Temperature Dependence of Photoluminescence of the Dilute Nitride Semiconductor GaN_xAs_{1-x}

by

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Abstract

The design of a closed cycle optical cryostat for semiconductor crystal characterization is discussed. The system designed and developed is capable of performing photoluminescence, resistivity, and Hall measurements as a function of temperature from 10 K to higher than 300 K. Preliminary photoluminescence experiments are carried out as a test of the system. Results from the photoluminescence measurements show evidence for the existence of nitrogen clusters in GaN_xAs_{1-x} . The clusters are shown to produce states with energies inside the band gap. It has also been found that the introduction of bismuth, as a surfactant, during the growth process tends to reduce the density of the nitrogen clusters in the material.

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Chapter 1

Introduction

In recent times the incorporation of small amounts of nitrogen into III-V semiconductor compounds (such as GaN_xAs_{1-x} and $InGaN_xAs_{1-x}$), has become a hot topic in experimental and theoretical physics. Interest in dilute nitrides has also grown in the industrial sector, primarily for 1.3 μ m vertical cavity surface emitting lasers (VSCELs) and cooler-less edge emitting lasers. The addition of a fraction of a percent of nitrogen can dramatically reduce the band gap of the alloyed material, allowing for the production of more technically favourable wavelength devices (1.3 μ m and 1.55 μ m). These new materials have several advantages over ones currently in use (InGaAsP/InP and InGaAs/InGaAsP)[1]. As an example, lasers made from the dilute nitride alloys are not as temperature sensitive due to a larger conduction band offset 2. This higher temperature stability is useful for the production of uncooled lasers. GaAs substrates, on which these alloys are grown are available in larger sizes and at a lower cost than InP substrates, leading to lower costs in device manufacturing. To date nitrogen's effect on the electrical, optical and material properties of the III-V compounds is not well understood.

There are also some disadvantages associated with the addition of nitrogen. For example, a large decrease in electron mobility and recombination ,

lifetime[3], and a reduction in photoluminescence intensity is observed[4]. In addition to these electrical and optical deficiencies, there are also some structural problems that arise with nitrogen incorporation. Because nitrogen is atomically smaller (atomic radius, $r_0 = 0.74\dot{A}$) than the arsenic, $(r_0 = 1.19 \dot{A})$), which it replaces, there is a large lattice constant mismatch between substrate and the epi-layer. This puts a large amount of strain on the grown epi-layer. This strain results in elastic and plastic relaxation processes that can lead to roughened surfaces and interfaces[5], as well as dislocations and cracks in the material. All this compromises the functionality of the material. The introduction of In along with N compensates for the size discrepancies correcting some of the lattice mismatch.

In order to achieve the very specific material properties for device fabrication, particularly in energy and intensity of the emitted photons, attempts are being made to improve the material by varying the growth parameters and techniques[6][7][8] to reach the desired characteristics. One area still largely unexplored in dilute nitride semiconductors is the dependence of the electronic and optical properties of these alloys on temperature, especially in the range 10 K to above 300 K. Also unknown is the effect which the various growth methods have on temperature dependent phenomena.

The following is a description of the development of an apparatus to carry out experiments characterizing the GaNAs samples. Only measurements on the temperature dependence of the photoluminescence of dilute nitride alloys will be discussed in the following pages. Chapter 2 gives some background information on materials at low temperature, necessary for the discussion of the design of the cryostat and a short introduction to dilute nitride semiconductors and photoluminescence. In chapter 3, the design of the cryostat is covered. Measurements on the temperature dependencies of photoluminescence (PL) is given in chapter 4, with concluding remarks in chapter 5. All design drawings and specifications for the cryostat can be found in the appendices.

