INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI®

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
CHARACTERIZATION OF DEEP LEVEL DEFECTS IN InGaAsN

DISSERTATION

Presented in partial fulfillment of the requirements for the degree of
Doctor of Philosophy in the Graduate School of The Ohio State University

by

Robert J. Kaplar, B.S., M.S.E.E.

The Ohio State University

2002

Dissertation committee:
Dr. Steven A. Ringel, advisor
Dr. Leonard J. Brillson
Dr. Betty Lise Anderson

Approved by:

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
ABSTRACT

This Dissertation describes the research that we have conducted to measure and understand the properties of deep level defects in In_{1-x}Ga_{x-1}As_{1-x}N_x alloys. This is a novel class of alloys in which the bandgap of the alloy may be tailored to a desired value, typically near 1.0 eV, while maintaining lattice-match to GaAs. This work has focused on the measurement of 1.05 eV alloys containing 7% indium and 2% nitrogen.

Measurements have been accomplished primarily through the use of deep level transient spectroscopy (DLTS). In unintentionally doped p-type material grown by metal-organic chemical vapor deposition (MOCVD), we have detected four hole traps: H1, H2, H3, and H4, located at 0.10, 0.23, 0.48, and ~0.5 eV above the valence band edge, respectively. All four defects give rise to broad DLTS spectra and are thus believed to be due to energy distributions within the semiconductor bandgap, as opposed to discrete levels. The concentrations of H1, H2, and H4 were all observed to be substantially reduced following thermal annealing, and the removal of H4 was found to correlate with greater photoluminescence intensity, a longer minority-carrier diffusion length, and improved device performance. By comparing measurements of 1.05 eV and 1.15 eV lattice-matched alloys, it was found that the deep level spectra of MOCVD-grown p-type InGaAsN are sensitive to nitrogen content, with more nitrogen leading to higher concentrations of deep levels. Further, deep level concentrations were found to depend...
on MOCVD precursor gas flow conditions, and the presence of excess carbon appeared to correlate with the concentration of H4. DLTS measurements of MBE-grown, unintentionally doped p-type InGaAsN have detected deep levels, E3' and E4', whose positions in the bandgap are roughly consistent with H3 and H4. Further, the positions of H1 and H3/H3' are approximately consistent with the theoretically predicted energies of A$_{\text{AsGa-NAs}}$ pairs and N-N split interstitials in GaAsN, respectively. In n-type MOCVD-grown InGaAsN doped with tin, four electron levels were measured, E1, E2, E3, and E4. E1 is a broad distribution of states extending from the bottom of the conduction band to approximately $E_C - 0.2$ eV, whereas E2, E3, and E4 appear to be broadened levels centered at 0.36, 0.34, and 0.40 eV below the conduction band edge, respectively. All of the levels appeared in annealed material, whereas the E2 level was absent in as-grown material. Further, a single hole trap, H6, was observed at 0.71 eV above the valence band edge in annealed material. This level is believed to be the same defect as E2 observed via hole rather than electron emission, and the E2/H6 defect was shown to be responsible for the reverse-bias generation current in an InGaAsN-based test diode. Moreover, the capture kinetics of E2/H6 are consistent with that of an extended defect, and the physical source of this defect is believed to be related to the nucleation conditions of the InGaAsN alloy on a GaAs surface. Capture kinetics experiments were also performed on E4 and it was demonstrated that this level is a point-like defect characterized by a thermally activated electron capture cross-section, the activation energy of which is 0.42 eV. Further, the saturation time of E4 is on the order of 300 ms, which is exceedingly long. In MBE-grown n-type (Si-doped) InGaAsN, two levels were observed, E1' and E4': these levels are approximately consistent with levels E1 and E4 observed in MOCVD-grown...
material. Capture kinetics experiments measured very long saturation times for both E1' and E4', suggesting that similar electron capture mechanisms are at work in these two levels. E4' was, like E4, found to be a point-like level characterized by a thermally activated electron capture cross-section, although with an activation energy of 0.26 eV. The positions of E1/E1' and E4/E4' are roughly coincident with states predicted by an alloy-fluctuation model put forth in the literature to describe the structure of the conduction band of GaAsN and InGaAsN alloys. Further, the presence of E3 appears to correlate with the use of tin as an n-type dopant, as this level is absent in DLTS spectra of MOCVD-grown material doped with tellurium. Finally, a minority-carrier hole trap, H5', was observed in n-type InGaAsN grown by MBE. Although the measured activation energy of this level was equal to that of H6 at 0.71 eV, it does not seem possible that these two levels are the same, since H6 was observed to correlate with E2. Thus, the origin of H5' is unknown, aside from the fact that it is observed in MBE-grown material only.
Dedicated to my grandfather.

John F. Kaplar
ACKNOWLEDGMENTS

I would like to thank my parents for raising me and for teaching me to appreciate knowledge and the value of an education. Without their influence I would never have had the motivation to reach the point of writing this dissertation.

I would like to thank Dr. Bob Brown for introducing me to physics. I would also like to thank my advisor, Dr. Steve Ringel, for his guidance and support – without him, my career would not have been possible.

I am grateful for the assistance and friendship of many of my fellow students and post-docs at Ohio State, in particular Aaron Arehart, John Boeckl, Adrian Hierro, and Daewon Kwon. Further, I would like to thank Mr. Jim Jones for technical assistance with just about anything that required it.

I am indebted to my collaborators and future co-workers at Sandia National Laboratories, particularly Dr. Andy Allerman, Dr. Steve Kurtz, and Dr. Rob Sieg. Without their assistance, this dissertation would not have been possible.

I would like to thank Alec Patton for his friendship throughout the course of my graduate studies.

Finally, I would like to thank Wendy for her unconditional love and support during the time that we have known each other. I look forward to spending the rest of my life with you.
VITA

July 17, 1972 ................................................... Born – Cleveland, Ohio, USA

1994 ............................................................. B.S. in Physics, Case Western Reserve University

1995 – 1996 ..................................................... M.S. candidate, Stanford University

1998 ............................................................. M.S. in Electrical Engineering, The Ohio State University

1998 – 2002 .................................................... Ph.D. candidate, The Ohio State University

2002 – ............................................................. Postdoctoral associate, Sandia National Laboratories

PUBLICATIONS


FIELDS OF STUDY

Major Field: Electrical Engineering

vii
3.3 Impact of carrier recombination and generation on device properties ........................................ 39
  3.3.1 Generation current in a \textit{pn} junction diode ................................................................. 40
  3.3.2 Impact of carrier recombination on device performance .................................................. 45
3.4 References ................................................................................................................................... 50

4. CAPACITANCE TRANSIENT SPECTROSCOPY ......................................................................... 51

  4.1 Introduction ............................................................................................................................. 51
  4.2 Characterization of ideal deep levels by DLTS .................................................................... 52
     4.2.1 Experimental technique ................................................................................................. 52
     4.2.2 Physics of carrier emission ............................................................................................ 55
     4.2.3 Extraction of trap parameters from DLTS spectra ......................................................... 60
  4.3 Characterization of non-ideal deep levels by DLTS ............................................................... 66
     4.3.1 Carrier capture kinetics of point versus extended defects ............................................. 67
     4.3.2 Defects characterized by a distribution of states within the bandgap ........................... 70
  4.4 References ................................................................................................................................ 75

5. CHARACTERIZATION OF DEEP LEVELS IN InGaAsN GROWN BY METAL-ORGANIC CHEMICAL VAPOR DEPOSITION .............................................................................. 76

  5.1 Introduction ............................................................................................................................. 76
  5.2 Characterization of \textit{p}-type InGaAsN grown by MOCVD ................................................... 77
     5.2.1 Sample growth and material electronic quality ............................................................... 77
     5.2.2 Deep level characterization ............................................................................................ 83
  5.3 Characterization of \textit{n}-type InGaAsN grown by MOCVD ................................................ 89
     5.3.1 Sample growth and measurement of carrier concentration .......................................... 89
     5.3.2 Deep level characterization ............................................................................................ 96
     5.3.3 Impact of deep levels on carrier transport ................................................................... 102
  5.4 References ................................................................................................................................... 105

6. CHARACTERIZATION OF DEEP LEVELS IN InGaAsN GROWN BY MOLECULAR BEAM EPITAXY ................................................................................................................. 106

  6.1 Introduction ............................................................................................................................. 106
  6.2 MBE growth and sample preparation .................................................................................... 107
  6.3 Properties of deep levels in \textit{p}-type InGaAsN grown by MBE ............................................ 109
  6.4 Properties of deep levels in \textit{n}-type InGaAsN grown by MBE ........................................... 112
  References .................................................................................................................................... 116

7. TOWARD THE IDENTIFICATION OF THE PHYSICAL SOURCES OF DEEP LEVELS IN InGaAsN ALLOYS ......................................................................................................................... 117

  7.1 Introduction ............................................................................................................................. 117
  7.2 Carrier capture kinetics in \textit{n}-type InGaAsN ...................................................................... 118
  7.3 Impact of MOCVD growth conditions on the properties of deep levels ............................ 126
     7.3.1 Impact of growth conditions on defect spectra of \textit{p}-InGaAsN ................................... 127
     7.3.2 Impact of growth conditions on defect spectra of \textit{n}-InGaAsN .................................. 133

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
### LIST OF TABLES

| Table 1.1 | Properties of GaAs, InAs, GaN (cubic), and InN (cubic) at 300 K. | 2 |
| Table 1.2 | Summary of current multi-junction solar cell technology as well as potential future InGaAsN-based high-efficiency solar cell structures. Shown are the materials and bandgaps necessary to achieve the theoretical efficiencies indicated. | 15 |
| Table 4.1 | Sampling times $t_1$ and $t_2$ for various rate windows used throughout the course of this research. Note that the ratio $t_2/t_1 = 2.5$ in all cases. | 55 |
| Table 5.1 | MOCVD precursor gases used to grown InGaAsN layers. | 77 |
| Table 5.2 | Properties of deep levels observed in $p$-type InGaAsN grown by MOCVD. Activation energies are measured from the valence band edge. | 88 |
| Table 5.3 | Properties of deep levels in $n$-type InGaAsN grown by MOCVD. | 100 |
| Table 6.1 | Trap parameters resulting from the analysis of the DLTS spectra of $p$-type MBE-grown InGaAsN presented in Figure 6.3. Concentration values were calculated from the “majority-carrier DLTS” curve. | 112 |
| Table 6.2 | Trap parameters resulting from the analysis of the DLTS spectra of $n$-type MBE-grown InGaAsN presented in Figure 6.4. Concentration values were calculated from the “majority-carrier DLTS” curve. | 114 |
| Table 7.1 | Summary of the electron capture kinetics of defects E4 and E4' as observed in annealed, $n$-type InGaAsN grown by MOCVD and MBE. | 126 |
| Table 7.2 | Properties of deep levels observed in bulk 1.05 eV In$_{0.07}$Ga$_{0.93}$As$_{0.98}$N$_{0.02}$ films lattice-matched to GaAs. $E_A$ is measured from the valence band edge in H-traps and from the conduction band edge in E-traps; note that the cross-section activation energies $E_{ac}$ have been taken into account for E4 and E4'. | 140 |
LIST OF FIGURES

Figure 1.1 Bandgap versus lattice constant for InGaAs, GaAsN, and InGaAsN alloys. For the In$_x$Ga$_{1-x}$As curve, 0 < $x$ < 0.60; for the GaAs$_{1-y}$N$_y$ curve, 0 < $y$ < 0.06. .............................................................................................................. 2

Figure 1.2 Equivalent circuit of a single-junction solar cell. The parasitic resistances $R_S$ and $R_P$ are included for reference, but are not considered in the text. ................................................................. 5

Figure 1.3 Schematic illustration of a simple GaAs-based p-on-n solar cell. The shaded regions on the top and bottom of the structure represent metal contacts; the contact layer is necessary to provide good ohmic conduction between the window layer and the top metal contact. ................. 7

Figure 1.4 Absorption coefficients of various semiconductors as a function of energy $E = h\nu/\lambda$. .................................................................................................... 8

Figure 1.5 Example of solar cell spectral response. Individual contributions from the non-depleted base, non-depleted emitter, and depleted base/emitter regions are shown. Again recall that $E = h\nu/\lambda$. ................................................... 9

Figure 1.6 Solar cell current-voltage relationship calculated using Equation (1.4). The parameters used were $J_{01} = 10^{12}$ A/cm$^2$, $J_{02} = 10^{10}$ A/cm$^2$, and $J_L = 10^4$ A/cm$^2$; the temperature is assumed to be 300 K. Note that in the literature, plots such as this are often rotated about the horizontal axis. An optimized load current is also shown ........................................................................... 10

Figure 1.7 Schematic illustration of a series-connected four-junction solar cell and the portions of the solar spectrum that each junction is sensitive to. ............. 12

Figure 1.8 (a) Schematic diagram of a dual-junction GaAs-In$_{0.5}$Ga$_{0.5}$P solar cell, and (b) IQE of the same solar cell under one-sun, AM0 conditions. .......... 14

Figure 1.9 Calculated band line-ups of (a) InP-InGaAsP and (b) GaAs-InGaAsN quantum wells. Note the large conduction band offset between the two materials in part (b). ................................................................. 17

Figure 1.10 Room-temperature pulsed operation of an edge-emitting InGaAsN based laser diode grown by GS-MBE. ....................................................... 18
Figure 2.1 Bandstructure of an In$_{0.04}$Ga$_{0.96}$As$_{0.99}$N$_{0.01}$ alloy calculated using Equation (2.2).  

Figure 2.2 Photoreflectance spectra of four GaAs$_{1-x}$N$_x$ samples of varying nitrogen content $x$. The notation is such that $E_-, E_-$, and $E_+\Delta_0$ correspond to transitions 1, 2, and 3 of Figure 2.1 above.

Figure 2.3 Comparison between the predictions of the band anti-crossing theory (lines) and the results of photoreflectance spectra of the pressure dependence of the $E_-$ and $E_+$ transitions in GaAs$_{0.985}$N$_{0.015}$ (open triangles) and In$_{0.05}$Ga$_{0.95}$As$_{0.988}$N$_{0.012}$ (filled triangles) alloys.

Figure 2.4 Calculated nitrogen localized states ("cluster states") and quasi-localized states ("perturbed host states") induced in GaAs$_{1-y}$N$_y$ alloys for various nitrogen concentrations $y$. The zero of the scale is the position of the conduction band minimum of the GaAs host; the vertical arrows indicate the CBM of each GaAsN alloy.

Figure 2.5 Strongly localized, defect-like states (cluster states) and quasi-localized states (perturbed host states) predicted to exist in In$_{0.06}$Ga$_{0.94}$As$_{0.98}$N$_{0.02}$. The zero of energy corresponds to the conduction band minimum of the alloy.

Figure 3.1 Schematic illustration of carrier capture and emission through a deep level.

Figure 3.2 Simulated generation current versus temperature curves resulting from a deep level 0.35 eV below the conduction band edge of a 1.05 eV bandgap material. Note the different activation energies resulting from the two cases $\tau_n = \tau_p$ and $\tau_n >> \tau_p$.

Figure 3.3 Current-voltage relationship of the solar cell model presented in Figure 1.6, except without the inclusion of the $J_L$ term. The dominance of the $n = 2$ recombination current at low forward bias is evident.

Figure 4.1 Schematic illustration of the capture and emission of electrons from a deep level in the upper half of the bandgap. The leading edge of the fill pulse defines $t = 0$.

Figure 4.2 Schematic illustration of various capacitance transients as a function of temperature, and the resulting DLTS signals. Note that the symbol $\delta C$ in the figure is equivalent to the negative of the $\Delta C$ used throughout the text; this difference is trivial, merely resulting in a reflection of the DLTS signal about the temperature axis.

Figure 4.3 Capacitance transient resulting from majority-carrier emission from a deep level with $N_F/N_D = 0.01$. 

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Figure 4.4. Capacitance transient resulting from minority-carrier emission from a deep level with \( N_T/N_D = 0.01 \) and \( p_{T0}/N_D = 0.001 \). ........................................... 59

Figure 4.5. Simulated DLTS spectra of an R-G center located 0.35 eV below the conduction band edge of an \( n \)-type, 1.05 eV bandgap material. The electron and hole capture cross-sections were both assumed to be equal to \( 1\times10^{15} \) cm\(^2\), and initial trap occupancy parameters were \( n_{T0} = 0.75N_T \) and \( p_{T0} = 0.25N_T \) with a trap density of \( N_T = 0.01N_D \). The curves were sampled using rate windows 200, 80, 50, and 20 s\(^{-1}\). ........................................... 65

Figure 4.6. Schematic illustration of the band-bending that occurs in the vicinity of an extended defect due to the capture of carriers. ........................................... 68

Figure 4.7. Schematic illustration of a broadened deep level. ........................................... 71

Figure 4.8. Simulated DLTS spectra of a broadened R-G center. The trap parameters and experimental conditions were the same as those used to generate the curves of Figure 4.5, except that the level was assumed to be broadened according to Equation (4.40) with \( \sigma_E = 0.02 \) eV. ........................................... 73

Figure 5.1. Solar cell sample structure used to facilitate DLTS measurements on \( p \)-type InGaAsN grown by MOCVD. The DLTS spectra shown in this section are due to deep levels in the low-doped base layer. ........................................... 78

Figure 5.2. Photoluminescence and absorption spectra of \( p \)-type InGaAsN grown by MOCVD. Note the prominent sub-band gap features in the spectrum of the as-grown material and the dominance of the bandgap transition in the annealed material. ........................................... 79

Figure 5.3. 300 K light-IV curves of as-grown and annealed InGaAsN solar cells. Note the improvement following annealing.3 ........................................... 80

Figure 5.4. Internal quantum efficiency for as-grown and annealed InGaAsN solar cells. Again note the substantial improvement following annealing.3 ............. 81

Figure 5.5. DLTS spectra of as-grown, \( p \)-type InGaAsN layers grown by MOCVD. The experimental conditions used were \( V_R = -0.80 \) V and \( V_F = -0.15 \) V for a duration of 1 ms. Note that the DLTS signal is expressed in units of concentration. ................................................................. 83

Figure 5.6. Representative TEM image of InGaAsN layers grown by MOCVD. The absence of dislocations in the image indicates that the dislocation density is lower than the TEM statistical detection limit of \( 10^7 \) cm\(^2\). ............. 84

Figure 5.7. DLTS spectra of annealed, \( p \)-type InGaAsN layers grown by MOCVD. The experimental conditions were the same as for the spectra of Figure xiv

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
5.5 except that \( V_F = 0.00 \) V. The DLTS signal is again expressed in units of concentration. ........................................... 85

**Figure 5.8** Arrhenius analysis of the DLTS spectra of the \( p \)-type InGaAsN shown in Figure 5.7......................................................... 86

**Figure 5.9** Direct comparison between DLTS spectra of as-grown and annealed \( p \)-type InGaAsN. The data shown were obtained using a rate window of 200 s\(^{-1}\)................................................................. 87

**Figure 5.10** Heterojunction solar cell structure used to facilitate DLTS measurements of deep levels in \( n \)-type InGaAsN layers................................. 90

**Figure 5.11** Carrier concentration profiles of \( n \)-type InGaAsN layers, as determined from capacitance-voltage measurements.......................... 91

**Figure 5.12** Calculated density of electron traps required to account for the observed change in carrier concentration after annealing, as observed in Figure 5.11. Activation energy is measured from the conduction band edge................................................................. 93

**Figure 5.13** Calculated density of hole traps required to account for the observed change in carrier concentration after annealing, as observed in Figure 5.11. Activation energy is measured from the valence band edge........ 95

**Figure 5.14** Majority-carrier DLTS spectra of as-grown and annealed \( n \)-InGaAsN layers. The spectra shown were obtained using a rate window of 10 s\(^{-1}\), and the pulse conditions used were \( V_R = -1.00 \) V and \( V_F = -0.20 \) V with a fill pulse duration of 1 ms. The inset shows the Arrhenius plot of \( \ln(\tau T^2) \) (\( \tau T^2 \) in sK\(^2\)) vs. 1000/\( T \) (K\(^{-1}\)) which was used to determine the activation energies and electron capture cross sections for levels E2, E3, and E4................................................. 97

**Figure 5.15** DLTS spectra of as-grown and annealed InGaAsN layers under conditions of minority-carrier injection. The pulse conditions used were \( V_R = -1.00 \) V and \( V_F = +0.22 \) V, and the pulse duration was 1 ms. The data shown were obtained for a rate window of 10 s\(^{-1}\). The inset shows the Arrhenius plot of \( \ln(\tau T^2) \) (\( \tau T^2 \) in sK\(^2\)) vs. 1000/\( T \) (K\(^{-1}\)) used to determine the activation energy and hole capture cross section of trap H1................................................................. 99

**Figure 5.16** Minority-carrier injection DLTS curves of two \( n \)-InGaAsN layers grown under identical conditions aside from the initial gas-flow transition from GaAs to InGaAsN growth. The flow conditions for each transition are indicated in the figure. The 10 s\(^{-1}\) rate window is shown...... 101
**Figure 5.17** Reverse-bias current-temperature data for the annealed InGaAsN test diode grown using the no DMHy, low AsH₃ gas-flow transition. $I_{rev}$ is the reverse-bias generation current measured at a voltage of $-1.0$ V. The straight line shows the fit to the data, which yielded an activation energy of $0.35$ eV, corresponding to the E2/H6 deep level.  

**Figure 6.1** Schematic illustration of the essential elements of an MBE growth system.  

**Figure 6.2** Schematic illustration of the solar cell structures used to facilitate DLTS measurements of MBE-grown InGaAsN. Two configurations were grown, $n^{+}$-on-$p$ and $p^{+}$-on-$n$; in both cases the defect spectra are due to deep levels in the low-doped base layers. The window layer consisted of $30\%$ Al on the group III sublattice.  

**Figure 6.3** DLTS spectra of annealed, $p$-type, MBE-grown InGaAsN. The data shown were obtained using a rate window of $200$ s⁻¹ and a reverse-bias voltage of $V_R = -1.00$ V; the magnitude of the fill pulse was either $-0.20$ V (majority-carrier DLTS) or $+0.29$ V (minority-carrier injection DLTS) for a duration of $1$ ms. The inset shows the plot of $\ln(\tau T^2)$ vs. $1000/T$ (K⁻¹) that was used to determine the activation energies and capture cross-sections of levels H3 and H4.  

**Figure 6.4** DLTS spectra of annealed, $n$-type, MBE-grown InGaAsN. The data shown were obtained using a rate window of $20$ s⁻¹ and a reverse-bias voltage of $V_R = -1.00$ V; the magnitude of the fill pulse was either $-0.20$ V (majority-carrier DLTS) or $+0.34$ V (minority-carrier injection DLTS) for a duration of $1$ ms. The inset shows the plot of $\ln(\tau T^2)$ vs. $1000/T$ (K⁻¹) that was used to determine the activation energies and capture cross-sections of levels E4' and H5'.  

**Figure 7.1** Results of majority-carrier fill-pulse experiments made on annealed, $n$-type InGaAsN grown by MOCVD. For comparison to Figure 5.14, the $1$ ms curve is marked with a vertical hash; the $10$ s⁻¹ rate window is again shown.  

**Figure 7.2** Carrier capture kinetics of defect E2. Fill pulse times of $0.01$, $0.0316$, $0.1 \ldots 316$ ms are shown; the points are spaced so as to appear linearly separated on a logarithmic scale.  

**Figure 7.3** Carrier capture kinetics of defect E4 in MOCVD-grown InGaAsN. The data indicate that the capture kinetics are consistent with a point defect characterized by a thermally activated electron capture cross-section.  

**Figure 7.4** Explanation of the shift in peak position corresponding to changes in the fill pulse time in terms of a broadened defect level.
Figure 7.5 Results of majority-carrier fill-pulse experiments made on annealed, n-type InGaAsN grown by MBE. For comparison to Figure 6.4, the 1 ms curve is marked with a vertical hash; the 20 s\(^{-1}\) rate window is shown. 124

Figure 7.6 Carrier capture kinetics of defect E4' in MBE-grown InGaAsN. The data indicate that the capture kinetics are consistent with a point defect characterized by a thermally activated electron capture cross-section. 125

Figure 7.7 Majority-carrier DLTS spectra of two as-grown, p-type (uid), 1.05 eV InGaAsN layers grown using different arsine flow rates. The data are shown for a rate window of 200 s\(^{-1}\). 128

Figure 7.8 Majority-carrier DLTS spectra of (a) as-grown and (b) annealed, p-type, 1.05 eV InGaAsN layers doped using different sources. The data are shown for a rate window of 20 s\(^{-1}\). 130

Figure 7.9 Majority-carrier spectra of as-grown, p-type (uid), lattice-matched InGaAsN layers, illustrating the effect of different nitrogen content. Also shown is the spectrum of a lattice-mismatched, n-type (uid) In\(_{0.02}\)Ga\(_{0.98}\)As layer. The data are shown for a rate window of 200 s\(^{-1}\). 133

Figure 7.10 Majority-carrier deep level spectra of annealed, n-type In\(_{0.07}\)Ga\(_{0.93}\)As\(_{0.98}\)N\(_{0.02}\) layers grown by MOCVD. The duration of the fill pulse was 1 ms; the 20 s\(^{-1}\) rate window is shown. 134

Figure 7.11 Arrhenius plots of all traps except for E1, E1', and H4. Primed traps, i.e. traps observed in MBE-grown material, are indicated by dotted lines. Note that the cross-section activation energies \(E_A\) have been taken into account for E4 and E4'. 140

Figure 8.1 Schematic illustration of the proposed device which could be used to facilitate DLTS measurements on InGaAsN quantum wells. 148
LIST OF SYMBOLS

\( \alpha \quad \) Absorption coefficient, \( \text{cm}^{-1} \)

\( a \quad \) Lattice constant, \( \text{Å} \); electron concentration constant, \( \text{K}^{3/2}\text{cm}^{-3} \)

\( a_n \quad \) Electric potential expansion coefficients, \( \text{Vcm}^n \)

\( A \quad \) Diode cross-sectional area, \( \text{cm}^2 \)

\( b \quad \) Bandgap bowing parameter, eV; hole concentration constant, \( \text{K}^{3/2}\text{cm}^3 \)

\( c_n \quad \) Electron capture coefficient, \( \text{cm}^3\text{s}^{-1} \)

\( c_p \quad \) Hole capture coefficient, \( \text{cm}^3\text{s}^{-1} \)

\( C \quad \) Capacitance, pF

\( C_\infty \quad \) Steady-state capacitance, pF

\( \Delta C \quad \) DLTS signal, pF

\( \Delta C_0 \quad \) DLTS signal coefficient, pF

\( \Delta \quad \) Spin-orbit split-off energy, eV

\( D_n \quad \) Electron diffusion coefficient, \( \text{cm}^2/\text{s} \)

\( D_p \quad \) Hole diffusion coefficient, \( \text{cm}^2/\text{s} \)

\( \varepsilon \quad \) Permittivity, F/cm

\( e_n \quad \) Electron emission rate, \( \text{s}^{-1} \)

\( e_p \quad \) Hole emission rate, \( \text{s}^{-1} \)

\( e_\omega \quad \) Quantum-well emission rate, \( \text{s}^{-1} \)

\( E \quad \) Energy, eV

\( E_\sigma \quad \) Capture cross-section activation energy, eV

\( E_g \quad \) Bandgap energy, eV

\( E_A \quad \) Activation energy, eV

\( E_C \quad \) Conduction band edge energy, eV

\( E_i \quad \) Valence band edge energy, eV

\( E_T \quad \) Trap energy, eV

\( E_M \quad \) Band anti-crossing matrix conduction band, eV

\( E_N \quad \) Band anti-crossing nitrogen-induced defect level, eV

\( E_- \quad \) Band anti-crossing upper conduction band branch, eV

\( E_+ \quad \) Band anti-crossing lower conduction band branch, eV

\( E_{\text{HH}} \quad \) Heavy-hole valence band energy, eV

\( E_{\text{LH}} \quad \) Light-hole valence band energy, eV

\( E_{SO} \quad \) Split-off valence band energy, eV

\( F_n \quad \) Electron quasi-Fermi level, eV

\( F_p \quad \) Hole quasi-Fermi level, eV

\( \gamma_n \quad \) Electron DLTS constant, \( \text{cm}^{-2}\text{s}^{-1}\text{K}^{-2} \)

