. 10.

Figure 9. Exciton diamagnetic shift as a function of magnetic field and 38 kbar at 2K for the 2% nitrogen InGaAsN alloy. The closed circles are the experimental points. The curves, $m_c = 0.067$ to 0.50, are theoretical diamagnetic shifts as a function of mass. The estimated InGaAsN conduction-band effective mass at 38 kbar is $m_c \sim 0.2$.

Figure 10. The 2-K pressure dependence of the conduction-band mass between ambient pressure and 40 kbar for the 2% nitrogen InGaAsN sample. The smooth curve drawn through the data provides an aid to the eye.

D. Conclusions

We have shown that while the first principles LDA calculation for the band structure of InGaAsN yields incorrect values for the bandgap energy, the predicted change in bandgap energy with pressure is in excellent agreement with experiment. Both experiment and calculations show that the lack of crossing of the G-like and X-like conduction bands is due to G-X mixing. The conduction-band effective mass was measured by three techniques with the result for 2% InGaAsN, lattice matched to GaAs, being that the ambient pressure conduction-band effective mass $m_c \sim 0.15$. The pressure dependence of the conduction-band mass is nonlinear and large. The current challenge of the LDA calculation is to account for this behavior.

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III. InGaAsN Solar Cells with 1.0 eV Bandgap, Lattice Matched to GaAs

A. Introduction

Multi-junction tandem solar cells are being developed as power sources for satellite systems operating in air mass zero (AM0) solar radiation. Models indicate that record efficiencies ($\approx 38\%$) would be obtained for tandem cells where a 1.0 eV bandgap cell is added in series to proven InGaP-GaAs tandem structures.¹ The $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ alloy system appears ideal for this application. Bandgaps of ≈ 1.0 eV are obtained for $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ with minimal N concentrations ($y > 0.02$), and the quaternary is lattice-matched to GaAs for compositions with $x \approx 3y$.^{2,3} Even at these low concentrations, N incorporation has proven problematic, and it remains a challenge to demonstrate thick (2-3 μm), high quality, $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ ($y > 0.02$) epilayers needed for solar cell development. In this paper, we present a status report on $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ properties, growth, and solar cell performance. Under specialized conditions, we demonstrate internal quantum efficiencies $>70\%$ for 1.0 eV bandgap solar cells.

B. Experimental

The structures in this work were grown in a vertical flow, high speed rotating disk, Emcore GS/3200 metalorganic chemical vapor deposition (MOCVD) reactor. $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ films were grown using trimethylindium (TMIn), trimethylgallium (TMG), 100% arsine and dimethylhydrazine (DMHy). Dimethylhydrazine was used as the nitrogen source since it has a lower disassociation temperature than ammonia and has a vapor pressure of approximately 110 torr at 18°C . Unintentionally doped InGaAsN was p-type. N-type material was achieved using silicon tetrachloride (SiCl_4). InGaAsN films for Hall and optical measurements were grown on semi-insulating GaAs orientated 2° off (100) towards $\langle 110 \rangle$. Lattice matched ($\Delta a/a < 8 \times 10^{-4}$) films were grown at 600°C and 60 torr using a V/III ratio of 97, a DMHy/V ratio of 0.97 and a TMIn/III ratio of 0.12. The growth rate was $10 \text{ \AA/s}$. These conditions resulted in films with an indium mole fraction of 0.07 (± 0.005) and a nitrogen mole fraction of 0.022 (± 0.003). The composition was determined by calibration growths of GaAsN and InGaAs along with double crystal x-ray diffraction measurements. The nitrogen composition was also confirmed from elastic recoil detection (ERD) measurements.

A significant increase in photoluminescence intensity was observed from these films following a post-growth anneal.⁴ Ex-situ, post-growth anneals were carried out in a rapid thermal anneal system under nitrogen using a sacrificial GaAs wafer in close proximity to the InGaAsN sample. The photoluminescence intensity was a maximum for samples annealed for either 700°C for 2 minutes or 650°C for 30 minutes. Secondary ion mass spectrometry measurements showed the residual carbon concentration of similar films to be $6\text{-}8 \times 10^{17} \text{ cm}^{-3}$. Carbon is incorporated during growth at sufficiently high

levels to possibly cause the background p-type conductivity and the observed ex-situ annealing behavior.