Chapter 2

Background

2.1 Materials at Low Temperatures

The first step in the project was to design and build a variable temperature closed cycle helium cryostat from a second-hand cryopump. In the design of this system the heat capacity, $C_V(T)$, and thermal conductivity, $\kappa(T)$, of the materials involved are of primary importance. The heat capacity of a material is important when the material is to be heated or cooled in some way. It relates the amount of energy necessary to raise or lower a unit mass one degree. Typically, the specific heat is considered to be constant above a given temperature, and below this point to be highly temperature dependent. The influence of temperature on the specific heat of different types of materials will be discussed below in a little more detail. It is also necessary to know the thermal conductivity of a material. Important whenever a material is to be heated to know how quickly thermal equilibrium will be reached or if using that particular material as a thermal conductor or insulator. Further notes on the thermal conductivity of materials will be covered later on, with special consideration given to metal alloys, such as stainless steel.

2.1.1 Heat Capacity

Heat capacity of a material is defined as the rate of change of energy, U, with temperature, T. For a given material, the specific heat has contributions from a variety of sources, most notably electrons and phonons. The phonon part can be best approximated by the Debye function,

$$C_V(T) = \frac{9N_A k_B}{M_m} (\frac{T}{\theta_D})^3 \int_0^{\frac{\theta_D}{T}} \frac{x^4 e^x}{(e^x - 1)^2} dx$$
(2.1)

Where θ_D is the Debye temperature, and M_m the molar mass (for MKS units, $\frac{J}{kg K}$). The above equation is derived using the elastic continuum model of a solid, in which the number of vibrational modes in the interval $\nu, \nu + d\nu$ is given by;

$$n_{modes} = 4\pi \left(\frac{1}{v_l^3} + \frac{2}{v_t^3}\right) V \nu^2 d\nu$$
(2.2)

Where V is the volume of the solid, v the wave velocities, and the subscripts l and t indicate longitudinal and transverse modes respectively. A maximum frequency, ν_m is given by the normalizing constraint that a solid with N atoms may have only 3N modes. This in turn gives the Debye temperature as:

$$\theta_D = \frac{h\nu_m}{k_B} \tag{2.3}$$

A full derivation of the Debye model for the specific heat can be found in any standard condensed matter physics text[10][11]. At low temperatures, $T < \theta_D$, the specific heat is predicted to have a T^3 dependence, known as the Debye T^3 law. It should be noted that for real solids it is generally necessary to go to much lower temperatures to have a pure T^3 behaviour. At temperatures $T > \theta_D$, the specific heat is a constant, and given by the Dulong-Petit relation[10][12], $C_v = \frac{3}{2}N_Ak_B$. At low temperatures the fraction of electrons, $\frac{NT}{T_F}$, within k_BT of the Fermi surface begins to contribute more to the specific heat: T_F is the Fermi temperature $\left(\frac{\varepsilon_F}{k_B}\right)$. This electronic component gives a linear dependence of the specific heat on temperature at very low temperatures. In metals it is the electrons that contribute most to the specific heat at low temperatures and phonons at higher temperatures, whereas insulators have only the phonon contribution.

For the purposes of the discussion to follow on the design of the cryostat, the properties of copper will be discussed in more detail. The basic picture of the cryostat is a copper sample mount, with a heater, weakly linked to a thermal sink operating at some low temperature. Therefore much consideration must be given to the initial cooling and subsequent reheating of the copper stage. Copper has a Debye temperature of 343 K, given by its $T \rightarrow 0$ limit. When a more accurate measure of the specific heat is needed the Debye temperature is assumed to be a function of temperature[12]. Shown in fig 2.1 as a function of temperature is the specific heat of copper. Three regions immediately stand out: for T < 40 K there is a T^3 dependence, above that (40 K< T < 100 K) there is a region of linear dependence, and then for T > 300 K $C_v(T)$ is a constant given by the Dulong-Petit relation as $385 \frac{J}{kgK}$.

2.1.2 Thermal Conductivity

Heat transfer by conduction depends both on the temperature gradient between two points as well as the thermal conductivity of the material bridging



Figure 2.1: Heat capacity of copper

them. Thermal conductivity can be approximated by a relation borrowed from the kinetic theory of gases:

$$\kappa(T) = \frac{1}{3}\rho C_V(T)vl \tag{2.4a}$$

Where $C_V(T)$ is the specific heat, v the velocity of the energy carrier, and l the mean free path of the energy carrier. Velocities of energy carriers are approximately 10⁷ m/s for electrons and the speed of sound for phonons, and both can be assumed to be relatively constant with temperature. The dependence of the specific heat on temperature has been covered in the previous section. What remains is the mean free path of the carriers involved.