\( \gamma_p \quad \) Hole DLTS constant, \( \text{cm}^{-2}\text{s}^{-1}\text{K}^{-2} \)

\( \Gamma \quad \) Photon flux, \( \text{cm}^{-2}\text{s}^{-1} \)

xviii
\( \Gamma_0 \quad \text{Incident photon flux (solar spectrum), } \text{cm}^{-2}\text{s}^{-1} \)

\( G \quad \text{Generation rate, } \text{cm}^{-3}\text{s}^{-1} \)

\( h \quad \text{Planck's constant, eV}s \)

\( J \quad \text{Current density, A/cm}^2 \)

\( J_{D1} \quad \text{Solar cell diffusion current density, A/cm}^2 \)

\( J_{D2} \quad \text{Solar cell recombination current density, A/cm}^2 \)

\( J_{0B} \quad \text{Solar cell base saturation current density, A/cm}^2 \)

\( J_{0E} \quad \text{Solar cell emitter saturation current density, A/cm}^2 \)

\( J_L \quad \text{Solar cell photo-generated (light) current density, A/cm}^2 \)

\( J_m \quad \text{Solar cell current density at maximum power output, A/cm}^2 \)

\( J_{sc} \quad \text{Solar cell short-circuit current density(A)} \)

\( k \quad \text{Boltzmann's constant, eV/K} \)

\( \lambda \quad \text{Wavelength, cm} \)

\( L_n \quad \text{Electron minority-carrier diffusion length, cm} \)

\( L_p \quad \text{Hole minority-carrier diffusion length, cm} \)

\( m_n \quad \text{Electron effective mass, kg} \)

\( m_p \quad \text{Hole effective mass, kg} \)

\( m_M \quad \text{Band anti-crossing matrix electron effective mass, kg} \)

\( n \quad \text{Electron density, cm}^{-3}; \text{Diode ideality factor, unitless} \)

\( n_T \quad \text{Density of filled traps, cm}^{-3} \)

\( n_{TE} \quad \text{Equilibrium density of filled traps, cm}^{-3} \)

\( n_{T0} \quad \text{Density of filled traps at end of DLTS fill pulse, cm}^{-3} \)

\( N \quad \text{Charge density, cm}^{-3} \)

\( N_A \quad \text{Acceptor density, cm}^{-3} \)

\( N_D \quad \text{Donor density, cm}^{-3} \)

\( N_C \quad \text{Conduction band edge density of states, cm}^{-3} \)

\( N_V \quad \text{Valence band edge density of states, cm}^{-3} \)

\( N_T \quad \text{Trap density, cm}^{-3} \)

\( p \quad \text{Hole density, cm}^{-3} \)

\( p_T \quad \text{Density of empty traps, cm}^{-3} \)

\( p_{TE} \quad \text{Equilibrium density of empty traps, cm}^{-3} \)

\( p_{T0} \quad \text{Density of empty traps at end of DLTS fill pulse, cm}^{-3} \)

\( \varphi \quad \text{Electric potential, V} \)

\( q \quad \text{Electron charge, C} \)

\( \rho \quad \text{Reflection coefficient, unitless} \)

\( r \quad \text{DLTS signal constant, unitless} \)

\( R \quad \text{Recombination rate, cm}^{-3}\text{s}^{-1} \)

\( R_L \quad \text{Solar cell load resistance, } \Omega \)

\( R_P \quad \text{Solar cell parallel (shunt) resistance, } \Omega \)

\( R_S \quad \text{Solar cell series resistance, } \Omega \)

\( \sigma_E \quad \text{Standard deviation of Gaussian trap density distribution, eV} \)

\( \sigma_n \quad \text{Electron capture cross-section, cm}^2 \)

\( \sigma_p \quad \text{Hole capture cross-section, cm}^2 \)

\( \tau_E \quad \text{Extended defect capture time constant, s} \)

\( \tau_g \quad \text{Generation lifetime, s} \)
\( \tau \) Recombination lifetime, s
\( \tau_n \) Electron minority-carrier lifetime, s; Electron emission time constant, s
\( \tau_p \) Hole minority-carrier lifetime, s
\( \tau_w \) Quantum-well emission time constant, s
\( RW \) Rate window, s\(^{-1}\)
\( S_n \) Electron surface recombination velocity, cm/s
\( S_p \) Hole surface recombination velocity, cm/s
\( t_f \) Fill pulse duration, s
\( U \) Recombination-generation rate, cm\(^{-3}\)s\(^{-1}\)
\( v_{th} \) Thermal velocity, cm/s
\( V \) Voltage, V
\( V_F \) Total fill pulse voltage \((V_F = V_R + V_P)\), V
\( V_P \) Magnitude of fill pulse, V
\( V_R \) Reverse-bias voltage, V
\( V_{bi} \) Built-in voltage, V
\( V_m \) Solar cell voltage at maximum power output, V
\( V_{oc} \) Solar cell open-circuit voltage, V
\( V_{MN} \) Band anti-crossing interaction term, eV
\( W_B \) Solar cell base width, cm
\( W_E \) Solar cell emitter width, cm
\( W_D \) Depletion width, cm; also \( x_D \)
\( x \) Distance, cm; Group III composition, unitless
\( x_D \) Depletion width, cm; also \( W_D \)
\( y \) Group V composition, unitless
CHAPTER I
INTRODUCTION AND MOTIVATION

1.1 Introduction

The In$_x$Ga$_{1-x}$As$_{1-y}$N$_y$ class of semiconductor alloys is a novel materials system which is potentially useful in a number of contexts, including high-efficiency multi-junction solar cells for space power applications as well as 1.30 and 1.55 μm optoelectronics for fiber-optic communications applications. Both of these areas of application are discussed in detail later in this chapter. The novel properties of the InGaAsN material stem from the large "bowing parameter" of the ternary GaAsN alloy for low nitrogen concentrations, "low" meaning [N] < 6% or so. For a ternary alloy A$_x$B$_{1-x}$C, the bandgap is given by

\[ E_g(x) = xE_g(AC) + (1-x)E_g(BC) - bx(1-x) \]  \hspace{1cm} (1.1)

where the quantity b is known as the bowing parameter. In a "typical" ternary III-V semiconductor alloy, the bowing parameter tends to be less than unity: e.g., for the InGaAs alloy, b = 0.40 eV. The ternary GaAsN alloy, however, is characterized by a bowing parameter that is not only considerably greater than unity, but one that is composition-dependent as well; for the composition range of interest, b is predicted to be roughly 16 eV. A plot of lattice constant a versus bandgap energy $E_g$ is shown in Figure 1.
The values of $a$ and $E_g$ used for the various binary compounds are listed in the table below the figure.

\begin{center}
\begin{tabular}{|c|c|c|c|}
\hline
Parameter & GaAs & InAs & GaN (cubic) & InN (cubic) \\
\hline
$E_g$ (eV) & 1.42 & 0.35 & 3.28 & 2.20 \\
$a$ (Å) & 5.65 & 6.06 & 4.52 & 4.98 \\
\hline
\end{tabular}
\end{center}

\textbf{Table 1.1} Properties of GaAs, InAs, GaN (cubic), and InN (cubic) at 300 K.\textsuperscript{23}

Note that the cubic form of GaN is considered, as opposed to the more common hexagonal structure; this is because the GaAsN alloys under consideration are cubic crystals, and a meaningful interpolation based on Equation (1.1) requires that the crystal structure be the same. For both branches of the plot, the values of the lattice constant $a$
were calculated by using a linear interpolation between the lattice constants of the two binary constituents; for the hypothetical ternary compound A_{x}B_{1-x}C, this is expressed by

\[ a(x) = xa(AC) + (1 - x)a(BC) \]  (1.2)

Due to the large GaAsN bowing parameter, we see from Figure 1.1 that the addition of a small amount of nitrogen to GaAs actually decreases the bandgap, even though the bandgap of GaN is larger than that of GaAs! This peculiar property may be exploited in that any lattice constant-bandgap combination within the shaded region of Figure 1.1 may be achieved though the use of the quaternary alloy In_{x}Ga_{1-x}As_{1-y}N_{y}. Further, extending Equation (1.2) to this alloy, we have

\[ a(x, y) = x(1 - y)a(InAs) + yxa(InN) + (1 - x)(1 - y)a(GaAs) + (1 - x)y(a(GaN)) \]  (1.3)

By substituting the appropriate values from Table 1.1 into Equation (1.3), it may be shown that the quaternary alloy is lattice-matched to GaAs for \( x = 3.5y \). This condition is indicated by the vertical line in Figure 1.1. Thus, it should be possible to grow InGaAsN lattice-matched to GaAs, anywhere within the bandgap range indicated by the line, simply by varying the indium and nitrogen fractions \( x \) and \( y \), so long as the ratio \( x = 3.5y \) is maintained! This opens up the possibility of growing thick, dislocation-free layers of material within a broad range of infrared bandgaps on standard GaAs substrates. Further, thin layers within roughly the same bandgap range may be grown on GaAs substrates in conditions of either tensile or compressive strain.

Despite the enormous potential of the InGaAsN alloy system, problems with material quality remain a major challenge. In particular, a large miscibility gap exists.
between GaN and GaAs, so that the growth of single-phase GaAsN and, hence, InGaAsN has been difficult. In fact, it has been observed that the incorporation of even a few atomic percent nitrogen requires a low growth temperature and a high nitrogen-source flux.\textsuperscript{4} Further, short minority-carrier diffusion lengths have been observed in InGaAsN solar cells, and these have adversely affected the performance of such devices.\textsuperscript{5,6,7} The cause of the short minority-carrier diffusion lengths is currently not well understood. The source may be intrinsic, for example localized regions of GaN owing to the poor miscibility of GaN and GaAs. On the other hand, the source may be extrinsic, for example impurities in the source materials, in particular in the nitrogen source. Further, conditions such as those that must be used to grow single-phase InGaAsN typically affect minority-carrier diffusion lengths in a negative fashion even in more conventional materials, further exacerbating any pre-existing intrinsic or extrinsic problems.\textsuperscript{8} Whether intrinsic, extrinsic, or a combination of the two, defects are likely to give rise to deep levels within the bandgap of the InGaAsN material, and in fact deep levels have been reported in both $p$-type\textsuperscript{9} and $n$-type\textsuperscript{10,11,12} InGaAsN grown by MOCVD as well as in both $p$- and $n$-type InGaAsN grown by MBE.\textsuperscript{13} The purpose of the research described herein and reported in references 9, 11, 12, and 13) is to identify deep level defects in InGaAsN and, if possible, to correlate these defects with growth conditions, physical sources, and device performance.

1.2 Application of InGaAsN to solar cells

The majority of the work presented in this Dissertation deals with the measurement of deep level defects in bulk InGaAsN layers grown for solar cell
applications. Thus, we will spend some time reviewing the physics of solar cell operation. We begin with a general discussion of single-junction solar cells and their properties, and follow this with a focused investigation of the specific role of InGaAsN alloys in high-efficiency, multi-junction solar cells.

1.2.1 Theory of single-junction solar cells

An equivalent circuit of a single-junction solar cell is shown in Figure 1.2 below. The model contains two diodes contributing current densities $J_{D1}$ (diffusion current) and $J_{D2}$ (recombination current), a current source contributing a current density $-J_L$, and series and parallel (or shunt) resistances $R_S$ and $R_P$. The load resistance is $R_L$.

For the purposes of this chapter, we shall ignore the parasitic resistances $R_S$ and $R_P$. The solar cell current is then given by

$$J = J_{D1} + J_{D2} - J_L = J_{o1}\left[\exp\left(\frac{qV}{kT}\right) - 1\right] + J_{o2}\left[\exp\left(\frac{qV}{2kT}\right) - 1\right] - J_L$$

(1.4)

The diodes $D1$ and $D2$ are $pn$ junctions; the top layer is known as the emitter, and the bottom layer is known as the base. The emitter layer is typically the thinner of the two.
layers, since a thinner layer allows light to pass into the base layer below it. For our purposes, we assume a \textit{p-on-n} configuration since, as we will see in later chapters, carrier transport in \textit{p}-type InGaAsN alloys is limited to extremely short distances; as a result, it will be beneficial to fabricate the thicker base layer out of \textit{n}-type InGaAsN, where transport may occur over relatively longer distances. The diffusion saturation current $J_{01}$ is then a sum of a component from the \textit{p}-type emitter and a component from the \textit{n}-type base, given by

$$J_{01} = J_{0B} + J_{0E} \quad (1.5)$$

Consider the emitter saturation current $J_{0E}$. It is given by

$$J_{0E} = q \left( \frac{n_c^2 D_n}{N_A L_n} \right) \left[ \frac{S_n L_n \cosh \left( \frac{W_E}{L_n} \right) + \sinh \left( \frac{W_E}{L_n} \right)}{\frac{S_n L_n \sinh \left( \frac{W_E}{L_n} \right) + \cosh \left( \frac{W_E}{L_n} \right)}{4}} \right] \quad (1.6)$$

The quantity $L_n$ is the \textit{electron minority-carrier diffusion length}. This quantity is the distance, on average, that a minority-carrier electron travels in a "sea" of majority-carrier holes prior to recombining; a precise definition of this quantity is given in Chapter 3. A related parameter is $S_n$, the \textit{electron surface recombination velocity}, which gives a measure of the rate at which minority-carrier electrons recombine at the top surface of the emitter layer. To minimize this recombination, a \textit{window} layer is often grown on top of the emitter; for this purpose, a material that "passivates" the surface (e.g. AlGaAs on GaAs) is deposited to reduce the surface recombination velocity. An expression similar to Equation (1.6) with the appropriate substitutions made (e.g. $W_E \rightarrow W_B$, $L_n \rightarrow L_p$) describes the base saturation current $J_{0B}$. Analogous to the window layer, a layer known
as a back surface reflector (BSR) is often inserted between the substrate and the base layer in order to passivate the back surface of the base as well as to improve the efficiency with which photo-generated carriers are collected. A schematic of a basic GaAs-based solar cell is illustrated in Figure 1.3 below.

![Figure 1.3 Schematic illustration of a simple GaAs-based p-on-n solar cell. The shaded regions on the top and bottom of the structure represent metal contacts; the contact layer is necessary to provide good ohmic conduction between the window layer and the top metal contact.](image)

We now turn our attention to the other two components of the solar cell current density, the recombination current density $J_{D2}$ and the photo-generated current density $J_L$. The former is addressed in detail in Chapter 3, so we will defer our discussion of it until then. The photo-generated current $J_L$, on the other hand, is the means through which the solar cell is able to generate useful power. Incident photons are absorbed by the semiconductor material and generate electron-hole pairs, which are then swept out of the solar cell by the built-in field of the junction and consequently constitute the current source shown in Figure 1.2. The differential photo-current generated in a region of width $dx$ is given by

\[ J_L \]
\[ dJ_x(\lambda, x) = q\alpha(\lambda)\Gamma(\lambda, x)dx \]  

(1.7)

where the quantity \( \alpha(\lambda) \) is the wavelength-dependent absorption coefficient. The absorption coefficient for a given material is zero for energies less than its bandgap and increases rapidly thereafter, as illustrated in Figure 1.4 below.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{absorption_coefficients.png}
\caption{Absorption coefficients of various semiconductors as a function of energy \( E = hc/\lambda \).}
\end{figure}

The quantity \( \Gamma(\lambda, x) \) is the photon flux at the wavelength \( \lambda \) and position \( x \). Its intensity decreases with position in a semiconductor material according to

\[ \Gamma(\lambda, x) = \Gamma_0(\lambda)(1 - \rho(\lambda))\exp[-\alpha(\lambda)x] \]  

(1.8)

where \( \rho(\lambda) \) is the reflection coefficient of the solar cell and \( \Gamma_0(\lambda) \) is the incident photon flux, i.e. the solar spectrum. The photo-current density due to absorption of light at
wavelength is obtained by integrating over the width of the active portion (i.e., the emitter and base layers) of the solar cell, so that

$$J_L(\lambda) = q\Gamma_0(\lambda)[1 - \rho(\lambda)] \int_{-w_e}^{w_e} \alpha(\lambda) \exp[-\alpha(\lambda)x]dx$$ (1.9)

The integral in this expression is equal to the efficiency with which photons are converted into electrons, and is known as the internal quantum efficiency, or IQE. Often the IQE is determined experimentally, in which case it is given by

$$\text{IQE}(\lambda) = \frac{J_L(\lambda)}{q\Gamma_0(\lambda)[1 - \rho(\lambda)]}$$ (1.10)

If the bracketed term containing the reflection coefficient is omitted, the remaining quantity is known as the external quantum efficiency or spectral response. An example of this is shown in Figure 1.5 below.

![Graph](image)

**Figure 1.5** Example of solar cell spectral response. Individual contributions from the non-depleted base, non-depleted emitter, and depleted base/emitter regions are shown. Again recall that $E = h\nu/\lambda$.  

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
The photo-generated current density may be obtained by integrating over the IQE and the incident photon flux, i.e.

\[ J_L = q \int \Gamma_n(\lambda)[1 - \rho(\lambda)]\text{IQE}(\lambda)d\lambda \]  

(1.11)

Obviously, the photo-current density will be larger if there is significant wavelength overlap between the IQE and the solar spectrum: this point will be returned to in the next section.

For purposes of illustration, a simulated solar cell current-voltage curve, calculated using Equation (1.4), is illustrated below.

\[ \text{Voltage (V)} \]
\[ \text{Power} \]
\[ \text{Load current} \]
\[ (V_o, J_o) \]
\[ \text{Cell current} \]

Figure 1.6  Solar cell current-voltage relationship calculated using Equation (1.4). The parameters used were \( J_{01} = 10^{-12} \text{ A/cm}^2 \), \( J_{02} = 10^{-10} \text{ A/cm}^2 \), and \( J_L = 10^{-2} \text{ A/cm}^2 \); the temperature is assumed to be 300 K. Note that in the literature, plots such as this are often rotated about the horizontal axis. An optimized load current is also shown.
A number of important points are illustrated in Figure 1.6. The first of these is the \textit{short-circuit current density}, $J_{sc}$, which is the current density at zero applied voltage. From Equation (1.4), this is

$$J_{sc} = -J_{o1} - J_{o2} - J_L = -J_L$$  \hfill (1.12)

As second important point evident in Figure 1.6 is the \textit{open-circuit voltage}, $V_{oc}$, defined as the voltage at which no current passes through the solar cell. For sufficiently large voltages, the $n = 1$ diffusion component will always dominate over the $n = 2$ recombination component of Equation (1.4); thus, if we neglect the latter component and set the current to zero, we find

$$V_{oc} = \frac{kT}{q} \ln \left( \frac{J_L}{J_{o1}} + 1 \right)$$  \hfill (1.13)

Generally, it is desirable to maximize $J_{sc}$ and $V_{oc}$. To illustrate this, we have shown in Figure 1.6 a plot of the power, $P = V I$, generated by the solar cell; note that it is negative, since the cell is producing power rather than consuming it. We see that the magnitude of the power reaches a maximum at the point $(V_m, J_m)$, and we have thus included in the plot the current due to an optimized load resistance $R_L = V_m/AJ_m$; the solar cell operates at the point where the cell current curve crosses the load current line. We thus see that the power delivered to the load will generally be higher for higher values of $I_{sc}$ and $V_{oc}$. The next section discusses methods of achieving this.

\textbf{1.2.2 Multi-junction solar cells}

It was mentioned in the previous section that the IQE of a solar cell is larger if there is significant overlap between the absorption coefficient and the incident solar
spectrum. It follows that, since the absorption coefficient of a semiconductor is fixed by the material’s bandgap, improvements in material quality can only go so far towards improving the overall efficiency of a solar cell. One way to overcome this limitation is to use multiple cells consisting of different materials – with each material possessing an optimally chosen bandgap – in concert to make more efficient use of the incident solar spectrum. Such high efficiency is particularly important for space applications such as satellite power systems. In such systems, solar cell “real estate” is at a premium, not only because of the technical problems associated with deploying extremely large solar panels, but also because of the enormous launch costs associated with each additional bit of weight due to added solar cell area. Thus, high-efficiency multi-junction solar cells have found extensive application in space power systems. In order to conserve area, such solar cells are composed of individual junctions grown one on top of another, connected in series rather than in parallel. The method by which a multi-junction series stack takes advantage of the whole solar spectrum is illustrated schematically below: the particular cell configuration shown will be discussed later in this section.

Figure 1.7 Schematic illustration of a series-connected four-junction solar cell and the portions of the solar spectrum that each junction is sensitive to.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Since the individual junctions such as those of Figure 1.7 are connected in series, it is not
the photo-generated current density that is improved through the use of multiple
junctions; indeed, since the current through the stack will be limited by the worst-
performing cell, each individual cell must be current-matched to all of the others in the
stack in order to maintain optimum performance. Thus, Equation (1.11) is applicable to
the IQEs resulting from each of the individual junctions, and not to the total IQE of the
multi-junction cell. Rather than increasing the photo-current density, it is the cell voltage
that is increased in this series-connected multi-junction configuration, since the voltages
of each of the individual junctions add to give the overall cell voltage. The increased cell
voltage coupled with the unperturbed density of cell current allows multi-junction solar
cells to produce more power for a given flux of solar radiation than their single-junction
counterparts, thus making them desirable for applications requiring high conversion
efficiency – applications such as space power systems. Finally, note that since solar cells
are composed of relatively thick layers (on the order of 1 μm or so), the materials of
which they are composed must be lattice-matched to their substrates in order to avoid the
formation of performance-degrading dislocations. This imposes a very strict limitation
on the types of materials that may be considered when trying to grow such devices.

The simplest multi-junction cell in common use is a dual-junction GaAs-
In_{0.5}Ga_{0.5}P configuration,^{16,17,18} the InGaP cell is placed on top since its bandgap (1.85
eV) is larger than that of GaAs (1.42 eV), thus allowing lower-energy photons that are
not absorbed by the top junction to pass through to the bottom junction to be collected
there. These two-junction cells are typically grown on GaAs substrates and have
achieved efficiencies of nearly 31% under one-sun, air-mass zero (AM0) conditions, i.e.
under conditions similar to what a satellite in Earth orbit would experience.\textsuperscript{5} A schematic diagram of such a two-junction cell is shown in Figure 1.8 below.

![Schematic diagram of a two-junction GaAs-In\textsubscript{0.5}Ga\textsubscript{0.5}P solar cell](image)

**Figure 1.8** (a) Schematic diagram of a dual-junction GaAs-In\textsubscript{0.5}Ga\textsubscript{0.5}P solar cell, and (b) IQE of the same solar cell under one-sun, AM0 conditions.\textsuperscript{17}

Also shown in the figure is the IQE of the dual-junction device. In this latter portion of the figure, note the distinct contributions from each portion of the spectrum due to each of the junctions: further, note that the IQE decreases in the long-wavelength region where the reflectivity $\rho$ is higher, in accordance with Equation (1.10).

A further improvement in collection efficiency can be achieved by inserting a third junction, composed of 0.67 eV bandgap Ge, below the GaAs junction and growing the entire structure on a strong, lightweight Ge substrate. This results in a solar cell which captures even more of the solar spectrum than the dual-junction cell. However, this is not the best way to extend the GaAs-InGaP dual-junction cell to a three-junction configuration, since the 0.67 eV bandgap of Ge does not result in optimum performance when coupled with the 1.85 and 1.42 eV bandgaps of the In\textsubscript{0.5}Ga\textsubscript{0.5}P and GaAs layers. Rather, simulations have shown that the replacement of the GaAs junction with a 1.25 eV
material would result in a theoretical one-sun AM0 efficiency of 38%, as opposed to 35% for the Ge-GaAs-InGaP configuration. Further, the insertion of a 1.05 eV material in between the GaAs and Ge layers of existing Ge-GaAs-InGaP three-junction devices would boost the efficiency of the resulting four-junction cell to 41%.\textsuperscript{6} From Figure 1.1 we see that InGaAsN can be grown lattice-matched to GaAs at both 1.05 and 1.25 eV, making it a good candidate for both of these possibilities. Moreover, the GaAs-InGaP two-junction device is theoretically less efficient than a 1.15-1.70 eV InGaAsN-InGaAsP device would be.\textsuperscript{19} Thus, the ability to grow good-quality bulk InGaAsN layers would enable a whole new range of high-efficiency solar cell structures to be created; see Table 1.2 below for a summary of these possibilities.

<table>
<thead>
<tr>
<th>Number of junctions</th>
<th>Current technology</th>
<th>Future technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-junction</td>
<td>GaAs-InGaP</td>
<td>InGaAsN-InGaAsP</td>
</tr>
<tr>
<td></td>
<td>1.42-1.85 eV</td>
<td>1.15-1.70 eV</td>
</tr>
<tr>
<td></td>
<td>31%</td>
<td>33%</td>
</tr>
<tr>
<td>3-junction</td>
<td>Ge-GaAs-InGaP</td>
<td>Ge-InGaAsN-InGaAsP</td>
</tr>
<tr>
<td></td>
<td>0.67-1.42-1.85 eV</td>
<td>0.67-1.25-1.85 eV</td>
</tr>
<tr>
<td></td>
<td>35%</td>
<td>38%</td>
</tr>
<tr>
<td>4-junction</td>
<td>–</td>
<td>Ge-InGaAsN-GaAs-InGaP</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.67-1.05-1.42-1.85 eV</td>
</tr>
<tr>
<td></td>
<td></td>
<td>41%</td>
</tr>
</tbody>
</table>

Table 1.2 Summary of current multi-junction solar cell technology as well as potential future InGaAsN-based high-efficiency solar cell structures. Shown are the materials and bandgaps necessary to achieve the theoretical efficiencies indicated.
Of course, the devices in the third column of the table are a long way from being realized, since many fundamental problems regarding the InGaAsN alloy remain unsolved. Indeed, to date single-junction InGaAsN solar cells have been inefficient;\textsuperscript{5,6,7} this is though to be due to the short minority-carrier diffusion lengths in InGaAsN, as well as to the general poor electronic quality of this class of materials. Obviously, a better understanding of the fundamental electronic properties of InGaAsN is necessary in order to realize the new classes of solar cells described above.

1.3 Application of InGaAsN to 1.30 and 1.55 \( \mu \text{m} \) optoelectronics

In this section we discuss another potential application of InGaAsN alloys, namely, for use as light sources for long-haul optical fiber communications systems. Current fiber-optic systems rely on light sources emitting at either 1.30 \( \mu \text{m} \) (0.95 eV) or 1.55 \( \mu \text{m} \) (0.80 eV), since it is for those wavelengths that the minimum loss in standard glass optical fiber is achieved. These sources are typically laser diodes fabricated from InP in conjunction with In\(_x\)Ga\(_{1-x}\)As\(_{1-y}\)P\(_y\) alloys, grown on InP substrates.\textsuperscript{20} However, such laser diodes exhibit poor temperature characteristics due to weak electron confinement, since only small conduction band offsets are achievable between InP and InGaAsP alloys.\textsuperscript{21,22} Further, the InP substrates that must be used to fabricate such structures are brittle and expensive compared to GaAs substrates. Thus, a material compatible with GaAs and having a bandgap in the range of 0.8 to 1.0 eV is desirable for optical communication system applications. Further, in order to avoid thermal problems similar to those associated with the InP-InGaAsP system, it would be advantageous for such a material to have a large conduction band offset with GaAs. The InGaAsN alloy was in
fact first investigated because it has these very properties. The diagram below shows calculated band line-ups for a conventional InP-InGaAsP quantum-well structure as well as a potential GaAs-InGaAsN-based quantum well, both of which are designed to be employed in a 1.3 µm laser diode; note the much larger conduction band offset in the InGaAsN-based structure. Also note that the In:N ratio in the InGaAsN layer shown is larger than 3.5; this is because InGaAsN layers for optoelectronic applications such as laser diodes are typically designed to exist in a state of compressive strain, rather than the lattice-matched condition that is necessary for the much thicker "bulk" layers used for multi-junction solar cell applications.

\[ \Delta E_c = 100 \text{ meV} \]

\[ \Delta E_v = 150 \text{ meV} \]

\[ \Delta E_v = 60 \text{ meV} \]

\[ \Delta E_v = 570 \text{ meV} \]

**Figure 1.9** Calculated band line-ups of (a) InP-InGaAsP and (b) GaAs-InGaAsN quantum wells. Note the large conduction band offset between the two materials in part (b).