C. Discussion

The optical properties of the InGaAsN films were extremely sensitive to N content, ex-situ annealing, and doping. Photoluminescence and optical absorption spectra are shown in Figure 1 for InGaAsN films grown under the same conditions and with nominally the same compositions as the n and p-type regions of the solar cell. Photoluminescence was measured with a Fourier transform spectrometer equipped with a cooled, North Coast Ge detector. In addition to the bandgap reduction, there was photoluminescence quenching in InGaAsN films with increasing N content. A band-edge photoluminescence peak was not observed in as-grown, $\text{In}_{0.07}\text{Ga}_{0.93}\text{As}_{0.98}\text{N}_{0.02}$ films at 300 K. After the ex-situ annealing process, described earlier, a band-edge photoluminescence peak, approximately 60 meV linewidth, was observed in our p-type films. (see Figure 1(a)) Annealing had negligible effect on the absorption spectra of the p-type films. (Absorption spectra are shown in Fig. 1(b). Baseline corrections have eliminated free carrier contributions to these spectra.) Consistent with these observations, deep-level-transient-spectroscopy (DLTS) results clearly show that annealing eliminates a midgap defect state present in our as-grown, p-type material.⁵ N-type doping with Si appears to introduce yet another defect or impurity into the InGaAsN. With Si doping, the band-edge photoluminescence was weak both before and after ex-situ annealing. (Fig. 1(a)) Also, the absorption spectrum for the Si doped material displayed a low energy tail. (Fig. 1(b)) DLTS measurements to identify the defect associated with Si doping are in progress.⁷

The solar cell described in this work consisted of a 1.0 μm thick, n-type ($2 \times 10^{17} \text{ cm}^{-3}$, Si doped) $\text{In}_{0.07}\text{Ga}_{0.93}\text{As}_{0.98}\text{N}_{0.02}$ emitter grown on a 1.0 μm thick, p-type ($4 \times 10^{16} \text{ cm}^{-3}$, background doped) base. The base doping concentration was determined from capacitance-voltage measurements, and emitter doping was determined from Hall measurements on similar, annealed material. The solar cell was grown on a p+ GaAs substrate. A 500 Å thick, $\text{Al}_{0.8}\text{Ga}_{0.2}\text{As}$ window layer and a 0.15 μm thick GaAs cap/contact layer (both doped n-type, $5 \times 10^{18} / \text{cm}^3$) were grown on top of the solar cell emitter. The $\text{Al}_{0.8}\text{Ga}_{0.2}\text{As}$ window prevented photogenerated holes from escaping from the n-type emitter, and the 300-400 meV $\text{In}_{0.07}\text{Ga}_{0.93}\text{As}_{0.98}\text{N}_{0.02}$ / GaAs conduction band offset produced a back-side reflector for electrons generated in the p-type base. Solar cells were processed with Pd/Ge/Au front grids and Be/Au back contacts and with an area of 0.25 cm^2 . Any ex-situ anneals of InGaAsN were performed prior to metallization. No antireflection coatings were applied.

Solar cell spectral response was determined by the ratio of the short-circuit cell photocurrent to that of a calibrated Ge detector. The internal quantum efficiency curves for both the annealed and as-grown cells are shown in Figure 2. The photoresponses extended out to the band-edge of the InGaAsN at 1.2 μm . (Due to irreproducibility in N composition, the solar cell bandgap was shifted to $\approx 0.04 \mu\text{m}$ longer wavelength than that of the optical samples shown in Fig.1) At wavelengths less than 0.9 μm , the solar cell

Figure 1. (a) Photoluminescence spectra for ex-situ annealed, p-type (background doped) and n-type (Si doped) $\text{In}_{0.07}\text{Ga}_{0.93}\text{As}_{0.98}\text{N}_{0.02}$ epitaxial films. (b) Absorption spectra for the samples in (a).

response was dominated by the GaAs cap, acting as a filter. Peak internal quantum efficiencies of $>70\%$ were obtained for the annealed cell. Comparing the annealed and as-grown cells, annealing improved the quantum efficiency by roughly a factor of 5. Comparing the performance of our thick n-type emitter solar cell with thin n-type emitter cells and other alternative designs, we found that negligible electron diffusion is occurring in the 1.0 eV p-type material (annealed or as-grown). To date, high quantum efficiencies have only been obtained with cell designs utilizing hole diffusion in n-type material.

