Deep levels in $p$-type InGaAsN lattice matched to GaAs

D. Kwon, R. J. Kaplar, and S. A. Ringel
The Ohio State University, Dept. of Electrical Engineering, Columbus, OH 43210-1272

A. A. Allerman, Steven R. Kurtz, and E.D. Jones
Sandia National Laboratories, Albuquerque, NM 87185-0603

ABSTRACT

Deep level transient spectroscopy (DLTS) measurements were utilized to investigate deep level defects in metal-organic chemical deposition (MOCVD)-grown unintentionally doped $p$-type InGaAsN films lattice matched to GaAs. The as-grown material displayed a high concentration of deep levels distributed within the bandgap, with a dominant hole trap at $E_v + 0.10$ eV. Post-growth annealing simplified the deep level spectra, enabling the identification of three distinct hole traps at $0.10$ eV, $0.23$ eV, and $0.48$ eV above the valence band edge, with concentrations of $3.5 \times 10^{14}$ cm$^{-3}$, $3.8 \times 10^{14}$ cm$^{-3}$, and $8.2 \times 10^{14}$ cm$^{-3}$, respectively. A direct comparison between the as-grown and annealed spectra revealed the presence of an additional midgap hole trap, with a concentration of $4 \times 10^{14}$ cm$^{-3}$ in the as-grown material. The concentration of this trap is sharply reduced by annealing, which correlates with improved material quality and minority carrier properties after annealing. Of the four hole traps detected, only the $0.48$ eV level is not influenced by annealing, suggesting this level may be important for processed InGaAsN devices in the future.
DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
Kondow et al. have proposed using the quaternary alloy semiconductor InGaAsN in long-wavelength (1.3-1.55 μm) laser diodes as an active layer material grown on GaAs substrates. Such laser diodes have potentially superior temperature characteristics compared to conventional InGaAsP/InP diodes. The high characteristic temperature ($T_0$ can be above 150 K) is primarily due to the large conduction band offset between InGaAsN and GaAs, which reduces the electron overflow from the active InGaAsN wells to the adjacent GaAs layers at high temperatures. The same group has reported InGaAsN/GaAs laser diodes which were operated in the continuous wave (CW) condition at room temperature with a lasing wavelength of 1.18 μm for which a characteristic temperature of 126 K was obtained. Thus far, several groups have reported the fabrication of operational InGaAsN/GaAs laser diodes by using different growth techniques such as gas-source molecular beam epitaxy (GSMBE), chemical beam epitaxy (CBE), and metal-organic chemical vapor deposition (MOCVD).

The InGaAsN alloys have also drawn recent attention from the solar cell community, since very high efficiencies have been predicted for multi-bandgap solar cells that can utilize a 1.0 eV bandgap sub-cell lattice-matched to GaAs or Ge. Recently, 1.0 eV bandgap solar cells utilizing InGaAsN material have been reported, but the minority carrier diffusion lengths in such solar cells were too short for efficient solar cell applications. However, more recent work has shown that the diffusion length increases considerably after post-growth annealing, resulting in internal quantum efficiencies in excess of 70 %. These results suggest that defects may play a significant role in device properties at this stage of InGaAsN development. Hence, in this paper, we report on the presence and thermal stability of deep levels in p-type InGaAsN.

$\text{In}_{0.07}\text{Ga}_{0.03}\text{As}_{0.98}\text{N}_{0.02}$ epitaxial layers were grown on (001) GaAs substrates by MOCVD. Details regarding the growth and composition can be found elsewhere. X-ray rocking curve
measurements indicated a lattice mismatch of 0.08% with the GaAs substrate, consistent with earlier results which showed that InGaAsN can be grown closely lattice matched to GaAs when the indium content is approximately three times the nitrogen content. The three to one lattice matching condition has been verified to hold up to a nitrogen mole fraction of 6%. The bandgap of the InGaAsN layers used in our study were determined by optical absorption measurements to be 1.05 eV at 300 K, as desired for multi-junction solar cell applications.

Figure 1 shows the device structure used for deep level transient spectroscopy (DLTS) measurements of p-type InGaAsN. After growth, Au-Ge-Ni alloy ohmic contacts were deposited on the top n-GaAs layer and Au-Be alloy ohmic contacts were evaporated on the p-GaAs substrate. This was followed by a mesa-etch around the contacts to facilitate DLTS measurements. To prepare the annealed samples, thermal annealing was performed at 650 °C for 30 minutes prior to contact deposition. Hall effect measurements on unintentionally doped InGaAsN layers grown under identical conditions as the DLTS samples but on semi-insulating GaAs substrates revealed a p-type background conductivity. The p-type background doping was confirmed in the DLTS test layers using capacitance-voltage (CV) profiling, with $N_A = 3.5 \times 10^{16}$ cm$^{-3}$ throughout the measured region for the as-grown sample and $N_A = 1.1 \times 10^{17}$ cm$^{-3}$ for the annealed sample. This increase in $N_A$ after annealing is typically observed, and measurements to determine whether this effect is related to the removal of possible donor-like compensating defects or the removal of passivating hydrogen are currently underway.