Several groups have reported the successful operation of InGaAsN-based laser diodes grown by a variety of techniques, including gas-source molecular beam epitaxy (GS-MBE), solid-source molecular beam epitaxy (SS-MBE), chemical beam epitaxy (CBE), and metal-organic chemical vapor deposition (MOCVD). These efforts have, to some degree, been successful; see, for example, the characteristics shown below for an edge-emitting InGaAsN-based laser diode grown by GS-MBE.
Despite the success that has been achieved to date in fabricating long-wavelength InGaAsN-based laser diodes, much room for improvement remains; for example, most (but not all) of the devices fabricated thus far have been demonstrated under conditions of pulsed, rather than continuous, operation only. Further, many of the fundamental material properties of thin, strained InGaAsN layers are unknown, and a further understanding of such properties would undoubtedly enable the design, growth, and fabrication of more efficient InGaAsN-based optoelectronic devices. In particular, the impact of deep levels on InGaAsN quantum wells has never been measured. This last point will be discussed further in Chapter 8.

Finally, we note that devices other than multi-junction solar cells and long-wavelength laser diodes may be achieved using InGaAsN alloys. For example, two recent papers have reported on the growth and fabrication of heterojunction bipolar transistors (HBTs) consisting of InGaAsN base layers. These transistors were found to have lower turn-voltages than conventional GaAs- and InP-based HBTs; such devices are therefore good candidates for application in low-power electronics. Indeed, InGaAsN...
is a suitable material for any application requiring a bandgap in the shaded region of Figure 1.1 — assuming, of course, that material of good electronic quality can be grown with regularity. Whether or not this can be done is a complex question, and answering one aspect of it is the topic of the remainder of this Dissertation.

1.4 Outline of this Dissertation

The remainder of this Dissertation is organized as follows. Chapter 2 covers the band theory of dilute nitride semiconductors, explaining some of the ideas that have been put forth in the literature to explain the origin of the extremely large bowing parameter $b$ that characterizes the family of GaAsN-like alloys. Chapter 3 covers recombination and generation of carriers through deep levels in the semiconductor bandgap and explains some of the consequences of these processes, and Chapter 4 explains in some detail the primary tool that we have used to characterize deep levels in this work, deep level transient spectroscopy (DLTS). Chapters 5 through 7 constitute the “heart” of the dissertation, as they present the results of our work on the characterization of deep levels in InGaAsN alloys. The first of these three chapters discusses our measurements of deep levels in material grown by metal-organic chemical vapor deposition (MOCVD); the second addresses the same sorts of measurements in material grown by molecular beam epitaxy (MBE); and the last begins to address the problem of determining the physical sources of the defects that were observed in Chapters 5 and 6. Chapter 8 concludes the document by presenting a discussion of some ideas for future work in this area.
1.5 References

1 S. H. Wei and A. Zunger. Phys. Rev. Lett. 76, 664 (1996). This reference contains values of $b$ for the both the InGaAs and GaAsN alloys discussed in this chapter, with the focus being on the calculation of the latter using first-principles techniques.


Other elements of the discussion of solar cell theory were drawn from S. A. Ringel, *EE830 class notes* (Ohio State University, Columbus, 1999).


2.1 Introduction

In this chapter we review two different theories that have been put forth to explain the large bowing parameter $b$ of GaAsN and InGaAsN alloys. We will find that both theories predict a large perturbation to the conduction band of the host material (either GaAs or InGaAs) whereas the valence band remains relatively unaffected in both scenarios. Not only is the bandgap dramatically reduced by the perturbation to the conduction band, but the electron effective mass is found to be dramatically increased. Thus, based on these theories, we might expect electron transport in GaAsN and InGaAsN alloys to be significantly different from transport in the host material, which, as is explained in Chapter 5, is indeed what is observed in such alloys. The two theories are called the band anti-crossing model and the alloy fluctuation model; the former postulates the existence of a nitrogen-induced, spatially localized energy level that interacts with the host material's conduction band to account for the reduced bandgap of the alloy material, whereas the latter suggests that both highly-localized and quasi-localized nitrogen-induced energy states hybridize to account for the curious behavior of the dilute nitride alloy's bandgap.
2.2 Band anti-crossing model

The first theory that we will discuss is the so-called band anti-crossing model. This model postulates the existence of a nitrogen-induced "defect" level $E_N$: this level, located 1.74 eV above the valence band edge of the host material, is thought to be a spatially-localized acceptor-like level, due primarily to structural relaxation and charge exchange resulting from the disparity in atomic orbital size and energy, respectively, of As and N atoms. Assuming that the nitrogen level $E_N$ interacts with the host (or matrix) material's conduction band $E_M(k)$, standard quantum-mechanical perturbation theory leads to the following Eigenvalue problem:

$$\begin{bmatrix} E - E_M(k) & V_{MN} \\ V_{MN} & E - E_N \end{bmatrix} = 0$$

(2.1)

where $V_{MN}$ describes the interaction between the levels $E_M$ and $E_N$; the value of $V_{MN}$ is composition-dependent, being around 0.4 eV for an alloy containing 2% nitrogen. Equation (2.1) has two solutions, or "branches," given by

$$2E_z(k) = E_N + E_M(k) \pm \sqrt{(E_N - E_M(k))^2 + 4V_{MN}^2}$$

(2.2)

The two solution branches are conduction-like bands resident in the dilute nitride alloy. The two branches repel each other in the sense that they diverge from one another in the $E$-$k$ plane, which gives rise to the term "anti-crossing" in the name of the model. Since the $E_z$ branch is lower in energy than its counterpart, it contains the overwhelming majority of the conduction electrons in the material and thus it is the branch that serves as the actual conduction band of the alloy. The calculated positions of the $E_z$ and $E_N$ bands relative to the various valence bands as well as the $E_N$ and $E_M$ levels of an

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
In$_{0.04}$Ga$_{0.96}$As$_{0.99}$N$_{0.01}$ alloy are illustrated in Figure 2.1 below. Note that the $E_\text{c}$ band falls well below the matrix conduction band $E_M$, thus explaining the large bowing parameter and associated reduction in alloy bandgap due to the presence of nitrogen in the alloy.

![Bandstructure of an In$_{0.04}$Ga$_{0.96}$As$_{0.99}$N$_{0.01}$ alloy calculated using Equation (2.2).](image)

Figure 2.1 Bandstructure of an In$_{0.04}$Ga$_{0.96}$As$_{0.99}$N$_{0.01}$ alloy calculated using Equation (2.2).  

Also indicated in the figure are three transitions, labeled 1, 2, and 3. These correspond to the transitions $(E_{HH}, E_{LH})$ to $E_\text{c}$, $(E_{HH}, E_{LH})$ to $E_\text{c}$, and $E_{SO}$ to $E_\text{c}$, where $E_{HH}$, $E_{LH}$, and $E_{SO}$ refer to the heavy-hole, light-hole, and split-off valence bands, respectively.

Photoreflectance spectra give experimental evidence for these three transitions in Figure 2.2 below for several indium-free samples of varying nitrogen content. Photoreflectance is a technique whereby energetic transitions in a material are detected by measuring differential variations in the absorptivity of the material as function of energy.  

The symbol $\Delta_0$ in this figure is indicative of the $\sim 0.34$ eV spin-orbit split
between the heavy- and light-hole and split-off valence bands. Note the reduction in the value of the $E_+ \rightarrow E_-$ transition, as well as the increasing difference in energy between $E_-$ and $E_+$, with increasing nitrogen content, consistent with the predictions of the band anti-crossing theory.

Figure 2.2 Photoreflectance spectra of four GaAs$_{1-x}$N$_x$ samples of varying nitrogen content $x$. The notation is such that $E_-, E_-, \text{ and } E_- \pm \Delta_n$ correspond to transitions 1, 2, and 3 of Figure 2.1 above$^{3}$.

Further, the matrix conduction band energy $E_M$ is expected to be pressure-dependent$^{2}$ and pressure-dependent photoreflectance measurements have been in good agreement with the predictions of the theory, as shown in Figure 2.3 below. The figure shows the results for both GaAs$_{0.985}N_{0.015}$ (open triangles) and In$_{0.05}$Ga$_{0.95}$As$_{0.988}N_{0.012}$ (filled triangles) alloys. We see that the agreement between theory and experiment is quite good except at very large pressures. Further, optical absorption measurements have also been in good agreement with the predictions of the band anti-crossing theory.$^4$
Figure 2.3 Comparison between the predictions of the band anti-crossing theory (lines) and the results of photoreflectance spectra of the pressure dependence of the $E_e$ and $E_\pm$ transitions in GaAs$_{0.995}$N$_{0.015}$ (open triangles) and In$_{0.05}$Ga$_{0.95}$As$_{0.988}$N$_{0.012}$ (filled triangles) alloys.

A final consequence of the band-anticrossing theory is an increase in the electron effective mass. The electron effective mass may be easily obtained from Equation (2.2) and is given by

$$\frac{1}{m_n^2(k)} = \frac{1}{2m_M(k)} \left\{ 1 \pm \frac{E_M(k) - E_V}{\sqrt{[E_M(k) - E_V]^2 + 4V_{MN}^2}} \right\}$$

where $m_M(k)$ is the electron effective mass of the host matrix. The results of Equation (2.3) have been compared to experimental values of the electron effective mass in In$_x$Ga$_{1-x}$N$_y$ alloys determined from energy-dependent reflectivity measurements, and it was found that disagreement between theory and experiment did not exceed roughly 20%.

We used Equation (2.3) to predict a $k = 0$ electron effective mass of $m_n = 0.2m_0$ in our InGaAsN samples. For this purpose, we used linear interpolation between the effective...
masses of GaAs and InAs to determine the value of $m_m$, and also assumed that $E_N$ and $V_{MN}$ were equal to the values given earlier in this section.

2.3 Alloy fluctuation model

Despite the apparent success of the band anti-crossing model in predicting the bandstructure of dilute nitride alloys, some researchers do not accept it and have proposed other explanations for the curious behavior of this class of materials. One such explanation is the so-called alloy fluctuation model.\textsuperscript{7,8,9,10} We consider first the case of the ternary GaAs$_{1-x}$N$_x$ alloy. In this model, we consider two types of nitrogen-induces states: highly localized, sub-bandgap, defect-like states (termed "cluster states") as well as quasi-localized perturbations within the conduction band (known as "perturbed host states").\textsuperscript{9} In the dilute "impurity limit" the cluster states appear as discrete energy levels within the bandgap, whereas the perturbed host states are, as the name implies, perturbations to the pre-existing, de-localized bandstructure of the host material. This is illustrated in Figure 2.4, parts (a) and (b), below. Note that the data of this figure were obtained via simulation of a random alloy consisting of a large (on the order of 10,000) number of lattice sites subject to periodic boundary conditions; thus the approach is different from the model of the previous section, which relied on analytical results. The states presented in Figure 2.4 therefore arise "naturally" without any imposed constraints. Also note that the valence band states resulting from these calculations were not observed to change much due to the addition of nitrogen, in agreement with the model of the previous section.
Figure 2.4 Calculated nitrogen localized states ("cluster states") and quasi-localized states ("perturbed host states") induced in GaAs\textsubscript{1-x}N\textsubscript{x} alloys for various nitrogen concentrations \( y \). The zero of the scale is the position of the conduction band minimum of the GaAs host; the vertical arrows indicate the CBM of each GaAsN alloy.

As the amount of nitrogen in the alloy is increased beyond the impurity limit, a number of changes occur to both types of states: these changes are illustrated in Figure 2.4, parts (c) through (h). The cluster states tend to stay fixed in position relative to the host conduction band minimum (CBM) and broaden. The perturbed host states, in contrast, not only broaden, but they move downward relative to the alloy CBM. This process results in a superposition of both localized and extended states at the conduction band edge (this localized-delocalized duality is known as an "alloy fluctuation." hence the name of the model) which is responsible for a variety of novel physical properties, including the observed dramatic dependence of bandgap on composition. As the nitrogen concentration increases further, the superposition of states delocalizes fully and the alloy
transitions into a "conventional" III-V system characterized by smoothly varying physical properties. Referring again to Figure 2.4, we see a strong concentration of states at roughly –0.2 eV; this group of states is located near the conduction band edge and, in fact, corresponds to the $E_-$ branch of the model of the previous section. Similarly, the group of states clustered near +0.4 eV is thought to represent the $E_+$ band; thus, in a sense, the predictions of the two models are consistent with each other. However, we must be careful to avoid oversimplifying the situation; e.g., we note that in the alloy fluctuation model, the $E_-$ state is much more localized than the $E_+$ state; thus, these two groups of states are not simply two different branches of a perturbed host conduction band. Finally we mention that the alloy fluctuation model makes a number of predictions that the band anti-crossing model does not; e.g., due to the localized-delocalized duality inherent in this description, it predicts strong exciton localization as well as a blueshift in photoluminescence energy at low temperatures. Experiments designed to test these aspects of the theory would undoubtedly shed much light on the theoretical aspects of the bandstructure of dilute nitride materials.

A further aspect of the alloy fluctuation theory distinguishes it from the band anti-crossing theory. This is the fact that in the latter theory, the use of either a GaAs or InGaAs host material made little difference; the nitrogen-induced perturbations could apply equally well to either "matrix" material. In the alloy fluctuation theory, however, the quaternary alloy is fundamentally different from the ternary alloy. This is because in a quaternary alloy, a distinction must be made between a random alloy and an ordered alloy; in the case of InGaAsN, we may make this distinction by noting that in the random alloy, a nitrogen atom should bond with equal probability to either an indium atom or a
gallium atom. However, simulations have shown that this is not the case; rather, nitrogen appears to bond preferentially to indium. This enhances the prevalence of In-N clusters, which may be explained as follows. Each nitrogen atom is characterized by a local environment described by \( \text{In}_m\text{Ga}_{4-m} \), where \( m = 0, 1, 2, 3, \) or \( 4 \); due to the preferential In-N bonding arrangement, neighborhoods characterized by a higher value of \( m \) will be statistically more prevalent than neighborhoods characterized by low \( m \). This effect tends to increase the bandgap of the quaternary InGaAsN alloy relative to the ternary GaAsN alloy, thus decreasing the bowing coefficient \( b \). Further, we find that the preponderance of In-rich nitrogen neighborhoods leads to a broad distribution of quai-localized states near the conduction band minimum of the quaternary alloy; additionally, a number of strongly localized, defect-like states are predicted to exist within the bandgap. This is illustrated Figure 2.5 below for the case of \( \text{In}_{0.10}\text{Ga}_{0.90}\text{As}_{0.98}\text{N}_{0.02} \). We will see in Chapters 5 and 6 that a shallow distribution of states is indeed observed just below in the conduction band edge of our \( \text{In}_{0.07}\text{Ga}_{0.93}\text{As}_{0.98}\text{N}_{0.02} \) alloys, and further, that states are observed in the vicinity of \( E_C - 0.3 \) eV. While unproven, it is certainly possible that these experimentally observed deep levels are indeed the same states as illustrated in Figure 2.5, and if that is the case, this suggests that these states and whatever limitations they impose on electronic material quality are intrinsic to the InGaAsN system and thus cannot be eliminated. The subject of the potential physical sources deep level defects will be discussed in detail in Chapter 7.
Figure 2.5 Strongly localized, defect-like states (cluster states) and quasi-localized states (perturbed host states) predicted to exist in In_{0.06}Ga_{0.94}As_{0.98}N_{0.02}. The zero of energy corresponds to the conduction band minimum of the alloy. \textsuperscript{x}

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
2.4 References


CHAPTER 3

CARRIER RECOMBINATION AND GENERATION

3.1 Introduction

Carrier recombination and generation through deep levels defects are processes which may have a significant impact upon the properties of semiconductor devices. For example, excessive carrier recombination may result in a significant loss of photocurrent in a solar cell.\(^1\) This chapter provides an overview of carrier recombination and generation, with the first portion of the chapter discussing the basic physics of the recombination-generation (R-G) processes that occur in semiconductor materials, and the second portion of the chapter discussing the impact of such processes on the performance of semiconductor devices. The purpose of this chapter is twofold. First of all, an understanding of the material contained herein is required in order to understand the experimental techniques employed throughout the course of this research to identify the properties of deep level defects in InGaAsN alloys. Second, it demonstrates the practical importance of deep level defects by establishing their ability to influence – usually in an undesirable fashion – the properties of semiconductor devices.

34

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
3.2 Shockley-Read-Hall theory

This section discusses the basic physics of carrier recombination and generation through deep levels, which is known as the Shockley-Read-Hall theory due to its independent derivations by Shockley and Read\textsuperscript{2} and by Hall.\textsuperscript{3} Our discussion, however, is based on that of Pierret\textsuperscript{4} with supplemental information obtained from Blakemore\textsuperscript{5} and Fahrenbruch and Bube.\textsuperscript{1} We begin by considering a deep level trap that may capture and emit carriers. We are interested in the rate at which the density of occupied traps $n_T$ changes with time, and we begin our investigation by examining Figure 3.1 below.

![Schematic illustration of carrier capture and emission through a deep level.](image)

**Figure 3.1** Schematic illustration of carrier capture and emission through a deep level.

We see that there are four different processes that contribute to changes in the trap occupancy, which are electron capture (A), electron emission (B), hole capture (C), and hole emission (D). Consider first electron capture. The rate at which this process occurs is proportional to both the density of electrons in the conduction band $n$ as well as the density of empty traps $p_T$. Since the trap occupancy increases whenever an electron is captured, the rate of change is positive and we may write
The proportionality constant \( c_a \) is known as the electron capture coefficient and has units of \( \text{cm}^3 \text{s}^{-1} \). We consider second the complimentary process, electron emission. In this case the rate of change in trap occupancy is proportional only to the density of filled traps, and moreover, it is negative since this process reduces the trap occupancy. We thus have

\[
\frac{dn_T}{dt} \bigg|_A = c_a n p_T
\]  

(3.1)

The proportionality constant \( e_a \) is the electron emission rate and has units of \( \text{s}^{-1} \). Similar arguments lead to analogous expressions for hole capture and emission:

\[
\frac{dn_T}{dt} \bigg|_B = -e_a n_T
\]  

(3.2)

\[
\frac{dn_T}{dt} \bigg|_C = -c_p n p_T
\]  

(3.3)

\[
\frac{dn_T}{dt} \bigg|_D = e_p P_T
\]  

(3.4)

The net rate of change in the trap occupancy is then obtained by summing the rates of the four processes, which results in

\[
\frac{dn_T}{dt} = c_a n p_T - e_a n_T - c_p n p_T + e_p P_T
\]  

(3.5)

At this point it is important to note that the capture and emission coefficients are not independent. To deduce the relationship between them, consider the processes of
electron capture and emission. In an equilibrium situation, the net rate of change in the trap occupancy due to these two complementary processes must be zero. We thus have

$$c_n n_{TE} - e_n n_{TE} = 0$$

(3.6)

where the additional subscripts are indicative of the equilibrium situation, and further, it has been assumed that the coefficients $c_n$ and $e_n$ are always equal to their equilibrium values. Solving for the emission rate yields

$$e_n = c_n n_{TE} = c_n n \exp\left(\frac{E_T - E_T}{kT}\right) = c_n N_c \exp\left(\frac{E_T - E_C}{kT}\right)$$

(3.7)

where the latter two equalities are easily demonstrated by considering standard expressions for carrier concentration and trap occupancy. A parallel derivation leads to an analogous expression for the hole emission rate, which is

$$e_p = c_p n, \exp\left(\frac{E_T - E_T}{kT}\right) = c_p N_v \exp\left(\frac{E_v - E_T}{kT}\right)$$

(3.8)

Assuming that the electron and hole capture cross sections are both constant, we see that the electron and hole emission rates are strong functions of the trap energy and the temperature.

We now turn our attention to the derivation of the R-G rate under steady-state conditions. By steady-state we mean a situation in which all of the variables characterizing the population of carriers within a volume of semiconductor material, e.g. $n$, $p$, $n_T$, etc., are constant in time, although this balance need not be achieved by an exact balance between each process and its inverse. In contrast, the term equilibrium implies that not only are the population variables constant in time, but each process is exactly
balanced by its inverse, as discussed in the previous paragraph. Thus, in the steady-state situation current may be present within a region of material due to the net creation or annihilation of carriers within that region. Nevertheless, \( n_T \) must remain constant in time within the region, so that from Equation (3.5) we have

\[
c_a n_T - e_a n_T - c_p p n_T + e_p p_T = 0
\]  

(3.9)

Using Equations (3.7) and (3.8) and recalling that \( p_T = N_T - n_T \), we may solve for \( n_T \) to obtain

\[
n_T = N_T \frac{c_a n + c_p n, \exp \left( \frac{E_i - E_r}{kT} \right)}{c_a \left[ n + n, \exp \left( \frac{E_r - E_i}{kT} \right) \right] + c_p \left[ p + n, \exp \left( \frac{E_i - E_r}{kT} \right) \right]}
\]  

(3.10)

Due to conservation of charge, in the steady-state situation the R-G rate due to electrons must be equal to the R-G rate due to holes. Considering the expressions for the electron capture and emission rates, we have

\[
U = c_a n p_T - e_a n_T = c_a \left[ n(N_T - n_T) - n, \exp \left( \frac{E_i - E_r}{kT} \right) n_T \right]
\]  

(3.11)

where we have used the symbol \( U \) to denote the net R-G rate. Substituting Equation (3.10) into Equation (3.11), we obtain (after a good bit of tedious mathematical manipulation) the expression for the steady-state recombination-generation rate, which is

\[
U = \frac{np - n^2}{\tau_p \left[ n + n, \exp \left( \frac{E_r - E_i}{kT} \right) \right] + \tau_e \left[ p + n, \exp \left( \frac{E_i - E_r}{kT} \right) \right]}
\]  

(3.12)
where the quantities \( \tau_n = (c_nN_T)^{-1} \) and \( \tau_p = (c_pN_T)^{-1} \) are known as, respectively, the electron and hole minority-carrier lifetimes. Physically, these quantities may be interpreted as the average time that a minority-carrier will survive in a sea of majority-carriers before recombining with one of them. Note that each minority-carrier lifetime depends only upon the appropriate capture coefficient and the trap density, and that an increase in either of these quantities will result in a decrease in the lifetime. The minority-carrier lifetimes are simply related to the minority-carrier diffusion lengths discussed in Chapter 1 by the relation

\[
L_{n,p} = \sqrt{D_{n,p} \tau_{n,p}}
\]  

(3.13)

where \( D_n \) and \( D_p \) are the electron and hole minority-carrier diffusion coefficients, respectively. Further, if \( U > 0 \), then we define the recombination rate \( R = U \); on the other hand, if \( U < 0 \), we define the generation rate \( G = -U \). As is obvious from the terminology, in the former situation the recombination of carriers is dominant, whereas in the latter situation the generation of carriers is the dominant process. Finally, it is evident that the right-hand side of Equation (3.12) has units of concentration divided by time. Thus, this equation is often expressed as an appropriate concentration divided by a time constant; for \( U < 0 \) this time constant is the generation lifetime \( \tau_g \), and for \( U > 0 \) it is the recombination lifetime \( \tau_r \).

3.3 Impact of carrier recombination and generation on device properties

In this section we wish to illustrate the impact that the R-G processes discussed above have on semiconductor devices. The material discussed below draws largely on the
textbooks by Neudeck\textsuperscript{8} and by Muller and Kamins\textsuperscript{9}, and is supplemented by information from the excellent book by Fahrenbruch and Bube\textsuperscript{1} on photovoltaics.

3.3.1 Generation current in a $pn$ junction diode

We first consider the current due to the generation of carriers through a deep level in a $pn$ junction diode under reverse bias. The first step is to re-write Equation (3.12) in terms of the applied voltage $V$. This done by noting that the $np$ product is equal to

$$np = n_i^2 \exp \left( \frac{qV}{kT} \right)$$  \hspace{1cm} (3.14)

which, when substituted into Equation (3.12), results in the expression

$$U = \frac{n_i^2 \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right]}{\tau_p \left[ n + n, \exp \left( \frac{E_T - E_r}{kT} \right) \right] + \tau_n \left[ p + n, \exp \left( \frac{E_r - E_T}{kT} \right) \right]}$$  \hspace{1cm} (3.15)

for the R-G rate. Since the diode is assumed to be under reverse bias, we have $V < 0$; we further assume that the magnitude of the voltage is large enough such that $\exp(qV/kT) \ll 1$. Under such conditions, Equation (3.15) becomes

$$G = \frac{n_i^2}{\tau_p \left[ n + n, \exp \left( \frac{E_T - E_r}{kT} \right) \right] + \tau_n \left[ p + n, \exp \left( \frac{E_r - E_T}{kT} \right) \right]}$$  \hspace{1cm} (3.16)

where we have made the substitution $G = -U$. This gives a generally applicable expression for the generation rate $G$. A specific case of this that is often a reasonable approximation to the situation in real materials is the case of equal electron and hole
minority-carrier lifetimes. \( \tau_n = \tau_p = \tau_0 \). Applying this assumption to Equation (3.16), we have

\[
G = \frac{n_i^2}{\tau_0 \left[ n + p + 2n_i \cosh \left( \frac{E_r - E_i}{kT} \right) \right]} 
\]

We may make a further simplification by noting that under reverse bias conditions \( n << n_i \) and \( p << n_i \). Therefore, the terms \( n \) and \( p \) in the above expression will always be much smaller than the hyperbolic cosine term, and Equation (3.17) simplifies to

\[
G = \frac{n_i}{2 \tau_0 \cosh \left( \frac{E_r - E_i}{kT} \right)} 
\]

Thus, the generation rate is inversely proportional to the hyperbolic cosine of the difference between the trap energy and the intrinsic Fermi level. However, as the trap energy deviates from midgap, a single exponential will tend to dominate this function, and consequentially the behavior of the generation rate will become exponential. We may therefore approximate Equation (3.18) by two equations, one for \( E_r > E_i \), and one for \( E_r < E_i \), which are

\[
E_r > E_i \Rightarrow G = \frac{n_i}{\tau_0 \exp \left( \frac{E_r - E_i}{kT} \right)} 
\]

\[
E_r < E_i \Rightarrow G = \frac{n_i}{\tau_0 \exp \left( \frac{E_i - E_r}{kT} \right)} 
\]
The intrinsic carrier concentration \( n_i \) may be eliminated by making use of the well-known expression

\[
    n_i = \sqrt{N_C N_v} \exp \left( \frac{-E_A}{2kT} \right)
\]

(3.20)

where \( N_C \) and \( N_v \) are the effective densities of states at the conduction and valence band edges, respectively, and \( E_v \) is the semiconductor bandgap. These two quantities are both proportional to \( T^{3/2} \), although this temperature dependence is very weak compared to the exponential dependence involving the bandgap, so for the present we will consider \( N_C \) and \( N_v \) to be constant in temperature. Equations (3.19) then become

\[
    E_T > E_i \Rightarrow G = \frac{\sqrt{N_C N_v}}{r_0} \exp \left( \frac{E_i - E_T}{kT} \right)
\]

\[
    E_T < E_i \Rightarrow G = \frac{\sqrt{N_C N_v}}{r_0} \exp \left( \frac{E_T - E_C}{kT} \right)
\]

(3.21)

To obtain the generation current density, we must multiply the generation rate by the electron charge \( q \) and the depletion width \( x_D \). We thus obtain

\[
    J_G = \frac{q x_D \sqrt{N_C N_v}}{r_0} \exp \left( \frac{-E_A}{kT} \right) = J_{Go} \exp \left( \frac{-E_A}{kT} \right)
\]

(3.22)

We note that the activation energy \( E_A \) is always larger than half the bandgap, since

\[
    E_T > E_i \Rightarrow E_A = E_T - E_i
\]

\[
    E_T < E_i \Rightarrow E_A = E_C - E_T
\]

(3.23)
Physically, this makes sense because it is the rate-limiting process, i.e. the slower of either the electron or hole emission processes, that determines the overall carrier generation rate. Since the emission rate of carriers from a trap level is a thermally activated process, the overall generation rate should be limited by the transition to the band further from the trap level, assuming that the electron and hole minority-carrier lifetimes are equal.