Previously, InGaAsN solar cells have displayed short minority carrier diffusion lengths, and their photocurrents have been dominated by electron-hole pairs generated in the depletion region. The highest internal quantum efficiency reported for an InGaAsN solar cell was $>60\%$ (@ 1.1 μm), achieved with a compensation-doped *p-i-n* device. Conventional p-n InGaAsN solar cells have displayed internal quantum efficiencies typically $<25\%$ (@ 1.1 μm).⁷ To estimate the minority carrier diffusion length in our cells, we measured the photocurrent response versus bias. Depletion widths were determined from capacitance-voltage measurements. As shown in Figure 3, the photocurrents of the annealed and as-grown cells displayed roughly the same dependence on depletion width, although the photocurrent was much larger for the annealed cell. Based on several diagnostic devices, we developed a model which included carrier collection from the n-type emitter and the depletion region. From the model, one finds

$\alpha L \approx 1.1$ and 0.35 for the annealed and as-grown samples, respectively, where α is the absorption coefficient and L is the minority carrier diffusion length. From absorption data, we estimate that the hole diffusion lengths are $0.6\text{--}0.8\text{ }\mu\text{m}$ (annealed) and $0.2\text{--}0.3\text{ }\mu\text{m}$ (as-grown). Despite the poor quality of the n-type material as indicated by optical studies, the improved efficiency of our annealed InGaAsN cell was due to diffusion of holes in the n-type emitter.

Figure 2. Internal quantum efficiency curves for as-grown (0V bias, $0.15\text{ }\mu\text{m}$ depletion width) and ex-situ annealed (0V bias, $0.26\text{ }\mu\text{m}$ depletion width) $\text{In}_{0.07}\text{Ga}_{0.93}\text{As}_{0.98}\text{N}_{0.02}$ solar cells with $1.0\text{ }\mu\text{m}$ thick, n-type emitters.

Solar cell current-voltage characteristics were measured under high flux, broadband illumination conditions. For various light intensities, open-circuit voltage (V_{OC}) and short-circuit current (I_{SC}) values for the annealed and as-grown cells are shown in Figure 4. Annealing decreased the saturation current (I_0) from $1.1 \times 10^{-6}\text{ A/cm}^2$ (as-grown) to $8.3 \times 10^{-7}\text{ A/cm}^2$ (annealed). Similarly, the diode ideality factor (n) approached unity with annealing. ($n=1.21$ annealed versus $n=1.33$ as-grown) For the solar cell shown, the open circuit voltage was low ($< 0.3\text{ V}$). As bandgap energy increases, we found that the open circuit voltage rapidly increased. For example, the open-circuit voltage of a high efficiency, 1.2 eV bandgap InGaAsN solar cell was 0.6 V for $I_{sc}=0.03\text{ A/cm}^2$

($I_0 = 1.1 \times 10^{-11}$ A/cm²). Hopefully, we will be able to demonstrate future improvements in minority carrier diffusion length and lifetime to approach the open-circuit voltages (0.6-0.7 V) which are theoretically predicted for 1.0 eV bandgap InGaAsN solar cells.

Figure 3. (a) Internal quantum efficiency vs depletion width for the as-grown and annealed solar cells. Model (solid lines) assumes that the ratio of the n- and p-type doping concentration is unchanged by annealing. (b) Measured solar cell open-circuit voltage (V_{oc}) and short-circuit current (I_{sc}) for various light intensities.

D. Conclusions

In summary, we have described the design, MOCVD growth, and processing of an InGaAsN solar cell with improved performance. Unlike previous cells, we have demonstrated viable minority carrier diffusion, and in our present devices, we realized >70% internal quantum efficiency. The hole diffusion length in annealed, n-type 1.0 eV bandgap InGaAsN was 0.6-0.8 μm, and we found that ex-situ annealing was required to turn-on the hole diffusion. Even with future realization of near-unity quantum efficiency, material-related improvements in minority carrier lifetime and diffusion length will be required to increase 1.0 eV bandgap InGaAsN cell open-circuit voltages from ~ 0.3 V. Optical studies indicated that there are defects present in the InGaAsN associated with both N incorporation and n-type, Si doping. Elimination of such defects should further improve the performance of InGaAsN solar cells.