Figure 2 shows typical DLTS spectra obtained for as-grown p-InGaAsN. The DLTS signal was calculated using the well-known formula:

$$N_T = \frac{2N_A \Delta C r^{r/(r-1)}}{C_0(T) \left(1 - r\right)}.$$

(1)
where $N_A$ is the doping density, $C_0(T)$ is the steady state capacitance value measured at the DLTS quiescent bias of $-0.8$ V, $r=t_2/t_1$ ($t_1$ and $t_2$ are the initial and final DLTS sampling times, respectively), and $\Delta C$ is change in capacitance between the times $t_1$ and $t_2$. $C_0(T)$ was determined by making a steady-state capacitance measurement during a temperature sweep and was stored prior to DLTS measurements. The as-grown DLTS spectrum is characterized by a shallow hole trap detected at $E_v+0.10$ eV (low temperature peak) and an overall broadness, indicating a distribution of deep levels is present within the bandgap of as-grown InGaAsN layers. The fact that the measured trap densities depend on the rate windows supports the existence of such deep level distributions, since the DLTS signal for each rate window is the result of hole emission from deep levels which have different thermal emission rates. This distribution may result from various sources, including dislocations and other extended defects, which give rise to band-like defect states, or it may be the result of many closely spaced discrete deep levels. However, cross-sectional transmission electron microscopy (TEM) studies on a similar sample suggest that dislocations are an unlikely source since no dislocations were detected, which implies a low threading dislocation that is below the statistical limit of $10^7$ cm$^{-2}$.\textsuperscript{14} Therefore, a distribution of isolated point defects and/or point defect clusters may be more likely sources for the broad deep level spectrum.

This claim is supported by figure 3, which shows the DLTS spectrum after annealing. As seen, the DLTS spectrum is significantly simplified, which not only implies a removal of point defects as discussed below, but also enables us to determine trap energy levels. To obtain the peak positions and trap densities, each DLTS spectrum was fitted using Gaussian functions. Figure 4 shows Arrhenius plots obtained for the DLTS spectra after annealing, from which the activation energies of the traps present in the annealed InGaAsN were calculated. Three hole
traps with energy levels of $0.10 \text{ eV}$, $0.23 \text{ eV}$, and $0.48 \text{ eV}$ above the valence band edge were found. By fitting the 200 sec$^{-1}$ spectrum, the concentrations for these three traps were determined 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. The fact that there is still some rate window dependence for the magnitude of the $0.48 \text{ eV}$ DLTS peak (i.e. the trap concentration) suggests that some deep level distribution may still present in these annealed layers.

Figure 5 shows a direct comparison between the DLTS spectra of the as-grown and the annealed samples for a rate window of 200 sec$^{-1}$. There are several important observations which may be made from this comparison. First, following the post-growth anneal, the overall trap density was reduced by over a factor of two. Second, following the anneal, the broad features of the spectra simplified, revealing well-defined individual DLTS peaks. Both of these observations imply that point defects are the dominant source of the as-grown deep level spectra and that they are at least partially removed by the anneal. Indeed, preliminary studies of the filling pulse dependence of the deep levels showed no strong evidence for dislocation related trapping kinetics, suggesting that either point defects or point defect clusters may be the source of the broad as-grown spectra. The third observation is that the $0.10 \text{ eV}$ trap (corresponding to the low temperature peak), which had been the dominant trap in terms of concentration in the as-grown sample, is no longer the dominant trap in the annealed sample. Finally, close inspection of Figure 5 indicates that another trap contributing a peak near 270 K can be identified in the as-grown sample. This fourth trap is difficult to discern by looking only at the broad as-grown spectra. Rather, its presence is revealed by its absence in the spectrum of the annealed sample when compared to the spectrum of the as-grown sample. The energy level of this midgap trap
was estimated to be in the range of $E_v + 0.46 \text{ eV}$ to $E_v + 0.50 \text{ eV}$. A more accurate determination could not be made due to the broadness of the as-grown DLTS spectra.