Note that in the preceding derivation we made several assumptions which led to the current-temperature relationship described by Equations (3.22) and (3.23), namely that $\tau_n = \tau_p$ and that $n$ and $p$ are both much less than $n_i$. These need not necessarily hold, however. For example, if $\tau_n \gg \tau_p$, then instead of Equation (3.17) we have

$$G = \frac{n_i^2}{\tau_n \left[ p + n \exp \left( \frac{E_i - E_T}{kT} \right) \right]} \quad (3.24)$$

Assuming that $p \ll n_i$ and following a procedure analogous to the one outlined above, we obtain

$$J_g = J_{g0} \exp \left( \frac{E_T - E_C}{kT} \right) = J_{g0} \exp \left( \frac{-E_A}{kT} \right) \quad (3.25)$$

as the appropriate current-temperature relationship. This has the same exponential form as did the expression derived for the $\tau_n = \tau_p$ case. although now the activation energy is given by $E_A = E_C - E_T$ irrespective of the position of the trap in the bandgap. It is thus once again the rate-limiting process that determines the activation energy. This is easily seen by noting that, since $\tau_n = (c_nN_T)^{-1}$ and $\tau_p = (c_pN_T)^{-1}$, $\tau_n \gg \tau_p$ implies that $c_n \ll c_p$.

From Equations (3.7) and (3.8) we see that $e_n$ and $e_p$ are proportional to $c_n$ and $c_p$. 

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
respectively; thus we have \( e_n << e_p \), indicating that electron emission is the slower, rate-limiting process, explaining why the activation energy obtained for this situation is always referenced to the conduction band. Similar results are obtained if we consider the case \( \tau_n << \tau_p \), the only difference being that \( E_A = E_T - E_A \); in this situation it is hole emission that is the slower, rate-limiting process. To illustrate the appearance of the reverse-bias current-temperature relationships discussed in this section, several simulated curves are shown below. For this purpose, we consider an R-G center located 0.35 eV below the conduction band edge of a 1.05 eV material.

![Graph showing simulated current-temperature curves](image)

**Figure 3.2** Simulated generation current versus temperature curves resulting from a deep level 0.35 eV below the conduction band edge of a 1.05 eV bandgap material. Note the different activation energies resulting from the two cases \( \tau_n = \tau_p \) and \( \tau_n >> \tau_p \).
3.3.2 Impact of carrier recombination on device performance

We consider first the impact of R-G processes on solar cell performance. Solar cells are devices that, in order to generate useful power, must be operated in the forward-bias regime; thus, carrier recombination dominates over carrier generation. The recombination of carriers will degrade the IQE of the solar cell, since some of the photo-generated electron-hole pairs will recombine shortly after they are created. From Equation (1.11), we see that this will reduce the photo-current $J_E$ of the solar cell; this, in turn, will reduce $J_w$, as given by Equation (1.12). Further, the magnitudes of the minority-carrier diffusion lengths, and thus the properties of deep levels, have an impact on the properties of the cell diffusion current. If we neglect surface recombination and consider bulk properties only, then $S_n = 0$ and Equation (1.6) for the emitter saturation current density simplifies to

$$ J_{0E} = q \left( \frac{n^0}{N_A} \right) \frac{D_n}{L_n} \frac{\sinh \left( \frac{W_E}{L_n} \right)}{\cosh \left( \frac{W_E}{L_n} \right)} $$

(3.26)

If a material contains a large density of traps, it will have a short minority-carrier lifetime and a correspondingly short minority-carrier diffusion length; consequently, the emitter layer of a solar cell fashioned out of such a material will most likely have $L_n << W_E$. For large arguments, sinh($x$) and cosh($x$) both approach infinity, so that the ratio of the two functions approaches unity. We are therefore left with

$$ J_{0E} = q \frac{n^0}{N_A} \frac{D_n}{L_n} $$

(3.27)
Thus, due to the extremely short electron diffusion length, the emitter saturation current does not depend on the emitter thickness. On the other hand, suppose that the opposite condition holds. In that case, we have $L_n \gg W_E$, and since $\cosh(x) \sim 1$ and $\sinh(x) \sim x$ for small $x$, Equation (3.26) simplifies to

$$J_{0E} = q \frac{n_i^2 D_e}{N_A W_E}$$  \hspace{1cm} (3.28)

Thus, in this case the emitter saturation current does depend on the emitter thickness.

Since the value of $W_E$ is fixed in a particular cell design, the value of the former equation will always be greater than the value of the latter, and poor material quality thus leads to a larger emitter saturation current. Of course, expressions similar to Equations (3.27) and (3.28) apply to the $n$-type solar cell base layers for which $L_p << W_B$ and $L_p \gg W_B$, respectively, which complement the $p$-type emitter layers; we may draw a similar conclusion regarding the base saturation current. These effects will adversely impact the open-circuit voltage, since, from Equation (1.13)

$$V_{oc} = \frac{kT}{q} \ln \left( \frac{J_L}{J_{01}} + 1 \right) = \frac{kT}{q} \ln \left( \frac{J_L}{J_{0B} + J_{0E}} + 1 \right)$$  \hspace{1cm} (3.29)

We see that not only is $V_{oc}$ reduced by the reduction in $J_L$, it is further degraded by the increases in $J_{0B}$ and $J_{0E}$. Ultimately, through the reductions of $J_{oc}$ and $V_{oc}$, the power produced by the solar cell is reduced by the presence of recombination through deep level defects.

As a final point in this chapter, we address the diode recombination current $J_{D2}$. For the purpose of illustration, we assume equal minority-carrier lifetimes. $\tau_n = \tau_p = \tau_0$.  

46
In a *pn* junction diode, recombination dominates over generation for \( V > 0 \), and Equation (3.15) becomes

\[
R = \frac{n_i^2 \exp\left(\frac{qV}{kT}\right)}{\tau_0 \left[ n + p + 2n_i \cosh\left(\frac{E_T - E_i}{kT}\right) \right]} \tag{3.30}
\]

Where we have made the substitution \( R = U \). We now wish to consider a worst-case scenario, which is the situation in which the recombination rate is a maximum. From a quick inspection of Equation (3.30) it is clear that this occurs for traps located at midgap, so that \( E_T = E_i \); thus the hyperbolic cosine term is equal to unity. Since we are in the forward bias regime, \( n + p >> 2n_i \), and we are left with

\[
R = \frac{n_i^2}{\tau_0 (n + p) \exp\left(\frac{qV}{kT}\right)} \tag{3.31}
\]

Recalling Equation (3.14) for the \( np \) product, it is easily shown that the denominator of this expression reaches a minimum for \( n = p \), which leads to

\[
R = \frac{n_i}{2\tau_0} \exp\left(\frac{qV}{2kT}\right) \tag{3.32}
\]

Finally, multiplying by \( q \) and \( x_D \) yields the recombination current density \( J_R \), given by

\[
J_R = \frac{q x_D n_i}{2\tau_0} \exp\left(\frac{qV}{2kT}\right) = J_{D2} \exp\left(\frac{qV}{2kT}\right) \tag{3.33}
\]

We thus see that \( J_R = J_{D2} \), and we have therefore explained the origin of the \( n = 2 \) current component of the solar cell model of Figure 1.2. This particular mechanism does not tend to dominate the behavior of an illuminated solar cell, however; recall from Chapter 1
that $J_{sc}$ is roughly equal to $J_L$ and that $V_{oc}$ depends upon the $n = 1$ saturation current $J_{01}$ as well as $J_L$. However, since $J_{01}$ is typically less than $J_{02}$ (true for sufficiently large bandgap materials, since $J_{01} \approx n_i^2$ and $J_{02} \approx n_i$, where $n_i \approx \exp(-E_g/kT)$), recombination current does tend to dominate the performance of $pn$ junctions at low reverse bias in the absence of photo-generation. This is illustrated below, which shows the dark current-voltage curve for the solar cell simulated in Figure 1.6.

![Current-voltage relationship of the solar cell model presented in Figure 1.6, except without the inclusion of the $J_L$ term. The dominance of the $n = 2$ recombination current at low forward bias is evident.](image)

Thus the $n = 2$ recombination current certainly does play a role in device performance, although it is not evident in the case of the illuminated solar cell. In particular, devices designed to emit light under forward bias conditions may be affected by its presence; this includes both light-emitting diodes and laser diodes. The latter of these is, of course, the second class of devices discussed in Chapter 1 as being a potential application of
InGaAsN alloys. Thus we have one more reason to try to understand the properties of deep levels in this class of alloys.
3.4 References


6 This assumption is typically valid in situations where the deviation from equilibrium is small, i.e. under conditions of "low-level injection." Under circumstances that deviate significantly from equilibrium, the validity of this assumption is undoubtedly open to question.

7 Strictly speaking, the minority-carrier lifetimes are given by sums $\tau_{n,p} = \Sigma_i \tau_{n,p}^i$, where the index $i$ represents various processes such as band-to-band, Auger, SRH, etc. We assume that the SHR mechanism is dominant and take the net lifetimes to be equal to the SRH lifetimes.


CHAPTER 4
CAPACITANCE TRANSIENT SPECTROSCOPY

4.1 Introduction

The primarily tool used throughout the course of this research to characterize the properties of deep level defects in bulk InGaAsN alloys has been Deep Level Transient Spectroscopy (DLTS). This is a technique whereby the properties of deep level defects are elucidated by analyzing the transient decay in the capacitance of either a Schottky or a one-sided $pn$ junction diode resulting from the emission of trapped carriers from the deep levels. The first part of this chapter discusses the basic physics of the measurement as well as the interpretation and analysis of spectra resulting from "ideal" point defects. This is followed by an examination of some of the modifications that must be made in the understanding of the technique in order to account for the properties of "non-ideal" defects, i.e. spatially extended defects (e.g. dislocations) or other types of defects that may be characterized by a "density of states" within the semiconductor bandgap. We will see in later chapters that the understanding of this latter class of defects is of critical importance in the characterization of InGaAsN alloys.
4.2 Characterization of ideal deep levels by DLTS

The DLTS technique was first proposed by Lang in 1974. It has since been discussed by numerous authors, and the discussion in this section is based largely on the overviews by Blood and Orton and by Schroeder. We begin by presenting an overview of the experimental technique, which is followed by a discussion of the physics of carrier emission. The section concludes by explaining how trap parameters may be obtained from DLTS spectra.

4.2.1 Experimental technique

The DLTS technique requires the use of either a Schottky or a one-sided \(pn\) junction diode as a "test vehicle" through which the properties of deep levels are measured. The diode is held at a fixed reverse-bias \(V_R\) the majority of the time; however, at regular intervals a pulse of voltage \(V_F\) (in our notation the symbol \(V_F\) refers to the total voltage applied to the sample during the pulse, not the magnitude of the pulse itself, which we term \(V_F\); thus \(V_F = V_R + V_P\)) of duration \(t_F\) is applied to the sample. We always have \(V_P > 0\), although its magnitude may vary, so that conditions may be set such that \(V_F < 0\) or \(V_F > 0\); we will see that in the former case only majority-carrier traps may be observed, whereas in the latter case both majority- and minority-carrier traps may be observed. The application of this pulse reduces the depletion width \(x_D\), and as a consequence deep levels that had been previously empty become filled with carriers. Following the removal of the pulse, the depletion depth relaxes back to a value near its original, or "quiescent," width: it is in fact slightly wider than it was prior to the application of the pulse, since charge trapped in the deep levels reduces the doping.

52

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
density in the material and consequently increases the depletion depth, as suggested by Equation (4.7) below. As time proceeds, the trapped carriers are emitted from the deep levels and cause the depletion width to relax back to its true quiescent value. This process is illustrated below for the case of electron capture and emission.

![Schematic illustration of the capture and emission of electrons from a deep level in the upper half of the bandgap. The leading edge of the fill pulse defines $t = 0$.](image)

The relaxation of the depletion depth gives rise to a capacitance transient that is sampled at times $t_1$ and $t_2$. Such a sampling scheme is known as boxcar sampling; the physics of the measurement lies entirely in the capacitance transient and is independent of the sampling technique. And other methods other than the boxcar technique exist, although none of them have been used during the course of the present research. A temperature scan is performed and the capacitance difference, or DLTS signal, $\Delta C = C(t_2) - C(t_1)$ is measured and plotted as a function of temperature. Considering electron emission, we saw in Equation (3.7) that the emission rate $e_n$ is a function of temperature, and thus the time required for the capacitance to relax back to its quiescent value varies with...
temperature. Thus $\Delta C$ is temperature-dependent as well; these concepts are illustrated below.

![Figure 4.2](image)

**Figure 4.2** Schematic illustration of various capacitance transients as a function of temperature, and the resulting DLTS signals. Note that the symbol $\delta C$ in the figure is equivalent to the negative of the $\Delta C$ used throughout the text; this difference is trivial, merely resulting in a reflection of the DLTS signal about the temperature axis.

From Figure 4.2, we see that for both low and high temperatures (corresponding to slow and fast electron emission rates, respectively) the DLTS signal is small, and that for some intermediate temperature the DLTS signal is maximum. It may be shown (by maximizing Equation (4.19), which is derived in Section 4.2.3) that the DLTS signal peaks when

$$e_n = \frac{\ln(t_2/t_1)}{t_2 - t_1}$$

(4.1)
Recalling that $e_n$ is a function of $T$, we see that by changing the values of $t_1$ and $t_2$ (which are typically selected such that the ratio $t_2/t_1$ is constant) and noting the temperatures at which the DLTS peaks occur, it is possible to obtain information about the deep level giving rise to the peaks in question. The method by which this is accomplished is discussed in Section 4.2.3. In the present research, eight different combinations of $t_1$ and $t_2$ were used at various times. These combinations are listed below. Note that we refer to the peak emission rate as the rate window RW; this is a common terminology and is entirely equivalent to the emission rate at the peak positions.

<table>
<thead>
<tr>
<th>RW (s$^{-1}$)</th>
<th>$t_1$ (s)</th>
<th>$t_2$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>6.10x10$^{-4}$</td>
<td>1.53x10$^{-3}$</td>
</tr>
<tr>
<td>400</td>
<td>1.53x10$^{-3}$</td>
<td>3.81x10$^{-3}$</td>
</tr>
<tr>
<td>200</td>
<td>3.05x10$^{-3}$</td>
<td>7.63x10$^{-3}$</td>
</tr>
<tr>
<td>80</td>
<td>7.63x10$^{-3}$</td>
<td>1.91x10$^{-2}$</td>
</tr>
<tr>
<td>50</td>
<td>1.22x10$^{-2}$</td>
<td>3.06x10$^{-2}$</td>
</tr>
<tr>
<td>20</td>
<td>3.06x10$^{-2}$</td>
<td>7.65x10$^{-2}$</td>
</tr>
<tr>
<td>10</td>
<td>6.10x10$^{-2}$</td>
<td>1.53x10$^{-1}$</td>
</tr>
<tr>
<td>4</td>
<td>1.53x10$^{-1}$</td>
<td>3.81x10$^{-1}$</td>
</tr>
</tbody>
</table>

Table 4.1 Sampling times $t_1$ and $t_2$ for various rate windows used throughout the course of this research. Note that the ratio $t_2/t_1 = 2.5$ in all cases.

4.2.2 Physics of carrier emission

We begin our discussion of majority-carrier emission from deep levels by considering an ideal deep level trap within the bandgap. The density of such a trap as a function of the energy is described by
\[ N_T(E) = N_T \delta(E - E_T) \]  

(4.2)

As was shown in Chapter 3, the rate at which the occupancy of the trap changes with time is given by

\[ \frac{dn_T}{dt} = c_e n p_T - e_n n_T - c_p p n_T + e_p p_T \]  

(4.3)

Following the removal of the DLTS fill pulse, electron and hole emission are the dominant processes, and we may therefore neglect the terms proportional to the electron and hole capture coefficients. The previous equation thus simplifies to

\[ \frac{dn_T}{dt} = -e_n n_T + e_p p_T \]  

(4.4)

For the purposes of this exposition we suppose that that the material is n-type. This does not limit the generality of the DLTS theory developed herein, however, since the expressions obtained for the capacitance transients in p-type material are virtually identical to those in n-type material, the only differences being obvious substitutions such as \( e_n \rightarrow e_p, N_D \rightarrow N_A \), etc. That being said, we now consider the case of majority-carrier emission in n-type material. In such a situation electron emission is the dominant process, so Equation (4.4) reduces to

\[ \frac{dn_T}{dt} = -e_n n_T \]  

(4.5)

the solution of which is

\[ n_T(t) = n_T \exp(-e_n t) = N_T \exp(-e_n t) \]  

(4.6)
where \( n_m \) is the initial density of filled traps; in writing the second equality, it has been assumed that the initial density of filled traps is equal to the total trap density \( N_T \). We will see below that this assumption is not true under all circumstances, and that deviations from it may be exploited in order to obtain, among other things, information regarding the spatial distribution of deep level defects. For the present, however, we shall assume that this assumption holds.

We now need to consider some properties of junctions. The capacitance of a Schottky or one-sided \( pn \) junction is given by

\[
C = \frac{\varepsilon A}{x_D} = \varepsilon A \left[ \frac{qN}{2\varepsilon (V_n - V)} \right]^{1/2} = \frac{\varepsilon A}{2\varepsilon (V_n - V)} \left( \frac{q(N_D - n_T)}{2\varepsilon (V_n - V)} \right)^{1/2}
\]

(4.7)

where it has been assumed that the donors are fully ionized so that the net density of charge \( N \) within the depletion region is equal to the donor density \( N_D \) minus the density of occupied traps \( n_T \). Further manipulation yields

\[
C(t) = C_\infty \left[ 1 - \frac{n_T}{N_D} \right]^{1/2} = C_\infty \left( 1 - \frac{n_T}{N_D} \right)^{1/2}
\]

(4.8)

where \( C_\infty \) is the steady-state or "quiescent" capacitance, i.e. the capacitance in the absence of carrier trapping. Making use of the well-known formula \((1 + x)^n \approx 1 + nx \) (valid for \( x \ll 1 \)) and substituting Equation (4.6) into Equation (4.8) we obtain

\[
C(t) = C_\infty \left[ 1 - \frac{N_T}{2N_D} \exp(-e_x t) \right]
\]

(4.9)

which describes the capacitance transient resulting from the emission of majority carriers from an ideal deep level defect. As an example, a transient computed using Equation...
(4.9) with $N_T/N_D = 0.01$ is shown below. We see that the transient is "upward going," which implies that the DLTS signal, $\Delta C = C(t_2) - C(t_1)$, is positive.

![Capacitance transient resulting from majority-carrier emission](image)

**Figure 4.3** Capacitance transient resulting from majority-carrier emission from a deep level with $N_T/N_D = 0.01$.

We now consider the case of minority-carrier emission from deep levels. The discussion is identical to that of the preceding case up to Equation (4.4). At this point the derivation deviates from the previous one by assuming that hole emission, as opposed to electron emission, is the dominant process. We then have

$$\frac{dn_T}{dt} = e_p p_T \Rightarrow \frac{dp_T}{dt} = -e_p p_T$$

(4.10)

where we have made use of the facts that the total trap density is equal to the density of filled traps plus the density of empty traps and that the total trap density is constant in time. The solution of this equation is

$$p_T(t) = p_{T0} \exp(-e_p t) \Rightarrow n_T(t) = N_T - p_{T0} \exp(-e_p t)$$

(4.11)
where the constant $p_m$ is density of empty traps at the end of the fill pulse. This number will depend upon the injection level in the material (and thus on the forward bias voltage $V_F$) and is in general difficult to determine. The implication of this is that the density of traps determined during a minority-carrier injection measurement represents a lower bound on the trap density, rather than the true trap density, since $p_m$ is less than or equal to $N_T$. Substituting Equation (4.11) into Equation (4.8) yields

$$C(t) = C_\infty \left[ 1 - \frac{N_T}{2N_D} + \frac{p_m}{2N_D} \exp(-e_p t) \right]$$

(4.12)

where it has been assumed that $p_m$ and $N_T$ are both much less than $N_D$. An example of a transient computed using this expression with $N_T/N_D = 0.01$ and $p_m/N_D = 0.001$ is shown below. We see that in this case the transient is “downward going” so that the DLTS signal resulting from minority-carrier emission is negative. Note also that the capacitance does not approach $C_\infty$ as $t \to \infty$, but rather saturates at a lesser value due to the presence of negative charge in the deep levels in the steady-state situation.

![Capacitance transient resulting from minority-carrier emission from a deep level with $N_T/N_D = 0.01$ and $p_m/N_D = 0.001$.](image)

**Figure 4.4.** Capacitance transient resulting from minority-carrier emission from a deep level with $N_T/N_D = 0.01$ and $p_m/N_D = 0.001$.  

59
4.2.3 Extraction of trap parameters from DLTS spectra

We begin this section by recalling from Chapter 3 the expression for the electron emission rate, which is

\[ e_n = c_n n, \exp \left( \frac{E_T - E_i}{kT} \right) = c_n N_C \exp \left( \frac{E_T - E_C}{kT} \right) \]  

(4.13)

Re-writing this equation in terms of the electron emission time constant (\( \tau_n = e_n^{-1} \)) and substituting in \( c_n = \sigma_n v_{th} \) yields

\[ \tau_n = \frac{1}{\sigma_n v_{th} N_C} \exp \left( \frac{E_C - E_T}{kT} \right) \]  

(4.14)

At this point we wish to write the temperature dependence of the product \( v_{th} N_C \) explicitly. It is given by

\[ v_{th} N_C = \left( \frac{3kT}{m_n} \right)^{\frac{1}{2}} 2 \left( \frac{2\pi m_n kT}{h^2} \right)^{\frac{1}{2}} = \gamma_n T^2 \]  

(4.15)

where the constant \( \gamma_n = 3.25 \times 10^{21} \left( m_n/m_0 \right) \text{cm}^{-2} \text{s}^{-1} \text{K}^{-2} \). Substituting this into Equation (4.14) results in

\[ \ln(\tau_n T^2) = \frac{E_C - E_T}{kT} - \ln(\sigma_n \gamma_n) = \frac{E_A}{kT} - \ln(\sigma_n \gamma_n) \]  

(4.16)

In this equation, \( T \) is the temperature at which a peak occurs for a DLTS scan taken using a rate window of \( e_n = \tau_n^{-1} \). Thus, a plot of \( \ln(\tau_n T^2) \) versus \( 1/kT \) has a slope of \( E_A = E_C - E_T \) and an intercept of \( -\ln(\sigma_n \gamma_n) \), thereby enabling the trap activation energy with respect to the conduction band edge as well as the electron capture cross-section to be determined from a sequence of measured \( (\tau_n, T) \) pairs. The horizontal axis of this "Arrhenius plot"
is in practice often in units of $1000/T$ instead of $1/kT$ (simply because the numbers for the former scale tend to be in the convenient range of 0 to 10), in which case the slope is $E_A/1000k$ rather than $E_A$. A similar expression applies to minority-carrier capture in $n$-type material with the appropriate substitutions made ($\tau_n \rightarrow \tau_p$, $E_C \rightarrow E_V$, etc.) as well as to majority- and minority-carrier capture in $p$-type material.

At this point we wish to take note of an important point that is frequently neglected in the analysis of DLTS data, namely, that the quantity $\sigma_n$ is actually temperature-dependent, and that the value obtained by a straightforward analysis of Equation (4.16) is in actuality the electron capture cross-section extrapolated to infinite temperature. The temperature dependence of the capture cross-section is often accurately described by

$$\sigma_n = \sigma_n^\infty \exp\left(-\frac{E_a}{kT}\right)$$

(4.17)

which, when substituted into Equation (4.16), yields

$$\ln(\tau_nT^2) = \frac{E_C - E_T + E_a}{kT} - \ln(\sigma_n^\infty \gamma_n)$$

(4.18)

Thus the measured activation energy $E_A$ may in fact be larger than the trap activation energy $E_C - E_T$ by an amount $E_a$. The latter value may be determined, however, by exploiting the fact that the occupancy of the trap at the end of the fill pulse depends upon the duration of the pulse.8 The DLTS signal $\Delta C = C(t_2) - C(t_1)$ for a majority-carrier trap in $n$-type material is, from Equation (4.9),

$$\Delta C = \Delta C_0 \left[ \exp(-e_n t_1) - \exp(-e_n t_2) \right]$$

(4.19)
where the quantity $\Delta C_0$ is given by

$$\Delta C_0 = C_\infty \frac{n_{T_0}}{2N_D} \quad (4.20)$$

Note that we have not assumed that $n_{T_0} = N_T$. In order to determine the value of $n_{T_0}$, we need to investigate the kinetics of electron capture, which is done by re-examining Equation (4.3) under the assumption that the term proportional to $c_n$ is dominant. Under such conditions we have

$$\frac{dn_T}{dt} = c_n n \rho_T = c_n n (N_T - n_T) \quad (4.21)$$

which, assuming that the trap is initially empty of electrons, has the solution

$$n_T(t) = N_T \left[ 1 - \exp(-c_n nt) \right] \quad (4.22)$$

The trap occupancy at the end of the fill pulse is thus given by the value of this expression at $t = t_F$, so that

$$n_{T_0} = N_T \left[ 1 - \exp(-c_n n t_F) \right] \quad (4.23)$$

Note that $n_{T_0} \to N_T$ for long fill pulse times, i.e. for $t_F \gg (c_n n)^{-1}$. Now suppose that we perform two different experiments, the only difference between them being that for the first we use a fill pulse of width $t_F < (c_n n)^{-1}$ and for the second we use a very long fill pulse. If we then measure the peak heights $\Delta C^f$ and $\Delta C^\infty$ for a given rate window and divide the former by the latter, we find that, using Equations (4.19), (4.20), and (4.23),

$$\frac{\Delta C^f}{\Delta C^\infty} = \frac{\Delta C^f_0}{\Delta C^\infty_0} = \frac{n_{T_0}^f}{N_T} = 1 - \exp(-c_n n t_F) = 1 - \exp(-\sigma_{\nu,th} n t_F) \quad (4.24)$$

62
Thus we may express the ratio of the peak heights in terms of the electron capture cross-section. Assuming that $n$ is constant over the temperature range of interest, we may rearrange this expression to obtain

$$\ln \left(1 - \frac{\Delta C^F}{\Delta C^-}\right) = -n t_F \left(\frac{3kT}{m_n}\right)^{1/2} \sigma_n^* \exp \left(\frac{-E_\sigma}{kT}\right)$$  \hspace{1cm} (4.25)

where we have substituted in the expressions for $\nu_{th}$ and $\sigma_n$. Grouping all of the constant terms into a single variable $\alpha_n$ and taking the natural logarithm of both sides results in

$$\ln \left[-T^{-1/2} \ln \left(1 - \frac{\Delta C^F}{\Delta C^-}\right)\right] = \ln(\alpha_n) - \frac{E_\sigma}{kT}$$  \hspace{1cm} (4.26)

Thus, a plot of the (somewhat complicated) expression on the left-hand side of this equation versus $1/kT$ will have a slope of $-E_\sigma$. Subtracting this from the value of the activation energy $E_A$ obtained by the method outlined above then allows one to determine the true activation energy $E_C - E_T$.