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IV. Deep levels in *p*-type InGaAsN lattice matched to GaAs

A. Introduction

Recently, the quaternary alloy semiconductor InGaAsN has drawn significant attention because of its potential applicability to infrared laser diodes and its possible use as a narrow band-gap layer in tandem solar cells. Long wavelength laser diodes are used as light sources for optical fiber communications because of their emission at the low-loss optical fiber windows of 1.3 and 1.55 μm [1]. Conventionally, GaInPAs/InP based laser diodes have been used for such applications. GaInPAs/InP laser diodes, however, show poor temperature characteristics due to the small conduction band offset of this material system [2]. Kondow *et al.* have instead proposed using the quaternary alloy InGaAsN grown on GaAs substrates for long-wavelength laser diodes [3]. They have demonstrated that InGaAsN/GaAs laser diodes display superior high temperature characteristics due to the type-I hetero-interfaces formed between InGaAsN and GaAs. Several research groups have concentrated on improving growth techniques to achieve

Au-Ge-Ni/Au
1500 Å n-GaAs (5×10^{18})
500 Å n-AlGaAs (5×10^{18})
1 μm n-InGaAsN (3×10^{17})
1 μm uid-InGaAsN
500 Å p-GaAs (2×10^{18})
P-GaAs Substrate
Au-Be

Figure 1. The device structure that was used for DLTS measurements. Hall measurements showed that the unintentionally doped InGaAsN layer is *p*-type [11].

better quality InGaAsN materials [3,4,5,6,7,8,9,10,11]. Recently, a 1.0 eV band-gap solar cell made of InGaAsN with an internal quantum efficiency greater than 70% has been reported [11]. However, because of the difficulty in growing N-containing quaternary materials, these materials may contain defects that impact their electrical quality. In this study, we report on deep level defects revealed by deep level transient spectroscopy (DLTS) in unintentionally doped *p*-type InGaAsN films grown on GaAs substrates. In addition, we investigate the thermal stability of deep traps by examining DLTS spectra before and after an anneal.

B. Experimental

The samples used in this study were grown by MOCVD. Details regarding the growth can be found elsewhere [11]. The device structure used for DLTS measurements is shown in Figure 1. The indium content was 7.0 % and the nitrogen content was 2.2 % for the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ layers. Au-Be alloy ohmic contacts were evaporated on the *p*-GaAs substrate and Au-Ge-Ni alloy ohmic contacts were evaporated on the top *n*-GaAs layer. After the evaporation the diodes were mesa-etched around the contacts. The diode area defined by the mesa was 1.11 mm^2 . Good rectifying current-voltage (I-V)

characteristics were observed for the diodes. Annealed samples were prepared by annealing the devices at 650 °C for 1800 seconds under the presence of nitrogen gas. The details concerning annealing also can be found elsewhere [11].

Figure 2. DLTS spectra of as-grown p-InGaAsN. The quiescent bias and fill pulse voltages were -0.8 V and -0.15 V, respectively. The fill pulse width was 1 msec. Numbers shown in the figure indicate rate windows in the unit of sec^{-1} .

DLTS was used to detect deep level defects. The trap concentrations were calculated from the well-known formula:

$$N_T = \frac{2N_A \Delta C}{C_0} \frac{r^{r/(r-1)}}{1-r}, \quad (1)$$

where N_A is the doping density, ΔC is the capacitance change between DLTS sampling times, C_0 is the steady state capacitance value under the applied reverse bias, and $r=t_2/t_1$, where t_1 and t_2 are the initial and final DLTS sampling times, respectively. The p-type background doping concentration was measured from capacitance-voltage (C-V) profiling and had a value of $3.5 \times 10^{16} \text{ cm}^{-3}$ for the unintentionally doped layer of the as-grown samples and $1.1 \times 10^{17} \text{ cm}^{-3}$ for the annealed samples. Hall measurements were carried out to verify the doping type of the InGaAsN layer and showed that the material is p-type [11]. The increase of doping concentration in p-InGaAsN after annealing has been observed, the source of which is under investigation [12]. Steady state capacitance measurements as a function of temperature were performed to obtain $C_0(T)$. The steady state C-T measurements were done under the same reverse bias condition (-0.8 V) as were the DLTS measurements.

C. Discussion

Figure 2 shows DLTS spectra of the as-grown *p*-InGaAsN for the different rate windows used. There are two interesting features to be pointed out in these spectra. The first is that the peaks are very broad and the second is that the trap density depends on the rate window. The above results strongly suggest that the energy distributions of the defect levels are not well defined at a single energy but are instead band-like. Band-like defect states typically appear in material with extended defects such as threading dislocations [13]. Figure 3 shows a typical cross sectional TEM of *p*-InGaAsN. The TEM image shows no sign of dislocations within the TEM resolution limit of 10^7 cm^{-2} demonstrating the good structural quality and lattice-matching of these thick layers. Hence, a more likely source is a high density of distributed point defects and/or point defect clusters. More intensive study of the physical nature of the defect sources, including the dependence of trap density on fill pulse width, is currently underway.