The simplification of the DLTS spectra and the reduction in overall trap density is consistent with the impact of annealing on the overall electronic quality of the InGaAsN layers reported previously. In that work, substantial increase in the band edge photoluminescence intensity and a three-fold increase in minority carrier diffusion length were observed for annealed versus as-grown InGaAsN layers. This correlation implies that thermally unstable deep levels play a substantial role in the overall InGaAsN material quality. It is tempting to attribute the improved electrical quality with the reduced concentration of the low temperature trap at $E_v + 0.10 \text{ eV}$ due to its dominance of the as-grown DLTS spectra and its sharp reduction in concentration after annealing. However, the thermally unstable midgap trap at $E_v + 0.46 \text{ to } E_v + 0.50 \text{ eV}$ is far more likely to be important due to the much greater recombination rate expected for midgap versus shallow levels. Indeed, fitting of the as-grown spectrum results in a trap concentration of $4 \times 10^{14} \text{ cm}^{-3}$ for the midgap level, which reduced to the $10^{13} \text{ cm}^{-3}$ range after annealing. The position of this trap in the bandgap and its removal by annealing correlates very well with the improved bulk properties of the material. Note, however, that while the traps at $0.10 \text{ eV}$ and $0.23 \text{ eV}$ as well as the fourth midgap trap are all thermally unstable, the $0.48 \text{ eV}$ trap concentration was not affected by the anneal. Hence, identification of the physical source of this trap and its removal may be important for future InGaAsN devices due to its midgap position and greater thermal stability compared with the other detected deep levels.

The work was supported by Sandia National Laboratories, NSF grant DMR-9458046, and an Ohio State interdisciplinary seed grant.
The work was supported by Sandia National Laboratories, NSF grant DMR-9458046, and an Ohio State interdisciplinary seed grant. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.
References


14 D. Kwon, R. J. Kaplar, J. J. Boeckl, S. A. Ringel, A. A. Allerman, S. R. Kurtz, and E. D.
Figure Captions

Figure 1. The device structure that was used for the DLTS measurements. Hall effect measurements performed on epilayers grown on semi-insulating GaAs showed that our unintentionally doped InGaAsN layers were p-type.

Figure 2. DLTS spectra of as-grown p-InGaAsN for different rate windows. The fill pulse and quiescent voltages were –0.15 V and –0.8 V, respectively, and the fill pulse width was 1 msec. We observed that the capacitance transient, directly measured on an oscilloscope, saturated for a pulse width of approximately 1 msec.

Figure 3. DLTS spectra of annealed p-InGaAsN for different rate windows. All the experimental conditions were the same as in Figure 2 except that the fill pulse voltage was 0.0 V. The energy levels indicated were obtained from Figure 4.

Figure 4. τT^2 versus 1000/T semi-log plots used to determine the trap energy levels in the annealed p-InGaAsN. The energy levels are measured from the valence band edge.

Figure 5. Comparison of the DLTS spectra of the as-grown and annealed samples for a rate window of 200 sec\(^{-1}\). The fourth trap, located near midgap, is indicated.
Figure 1

<table>
<thead>
<tr>
<th>Au-Ge-Ni/Au</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1500 Å $n$-GaAs ($5 \times 10^{18}$ cm$^{-3}$)</td>
<td></td>
</tr>
<tr>
<td>500 Å $n$-AlGaAs ($5 \times 10^{18}$ cm$^{-3}$)</td>
<td></td>
</tr>
<tr>
<td>1 μm $n$-InGaAsN ($3 \times 10^{17}$ cm$^{-3}$)</td>
<td></td>
</tr>
<tr>
<td>1 μm uid ($p$)-InGaAsN</td>
<td></td>
</tr>
<tr>
<td>500 Å $p$-GaAs ($2 \times 10^{18}$ cm$^{-3}$)</td>
<td></td>
</tr>
<tr>
<td>$p^+$-GaAs Substrate</td>
<td></td>
</tr>
</tbody>
</table>

Au-Be
Figure 2

[Graph showing DLTS signal (cm$^{-3}$) vs. Temperature (K) for different rate windows (sec$^{-1}$) of As-grown p-InGaAsN.]
Figure 3

Temperature (K)

Rate window (sec$^{-1}$)

Annealed $p$-InGaAsN

DLTS signal (cm$^{-3}$)

HT3 (0.48 eV)
HT2 (0.23 eV)
HT1 (0.10 eV)
Figure 4

The graph shows the relationship between \( \tau T^2 \) (sec-K^2) and \( 1000/T \) (K^-1). The data points indicate three different states:

- **HT3 (0.48 eV)**
- **HT2 (0.23 eV)**
- **HT1 (0.10 eV)**
Figure 5

Rate window = 200 sec$^{-1}$

DLTS signal (cm$^3$)

$2 \times 10^{15}$

$1 \times 10^{15}$

Temperature (K)

$0$ $50$ $100$ $150$ $200$ $250$ $300$ $350$

As-grown

Annealed

4th trap