Aside from the trap activation energy and capture cross section, it is often desirable to know the density of traps within a semiconductor material. This information may be obtained in a fairly straightforward fashion by the method outlined below. Suppose that we are at a temperature where a peak occurs for a given rate window. The emission rate is then given by Equation (4.1) and the DLTS signal. Equation (4.19). becomes

$$\Delta C = \Delta C_0 \left\{ \exp \left[\ln\left(t_1/t_2\right)\right] - \exp \left[\ln\left(t_1/t_2\right) \left(1 - t_1/t_2\right)\right]\right\} = \frac{\Delta C_0}{r}$$  \hspace{1cm} (4.27)
Note that the factor $r$ depends only upon the ratio $t_2/t_1$. As discussed in section 4.2.1, $t_2/t_1 = 2.5$ independent of rate window for the DLTS system used throughout the course of this research, and inserting this into the above expression results in $r \approx 3$. Recalling the definition of $\Delta C_0$, Equation (4.20), we then have

$$\Delta C = \frac{\Delta C_0}{r} = \frac{C_0 N_T}{2rN_D} \Rightarrow N_T = 2rN_D \frac{\Delta C}{C_0}$$ (4.28)

which gives an approximate expression for the trap density in terms of the measurable parameters $N_D$, $\Delta C$, and $C_0$. This equation may be multiplied by correction terms in order to take into account various factors, e.g. the variation in the magnitude of the DLTS signal $\Delta C$ due to a change in the fill pulse voltage $V_F$. Such corrections are frequently within the experimental error of the measurement, however, and will thus not be discussed here; the interested reader is referred to the overview by Blood and Orton for a more thorough discussion of this topic.\(^2\)

In order to illustrate the general properties of DLTS spectra arising due to “ideal” deep levels, simulations of DLTS experiments were performed. For this purpose it was supposed that a defect exists 0.35 eV below the conduction band edge of a 1.05 eV bandgap, $n$-type material; further, it was assumed that both electron and hole emission occur (i.e., the deep level is an R-G center) and that the electron and hole capture cross-sections are both equal to $1 \times 10^{-15}$ cm$^2$. The trap occupancy levels at the end of the fill pulse were assumed to be $n_{T0} = 0.75N_T$ and $p_{T0} = 0.25N_T$ with a trap density of $N_T = 0.01N_D$. The simulated DLTS spectra obtained for four rate windows are shown below.
Figure 4.5 Simulated DLTS spectra of an R-G center located 0.35 eV below the conduction band edge of an n-type, 1.05 eV bandgap material. The electron and hole capture cross-sections were both assumed to be equal to $1 \times 10^{-13} \text{ cm}^2$, and initial trap occupancy parameters were $n_0 = 0.75 N_T$ and $p_0 = 0.25 N_T$ with a trap density of $N_T = 0.01 N_D$. The curves were sampled using rate windows 200, 80, 50, and 20 s$^{-1}$.

A number of features are evident from the simulated curves. First of all, we see that the peaks resulting from majority-carrier electron emission are positive and that the peaks resulting from minority-carrier hole emission are negative, as expected. Further, the peaks resulting from electron emission (0.35 eV) occur at a lower temperature than the peaks resulting from hole emission (0.70 eV), which may be understood by examining the expression for the emission rate, Equation (3.7). From this equation, we see that a smaller activation energy requires a smaller temperature to achieve a given emission rate. Since the DLTS peak occurs at the temperature where the emission rate equals the rate window, peaks resulting from lower-energy transitions should occur at lower temperatures. This also explains why the peaks shift towards lower temperatures as the
rate window is decreased. We also see that the peak height for a given transition is independent of rate window, as is expected from Equation (4.27). Finally, we take note of the shape of the DLTS peaks. They are slightly asymmetric, with the low-temperature tail being slightly broader than the high-temperature tail. Further, they are narrow; for example, for the 20 s\(^{-1}\) rate window, the ratio of the full-width at half-maximum to the peak temperature was calculated to be 0.10 for both the electron emission peak and the hole emission peak. Indeed, it may be shown that this ratio is ~0.1 for all of the rate windows listed in Table 4.1.\(^9\) We will see below that deviations from the ideal delta function trap distribution given by Equation (4.2) result in broad DLTS peaks whose height is not independent of the rate window; thus, these two factors give a good indication of the “ideality” of the deep level responsible for the peak in question.

4.3 Characterization of non-ideal deep levels by DLTS

In this section we discuss the analysis of DLTS spectra resulting from deep levels due to non-ideal defects, where the term “non-ideal” generally refers to defects that are not confined to a single point in real space. The first part of this section covers the carrier capture kinetics associated with point defects versus those associated with line defects (i.e. dislocations) and how these differences manifest themselves in DLTS spectra. Analysis of these differences thus enables one to obtain information regarding the physical nature of the defects under investigation. Further, since non-ideal defects are not perfectly localized in real space, their \(k\)-space representations will not be entirely delocalized, and they thus tend to give rise to a narrow distribution of energy levels within the bandgap, as opposed to the discrete energy levels characteristic of “ideal”
point defects. The latter portion of this section therefore discusses modifications that must be made to the DLTS theory presented above in order to take into account deep levels "distributions" within the bandgap. Our discussion of these topics will once again assume that the material under study is n-type.

4.3.1 Carrier capture kinetics of point versus extended defects

We have in fact already discussed the capture kinetics associated with ideal point defects as part of our analysis of the temperature-dependent capture cross-section discussed in the previous section. There we derived an expression for the ratio of the DLTS peak height obtained for a pulse of duration \( t_F < (c_n n)^{-1} \) to the peak height resulting from a very long pulse. Equation (4.24), which we repeat here for convenience:

\[
\frac{\Delta C^f}{\Delta C^n} = 1 - \exp(-c_n nt_F)
\]

(4.29)

Re-arranging this equation results in the expression

\[
\ln\left(1 - \frac{\Delta C^f}{\Delta C^n}\right) = -c_n nt_F
\]

(4.30)

Thus, if the defect giving rise to the peak under study is an ideal point defect, a plot of the left-hand side of this expression versus the fill pulse time \( t_F \) should be a straight line. Note that this discussion applies to majority-carrier spectra only; the result is not necessarily true for minority-carrier traps due to the dependence of the peak height on the injection level. This latter effect may or may not be the dominant mechanism by which the peak height is established, thus rendering the results of any fill pulse experiments suspicious.
To analyze the carrier capture kinetics of extended defects, it is necessary to return to the expression for the rate of change of trap occupancy when electron capture is dominant. Equation (4.21), which we repeat here:

\[
\frac{dn_T}{dt} = c_n n (N_T - n_T) \tag{4.31}
\]

This equation must be modified, however, if it is to accurately describe the carrier capture kinetics of an extended defect. As carriers are captured, a time-dependent potential energy \( \varphi(t) \) builds up around the defect and influences the subsequent capture of electrons. This is illustrated in the figure below.

\[\text{Figure 4.6} \quad \text{Schematic illustration of the band-bending that occurs in the vicinity of an extended defect due to the capture of carriers.}\]

Electrons must overcome the potential barrier \( \varphi(t) \) if they are to be captured by the defect. Assuming Boltzmann statistics, the probability for an electron to do this is proportional to \( \exp[-\varphi(t)/kT] \), and Equation (4.31) becomes

\[
\frac{dn_T}{dt} = c_n n (N_T - n_T) \exp\left[\frac{-\varphi(t)}{kT}\right] \tag{4.32}
\]

The exact nature of the potential \( \varphi(t) \) will of course depend upon the geometry of the extended defect in question (line defect, point defect cluster, etc.) In all cases, however.
the potential must be a function of the density of filled traps \( n_T(t) \). Thus we may write

\[
\varphi(t) = a_1 n_T(t) + a_2 n_T^2(t) + \ldots
\]  

(4.33)

where the coefficients \( a_n \) are constants whose values will depend upon the precise geometric arrangement of the carrier capture centers. Note that we have omitted the constant \( a_0 \) term, since the potential must be zero if no charge is trapped. For sufficiently short times, we may neglect the higher order terms and assume that \( \varphi(t) = a_1 n_T(t) \): substituting this into Equation (4.32) we obtain

\[
\frac{dn_T}{dt} = c_s n(N_T - n_T) \exp\left( -\frac{q d_T n_T}{kT} \right)
\]  

(4.34)

which is the differential equation that approximately describes the carrier capture kinetics \( n_T(t) \) for an extended defect. Assuming that \( N_T >> n_T \) (true for the short-time approximation invoked above) and further supposing an initial condition \( n_T(0) = 0 \), the solution of this equation is given by

\[
n_T(t) = \frac{kT}{qa_1} \ln\left( 1 + \frac{t}{\tau_E} \right)
\]  

(4.35)

where the time constant \( \tau_E \) is equal to

\[
\tau_E = \frac{\tau_s kT}{n qa_1}
\]  

(4.36)

Now, from Equations (4.20) and (4.27), the DLTS peak height is proportional to the density of occupied traps at the end of the fill pulse, \( n_{T0} = n_T(t_F) \). We thus have
\[
\Delta C = \frac{C_m}{2\pi N_D} \frac{kT}{qa_i} \ln \left( 1 + \frac{t_F}{\tau_E} \right) = \Delta C_E \ln \left( 1 + \frac{t_F}{\tau_E} \right)
\]

(4.37)

For situations where \( t_F \ll \tau_E \) (which is often the case experimentally), Equation (4.37) may be approximated by

\[
\Delta C = \Delta C_E \ln \left( \frac{t_F}{\tau_E} \right) = \Delta C_E \ln(t_F) - \Delta C_E \ln(\tau_E)
\]

(4.38)

We thus see that, for an extended defect, the DLTS peak height is proportional to the natural logarithm of the fill pulse time. This behavior is markedly different than the behavior derived above for the case of carrier capture at a point defect. By varying the fill pulse time one may, therefore, obtain information regarding the spatial extent of a particular defect and thus insight into the physical source of the defect.

4.3.2 Defects characterized by a distribution of states within the bandgap

We now turn our attention towards the properties of defects that may be described by a distribution of states within the bandgap. As was mentioned in the introduction to this section, defects that are not perfectly localized in real space will give rise to \( k \)-space representations that are not entirely delocalized. Thus the dispersion relation \( E(k) \) corresponding to the defect will have a slight curvature and will therefore give rise to a distribution of states within the bandgap, as opposed to the discrete energy levels characteristic of "ideal" point defects. We describe such a distribution by

\[
N_T(E) = N_T g_T(E)
\]

(4.39)
where the function $g_T(E)$ is normalized such that its integral is unity. Typically such distributions will be "broadened" levels characterized by a peak that falls off with energy. An example of such a distribution is given below.

$$g_T(E) = \frac{1}{\sqrt{2\pi \sigma_E}} \exp\left[-\frac{(E - E_T)^2}{2\sigma_E^2}\right]$$

(4.40)

where the standard deviation $\sigma_E$ provides a measure of the broadness of the distribution.

We now consider electron emission from a narrow portion of the distribution centered at energy $E$ and having width $dE$. Emission from this portion of the spectrum gives rise to a differential trap occupancy $dn_T(t)$ given by

$$dn_T(t) = N_T g_T(E) \exp[-e_s(E)t]dE$$

(4.41)
which is the analogue of Equation (4.6). Note that the energy dependence of the electron emission rate must now be considered. An expression for $e_n$ was derived in Equation (3.7) assuming a single trap level $E_r$; for the present case, the appropriate analogue is

$$
e_n(E) = c_n N_C \exp \left( \frac{E - E_C}{kT} \right)$$

(4.42)

We must now consider the contributions to the trap occupancy from each energy interval $dE$; thus we integrate Equation (4.41) over the bandgap to obtain the trap occupancy as a function of time, which is

$$n_r(t) = N_r \int_{E_1}^{E_F} g_r(E) \exp[-e_n(E)] dE$$

(4.43)

Finally, substituting this into the expression for the diode capacitance, Equation (4.8), results in the expression for the capacitance transient due to a broadened defect distribution:

$$C(t) = C_0 \left[ 1 - N_r \int_{E_1}^{E_F} \frac{g_r(E) \exp[-e_n(E)t]}{2N_D} dE \right]$$

(4.44)

The transient is thus essentially a sum of exponential functions weighted by the normalized trap distribution density $g_r(E)$. The DLTS signal $\Delta C$ is once again defined by the familiar expression $\Delta C = C(t_2) - C(t_1)$.

In order to understand the impact of level broadening on DLTS spectra, we have performed simulations of DLTS measurements of broadened deep levels. The trap parameters and experimental conditions were taken to be the same as those that were used for the simulation of the ideal DLTS curves presented in Figure 4.5, although in this

72
case the deep level was assumed to be broadened according to Equation (4.40) with $\sigma_E = 0.02$ eV. The results of these simulations are shown below.

![Simulated DLTS spectra of a broadened R-G center.](image)

**Figure 4.8** Simulated DLTS spectra of a broadened R-G center. The trap parameters and experimental conditions were the same as those used to generate the curves of Figure 4.5, except that the level was assumed to be broadened according to Equation (4.40) with $\sigma_E = 0.02$ eV.

A cursory inspection of Figure 4.8 suggests that it is very similar to Figure 4.5, which showed simulated DLTS curves arising from an ideal R-G center. The two figures are indeed similar, but careful comparison reveals that some differences do exist. For example, we see that in the present situation the peak height is *not* independent of rate window. Rather, smaller rate windows result in smaller peak heights; this is particularly evident in the peaks resulting from electron emission, but careful inspection will reveal that it is also true for the peaks resulting from hole emission. This is due to the expression of the capacitance transient as an integral, given by Equation (4.44); thus the simple difference of exponentials which led to the independence of peak height on rate window becomes significant.
window. Equation (4.27), no longer holds. It follows that for any finite rate window, the peak height must be smaller than the peak height in the ideal case; indeed, we see that the peaks of Figure 4.8 are roughly 75% the heights of the corresponding peaks of Figure 4.5. Finally, the DLTS peaks resulting from broadened deep levels are themselves, not surprisingly, broadened. In the example being discussed here, we find that the full-width at half-maximum ratios for the 20 s\(^{-1}\) rate window are 0.17 and 0.12 for the electron and hole emission peaks, respectively; recall that without broadening, the ratios for both peaks were equal to 0.10. Fortunately, the temperatures at which a peak corresponding to a particular rate window occurs does not shift as a result of level broadening,\(^{12}\) so that Equation (4.16) – or one of its variants such as Equation (4.18) – may still be used to determine trap parameters from measured peak positions.
4.4 References


4. One such technique is known as the “Covariant Method of Linear Predictive Modeling,” or CMLPM; see, for example, F. R. Shapiro, S. D. Senturia, and D. Adler. J. Appl. Phys. 55, 3453 (1984).

5. Numerous texts discuss the properties of pn junctions. See, for example, G. W. Neudeck. The pn Junction Diode (Addison-Wesley, Reading, MA, 1989).


7. Fundamental relations between various semiconductor parameters such as this are discussed in numerous textbooks. A good reference is R. F. Pierret. Advanced Semiconductor Fundamentals (Addison-Wesley, Reading, MA, 1989).


CHAPTER 5

CHARACTERIZATION OF DEEP LEVELS IN InGaAsN GROWN BY METAL-ORGANIC CHEMICAL VAPOR DEPOSITION

5.1 Introduction

All of the samples investigated during the course of this study were obtained from Sandia National Laboratories as part of a collaboration between that organization and Ohio State University. This chapter discusses the characterization of deep levels in InGaAsN layers grown using the metal-organic chemical vapor deposition (MOCVD) technique, which is a technique whereby gas-phase "precursors" are introduced into a chamber. The precursors pass over a heated substrate and decompose at the surface of the substrate, which results in the growth of the desired epitaxial layer. The precursors used to introduce the group III atoms are metal-organic compounds, typically consisting of the metal molecule of interest (e.g., In or Ga) bonded to a number of methyl (CH$_3$) or ethyl (C$_2$H$_5$) groups. The group V atoms are introduced through the use of hydrogen-containing precursor gases such as arsine (AsH$_3$), and dopant atoms are introduced via metal-organic compounds or other compounds such as carbon tetrachloride (CCl$_4$). The precursors used for InGaAsN growth during the course of this research are listed in Table 5.1.
<table>
<thead>
<tr>
<th>Atom</th>
<th>Function</th>
<th>Source</th>
<th>Symbol</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indium</td>
<td>Group III</td>
<td>Trimethylindium</td>
<td>TMIn</td>
<td>In(CH$_3$)$_3$</td>
</tr>
<tr>
<td>Gallium</td>
<td>Group III</td>
<td>Trimethylgallium</td>
<td>TMGa</td>
<td>Ga(CH$_3$)$_3$</td>
</tr>
<tr>
<td>Gallium</td>
<td>Group III</td>
<td>Triethylgallium</td>
<td>TEGa</td>
<td>Ga(C$_2$H$_5$)$_3$</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Group V</td>
<td>Arsine</td>
<td>AsH$_3$</td>
<td>AsH$_3$</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Group V</td>
<td>Dimethylhydrazine</td>
<td>DMHy</td>
<td>H$_2$NN(CH$_3$)$_2$</td>
</tr>
<tr>
<td>Zinc</td>
<td>Dopant (p)</td>
<td>Dimethylicyclopentadiene</td>
<td>DMZn</td>
<td>Zn(CH$_3$)$_2$</td>
</tr>
<tr>
<td>Carbon</td>
<td>Dopant (p)</td>
<td>Carbon tetrachloride</td>
<td>CCl$_4$</td>
<td>CCl$_4$</td>
</tr>
<tr>
<td>Tin</td>
<td>Dopant (n)</td>
<td>Tetraethyltin</td>
<td>TESn</td>
<td>Sn(C$_2$H$_5$)$_4$</td>
</tr>
<tr>
<td>Tellurium</td>
<td>Dopant (n)</td>
<td>Diethyltellurium</td>
<td>DETe</td>
<td>Te(C$_2$H$_5$)$_2$</td>
</tr>
</tbody>
</table>

**Table 5.1** MOCVD precursor gases used to grown InGaAsN layers.

5.2 **Characterization of p-type InGaAsN grown by MOCVD**

This section begins with a presentation of the growth of the test structures used to characterize p-type InGaAsN alloys. The electronic quality of such alloys is discussed, including the curious impact of thermal annealing on the properties of InGaAsN. Following that, we proceed to the characterization of deep levels in p-type material by DLTS and the influence of thermal annealing on the properties of these levels.

5.2.1 **Sample growth and material electronic quality**

The solar cell sample structure used to facilitate DLTS measurements on p-type InGaAsN grown by MOCVD is shown below in Figure 5.1.
The MOCVD precursor gases used for the In, Ga, As, and N components of the material were TMIn, TMGa, AsH₃, and DMHy, respectively. Si sourced from SiCl₄ was used to achieve n-type doping. The growth temperature of the InGaAsN layers was 600°C and the pressure was 60 Torr, with a V/III ratio of 97, a DMHy/V ratio of 0.97, and a TMIn/V ratio of 0.12. The compositions of the base and emitter layers resulting from these growth conditions were both 7% In and 2% N, i.e. In₀.₀₇Ga₀.₉₃As₀.₉₈N₀.₀₂. Optical absorption measurements indicated a 300 K bandgap of 1.05 eV; as discussed in Chapter 1, this bandgap is desirable for multi-junction solar cell applications. Further, double crystal x-ray diffraction (DCXRD) measurements demonstrated a lattice mismatch of 0.08% with the GaAs substrate. After growth, the wafer was diced into a number of pieces, and some of them were subjected to thermal annealing at 650 °C for 30 minutes. Following annealing, Au-Ge-Ni and Au-Be alloy ohmic contacts were deposited on the top n-GaAs and bottom p-GaAs layers, respectively, of all of the pieces. This was
followed by mesa-etching around the contacts to define the diode area. 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; as discussed below, it is believed that this may be due to the incorporation of background carbon into the InGaAsN film during growth.

The impact of the thermal annealing process on the electronic quality of the material is rather startling. An example of this is illustrated below for a $p$-type InGaAsN layer grown under identical conditions to the base layer of the solar cell structure shown in Figure 5.1.

![Figure 5.2 Photoluminescence and absorption spectra of $p$-type InGaAsN grown by MOCVD. Note the prominent sub-bandgap features in the spectrum of the as-grown material and the dominance of the bandgap transition in the annealed material.](image)

Figure 5.2 shows photoluminescence (PL) spectra of as-grown (200 K) and annealed (300 K) InGaAsN layers, as well as the 300 K absorption spectrum of the as-grown material as
a reference. The PL technique is an experiment in which photons incident on a material excite electrons into high-energy states; the electrons subsequently fall into empty, lower-energy states and emit photons at wavelengths corresponding to the magnitudes of the transitions. The intensity as a function of energy (or, equivalently, wavelength) is recorded, with peaks corresponding to prominent transition energies. We see that in the particular experiment for which the data are shown, no spectrum could be obtained for the as-grown sample at room temperature due to its extremely poor electronic quality! We see that at 200 K the PL spectrum is dominated by a broad, sub-bandgap feature, which is suggestive of deep level defects in the material. Following annealing, we see that not only is a PL spectrum obtainable, but that the dominant feature is now the band-to-band transition.

Thermal annealing had a positive impact on solar cell properties as well. For example, the light-IV curves of both as-grown and annealed solar cells are shown below.

![Figure 5.3](image_url) 300 K light-IV curves of as-grown and annealed InGaAsN solar cells. Note the improvement following annealing.3

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
We see that both the open-circuit voltage \(V_{oc}\) and the short-circuit current density \(J_{sc} = I_{sc} / A\) improve after annealing. As was discussed in Chapter 1, this is indicative of a lengthening of the minority-carrier diffusion lengths \(L_n\) and \(L_p\), or equivalently, an increase in the minority-carrier lifetimes \(\tau_n\) and \(\tau_p\). This latter change may be correlated with a reduction in trap density, as discussed in Chapter 4. Further evidence for the improvement of \(L_n\) and \(L_p\) after annealing is shown in the plot of the solar cell internal quantum efficiency (IQE) below.

![Figure 5.4 Internal quantum efficiency for as-grown and annealed InGaAsN solar cells. Again note the substantial improvement following annealing.](image)

We see a substantial improvement in the IQE of the solar cell after thermal annealing. Estimates of the electron and hole minority-carrier diffusion lengths were made from IQE-voltage data and indicated negligible electron diffusion lengths in the \(p\)-type base layers of both as-grown and annealed material \((L_n < 0.01 \, \mu m)\), whereas in the \(n\)-type emitter the hole diffusion length was found to improve from \(L_p \sim 0.2 \, \mu m\) in as-grown...
material to $L_p \sim 1.0 \mu m$ in annealed material. It is perhaps not surprising that electron transport is so limited in InGaAsN, since it is thought to be almost entirely the conduction band that is affected by the incorporation of N in GaAs and InGaAs, as was discussed in Chapter 2. Whether or not this limitation is due to deep level defects or to some other aspect of N incorporation in this class of alloys will be discussed in Chapter 7.$^5$

To complement the Hall data mentioned above, capacitance-voltage (CV) profiling was used to determine the doping in the base layers of the actual DLTS test structures employed. The CV measurement is performed by measuring the small-signal capacitance of the test diode (the capacitance meter used for the present research measures at a frequency of 1 MHz) as a function of reverse-bias voltage. For a one-sided $p^*n$ junction such as the sample currently under investigation, the net hole concentration profile is given by$^6$

$$N_A(x) = -\frac{2}{q\varepsilon A^2} \left( \frac{dC}{dV} \right)^{-1}$$  \hspace{1cm} (5.1)

Note that for a one-sided $p^+n$ diode, the same expression applies except that the net donor concentration $N_A$ is replaced by the net acceptor concentration $N_D$. The case of a two-sided $pn$ junction is more complex and is in any case not applicable to the sample structures studied throughout the course of this research, so it will not be discussed here.

From our CV measurements, the background doping in the DLTS test layers was found to be $p$-type (in qualitative agreement with the Hall measurements mentioned above) and the magnitudes were $N_A = 3.5 \times 10^{16}$ cm$^{-3}$ 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 was thought to be due to the
de-passivation of background acceptors in the material; this hypothesis is examined in more detail in the discussion of $n$-type MOCVD-grown material presented in Section 5.3.

5.2.2 Deep level characterization

DLTS measurements were performed first on the as-grown InGaAsN base layers of the sample shown in Figure 5.1, the results of which are shown below.

![DLTS spectra](image)

**Figure 5.5** DLTS spectra of as-grown, $p$-type InGaAsN layers grown by MOCVD. The experimental conditions used were $V_R = -0.80$ V and $V_F = -0.15$ V for a duration of 1 ms. Note that the DLTS signal is expressed in units of concentration.

Note that the DLTS signal in Figure 5.5 is expressed in units of cm$^{-3}$, since the DLTS capacitance difference $\Delta C$ has been converted to trap concentration using Equation (4.28); when such a conversion is made, however, it is important to keep in mind that the values of the trap concentration on the vertical axis are applicable at the peak positions only, and not to the entire spectrum. That said, we see that the DLTS spectra are dominated by a low-temperature peak indicative of a shallow hole trap: further, the spectra are characterized by an overall broadness, suggesting that a distribution of deep
levels is present within the bandgap of the material. As discussed in Chapter 4, the fact that the heights of the DLTS peaks depend on the rate window used supports the existence of such deep level distributions. Also alluded to in Chapter 4 are the potential causes of such a distribution, including dislocations and other extended defects such as point defect clusters; further, as discussed in Chapter 2, intrinsic band-related states may play a role. A more detailed discussion of potential physical sources of the observed deep levels will be undertaken in Chapter 7. For the present, we note that cross-sectional transmission electron microscopy (TEM) studies on a sample similar to that for which the DLTS data were taken suggest that dislocations are an unlikely source. A representative image is shown below.

![Figure 5.6 Representative TEM image of InGaAsN layers grown by MOCVD. The absence of dislocations in the image indicates that the dislocation density is lower than the TEM statistical detection limit of $10^7$ cm$^{-2}$.](image)

84

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
We see that no dislocations are visible in the image. While this does not necessarily mean that there are no dislocations in the film, it does imply that the threading dislocation density is below the TEM statistical detection limit of $10^7 \text{ cm}^{-2}$, thus implying that dislocations are not a likely source of deep levels in the material; given the minimal lattice-mismatch with the substrate (0.08%), this result is not really surprising.

The DLTS spectra of the $p$-type base layer after annealing were studied next; these spectra are shown below in Figure 5.7.

![DLTS spectra](image)

**Figure 5.7** DLTS spectra of annealed, $p$-type InGaAsN layers grown by MOCVD. The experimental conditions were the same as for the spectra of Figure 5.5 except that $V_F = 0.00 \text{ V}$. The DLTS signal is again expressed in units of concentration.

Comparing the above spectra with those of Figure 5.5, we see that the overall magnitude of the DLTS spectrum is reduced and that the features are more clearly resolved. This not only implies that a removal of point defects occurred during the anneal, but it also enabled us to determine trap energy levels and densities. To do this, each DLTS spectrum was fitted using Gaussian functions. Figure 5.8 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.

![Graph](image)

**Figure 5.8** Arrhenius analysis of the DLTS spectra of the p-type InGaAsN shown in Figure 5.7.

Three hole traps with energy levels of 0.10 eV (H1), 0.23 eV (H2), and 0.48 eV (H3) above the valence band edge were found. By fitting the 200 s⁻¹ spectrum, the concentrations for these three traps were estimated to be $3 \times 10^{14}$ cm⁻³, $4 \times 10^{14}$ cm⁻³, and $8 \times 10^{14}$ cm⁻³, respectively. The fact that there is still some rate window dependence for the magnitude of the peaks again suggests that the deep levels giving rise to these spectra are distributions of energy states within the bandgap. In agreement with this, we also note that the DLTS peaks are quite broad; for example, the ratio of the full-width to half-maximum for peak H3 is roughly 0.4 for the 200 s⁻¹ rate window.
Finally, in order to observe the changes due to annealing more directly, we plot the DLTS spectra of the as-grown and the annealed layers on the same set of axes, as shown below.

![DLTS Spectra Comparison](image)

**Figure 5.9** Direct comparison between DLTS spectra of as-grown and annealed p-type InGaAsN. The data shown were obtained using a rate window of 200 s$^{-1}$.