Figure 4 shows DLTS spectra of the annealed sample for the different rate windows used. Unlike the spectra for the as-grown sample, the peaks are narrow enough to be easily resolved. Figure 5 shows Arrhenius plots from which the activation energies of the traps were calculated. To find the peak positions and the densities of each trap, we fit the N_T vs. T curves using Gaussian functions. Three majority carrier (hole) traps were found with energy levels of 0.10 eV, 0.23 eV, and 0.48 eV above the valence band edge. The concentrations of these traps were found to be $3.5 \times 10^{14} \text{ cm}^{-3}$, $3.8 \times 10^{14} \text{ cm}^{-3}$, and $8.2 \times 10^{14} \text{ cm}^{-3}$, respectively. Comparison of the DLTS spectra of the as-grown and the annealed samples for a fixed rate window shows that the broad deep level distribution

throughout the bandgap is reduced due to the post-growth annealing. In particular, the densities of the shallower traps (those with energy levels of 0.10 eV and 0.23 eV) are significantly reduced, and their thermal annealing behavior suggests that they are likely to be related to point defects within the InGaAsN. Correlating with this reduction in the trap density, InGaAsN was observed to have improved bulk properties, with large increases in photoluminescence and quantum efficiency following the anneal [11]. This indicates that the as-grown deep levels severely degrade carrier diffusion lengths in *p*-InGaAsN. However, close inspection of Figures 2 and 4 reveal that the concentration of the hole trap of $E_v + 0.48 \text{ eV}$ is not affected by the anneal, indicating a greater thermal stability for this defect as compared to the

Figure 3. Cross sectional TEM of an as-grown *p*-InGaAsN showing no sign of dislocations within the resolution limit of 10^7 cm^{-2} .

Figure 4. DLTS spectra of annealed p-InGaAsN. The quiescent bias and fill pulse voltages were -0.8 V and 0.0 V, respectively. The fill pulse width was 1 msec. Unlike the DLTS spectra for as-grown p-InGaAsN samples, peaks are narrow and resolvable.

Figure 5. $\ln(\tau T^2)$ versus $1000/T$ plots for annealed p-InGaAsN. The energy values in the parentheses are measured from the valence band edge since these are hole traps.

several distribution of shallow and deep traps. Moreover, this trap has been detected in p-InGaAsN grown under a wide range of MOCVD growth conditions, implying its source may be of a different nature than the thermally unstable deep levels. Since this trap is the dominant level after annealing, and since it is near midgap, it is likely to be important in limiting minority carriers lifetimes of the annealed p-InGaAsN, and perhaps subsequent device performance.

D. Conclusions

DLTS measurements were performed on unintentionally doped *p*-type InGaAsN films grown on GaAs. Broad DLTS spectra measured in as-grown *p*-InGaAsN suggest that there exists a distribution of deep defect states throughout the band-gap of the as-grown *p*-InGaAsN material. Moreover, the densities of the traps in the as-grown samples exceed 10^{15} cm^{-3} . Cross sectional TEM measurements indicate that, within the TEM resolution limit of 10^7 cm^{-2} , the traps are not likely to be due to threading dislocations. DLTS revealed three distinct hole traps in annealed samples. The energy levels of these traps are 0.10 eV, 0.23 eV, and 0.48 eV above the valence band edge and the concentrations are $3.5 \times 10^{14} \text{ cm}^{-3}$, $3.8 \times 10^{14} \text{ cm}^{-3}$, and $8.2 \times 10^{14} \text{ cm}^{-3}$, respectively. The concentrations of the two distinct shallower traps at 0.10 eV and 0.23 eV and the overall trap distribution were reduced considerably following the anneal, indicating that these traps are not thermally stable. In contrast, the concentration of a deep trap at 0.48 eV is unaffected by the anneal. The overall reduction in trap density is correlated with improved photoluminescence and quantum efficiency. However, since the 0.48 eV hole trap is both a midgap level and the dominant remaining trap after annealing, it is likely to be an important defect for limiting minority carrier properties in this material.

E. References

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