There are several important observations which may be made from the comparison shown in Figure 5.9. First, following the post-growth annealing, the overall trap density was greatly reduced; second, following annealing, the broad features of the spectra simplified, revealing well-defined individual DLTS peaks. Both of these observations were alluded to above and imply that point defects are the dominant source of the as-grown deep level spectra and that they are at least partially removed by annealing. The third observation is that trap H1, 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 5.9 indicates that another trap contributing a peak near 270 K can be identified in the as-grown sample. This fourth trap, H4, 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 $E_V + 0.5$ eV; a more accurate determination could not be made due to the broadness of the as-grown DLTS spectra. The properties of the deep levels observed in this p-type InGaAsN are summarized in Table 5.2 below.

<table>
<thead>
<tr>
<th>Trap</th>
<th>Activation energy (eV)</th>
<th>Concentration, annealed (cm$^{-3}$)</th>
<th>Thermally stable?</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>0.10</td>
<td>$3 \times 10^{14}$</td>
<td>No</td>
</tr>
<tr>
<td>H2</td>
<td>0.23</td>
<td>$4 \times 10^{14}$</td>
<td>No</td>
</tr>
<tr>
<td>H3</td>
<td>0.48</td>
<td>$8 \times 10^{14}$</td>
<td>Yes</td>
</tr>
<tr>
<td>H4</td>
<td>$-0.5$</td>
<td>–</td>
<td>No</td>
</tr>
</tbody>
</table>

**Table 5.2** Properties of deep levels observed in p-type InGaAsN grown by MOCVD. Activation energies are measured from the valence band edge.

The simplification of the DLTS spectra and the reduction in overall trap density is consistent with the impact of annealing on the electronic quality of the InGaAsN layers discussed earlier in this section. 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 H1 due to its dominance of the as-grown DLTS spectra and its sharp
reduction in concentration after annealing. However, the thermally unstable midgap trap H4 is far more likely to be important due to the much greater recombination rate expected for midgap versus shallow levels, as discussed in Chapter 3. The position of this trap in the bandgap and its removal by annealing correlates very well with the improved bulk properties of the material; however, this correlation does not necessarily establish a causal relationship between the removal of the trap and improved material properties. The potential physical sources of deep levels will be discussed in detail in Chapter 7.

5.3 Characterization of n-type InGaAsN grown by MOCVD

This section discusses the characterization of n-type InGaAsN grown by MOCVD. We first discuss sample growth, which is followed by an in-depth discussion of the measurement of the change in carrier concentration due to thermal annealing and a detailed analysis of possible explanations for this. This is followed by DLTS characterization of deep levels in n-type material and the impact of thermal annealing on their properties. Finally, we conclude the section by establishing a connection between the deep levels observed by DLTS and carrier transport as determined by reverse-bias current-temperature measurements.

5.3.1 Sample growth and measurement of carrier concentration

The n-InGaAsN film used to characterize deep levels was grown by MOCVD on an (001) GaAs substrate at a nominal temperature of 588°C. Growth conditions, including the precursor gases used and the gas partial pressures, were similar to those used to grow the solar cell structure of the previous section, the major difference being that in the present case TESn was used to introduce Sn as an n-type dopant. The growth
parameters were again designed to achieve indium and nitrogen mole fractions of $x = 0.07$ and $y = 0.02$, respectively, and the bandgap was determined to be 1.05 eV via optical absorption measurements. Double crystal x-ray diffraction measurements (DCXRD) verified that the InGaAsN layer was lattice-matched to the GaAs substrate to within 0.06%. Annealing, contact deposition, and etching were accomplished by the same procedure as described in the previous section. A schematic of the sample structure is shown in Figure 5.10. Note that in this case the sample is a heterojunction solar cell consisting of an $n$-InGaAsN emitter grown on a $p^+$-GaAs base. As we will shall see subsequently, the heterojunction at the base-emitter interface appears to have an impact on the properties of the deep levels present in the InGaAsN layer. Finally, we note that the Al content in the window and BSR layers was 30%.

![Figure 5.10](image)

150 nm GaAs contact ($n^+$)  
50 nm AlGaAs window ($n^+$)  
1000 nm InGaAsN emitter (n)  
200 nm GaAs base ($p^+$)  
200 nm AlGaAs BSR ($p^+$)  
GaAs substrate ($p^+$)

Figure 5.10  Heterojunction solar cell structure used to facilitate DLTS measurements of deep levels in $n$-type InGaAsN layers.

Capacitance-voltage profiling of both as-grown and annealed samples was performed in order to determine the net electron concentration in the $n$-type InGaAsN.
layers, and the results of these measurements are shown in Figure 5.11. The reverse-bias voltage was varied from -2.0 V to 0.0 V to obtain the profiles shown. From the figure, we see that the net electron concentration decreased by ~1.5×10^{17} \text{ cm}^{-3} following annealing. Recall that in the p-type material, an increase in net hole concentration of ~2.5×10^{17} \text{ cm}^{-3} was observed, and it was suggested that this increase was due to de-passivation of background carbon acceptors during annealing. Secondary ion mass spectroscopy (SIMS) indicates that a carbon concentration of ~3×10^{17} \text{ cm}^{-3} exists in n-type InGaAsN layers grown under similar conditions as those used for the sample of Figure 5.10, and this, coupled with the fact that in both types of material the sign of the change in net carrier concentration is consistent with an increase in hole concentration after annealing, supports the assertion that de-passivation of background carbon is responsible for the change in net electron concentration.

![Figure 5.11 Carrier concentration profiles of n-type InGaASN layers, as determined from capacitance-voltage measurements.](image)

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Despite the consistency of the above explanation, it does not allow us to entirely discount the role of traps. Thus, we performed a calculation to evaluate whether or not traps could be at least partially responsible for the observed change in carrier concentration in the n-type layers. We first assumed the presence of an electron trap in the material, initially passivated and thus empty of electrons. We then sought to determine how many such traps would need to be de-passivated, i.e. to become capable of effectively trapping electrons, to account for the observed decrease in carrier concentration. The density of traps filled with electrons $n_T$ is given by the Fermi-Dirac function\(^{10}\)

$$n_T = \frac{N_f}{1 + \exp\left(\frac{E_T - E_F}{kT}\right)} \quad (5.2)$$

The Fermi level is given by

$$E_F = E_C + kT \ln\left(\frac{n}{N_C}\right) \quad (5.3)$$

Combining these two expressions gives

$$N_T = n_T \left(1 + \frac{N_C}{n} e^{-E_A/kT}\right) \quad (5.4)$$

where $E_A = E_C - E_T$ is the activation energy of the deep level measured with respect to the conduction band edge. Finally, substituting in the expression for the conduction band-edge density of states.

$$N_C = 2 \left(\frac{2\pi m^*_e kT}{\hbar^2}\right)^{3/2} = aT^{3/2} \quad (5.5)$$
yields the expression that was used for the calculation, which is

\[ N_T = n_T (1 + an_T^{-1/2} e^{-E/AkT}) \]  \hspace{1cm} (5.6)

where \( a \) is a constant equal to \( 4 \times 10^{14} \) K\(^{-3/2}\) cm\(^{-3}\). To determine this value, the electron effective mass was assumed to be \( m_n = 0.2m_0 \), which was calculated using Equation (2.3) of the band-anticrossing model presented in Chapter 2.\(^{11}\) It was assumed that the number of traps filled after de-passivation was equal to the change in carrier concentration, so that \( n_T = 1.5 \times 10^{17} \) cm\(^{-3}\). Further, since the trap is assumed to be active only after annealing, we used the post-annealing value for the carrier concentration, \( n = 4.0 \times 10^{17} \) cm\(^{-3}\); note that, for the purposes of the calculation, it was assumed that no compensating holes were present, since only the effects of majority-carrier deep levels were considered. The 300 K values of \( n_T \) and \( n \) were assumed to hold at all temperatures, which is a reasonable assumption over the temperature range considered.\(^{10}\) The results of the calculation for \( T = 100, 200, 300, \) and \( 400 \) K are shown below.

**Figure 5.12** Calculated density of electron traps required to account for the observed change in carrier concentration after annealing, as observed in Figure 5.11. Activation energy is measured from the conduction band edge.
We see that, e.g., at 300 K the de-passivation of slightly more than $1 \times 10^{18}$ cm$^{-3}$ electron traps located just below the conduction band edge would be required to account for the observed decrease in electron concentration. Further, the density of traps required saturates at the observed change in carrier concentration, $1.5 \times 10^{17}$ cm$^{-3}$, at an activation energy of approximately 0.2 eV. We will see below that based on DLTS measurements of our samples, only a single electron trap was observed to be present in only the annealed material, and that this trap has an activation energy of $E_A = 0.36$ eV and a density of $N_T = 2 \times 10^{15}$ cm$^{-3}$. We see that the latter number is roughly two orders of magnitude lower than the required defect density indicated in the plot for this activation energy. Thus, it seems unlikely that majority-carrier deep levels are responsible for the change in carrier concentration observed after annealing.

Another possibility is that minority-carrier hole traps are passivated during annealing, thus liberating holes (possibly due to excess carbon already active prior to annealing) and compensating the n-type material. Note that this process is essentially equivalent to the proposed activation of excess carbon acceptors during annealing, aside from the assumption that holes are readily available from some other source. The number of traps filled with holes $p_T$ is given by

$$p_T = N_T \left(1 - \frac{1}{1 + e^{(E_r - E_T) / kT}}\right)$$

and following a procedure similar to the one outlined above, we obtain

$$N_T = p_T \frac{1 + (p/N_v)e^{E_r/kT}}{(p/N_v)e^{E_v/kT}}$$

94
In this case, the activation energy $E_A$ is measured from the valence band edge. As discussed in Chapter 2, it has been demonstrated that the addition of nitrogen to InGaAs does not appreciably affect the valence band structure of the host material, so that $m_p$(InGaAsN) ~ $m_p$(InGaAs). Since the indium content of our samples is only about 7%, we assumed that $m_p$ is the same as that for GaAs, namely, $m_p = 0.5m_0$.\(^{10}\) We thus obtain the result

$$N_T = \frac{P_T}{1 + \frac{bP_T}{T} - \frac{E_A}{kT}}$$

where $b = 6 \times 10^{-16}$ K$^{3/2}$ cm$^3$. It was assumed that the number of holes initially trapped was equal to the measured change in carrier concentration, so that $P_T = 1.5 \times 10^{17}$ cm$^{-3}$. Further, since the carbon concentration measured by SIMS was roughly $3 \times 10^{17}$ cm$^{-3}$, we set the hole concentration $p$ equal to this value. The results of the calculation are shown below.

**Figure 5.13** Calculated density of hole traps required to account for the observed change in carrier concentration after annealing, as observed in Figure 5.11. Activation energy is measured from the valence band edge.
Comparing this to our experimental results, we will see below that the only hole trap observed our material was present in the annealed sample only, so it does not fit the stipulations of this model, which requires that the deep level be active in the as-grown material only. Moreover, even if this latter situation were the case, the trap in question is characterized by $E_A = 0.71$ eV and $N_T = 8 \times 10^{14}$ cm$^{-3}$, which is inconsistent with the results shown above. Thus, we see that minority-carrier hole traps are likely not responsible for the observed change in carrier concentration. We are therefore left with our original hypothesis, namely, that a portion of the background carbon in the material is activated by the thermal annealing process, introducing compensating holes into the sample.

5.3.2 Deep level characterization

The results of DLTS measurements on both the as-grown and annealed $n$-InGaAsN layers are shown in Figure 5.14. For these measurements, the pulse conditions were $V_R = -1.00$ V and $V_F = -0.20$ V, with a fill pulse duration of 1 ms; the 10 s$^{-1}$ rate window is shown. Although it is not evident from the figure, we point out that the peak heights were observed to be dependent upon the rate window used, as was the case for the data of Figure 5.5 and Figure 5.7, again suggesting that the DLTS peaks are due to energy distributions within the bandgap; however, since this point has already been demonstrated for $p$-type material, the additional rate windows are suppressed from this point forward for clarity. Since $V_F < 0$, only peaks resulting from majority-carrier (electron) trapping may be seen in Figure 5.14. Three peaks, labeled E1, E3, and E4, are clearly discernable in the spectrum of the as-grown sample. The DLTS spectra of the as-
grown sample were fit using Gaussian functions in order to obtain the Arrhenius analysis of peaks E3 and E4 shown in the inset of the figure. The activation energies and electron capture cross sections obtained from this analysis, as well as the trap concentrations, are listed in Table 5.3. Since we are dealing with n-type material, when determining the capture cross sections, an electron effective mass of \( m_n = 0.2m_0 \) was again used.

![DLTS spectra](image)

**Figure 5.14** Majority-carrier DLTS spectra of as-grown and annealed n-InGaAsN layers. The spectra shown were obtained using a rate window of 10 s\(^{-1}\), and the pulse conditions used were \( V_R = -1.00 \) V and \( V_F = -0.20 \) V with a fill pulse duration of 1 ms. The inset shows the Arrhenius plot of \( \ln(\tau^2) \) (\( \tau^2 \) in sK\(^2\)) vs. \( 1000/T \) (K\(^{-1}\)) which was used to determine the activation energies and electron capture cross sections for levels E2, E3, and E4.

In contrast to the case for peaks E3 and E4, peak E1 could not be fit using a single Gaussian function, and in fact it appears that E1 is a very broad signal that extends to low temperature. The broadness and position of E1 suggest that it is likely the signature of a continuous trap distribution located just below the conduction band edge. By considering
the temperature of the trailing edge of the E1 DLTS signal relative to the position of peak E3, the low-energy edge of the proposed trap distribution was estimated to be approximately $E_C - 0.2$ eV. The calculation used to make this estimate assumed that traps E1 and E3 have equal electron capture cross sections, which is not necessarily the case, however. Finally, from Figure 5.14, we see that an additional trap (E2) is present in the annealed sample. This behavior is in sharp contrast to the behavior of deep levels in $p$-type InGaAsN, where, as shown in the previous section, trap concentrations were observed to either stay the same or to decrease following post-growth annealing.

Potential explanations for this will be addressed in Chapter 7. Gaussian functions were fit to the spectra of the annealed sample and an analysis similar to that described previously resulted in an activation energy of $E_C - E_T = 0.36$ eV for trap E2. In all cases the DLTS peaks were very broad, supporting the assertion that these peaks are due to broad distributions of deep level states within the bandgap.

While electron traps in $n$-type InGaAsN are of fundamental scientific interest, the performance of minority-carrier devices (such as solar cells) based on this material is likely to be very sensitive to the presence of minority-carrier hole traps. This, coupled with the fact that $L_p$ in $n$-type material is of a reasonable length, prompted us to perform minority-carrier DLTS measurements on these samples. As discussed in Chapter 4, this is accomplished by forward-biasing each sample during the fill pulse in order to inject holes across the $pn$ junction. Figure 5.15 shows DLTS spectra of the same as-grown and annealed $n$-InGaAsN layers for which the data of Figure 5.14 were obtained, but under conditions of minority-carrier hole injection. The pulse conditions used to obtain these spectra were $V_R = -1.00$ V and $V_F = +0.22$ V; again, the fill pulse duration was 1 ms and...
the 10 s⁻¹ rate window is shown in the figure. Under steady-state conditions, a forward bias voltage of 0.22 V corresponded to a current of approximately 1.0×10⁻⁶ A (1.3×10⁻⁴ A/cm²) at 300 K for both the as-grown and annealed samples.

![DLTS spectra](image)

**Figure 5.15** DLTS spectra of as-grown and annealed InGaAsN layers under conditions of minority-carrier injection. The pulse conditions used were \( V_R = -1.00 \) V and \( V_F = +0.22 \) V, and the pulse duration was 1 ms. The data shown were obtained for a rate window of 10 s⁻¹. The inset shows the Arrhenius plot of \( \ln(\tau^2) \) (\( \tau^2 \) in sK²) vs. \( 1000/T \) (K⁻¹) used to determine the activation energy and hole capture cross section of trap H1.

We see that the spectrum of the as-grown sample under conditions of minority-carrier injection is qualitatively similar to the corresponding spectrum under reverse-bias conditions, with peaks E1, E3, and E4 clearly visible. In contrast, the spectrum of the annealed sample under conditions of minority-carrier injection is markedly different from the spectrum of the same sample under majority-carrier only trapping conditions. In particular, a large high-temperature negative peak (H6) is clearly visible in the spectrum.
of the annealed sample shown in Figure 5.15. Since the magnitude of the minority-carrier DLTS signal depends on the injection level, the height of peak H6 may be used only to determine a lower bound on the trap concentration. This lower bound, $2 \times 10^{14} \text{cm}^{-3}$, was determined from curve-fits to the annealed minority-carrier spectra, and an activation energy of $E_T - E_V = 0.71 \text{eV}$ was obtained from the Arrhenius analysis shown in the inset of Figure 5.15. The activation energies of traps E2 and H6 thus add to 1.07 eV, which is close to the 1.05 eV bandgap of the InGaAsN material. This, coupled with the appearance of both traps after annealing, suggests that E2 and H6 may be the same trap observed under conditions of electron and hole emission, respectively. Since the E2/H6 defect is able to communicate with both the conduction and valence bands, it is likely to be an efficient recombination-generation center, an assertion which is investigated in the next section.

<table>
<thead>
<tr>
<th>Trap</th>
<th>Activation energy (eV)</th>
<th>$T \rightarrow \infty$ capture cross-section (cm$^2$)</th>
<th>Concentration, as-grown (cm$^{-3}$)</th>
<th>Concentration, annealed (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>$0 &lt; E_A &lt; E_C - 0.2$</td>
<td>–</td>
<td>$4 \times 10^{14}$</td>
<td>$4 \times 10^{14}$</td>
</tr>
<tr>
<td>E2</td>
<td>$E_C - 0.36$</td>
<td>$9 \times 10^{-16}$</td>
<td>–</td>
<td>$2 \times 10^{15}$</td>
</tr>
<tr>
<td>E3</td>
<td>$E_C - 0.34$</td>
<td>$7 \times 10^{-19}$</td>
<td>$2 \times 10^{14}$</td>
<td>$2 \times 10^{14}$</td>
</tr>
<tr>
<td>E4</td>
<td>$E_C - 0.82$</td>
<td>$1 \times 10^{-13}$</td>
<td>$8 \times 10^{14}$</td>
<td>$6 \times 10^{14}$</td>
</tr>
<tr>
<td>H6</td>
<td>$E_V + 0.71$</td>
<td>$3 \times 10^{-16}$</td>
<td>–</td>
<td>$8 \times 10^{14}$</td>
</tr>
</tbody>
</table>

**Table 5.3** Properties of deep levels in $n$-type InGaAsN grown by MOCVD.

As a final point in this section, we examine the DLTS spectra of a second annealed $n$-InGaAsN layer grown by MOCVD. The second InGaAsN layer is the emitter.
layer of a solar cell identical in structure to that shown in Figure 5.10. Further, the conditions under which the second layer was grown were identical to the growth conditions for the layer discussed in the preceding paragraphs. Indeed, the only difference between the two annealed layers is the gas-flow transition used to change from GaAs growth to InGaAsN growth at the base-emitter interface of the solar cell. In this context, the term "transition" means the gas flow during the period of time in between the growth of the two layers, after the group III precursor gases of the base layer have been shut off and before the corresponding gases of the emitter layer have been introduced into the chamber. In the first case, i.e. the sample discussed in the preceding paragraphs, this transition was accomplished without any DMHy flow, and only a moderate flow of AsH3. In contrast, for the second sample, the group V flows were the same as those used subsequently to grow the InGaAsN emitter layer. Representative results of DLTS measurements compared to the measurements of the first sample are shown below.

![Minority-carrier injection DLTS curves of two $n$-InGaAsN layers grown under identical conditions aside from the initial gas-flow transition from GaAs to InGaAsN growth. The flow conditions for each transition are indicated in the figure. The 10 s$^{-1}$ rate window is shown.](image)

**Figure 5.16** Minority-carrier injection DLTS curves of two $n$-InGaAsN layers grown under identical conditions aside from the initial gas-flow transition from GaAs to InGaAsN growth. The flow conditions for each transition are indicated in the figure. The 10 s$^{-1}$ rate window is shown.
The DLTS measurements were performed on the second sample under conditions of minority-carrier injection (so that both electron and hole traps may potentially be observed) identical to those used to perform the measurements shown in Figure 5.15, utilizing a forward-bias current of 1 μA. From Figure 5.16, we see that both E2 and H6 are missing from the spectrum of the sample grown using the higher DMHy and AsH3 flows. Not only does this support the assertion that E2 and H6 are the same level, but it also suggests that the combined E2/H6 level is related in some way to the conditions that occur during the initial nucleation of the InGaAsN layer. Thus we have not only begun to understand the physical source of this defect, but we have established a link between the bulk properties of the film (the deep level) and its surface properties (the initial nucleation conditions). We will examine the interesting properties of this defect further in the next section and in Chapter 7.

5.3.3 Impact of deep levels on carrier transport

Since E2/H6 has the potential to be an efficient combination-generation center, we decided to ascertain the possible impact of this level on device performance. To accomplish this, a current-temperature (I-T) measurement was performed on the annealed test diode grown using the no DMHy, low AsH3 base-emitter junction transition, in which the defect is present. For this measurement, the diode was held at a fixed reverse bias of −1.0 V (the same reverse bias as used for the DLTS measurements; also sufficient for generation to dominate over recombination, as discussed in Chapter 3) and the current was measured as a function of temperature. The results of this measurement are shown below.
Figure 5.17 Reverse-bias current-temperature data for the annealed InGaAsN test diode grown using the no DMHy, low AsH3 gas-flow transition. $I_{rev}$ is the reverse-bias generation current measured at a voltage of -1.0 V. The straight line shows the fit to the data, which yielded an activation energy of 0.35 eV, corresponding to the E2/H6 deep level.

As discussed in Chapter 3, if the reverse-bias current $I_{rev}$ is dominated by generation of carriers via a single deep level, a plot of $\ln(I_{rev})$ vs. 1000/T should be a straight line, with the slope of the line giving the activation energy of the deep level responsible for the current. We see from Figure 5.17 that the plot of $\ln(I_{rev})$ vs. 1000/T does indeed approximate a straight line, the fit to which yielded an activation energy of 0.35 eV. This is very close to the 0.36 eV activation energy of E2, suggesting that E2/H6 is responsible for the reverse bias generation current in the sample. Note that the activation energy determined from the I-T measurement is also close to the 0.34 eV activation energy of E3, although it is unlikely that this defect is responsible for the observed generation current. Not only is E3 present in a much lower concentration than E2/H6, but its
electron capture cross section (which is proportional to the carrier generation rate) is much smaller than that of E2/H6. Further, there is no evidence from DLTS that E3 is able to communicate with the valence band. Finally, we note that that the deep level to conduction band (E2 to CB) transition must be the rate-limiting transition, rather than the larger energy valence-band to deep level (VB to H6) transition, since the activation energy measured is less than half of the bandgap. Thus something other than thermal excitation must limit the rate at which the E2/H6 defect generates carriers. Based on our DLTS measurements, the electron and hole capture cross-sections appear to be similar to each other in magnitude, thus suggesting that a very small value of $\sigma_i$ is not the factor limiting the generation process. Rather, based on sketches of the band diagram of the test diode, it is suspected by the author that the electron population is limited by the presence of the GaAs/InGaAsN heterojunction; however, other explanations may exist as well.

Extension of the IVT analysis of Chapter 3 to include the case of transport in a heterojunction diode would undoubtedly shed some light on this matter, and this is certainly work that could be undertaken in the future to extend and refine this research.
5.4 References


2 Details regarding the growth and characterization of this material by techniques other than DLTS may be found in Steven R. Kurtz, A. A. Allerman, E. D. Jones, J. M. Gee, and J. J. Banas, Appl. Phys. Lett. 74, 729 (1999).

3 Photoluminescence, Hall, solar cell characterization, and SIMS measurements were performed by our collaborators at Sandia National Laboratories.

4 Many references discuss the theory and application of the photoluminescence technique: see, for example, J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1975).

5 Temperature-dependent Hall data point to the existence of transport-limiting, large-scale inhomogeneities in this class of alloys, similar to the structure of polycrystalline Si. For a discussion of this topic, see Steven R. Kurtz, A. A. Allerman, C. H. Seeger, R. M. Sieg, and E. D. Jones, Appl. Phys. Lett. 77, 400 (2000).


7 Many of the results discussed in this section were reported in D. Kwon, R. J. Kaplar, S. A. Ringel, A. A. Allerman, Steven R. Kurtz, and E. D. Jones, Appl. Phys. Lett. 74, 2830 (1999).

8 The author would like to thank John Boeckl for obtaining this TEM image.

9 Details regarding the growth and characterization of these samples by DLTS and IVT may be found in R. J. Kaplar, A. R. Arehart, S. A. Ringel, A. A. Allerman, R. M. Sieg, and Steven R. Kurtz, J. Appl. Phys. 90, 3405 (2001).

10 One of many possible references for this expression is R. F. Pierret, *Advanced Semiconductor Fundamentals* (Addison-Wesley, Reading, MA, 1989).

6.1 Introduction

In the molecular beam epitaxy (MBE) growth technique, streams of atoms (e.g. Ga and As$_2$), typically evaporated from a solid effusion source, pass through an ultra-high vacuum (UHV, referring to a regime where the pressure is on the order of $10^{-9}$ Torr or lower) chamber and impinge on a heated substrate, resulting in epitaxial growth. A schematic illustration of an MBE setup is shown below.

![Schematic illustration of the essential elements of an MBE growth system.](image)

Figure 6.1 Schematic illustration of the essential elements of an MBE growth system.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
The term "molecular beam" refers to the condition on the mean free path of the constituent atoms and/or molecules evaporated from the solid sources, which due to the extremely low chamber pressure is typically on the order of the distance from the effusion source to the growth surface. Thus, the bulk of the constituent atoms and/or molecules proceed directly, in a so-called "molecular beam," from the source to the substrate without undergoing collisions with other molecules. This permits one to exercise very precise control over the growth process. Further, since no C- or H-containing precursor gases (such as those used for MOCVD growth) are employed, and since the entire process occurs in a clean UHV environment, contamination by these and other impurities tends to minimal. Thus, examination of the deep level spectra of InGaAsN grown by MBE should yield some insight into the physical sources of the deep levels observed, particularly when compared with spectra derived from MOCVD-grown material. Thus, in the present chapter we examine the deep level spectra of InGaAsN grown by MBE.

6.2 MBE growth and sample preparation

The InGaAsN layers studied were grown by MBE at Sandia National Laboratories using conventional solid sources for all of the constituents aside from nitrogen, for which an RF plasma source was used. The elemental fluxes were adjusted so as to achieve an In$_{0.07}$Ga$_{0.93}$As$_{0.98}$N$_{0.02}$ alloy: lattice-match to GaAs was verified by DCXRD, and a bandgap of 1.05 eV was confirmed by optical absorption measurements. This composition is identical (within experimental error) to the MOCVD-grown material studied in the previous chapter; this equality was intentional in order to facilitate
comparison between the two growth techniques. The substrate temperature during growth was 430°C, and all samples were subjected to a post-growth anneal at 900°C for 10 seconds. Annealing was found to improve photoluminescence efficiency, which is consistent with the observations of MOCVD-grown material discussed in the previous chapter. DLTS measurements were performed on both n''-emitter on p-base and p''-emitter on n-base solar cells; a schematic of the test structures employed is shown below.

<table>
<thead>
<tr>
<th>30 nm GaAs contact (n+/p+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40 nm AlGaAs window (n+/p+)</td>
</tr>
<tr>
<td>100 nm InGaAsN emitter (n+/p+)</td>
</tr>
<tr>
<td>1000 nm InGaAsN base (p/n)</td>
</tr>
<tr>
<td>30 nm GaAs BSR (p+/n+)</td>
</tr>
<tr>
<td>GaAs substrate (p+/n+)</td>
</tr>
</tbody>
</table>

**Figure 6.2** Schematic illustration of the solar cell structures used to facilitate DLTS measurements of MBE-grown InGaAsN. Two configurations were grown, n''-on-p and p''-on-n; in both cases the defect spectra are due to deep levels in the low-doped base layers. The window layer consisted of 30% Al on the group III sublattice.

Si was used to achieve n-type doping in the epitaxial layers labeled n and n'', and Be was used to achieve p-type doping in the epitaxial layers labeled p''; the p-layer was, in contrast, unintentionally doped. Note that for each configuration, the defect spectra are due to deep levels in the low-doped base layer, for which the dopant concentrations were $p = 7.8 \times 10^{16}$ cm$^{-3}$ and $n = 1.2 \times 10^{17}$ cm$^{-3}$ as determined by capacitance-voltage measurements. Thus, in the n''-on-p structure, information regarding deep levels in p-
type material is obtained; in contrast, in the $p^*$-on-$n$ structure, the data give information regarding deep levels in $n$-type material.

### 6.3 Properties of deep levels in $p$-type InGaAsN grown by MBE

Figure 6.3 shows representative DLTS spectra resulting from measurements made on the $p$-type base layer of the $n^*$-on-$p$ solar cell structure.

![DLTS spectra](image.png)

**Figure 6.3** DLTS spectra of annealed, $p$-type, MBE-grown InGaAsN. The data shown were obtained using a rate window of 200 s$^{-1}$ and a reverse-bias voltage of $V_R = -1.00$ V; the magnitude of the fill pulse was either $-0.20$ V (majority-carrier DLTS) or $+0.29$ V (minority-carrier injection DLTS) for a duration of 1 ms. The inset shows the plot of $\ln(\tau T^2)$ ($\tau T^2$ in sK$^2$) vs. $1000/T$ (K$^{-1}$) that was used to determine the activation energies and capture cross-sections of levels H3 and H4.

The reverse-bias voltage was $V_R = -1.00$ V and the data were sampled using rate windows of 200, 80, 50, and 20 s$^{-1}$; for clarity, only the spectra obtained using the 200 s$^{-1}$ rate window are shown. The duration of the fill pulse was 1 ms and its magnitude was either $V_F = -0.20$ V or $V_F = +0.29$ V, with the latter value corresponding to a forward...
current of 1 μA (1.3×10^{-4} A/cm^2) passing through the test diode. Recall that in the former case the DLTS spectra are due to hole traps exclusively, whereas in the latter case both electron and hole traps may be observed. We see that the two spectra shown in Figure 6.3 are identical aside from a difference in magnitude, which is a result of the disparity in the volumes of material sampled by the two measurements. Thus, based on the data shown, only hole traps are present in the p-type InGaAsN layer measured.

Clearly evident in the spectra of Figure 6.3 are two well-defined positive peaks corresponding to majority-carrier hole traps: H3', located at ~200 K, and H4', located at ~300 K. At this point we wish to address the issue of the naming of the defects observed in this work. The levels observed in the MOCVD-grown material of the previous chapter have of course been given original names, H1 through H4 and E1 through E4 as well as E6. Levels observed in the present chapter that are thought to be similar to those observed in MOCVD-grown material have been given names that correspond to the name in the previous chapter but with the addition of a prime. Thus, e.g., H4 and H4' are thought to have similar properties but are observed in MOCVD- and MBE-grown material, respectively. In this way it is possible to establish correlations between levels observed in material grown by the two techniques while still acknowledging potential differences between them. Levels that are believed to be completely distinct between the two growth techniques are given entirely different names: the names of levels unique to MBE-grown material always are primed. With the issue of naming clarified, we continue our discussion of Figure 6.3 by noting that it is clear that the DLTS spectrum is non-zero for temperatures below the minimum measured temperature of 100 K, indicating that traps shallower than H3' and H4' are present in the material. Note that the “hump” visible
at around 225 K in both spectra is not a trap-generated peak, since its position was not observed to shift in temperature with changes in the rate window. The origin of this hump is thought to be due to a deviation of the test diode from an ideal depletion capacitor, e.g. due to a stray capacitance associated with the sample mounting configuration. The Arrhenius analysis of traps H3' and H4' is shown in the inset of Figure 6.3, and the results of this analysis are presented in Table 6.1; we see that H3' and H4' are located 0.37 eV and 0.51 eV above the valence band edge, respectively. Since the valence band structure of InGaAsN is thought to be similar to that of GaAs, a hole effective mass equal to that of GaAs, \( m_p = 0.5 m_0 \), was used when calculating the hole capture cross-sections. We see that the hole capture cross-sections listed for both levels are rather large (3\( \times \)10\(^{-13}\) cm\(^2\) and 4\( \times \)10\(^{-14}\) cm\(^2\) for H3' and H4', respectively); such large values suggest that the capture cross-sections may be strongly temperature-dependent, since the values presented in Table 6.1 are the cross-sections extrapolated to infinite temperature. If this is the case, it is possible that the activation energies listed are larger than the true trap activation energies by amounts \( E_d \), where \( E_d \) is the activation energy associated with the temperature-dependent capture cross-section of trap \( i \). The subject of thermally activated capture cross-sections will be discussed in the next chapter. Finally, we note that the peaks resulting from traps H3' and H4' are both very broad. Indeed, the ratio of the full-width at half-maximum to the peak temperature (FWHM/\( T_P \)) was found to be 0.42 for H3' and 0.27 for H4' for the 200 s\(^{-1}\) rate window; in contrast, this ratio is expected to be approximately 0.1 for a deep level due to an ideal point defect. This suggests that these deep levels are due to continuous distributions of states, as discussed in Chapter 4, as opposed to two well-defined individual energy levels.
### Table 6.1

<table>
<thead>
<tr>
<th>Trap</th>
<th>Activation energy (eV)</th>
<th>$T \rightarrow \infty$ capture cross-section (cm$^2$)</th>
<th>Concentration (cm$^3$)</th>
<th>FWHM/$T_p$ $200 \text{ s}^{-1}$ RW</th>
</tr>
</thead>
<tbody>
<tr>
<td>H3\textsuperscript{'}</td>
<td>$E_V + 0.37$</td>
<td>$3 \times 10^{13}$</td>
<td>$3 \times 10^{14}$</td>
<td>0.42</td>
</tr>
<tr>
<td>H4\textsuperscript{'}</td>
<td>$E_V + 0.51$</td>
<td>$4 \times 10^{14}$</td>
<td>$1 \times 10^{14}$</td>
<td>0.27</td>
</tr>
</tbody>
</table>

6.4 Properties of deep levels in $n$-type InGaAsN grown by MBE

The results of DLTS measurements made on the $n$-type base layer of the $p^\ast$-on-$n$ solar cell structure are shown in Figure 6.4.

![Figure 6.4](image-url)

**Figure 6.4** DLTS spectra of annealed, $n$-type, MBE-grown InGaAsN. The data shown were obtained using a rate window of $20 \text{ s}^{-1}$ and a reverse-bias voltage of $V_R = -1.00 \text{ V}$; the magnitude of the fill pulse was either $-0.20 \text{ V}$ (majority-carrier DLTS) or $+0.34 \text{ V}$ (minority-carrier injection DLTS) for a duration of 1 ms. The inset shows the plot of $\ln(t^2)$ (for $t^2$ in sK$^2$) vs. $1000/T$ (K$^{-1}$) that was used to determine the activation energies and capture cross-sections of levels E4\textsuperscript{'} and H5\textsuperscript{'}.
The same rate windows as those employed to measure the $p$-type material were used, although in the present case the 20 s$^{-1}$ rate window is shown in the figure. The fill pulse parameters were likewise similar to those used in the previous situation, the only difference being that the voltage required to achieve a forward-bias current of 1 µA was $V_F = +0.34$ V. In the $n$-type material electrons are the majority-carriers and holes are the minority-carriers, so that $V_F = -0.20$ V allows one to observe electron traps only, whereas $V_F = +0.34$ V results in spectra due to both electron and hole traps. We will examine the former case first. From Figure 6.4, we see that the low-temperature end of the spectrum (up to $-275$ K) is dominated by a broad signal, $E1'$, from which individual peaks are difficult to distinguish. This feature is typical of the DLTS spectra of $n$-type InGaAsN alloys grown by MOCVD and is indicative of a continuous distribution of shallow defect bands located just below the conduction band edge, as discussed in the previous chapter. Also present in the spectrum of Figure 6.4 is a distinct peak at $-360$ K labeled $E4'$. The Arrhenius analysis of this peak is shown in the inset of the figure and the results are listed in Table 6.2: from the table we see that $E4'$ was found to be located 0.56 eV below the conduction band edge and to have an electron capture cross-section of $2 \times 10^{-17}$ cm$^2$.

Since we are now dealing with the perturbed conduction band, we cannot assume that $m_n$ is equal to its value in GaAs when calculating the magnitude of the electron capture cross-section. Rather, Equation (2.3) of the band-anticrossing model discussed in Chapter 2 was used to determine the electron effective mass, which was found to be $m_n = 0.2m_0$. We note that the ratio FWHM/$T_p$ for $E4'$ was 0.15 for the 200 s$^{-1}$ rate window, slightly broader than the value expected for an ideal point defect. Also clearly evident in Figure 6.4 is a negative peak, due to a minority-carrier hole trap, in the curve obtained for
\( V_F > 0 \). The Arrhenius analysis of this trap, labeled \( H5' \), resulted in an activation energy of \( 0.71 \text{ eV} \) above the valence band edge and a hole capture cross-section of \( 3 \times 10^{-15} \text{ cm}^2 \).

Note that the obtained concentration of \( 2 \times 10^{14} \text{ cm}^{-3} \) is only a lower bound on the trap concentration, since in a forward-bias DLTS experiment the peak height depends upon the injection level as well as the trap density, as discussed in Chapter 4. For this negative peak, the ratio \( \text{FWHM/T}_p \) was found to be 0.19, again indicating that the peak is due to a continuous distribution of states.

<table>
<thead>
<tr>
<th>Trap</th>
<th>Activation energy (eV)</th>
<th>( T \to \infty ) capture cross-section (cm(^2))</th>
<th>Concentration (cm(^{-3}))</th>
<th>( \text{FWHM/T}_p ) 200 s(^{-1}) RW</th>
</tr>
</thead>
<tbody>
<tr>
<td>( H5' )</td>
<td>( E_V + 0.71 )</td>
<td>( 3 \times 10^{15} )</td>
<td>( &gt;2 \times 10^{14} )</td>
<td>0.19</td>
</tr>
<tr>
<td>( E1' )</td>
<td>( 0 &lt; E_A &lt; E_C - 0.35 )</td>
<td>–</td>
<td>( \sim 1 \times 10^{14} )</td>
<td>–</td>
</tr>
<tr>
<td>( E4' )</td>
<td>( E_C - 0.56 )</td>
<td>( 2 \times 10^{17} )</td>
<td>( 3 \times 10^{13} )</td>
<td>0.15</td>
</tr>
</tbody>
</table>

**Table 6.2** Trap parameters resulting from the analysis of the DLTS spectra of \( n \)-type MBE-grown InGaAsN presented in Figure 6.4. Concentration values were calculated from the "majority-carrier DLTS" curve.

We conclude this chapter by noting that levels \( H3', H4', E1', \) and \( E4' \) appear to be roughly consistent with the deep levels of the same (unprimed) names identified in InGaAsN grown by MOCVD in the previous chapter. If we assume that these levels are indeed the same, we may come to the conclusion that these four levels are due to physical sources that are unrelated to the specific growth technique used. It also suggests that these defects are due to intrinsic (i.e. nitrogen-related) sources; however, we point out that not all extrinsic sources are ruled out by this comparison. For example, carbon...
impurities are definitely present in the MOCVD-grown material and are probably present in the MBE-grown layers as well; thus carbon remains a potential extrinsic source of deep levels. The physical sources of the deep levels observed thus far is the subject of the next chapter.
References


CHAPTER 7

TOWARD THE IDENTIFICATION OF THE PHYSICAL SOURCES OF DEEP LEVELS IN InGaAsN ALLOYS

7.1 Introduction

This chapter makes an effort to begin understanding the properties of the physical sources of the deep level defects observed in Chapters 5 and 6. We begin by looking at the carrier capture kinetics of several of the deep levels catalogued in the previous chapters, and from this ascertain whether the sources of the deep levels are due to point or extended sources. We further examine the possibility of temperature-dependent capture cross-sections, hinted at previously. Following this, we examine the impact of composition, dopants, and growth conditions on the deep level spectra of both p- and n-type InGaAsN grown by MOCVD in an effort to understand which, if any, of these factors serve as sources of deep levels. Finally, we conclude the chapter by comparing our DLTS results to some intrinsic, nitrogen-related defects that have been predicted to exist in GaAsN and InGaAsN alloys. These investigations all attempt to address the larger question hinted at in previously, namely, are the deep levels that we have observed due to extrinsic sources — such as impurities, growth technique, etc. — or are they due to intrinsic sources related to the large perturbations introduced by the presence of nitrogen.
in InGaAs? We will see that the data point towards both options, depending on the deep level in question.

7.2 Carrier capture kinetics in n-type InGaAsN

In Chapter 4, we saw that by varying the duration of the DLTS fill pulse and observing the resulting dependence of the height of a given DLTS peak, information may be obtained regarding the spatial nature (i.e., point-like or extended) of the physical defect responsible for the peak. The appropriate dependences for point and extended defects were given by Equations (4.30) and (4.38), respectively, which we repeat here for convenience:

Point defect:
\[
\ln \left(1 - \frac{\Delta C^F}{\Delta C^\infty}\right) = -c_s n F \quad (7.1)
\]

Extended defect:
\[
\Delta C = \Delta C_E \ln \left(1 + \frac{t_F}{\tau_E}\right) = \Delta C_E \ln \left(\frac{t_F}{\tau_E}\right) \quad (7.2)
\]

Further, we found that for point defects, Equation (4.30)/(7.1) may be extended to determine the activation energy \(E_a\) of a thermally-activated capture cross-section. This was given by Equation (4.26), which we also repeat here:

\[
\ln \left[-T^{-1/2} \ln \left(1 - \frac{\Delta C^F}{\Delta C^\infty}\right)\right] = \ln(\alpha_n) - \frac{E_a}{kT} \quad (7.3)
\]

In this section, we apply these expressions in an effort to understand the physical nature of the sources of some of the deep levels that we observed in Chapters 5 and 6. In particular, we will study the properties of the deep levels that we observed in \(n\)-type
InGaAsN grown by both MOCVD and by MBE. We focus on annealed n-type material since that is the material of greater technological interest, thanks to the longer minority-carrier diffusion length as compared to p-type material.

We begin our study of carrier capture kinetics by examining the E2 and E4 defects observed in n-type InGaAsN grown by MOCVD; the properties of these defects are listed in Table 5.3. Figure 7.1 below shows the results of majority-carrier fill-pulse experiments on the material in question.

![Figure 7.1 Results of majority-carrier fill-pulse experiments made on annealed, n-type InGaAsN grown by MOCVD. For comparison to Figure 5.14, the 1 ms curve is marked with a vertical hash; the 10 s\(^{-1}\) rate window is again shown.](image)

From Figure 7.1, we see a marked dependence of both peaks E2 and E4 on the fill pulse time. In particular, we see that E4 saturates very slowly; indeed, it appears to saturate only between fill pulse times of \(t_F = 100\) and 316 ms. A saturation time of this magnitude is exceedingly long (316 ms is the longest fill pulse that our DLTS system is capable of...
achieving) and suggests that E4 is certainly not a typical deep-level defect; indeed, most
defects are completely saturated at 1 ms,\textsuperscript{1,2} which is why that value was used in Chapters
5 and 6. Further, based on the data shown, it appears that we must revise our estimate of
the concentration of E4. We see that the value given in Table 5.3 is $6 \times 10^{14}$ cm$^{-3}$.
although from the data of Figure 7.1 it appears that the saturated peak height is roughly
14 times the peak height obtained for a 1 ms fill pulse; thus multiplying the 1 ms value by
a factor of 14, we obtain a revised concentration of $8 \times 10^{15}$ cm$^{-3}$. In contrast, the E2
defect appears to be nearly saturated at 1 ms, and a revision of the concentration given in
Table 5.3 is therefore not necessary.

We now turn our attention to the specific capture kinetics of the E2 and E4 levels:
we consider first E2, the capture kinetics for which are shown below. From Figure 7.2,
we see that the capture kinetics of E2 are consistent with that of an extended defect, with
the peak height being proportional to the logarithm of the fill pulse time (recall that the
base-$e$ and base-10 logarithms are simply related by $\ln(x) = 2.3 \cdot \log(x)$), at least within a
range of fill pulse times. The areas where the proportionally is not applicable are at long
fill pulse times, where the trap is saturated, and at short fill pulse times, where the fill
pulse time $t_F$ is on the order of the time constant $\tau_L$, the simple logarithmic dependence is
not applicable. Recall from Chapter 5 that the E2 defect, along with its counterpart H6, is
thought to be due to the initial nucleation conditions at the GaAs/InGaAsN
heterointerface. Based on the data of Figure 7.2, it appears that improper nucleation
conditions introduce an extended defect of some sort into the material. Due to the close
lattice-match between the InGaAsN layers and the GaAs substrates observed throughout
the course of this research, it seems unlikely that the extended defect is a dislocation;

120

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
Figure 7.2 Carrier capture kinetics of defect E2. Fill pulse times of 0.01, 0.0316, 0.1 \ldots 316 ms are shown; the points are spaced so as to appear linearly separated on a logarithmic scale.

rather, some other extended geometry (point defect cluster, etc.) seems more likely to be the physical source of this level. This extended source, in turn, gives rise to a recombination-generation center.

In contrast, the capture kinetics of E4 appear to be consistent with those of a point-like defect, as we will see below. First, from Table 5.3 we observe that the activation energy and electron capture cross-section for this defect are 0.82 eV and $1 \times 10^{13}$ cm$^2$, respectively, both of which are rather large. This suggests that the capture cross-section of this deep level may be temperature-dependent, as given by Equation (4.17), and we thus suspect that Equation (7.3) may describe the capture kinetics of the defect. This is born out in the data shown in Figure 7.3 below. To construct this figure, two experimental parameters were adjusted: in order to adjust the peak's temperature,
different rate windows (50, 20, 10, and 4 \text{s}^{-1}) were used; and to adjust the peak's height, fill pulse times of 1 ms (giving $\Delta C^f$) and 316 ms (giving $\Delta C^\infty$) were used. Note that using a value other than 1 ms should result in the same value of $E_\sigma$, although the value of $\alpha_r$ in Equation (7.3) will be different.

![Graph](image)

**Figure 7.3** Carrier capture kinetics of defect E4 in MOCVD-grown InGaAsN. The data indicate that the capture kinetics are consistent with a point defect characterized by a thermally activated electron capture cross-section.

The fact that the data points of Figure 7.3 lie in a straight line tell us that not only are the carrier capture kinetics consistent with those of a point-like defect, but further, that the electron capture cross-section is thermally activated – according to Equation (4.17) – and that the activation energy is $E_\sigma = 0.42 \text{ eV}$. We note that the measured activation energy of the defect was 0.82 eV; thus, based on this analysis, we conclude that the defect is really located at $E_C - E_T = 0.40 \text{ eV}$. Further, the 350 K capture cross-section is much
smaller than the $T \to \infty$ value listed in Table 5.3, being roughly $1\times10^{-19}$ cm$^2$. These numbers are somewhat more reasonable than those listed in Chapter 5; this is particularly true of $E_A$, since 0.82 eV is actually much closer to the valence band than to the conduction band! This, in addition to the very slow saturation time of $E_4$, suggests that the physical source of this defect is unusual.

We continue our elucidation of the properties of the $E_2$ and $H_4$ defects by recalling that, in Chapter 5, we found reason to believe that both levels are distributions of deep states within the bandgap, as opposed to discrete energy levels. Further evidence for this may be obtained by examining the data of Figure 7.1, where we see that the positions of both peaks shift with changes in the fill pulse time. This is explained in Figure 7.4 by making reference to the broadened deep level model of Chapter 4.3:

![Figure 7.4 Explanation of the shift in peak position corresponding to changes in the fill pulse time in terms of a broadened defect level.]

The shaded region of the figure represents the fraction of traps that are occupied at the end of the fill pulse; we see that, since electrons tend to settle into the lower-energy states available to them, the lower-energy portion of the distribution is filled, whereas the higher-energy portion is not. Thus, for the situation shown, an average trapped electron has an energy that is lower than the peak energy of the trap distribution; these energies
are indicated in the figure by the lower and upper arrows, respectively. Thus, for a
trapped electron to be emitted to the conduction band, it must on average make a larger
jump if the trap distribution is not completely filled, compared to the situation where the
distribution is saturated. A larger transition corresponds to a higher DLTS peak
temperature; thus, based on this argument, shorter fill pulse times (which will not fill the
trap distribution completely) should be characterized by a higher peak temperature. This
is indeed what is observed in Figure 7.1 for peaks E2 and E4, lending further support to
the idea that these levels are distributions of levels as opposed to discrete energy states.

We now move on to discuss the majority-carrier capture kinetics of deep levels in
n-type InGaAsN grown by MBE. the data for which are shown below.

\[ t_F = 0.316, 1.0, 3.16 \ldots 316 \text{ ms} \]

From Figure 7.5 we see that, as was the case for the MOCVD-grown material, there is a
significant dependence of the peak heights (in this case E1' and E4') on rate window. We

Figure 7.5 Results of majority-carrier fill-pulse experiments made on
annealed, n-type InGaAsN grown by MBE. For comparison to Figure 6.4.
the 1 ms curve is marked with a vertical hash; the 20 s\(^{-1}\) rate window is
shown.

From Figure 7.5 we see that, as was the case for the MOCVD-grown material, there is a
significant dependence of the peak heights (in this case E1' and E4') on rate window. We

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
thus need to revise the values of the concentrations of E1' and E4' listed in Table 6.2 by multiplying by factors of 2 and 8, respectively, to arrive at a concentration of $2 \times 10^{14}$ cm$^{-3}$ for both levels. Further, from Figure 7.5 we see that the behavior of both E1' and E4' is similar to the behavior of E4 in the MOCVD-grown sample, since the saturation time is on the order of 300 ms for both levels. This suggests that the charge capture mechanisms of these two defects are similar to each other. While we did not attempt to analyze quantitatively the capture kinetics of E1' due to its extreme broadness and the resulting uncertainty in peak positions and heights, we did perform an analysis of E4' similar to that carried out on E4 in the MOCVD-grown material. The results of this analysis are shown below.

![Diagram](image)

**Figure 7.6** Carrier capture kinetics of defect E4' in MBE-grown InGaAsN. The data indicate that the capture kinetics are consistent with a point defect characterized by a thermally activated electron capture cross-section.

From Figure 7.6 we see that the electron capture kinetics are consistent with a point-like defect characterized by a thermally activated capture cross-section, and that the activation
energy of the cross-section is $E_a = 0.26$ eV; this is slightly less than two-thirds of the value obtained for the E4 defect in MOCVD-grown material. In Table 6.2, the values of the activation energy and $T \rightarrow \infty$ capture cross-section were 0.56 eV and $2 \times 10^{17}$ cm$^2$, respectively; based on the information presented in this section, these values must be revised to 0.30 eV and $3 \times 10^{21}$ cm$^2$. The first value is certainly reasonable, and in fact not far off from the 0.40 eV measured for the same level in MOCVD-grown material. The latter value is, however, quite small; however, we should keep in mind that the capture cross-sections obtained throughout this Dissertation are exponential functions of fit parameters; thus, errors in the curve-fits are likely to be magnified when calculating the carrier capture cross-sections, which may account for the very small value obtained.

A summary of the capture kinetics of the E4 and E4' defects is given below.

<table>
<thead>
<tr>
<th>Defect</th>
<th>$E_a$ (eV)</th>
<th>$E_C - E_T$ (eV)</th>
<th>$350 \text{ K } \sigma_r$ (cm$^2$)</th>
<th>$N_T$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E4 (MOCVD)</td>
<td>0.42</td>
<td>0.40</td>
<td>$1 \times 10^{19}$</td>
<td>$8 \times 10^{15}$</td>
</tr>
<tr>
<td>E4' (MBE)</td>
<td>0.26</td>
<td>0.30</td>
<td>$3 \times 10^{21}$</td>
<td>$2 \times 10^{14}$</td>
</tr>
</tbody>
</table>

**Table 7.1** Summary of the electron capture kinetics of defects E4 and E4' as observed in annealed, $n$-type InGaAsN grown by MOCVD and MBE.

### 7.3 Impact of MOCVD growth conditions on the properties of deep levels

We have already seen that several of the defects observed in MOCVD-grown material have counterparts in MBE-grown material, namely the H3/H3', H4/H4', E1/E1', and E4/E4' pairs; further, the unusual electron capture mechanisms of E1, E4, E4' appear to be similar to each other. Further, we have seen that the E2/H6 defect appears to be an
extended defect associated with the nucleation conditions between an InGaAsN layer and a GaAs substrate. However, these defects as well as the others observed have, to this point, been discussed based on their observation in a limited number of samples, and thus subject to a limited range of growth conditions. In this section, we therefore examine the impact of MOCVD growth conditions on the properties of deep level defects in both $p$- and $n$-type InGaAsN alloys.

### 7.3.1 Impact of growth conditions on defect spectra of $p$-InGaAsN

We first examine the impact of growth conditions on the deep level spectra of $p$-type InGaAsN grown by MOCVD. Figure 7.7 shows the majority-carrier DLTS spectra of two as-grown, $p$-type (uid), 1.05 eV InGaAsN layers grown using different arsine flow rates; the other growth parameters were adjusted accordingly in order to achieve the desired composition. These layers were the base layers of $n^*$-GaAs on $p$-InGaAsN heterojunction diodes: the structures were similar to those shown in Figure 5.1 with a GaAs emitter substituted for the InGaAsN emitter. The spectra, in particular that of the layer grown using the low arsine flow, generally resemble the as-grown spectrum of Figure 5.5, being characterized by very broad peaks most likely resulting from distributions of deep levels within the bandgap. It is evident from the spectra of Figure 7.7 that the arsine flow rate has a significant effect on the concentrations of deep levels as well as on their distribution. In particular, the material grown using the high arsine flow rate exhibits a lower trap concentration than the material grown using the low arsine flow rate. The reasons for this are unknown, although it has been suggested that the deep
levels in this $p$-type material are in some way carbon-related, and that the larger atomic hydrogen concentration resulting from the higher arsine flow rate consumes and volatizes excess carbon at the growth surface: this would in turn reduce the concentrations of carbon-related deep levels. However, SIMS data is lacking for the InGaAsN layers presently under discussion, making it impossible to directly correlate carbon concentration with defect density. While it does seem that carbon may have some impact on the deep level spectra of as-grown $p$-InGaAsN (more on this below), it is possible that some of the defects evident in Figure 7.7 are not related to carbon at all, but rather are “intrinsic” nitrogen-related defects, much as the E1 and E4 defects in $n$-type InGaAsN are thought to be. If this is indeed the case, then it must be a complex interplay between the various precursor gases that leads to the observed dependence of deep level
concentration on arsine flow. Despite these uncertainties, we may nonetheless accept the
data of Figure 7.7 on an empirical basis, in which case we simply state that growth
conditions do have some impact on the deep level distribution in p-type InGaAsN.

The influence of dopant type on deep levels in InGaAsN has been investigated in
Figure 7.8, which shows majority-carrier DLTS spectra of p-type. 1.05 eV InGaAsN
layers, grown using the high arsine flow conditions of Figure 7.7. Three dopant types
were examined: uid (this layer is the same as the one labeled “high arsine flow” in Figure
7.7; as discussed previously, it is believed that the p-type nature of the film is due to
background carbon acceptors), Zn-doped (introduced using DMZn), and C-doped
(introduced using CCl₄), as indicated in the figures. If dopant atoms are responsible for
deep levels – either directly or via interactions with other atoms such as nitrogen –
differences in the defect spectra should be observed. For example, in order to achieve p-
type doping, zinc and carbon atoms must substitute on group III and group V lattice sites.
respectively. Thus, some of the nitrogen atoms must be bonded differently in the various
layers studied, keeping opening the possibility that the properties of nitrogen-related deep
levels may be different due to the different dopant atoms.

Spectra for both as-grown and annealed layers are shown in Figure 7.8, parts (a)
and (b) respectively. The sample structures were all the same, a p⁺-GaAs on n-InGaAsN
heterojunction structure comparable to that described in the preceding paragraphs.
Examining first the spectra of the as-grown layers, it is evident that the distributions of
deep levels in the uid and Zn-doped samples are similar to each other, aside from some
small differences at low temperature. Further, these spectra are qualitatively similar to
the as-grown spectra of Figure 5.5, although the trap concentrations are much reduced.

129
Figure 7.8 Majority-carrier DLTS spectra of (a) as-grown and (b) annealed, $p$-type, 1.05 eV InGaAsN layers doped using different sources. The data are shown for a rate window of 20 s$^{-1}$.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
This latter observation reflects an overall improvement in the conditions used to grow InGaAsN, since the material of Figure 7.8 was grown at a later date than the material of Figure 5.5. Further, CV profiling of the uid and Zn-doped layers of Figure 7.8 (a) revealed a net carrier concentration of $\sim 3 \times 10^{16} \text{ cm}^{-3}$ in each, which is surprising given that the target doping in the Zn layer was $7 \times 10^{17} \text{ cm}^{-3}$. In contrast, the net carrier concentration in the as-grown C-doped layer was $\sim 2 \times 10^{17} \text{ cm}^{-3}$, and further, the DLTS spectrum of this layer looks somewhat different than those of the uid and Zn-doped layers. In particular, the peak present at $\sim 250 \text{ K}$ in the spectra of the uid and Zn-doped layers seems to be suppressed in the spectrum of the C-doped layer, whereas the peak at $\sim 300 \text{ K}$ that is dominant in the latter layer is not as evident in the other two. It is possible that this may reflect an increase in concentration of H4 relative to H3 due to carbon doping in as-grown material, since those two defects appear in the temperature ranges mentioned in the previous sentence. The disparity between the uid and the C-doped layers is particularly surprising, since the former layer is thought to be doped by background carbon impurities. However, without corroborating measurements such as SIMS, it is impossible to know exactly how the presence and/or concentration of excess carbon influences the structure and, hence, the deep levels present in as-grown InGaAsN.

Following annealing, it is seen from Figure 7.8 (b) that the DLTS spectra of the uid, Zn-doped, and C-doped InGaAsN layers are all very similar to each other, which suggests that the defect distributions in these layers after annealing are independent of the type of dopant atom present. An overall decrease in deep level concentration is not observed, perhaps due to the already low concentrations present in the as-grown material. Finally, CV profiling revealed a net carrier concentration of $\sim 5 \times 10^{17} \text{ cm}^{-3}$ in each of the layers of
Figure 7.8 (b). The observed increase in carrier concentration is consistent with what was observed in Chapter 5 and suggests that the doping of the annealed layers is dominated by background acceptors.

Finally, the influence of nitrogen content on the deep level spectra of as-grown, p-type InGaAsN was examined. Figure 7.9 shows the majority-carrier spectra of two uid, p-type, lattice-matched InGaAsN layers grown using the low arsine flow growth conditions discussed above. The sample structures were again $p^+$-GaAs on $n$-InGaAsN heterojunctions. One of the layers contained 2% nitrogen (In$_{0.07}$Ga$_{0.93}$As$_{0.98}$N$_{0.02}$) and had a bandgap of 1.05 eV, the same as all of the material that we have discussed up to this point has had; the other contained 1% nitrogen (In$_{0.035}$Ga$_{0.965}$As$_{0.99}$N$_{0.01}$) and had a bandgap of 1.15 eV. Recall from Chapter 1 that the latter composition may be useful in the fabrication of an optimized dual-junction solar cell. It is clear from Figure 7.9 that the layer containing 1% nitrogen exhibits a lower overall trap concentration than the sample containing 2% nitrogen, suggesting that the deep level defects present are attributable to the presence of nitrogen. Further supporting this assertion is the DLTS spectrum obtained by measuring an MOCVD-grown In$_{0.02}$Ga$_{0.98}$As layer containing no nitrogen; thus it is slightly lattice-mismatched to the GaAs substrate. This particular layer, while unintentionally doped, was $n$-type rather than $p$-type; nevertheless, it demonstrates that deep level concentrations are in general much lower in an alloy containing no nitrogen than alloys containing even a small percentage of nitrogen.
Figure 7.9 Majority-carrier spectra of as-grown, p-type (uid), lattice-matched InGaAsN layers, illustrating the effect of different nitrogen content. Also shown is the spectrum of a lattice-mismatched, n-type (uid) In$_{0.05}$Ga$_{0.95}$As layer. The data are shown for a rate window of 200 s$^{-1}$.

7.3.2 Impact of growth conditions on defect spectra of n-InGaAsN

Analogous to the study of unintentional, zinc, and carbon p-type doping discussed in the previous section, we undertook a study of tin and tellurium n-type doping in InGaAsN. Two $p^*$-on-n In$_{0.07}$Ga$_{0.93}$As$_{0.98}$N$_{0.02}$ homojunction solar cell samples were grown; both structures were similar to the $p$-on-$n$ configuration shown in Figure 6.2.

Although when referencing this figure, it is important to keep in mind that the growth technique used in the present experiment was MOCVD, not MBE. For the experiments that follow, it is the base layer of the solar cell that is measured. The two samples were identical except that one was doped with tin obtained from DESn, and the other was doped with tellurium obtained from TETe; see Table 5.1 for a description of these two precursor gases. The samples were grown under conditions similar to those used to grow 133

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
the samples described in Chapter 5, except that gallium source was TEGa instead of TMGa; also as described in Chapter 5, both samples were subjected to post-growth thermal annealing. The majority-carrier deep level spectra of the two samples, obtained using a rate window of 20 s\(^{-1}\) and a fill pulse time of 1 ms, are shown below.

![DLS Spectra](image)

**Figure 7.10** Majority-carrier deep level spectra of annealed, \(n\)-type In\(_{0.07}\)Ga\(_{0.93}\)As\(_{0.98}\)N\(_{0.02}\) layers grown by MOCVD. The duration of the fill pulse was 1 ms; the 20 s\(^{-1}\) rate window is shown.

Looking first at the spectrum of the Sn-doped sample, we see that it is very similar to the spectrum of the Sn-doped heterojunction sample shown in Figure 5.14, with peaks corresponding to the traps E1, E2, E3, and E4 elucidated in Chapter 5; further, the peak heights are not far off of what was observed there. Regarding E2, keep in mind that even though we are now examining a homojunction sample, we are looking at the base layer, which is grown directly on a GaAs BSR layer; thus, this layer is likely subject to the same nucleation issues that the layers studied in Chapter 5 were. The similarity between
the present Sn-doped spectrum and that of Chapter 5 suggests that the use of the TEGa precursor gas in place of the TMGa precursor gas has little, if any, impact on the deep level spectrum of the material. The spectrum of the Te-doped layer, however, looks somewhat different from the spectrum of the Sn-doped layer. We have tentatively identified the peaks E1 and E2, and we do not see any sign of E3; however, all three peaks are much reduced in magnitude from the corresponding peaks in the Sn-doped material. Further, the peak labeled “E4?” appears at first glance to be a high-temperature peak similar to E4, although direct comparison of the two spectra reveals that it is in fact shifted to a somewhat higher temperature. Thus it is unclear whether the high-temperature peak in the spectrum of the Te-doped sample is in fact E4 or not, which is why the name has had a question mark appended to it. Despite this uncertainty, the overall trends in these data thus suggest that the n-type dopant does play some role in the determination of the deep level spectrum of n-type InGaAsN grown by MOCVD. The absence of Sn, in particular, correlates with the absence of E3. Assuming that the two peaks labeled E4 in Figure 7.10 are indeed the same defect (which is the opinion of the author), it is apparent that the position of E4 may vary slightly from sample to sample. Of course, this has already been established by comparing the activation energy of E4 in MOCVD-grown material (0.40 eV) with the corresponding activation energy in MBE-grown material (0.30 eV).

7.4 Summary of possible physical sources of deep levels

In this section we summarize the properties of the deep levels that we have observed during the course of this research. Towards this goal, we suggest a number of
physical sources for these defects; however, the reader is advised that these assignments are tentative and are based only on the best estimates made by the author. The subject of the physical sources of deep level defects is a complex one, and much more research needs to be completed before the sources of deep level defects in this unusual material are definitively assigned. Of particular importance to keep in mind is the fact that we have examined bulk, lattice-matched films of a single bandgap (1.05 eV, aside from the one 1.15 eV sample) only. Thus the variation of the properties of the deep levels summarized herein with nitrogen composition almost completely unknown, and the effects of properties such as strain (i.e., the In:N ratio) have not been examined at all.

We begin by reviewing the deep levels observed in $p$-type InGaAsN grown by MOCVD. Four hole traps were seen: $H_1$, $H_2$, $H_3$, and $H_4$, located at 0.10, 0.23, 0.48, and $\sim0.5$ eV above the valence band edge. All four defects give rise to broad DLTS spectra and are thus believed to be due to energy distributions within the semiconductor bandgap, as opposed to discrete levels. The concentrations of $H_1$, $H_2$, and $H_4$ were all observed to be substantially reduced following thermal annealing, and the removal of $H_4$ was found to correlate with greater photoluminescence intensity, a longer minority-carrier diffusion length, and improved solar cell performance. The deep level spectra of MOCVD-grown $p$-type InGaAsN were observed to be sensitive to nitrogen content as well as to precursor gas flow conditions, with deep level concentrations correlated with both of these variables. Further, the presence of excess carbon seems to have an impact on the deep level spectra, with the concentrations of carbon and $H_4$ appearing to correlate; however, the true relationship between carbon concentration and deep level properties is not fully clear. DLTS measurements of MBE-grown $p$-InGaAsN have...

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
detected two deep levels, H3' and H4', located 0.37 and 0.51 eV above the valence band edge, respectively. These two levels appear to be similar to H3 and H4 as observed in MOCVD-grown material. Regarding physical sources, we have already mentioned the impact of carbon. Aside from this, we note that deep levels have been predicted to exist at 0.05 eV and 0.38 eV above the valence band edge of 1.05 eV GaAsN; these levels are due to AsGa-NAs pairs and N-N split interstitials, respectively. We see that these energies correspond roughly to those measured for H1 and H3/H3'; however, assignment of these two defects as the physical sources of the H1 and H3/H3' levels is highly speculative.

Moving on to n-type InGaAsN, we recall that we observed four electron levels, E1, E2, E3, and E4, in MOCVD-grown material. E1 was observed to be a broad distribution extending from the bottom of the conduction band to approximately $E_C - 0.2$ eV, whereas the levels E2, E3, and E4 were thought to be broadened levels centered at 0.36, 0.34, and 0.40 eV below the conduction band edge, respectively. All of the levels appeared in annealed material, whereas the E2 level was absent in as-grown material. Further, a single hole trap, H6, was observed at 0.71 eV above the valence band edge. This level, like E2, was absent in as-grown material and is believed to be the same level as E2 observed by hole rather than electron emission. The E2/H6 defect was shown to be responsible for the reverse-bias generation current in an InGaAsN-based test diode. Moreover, the capture kinetics of E2/H6 are consistent with that of a line defect, and the physical source of this defect is believed to be related to the nucleation conditions of the InGaAsN alloy on a GaAs surface. Capture kinetics experiments were also performed on E4 and it was demonstrated that this level is a point-like defect characterized by a thermally activated electron capture cross-section, the activation energy of which is a
very large 0.42 eV. Further, the saturation time of E4 is on the order of 300 ms, which is exceedingly long. In MBE-grown n-type InGaAsN, defects similar to E1 and E4 were observed, which were named E1' and E4'. E1' was found to be a broad distribution of levels, although in this case the lower end of the distribution was estimated to be located at approximately $E_C - 0.35$ eV; further, E4' was located 0.30 eV below the conduction band edge. Capture kinetics experiments observed very long saturation times, again on the order of 300 ms, for both E1' and E4', suggesting that similar electron capture mechanisms are at work in these two levels. E4' was again consistent with a point-like level characterized by a thermally activated electron capture cross-section, this time having an activation energy of 0.27 eV. Regarding physical sources, we note that the alloy fluctuation model predicts the presence of a distribution of states located just below the conduction band edge, consistent with the location of E1/E1'; further, the same model predicts the existence of another distribution roughly 0.3 eV below the conduction band edge, which is roughly consistent with the position of E4/E4' in the bandgap. Given the similar and unusual electron capture characteristics of these levels, it is conceivable that they are intrinsic, nitrogen-induced levels predicted by this model. However, we also point out that a N-As split interstitial has been predicted to give rise to a level at $E_C - 0.42$ eV — consistent with the location of E4 — in lattice-matched InGaAsN alloys of this composition. The similarities between E1/E1' and E4/E4' suggest to the author that the alloy-fluctuation explanation is the more likely; we nevertheless use this example to reiterate the fact that the assignment of physical sources herein is speculative at this point.

We also note that the absence of E3 has been observed to correlate with the absence of tin doping in n-type material grown by MOCVD. Finally, a minority-carrier hole trap, H5'.
was observed in \( n \)-type InGaAsN grown by MBE. Although the measured activation energy of this level was equal to that of H6 at 0.71 eV, it does not seem possible that these two levels are the same, since H6 was observed to correlate with E2. Thus, the origin of H5' is completely unknown, aside from the fact that it is observed in MBE-grown material only. The properties of the deep levels outlined in this and the previous paragraph are summarized in Table 7.2 on the next page. Shown below the table is a "master" Arrhenius plot of all of the traps characterized throughout the course of this research, except for E1, E1', and H4, for which no Arrhenius analysis was possible. Figure 7.11 serves as a "map" of the various defects in emission-rate / temperature space, allowing one to easily compare the properties of the various levels at a glance. The slope of each line is proportional to the activation energy of the corresponding level and the intercept is related to the \( T \to \infty \) capture cross-section; thus levels possessing similar electrical properties should be grouped together. Regarding direct comparisons, the most important are undoubtedly between H3 and H3' as well as E4 and E4'; in both cases the unprimed and primed levels appear to deviate from each other due to discrepancies in the capture cross-sections. One potential explanation for this is that the local environments surrounding these defects are dissimilar due to the different growth techniques employed, thus resulting in variations in the capture kinetics between the levels; in any case, this discrepancy unquestionably calls for further investigation of these levels, especially in light of the qualitative and quantitative agreement of the other properties of these levels.
<table>
<thead>
<tr>
<th>Level</th>
<th>$E_a$ (eV)</th>
<th>Observed in</th>
<th>Possible source</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>0.10</td>
<td>$p$-MOCVD</td>
<td>As$<em>{Ga}$-N$</em>{As}$ pair$^7$</td>
</tr>
<tr>
<td>H2</td>
<td>0.23</td>
<td>$p$-MOCVD</td>
<td>Unknown</td>
</tr>
<tr>
<td>H3/H3'</td>
<td>0.48/0.37</td>
<td>$p$-MOCVD/p-MBE</td>
<td>N-N split interstitial$^7$</td>
</tr>
<tr>
<td>H4/H4'</td>
<td>0.5/0.51</td>
<td>$p$-MOCVD/p-MBE</td>
<td>Carbon doping</td>
</tr>
<tr>
<td>H5'</td>
<td>0.71</td>
<td>$n$-MBE</td>
<td>Unknown</td>
</tr>
<tr>
<td>E1/E1'</td>
<td>&lt;0.2/&lt;0.35</td>
<td>$n$-MOCVD/n-MBE</td>
<td>Alloy fluctuation$^8$</td>
</tr>
<tr>
<td>E2/H6</td>
<td>0.36/0.71</td>
<td>$n$-MOCVD</td>
<td>MOCVD nucleation</td>
</tr>
<tr>
<td>E3</td>
<td>0.34</td>
<td>$n$-MOCVD</td>
<td>Tin doping</td>
</tr>
<tr>
<td>E4/E4'</td>
<td>0.40/0.30</td>
<td>$n$-MOCVD/n-MBE</td>
<td>Alloy fluctuation$^8$</td>
</tr>
</tbody>
</table>

Table 7.2 Properties of deep levels observed in bulk 1.05 eV In$_{0.07}$Ga$_{0.93}$As$_{0.88}$N$_{0.02}$ films lattice-matched to GaAs. $E_a$ is measured from the valence band edge in H-traps and from the conduction band edge in E-traps; note that the cross-section activation energies $E_c$ have been taken into account for E4 and E4'.

Figure 7.11 Arrhenius plots of all traps except for E1, E1', and H4. Primed traps, i.e. traps observed in MBE-grown material, are indicated by dotted lines. Note that the cross-section activation energies $E_c$ have been taken into account for E4 and E4'.
7.5 References


CHAPTER 8

PROPOSED FUTURE WORK

8.1 Introduction

Of course, no research project is ever truly complete, since new ideas and avenues of exploration are always available. This final chapter outlines a few ideas regarding potential future investigations into the nature of deep level defects in InGaAsN alloys. The remainder of the chapter is divided into three sections, with the first describing what is perhaps the most straightforward extension of the research presented in this Dissertation, namely, the continued investigation of factors such as growth conditions, composition, impurities, etc. The latter two sections of this chapter, however, deviate significantly from what has been presented thus far; the first of these sections of these proposes a novel method of analyzing DLTS data, while the second addresses the measurement of deep levels in quantum-well structures.

8.2 Extension of current work

To extend and refine our knowledge of the properties and physical origins of deep level defects in InGaAsN alloys, further effort could be made to correlate the growth parameters of both p- and n-type InGaAsN with the defect spectra of the material. For MOCVD-grown material, potential studies could include a detailed investigation of the
effects of changing the flow rates of the various precursor gases, including DMHy; an investigation of the influence of in-situ vs. ex-situ annealing; and an examination of the differences (if any) between the DLTS spectra of InGaAsN layers grown on Ge substrates vs. those grown on standard GaAs substrates. This latter point is potentially related to the issue of the influence of interfaces and nucleation conditions on bulk deep levels, as discussed in Chapters 5 and 7. These measurements could be made on pn junction samples, as has been done up to this point; however, it would be potentially advantageous to make some of these measurements on Schottky diodes instead. This is because the latter device structure is simpler and fabrication and control of experimental conditions is thus more straightforward. Unfortunately, preliminary efforts to fabricate Schottky diodes on both p- and n-type InGaAsN have been unsuccessful.

Further, the correlation of experimental techniques other than DLTS with measured defect spectra could prove to be quite fruitful. For example, Fourier transform infrared spectroscopy (FTIR) could be used to examine the bonding structure of InGaAsN both before and after annealing, and changes could potentially be correlated with changes in the defect spectra of the material; this would, of course, provide some insight into the physical origin of the deep levels observed by DLTS. Indeed, FTIR has demonstrated structural changes in InGaAsN as a result of thermal annealing, including the transformation of local nitrogen environments from Ga$_4$N into Ga$_3$InN, as well the change of the hydrogen-impurity bonding configuration from NH to NH$_2$. Further, hydrogenation experiments could be performed not only in an attempt to passivate deep level defects, but also to obtain further information regarding the changes in carrier concentration which are observed after annealing. In particular, if hydrogen is indeed
involved in the changes in carrier concentration observed after annealing, might not it be possible to reverse the annealing process by re-introducing hydrogen into the material? If so, might this have some impact on deep levels in the material, and on its electronic quality in general? Preliminary plasma hydrogenation and Hall effect experiments suggest that the annealing process is not reversible. Indeed, the introduction of hydrogen into InGaAsN layers was not observed to return carrier concentrations to pre-annealing levels, although it was observed to decrease carrier mobility in both $p$- and $n$-type samples. Thus, it appears that hydrogen does play some role in the electronic quality of InGaAsN, although whether this is related in some way to deep level defects is unknown. Clearly more work is required to sort out complex issues such as this.

### 8.3 Novel DLTS analysis techniques

A problem that we were forced to deal with repeatedly throughout the course of this research was to try to apply standard DLTS analysis techniques, as described in Chapter 4, to the very broad spectra that were found to characterize InGaAsN alloys. The expressions used to determine activation energies, capture cross-sections, and trap concentrations — such as Equations (4.16) and (4.28) — were derived assuming ideal “delta-function” trap levels, and modifications such as the broadened level model of Equation (4.40) are really only perturbations to the ideal model. Deep levels in InGaAsN appear to deviate significantly from the delta-function model, however, resulting in very broad, convoluted DLTS spectra which were very difficult to fit. In this section we deviate considerably from the delta-function model and assume that a continuous
distribution of states exits over the entire bandgap; we then propose an analysis technique to extract this distribution from a single DLTS temperature scan.

We begin by considering Equation (4.44) for the capacitance due to a broadened deep level, again supposing that electron emission dominates in an n-type material. Since we are now assuming a continuous distribution of states over the entire bandgap, we use the more general expression $N_{rf}(E)$ in place of $N_{rgf}(E)$. With this in mind, we form the DLTS signal $\Delta C = C(t_2) - C(t_1)$ due to the distribution of states:

$$\Delta C = \frac{C_w}{2N_D} \int_0^E N_{rf}(E) \left[ \exp\left(-e_a(E) t_1\right) - \exp\left(-e_a(E) t_2\right) \right] dE$$  \hspace{1cm} (8.1)

where the energy-dependent emission rate is given by Equation (4.42), which we repeat here for convenience:

$$e_a(E) = c_aN_c \exp\left(\frac{E - E_c}{kT}\right)$$  \hspace{1cm} (8.2)

We now wish to evaluate Equations (8.1) and (8.2) numerically. To do this, we discretize the variable $T$ into a vector of length $(I + 1)$ such that

$$T \rightarrow T_i \text{ where } i = 0 \ldots I$$  \hspace{1cm} (8.3)

We perform a similar operation on the variable $E$, giving

$$E \rightarrow E_j \text{ where } j = 0 \ldots J \text{ and } J = E_g / \Delta E$$  \hspace{1cm} (8.4)

These discretizations allow us to convert the integral of Equation (8.1) into a summation, which is given by

$$\Delta C' = \frac{C_w}{2N_D} \sum_{j=0}^{I} N_{rf}^{(j)} \left[ \exp(-e_a^{(j)} t_1) - \exp(-e_a^{(j)} t_2) \right] \Delta E$$  \hspace{1cm} (8.5)
where the variables $N_T$ and $e_n$ are given by

$$N_T = N_T(E_j)$$

(8.6)

and

$$e_n = c_n N_e \exp \left( \frac{E_j - E_c}{kT} \right)$$

(8.7)

Note that we have assumed that the capture coefficient is independent of energy, which is likely not true. Worse yet, we assume that its value is known at the outset of the analysis, which it is not! One potential way around this problem may be to use conventional techniques to obtain a first estimate for the value of $c_n$ (recall that $c_n = \sigma_{tin}$) and then to use an iterative procedure to refine its value, perhaps as a function of energy, in conjunction with the distribution $N_T(E)$. For our present purpose, which is merely to provide the outline of a possible technique that may be used to elucidate the nature of a continuous trap distribution in the bandgap, we assume that $c_n$ is constant and known.

We may then write Equation (8.5) as a matrix equation:

$$\Delta C' = M'' N'_T \rightarrow \DeltaC = \overline{M} \cdot \overline{N}_T$$

(8.8)

where the single overhead bars indicate vector quantities and the double overhead bars indicate matrix quantities. From Equation (8.5), the elements $M''$ are seen to be

$$M'' = \frac{C \Delta E}{2N_D} \left[ \exp(-e''_n t_1) - \exp(-e''_n t_2) \right]$$

(8.9)

Finally, Equation (8.8) may be inverted to obtain the trap distribution, which is

$$\overline{N}_T = \overline{M}^{-1} \cdot \DeltaC$$

(8.10)
However, in order for \( M \) to be invertible, it must be square; thus, we must sample \( T \) and \( E \) such that \( I = J \). This should pose no difficulty, as the selection of \( \Delta E \) is entirely arbitrary. However, since the square matrix \( M \) has \((I + 1)\) rows and \((I + 1)\) columns, it is potentially quite large and thus its inversion is a computationally intensive task. Coupled with the fact that the process may need to be applied iteratively in order to obtain the energy-dependent capture cross-section as well as the trap distribution, it appears that the proposed technique may become quite complex. Nevertheless, it is perhaps a first step towards establishing a more realistic view of the deep states that exist within the bandgap of InGaAsN alloys. Further, it only requires a single temperature scan sampled at times \( t_1 \) and \( t_2 \), so it is potentially less time-consuming than traditional techniques in terms of experimental effort.

8.4 Measurement of quantum well structures

To date, this research has focused on the determination of deep levels in bulk, lattice-matched InGaAsN material through the use of DLTS measurements performed on solar cell structures. However, as discussed in Chapter 1.1.30 and 1.55 µm optoelectronic devices such as quantum-well lasers are another important potential application of InGaAsN alloys.\(^{2,3.4,5,6,7,8,9,10}\) It would likely be illuminating to undertake a study of deep levels in InGaAsN-based quantum-well structures, grown by either MOCVD or MBE, to complement our work on bulk material. Such quantum wells are typically composed of very thin (on the order of 100 Å or so) InGaAsN layers embedded within GaAs. Unlike InGaAsN layers for solar cell applications, quantum-well layers do not necessarily need to be lattice-matched to the surrounding GaAs; this is because such
very thin layers often do not exceed the critical thickness of the well material, thus permitting strained layers to be grown dislocation-free. In fact, in order to achieve the longest possible emission wavelength, the majority of InGaAsN-based quantum-well devices have been grown such that the In:N ratio is much larger than 3.5:1 (typically x ~ 0.3 and y ~ 0.01 or less), resulting in material that is compressively strained on the order of 2%. Thus, we do not necessarily expect deep levels in quantum-well layers to be similar to those observed in bulk material. Unfortunately, and perhaps not surprisingly, the measurement of deep levels in quantum-well structures is more complex than the measurement of bulk deep levels, as we will see below. To facilitate deep level measurements of quantum-well material, one-sided $pn$ junction diodes could be grown as test vehicles. The quantum-well layers of interest would be embedded into the low-doped side of the junction, such that they lie within the portion of the diode that is normally probed during a DLTS experiment. Such a configuration is illustrated schematically in Figure 8.1, which shows a $p^+n$ arrangement. Deep levels within the quantum-well layers should fill and empty as levels do in bulk material, and the data resulting from these processes may be analyzed in the manner discussed in Chapter 4.

![Figure 8.1](image)

**Figure 8.1** Schematic illustration of the proposed device which could be used to facilitate DLTS measurements on InGaAsN quantum wells.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.
However, in addition to emission from deep levels to the band edges of the quantum-well material, emission from the quantum-well energy levels to the band edges of the host material may be observed. In our case, the quantum wells under study result from the conduction band offset between GaAs and InGaAsN; this offset will introduce additional peaks into the DLTS spectra of n-type quantum-well material, since we are likely to observe electron emission from the lowest energy level $E_t$ of these quantum wells to the conduction band edge of the GaAs host. The "activation energy" $E_C - E_1$ may be determined through the use of an expression similar to Equation (4.16), although in this case a plot of $-\ln(\tau_n T)$ vs. $1/kT$ has a slope of $(E_C - E_1)$. Here $\tau_n$ is equal to the rate window of the DLTS experiment, although here its physical significance is that it is the inverse of the well emission rate $e_w$. Thus, the behavior of the peak temperature shift should provide a means by which to experimentally distinguish DLTS peaks due to deep levels from those due to quantum-well levels. It should also be possible to determine the conduction band offset $\Delta E_C = (E_C - E_1) + E_1$, since the quantum well energy level $E_t$ may be readily determined by standard methods. Further, since the band discontinuity between GaAs and InGaAsN occurs primarily in the conduction band, the value of $\Delta E_C$ determined from such experiments should be approximately equal to the difference between the bandgaps of the two materials. Finally, it should be pointed out that the analysis of the data resulting from DLTS measurements on quantum-well structures may be complicated by emission from surface states at the host-well boundaries.
8.5 References


12. See references 2-10.


J. S. Blakemore, Semiconductor Statistics (Dover, New York, 1987).


151


S. A. Ringel, *EE830 class notes* (Ohio State University, Columbus, 1999).