In the case of electrons, the same processes that limit the electrical conductivity also affect the thermal conductivity, i.e. scattering off phonons and impurities in the crystal. One can invoke the Weidemann-Franz law, shown below, to find the thermal conductivity from the electrical conductivity.

$$\rho\kappa(T) = LT \tag{2.5}$$

In equation 2.5 L is the Lorentz constant, having a value of $2.45 \times 10^{-8} \frac{V^2}{K^2}$. Note that this is only applicable where the mean free path is the same for electrical and thermal transport[11]. At temperatures, $T > \theta_D$, electron-phonon scattering is the major process involved. At these temperatures the wave vectors **k**, of the electrons, and **q**, of the phonons are comparable in magnitude. This gives rise to an inverse relationship between mean free path and temperature:

$$l = M_a k_B \frac{\theta_D}{T} \tag{2.6}$$

Where M_a is the atomic mass. At low temperatures, where impurity scattering dominates, the mean free path is constant, and therefore the electron thermal conductivity has a linear dependence on temperature.

Phonon thermal conductivity depends heavily on both the wavelength of the phonon and temperature, as well as the type of scattering mechanism. At high temperatures the phonons are chiefly scattered by other phonons, so-called Umklapp processes, giving rise to a T^{-1} in $\kappa(T)$. relation. At lower temperatures, $T \ll \theta_D$, where phonons are rare, crystal impurities have the greatest effect on the thermal conductivity. In this temperature regime long wavelength phonons are more likely to be excited. As a result planar defects affect the conductivity more than point defects do. Therefore, we need only concern ourselves with the types of impurities and their respective densities. Depending on the type of impurity, different temperature dependencies are found. Table 2.1 shows the relation between several types of impurities and their effect on the temperature dependence of the thermal conductivity.

Impurity	Temperature Dependence of $\kappa(T)$
Grain Boundaries	T^3
Dislocations	T^2 ,
Point Defects	T^{-1}

Table 2.1: Temperature dependencies of phonon thermal conductivity for various types of crystal impurities[12]

Impurities also play the major role when their densities are quite high, as in alloys. Stainless steel is typically comprised of iron with 11% chromium along with a variety of other elements, (C, Mn, Mo, Ni, Si, Ti), at 1% or less. In treating the thermal conductivity of stainless steel, one can think of it as a metal with a very large number of impurities. Due to the high density of impurities, the thermal conductivity becomes comparable with the electronic component. At low temperatures, there is most predominately a linear dependency. For intermediate temperature ranges, all scattering mechanisms can play significant roles lending to a nearly constant value from T = 150 K to T = 300 K. Above these temperatures a T^{α} relationship is seen, with $\alpha < 1$. Fig. 2.2 shows the thermal conductivity of stainless steel as a function of temperature.

Heat Transfer Through Solids

The heat flow, \dot{Q} , along a solid of cross-section, A, under the influence of a temperature gradient, $\frac{dT}{dx}$, is given by:

$$\dot{Q} = \kappa(T) A \frac{dT}{dx} \tag{2.7}$$



Figure 2.2: Thermal conductivity of stainless steel

Where $\kappa(T)$ is the thermal conductivity of the material as a function of temperature, and A, its cross-sectional area. If its ends are at temperatures T_2 and T_1 respectively, and is of length, l, with uniform cross-sectional area, then the equation can be rewritten as:

$$\dot{Q} = \frac{A}{l} \int_{T_1}^{T_2} \kappa(T) dT \tag{2.8}$$

The above equation will be used later on to establish the proper ratio of area to length needed for the temperature ranges of the thermal bridges between the cold head and sample stage, as well as calculating the amount of heat conducted along any leads into the sample.

2.2 III-V Semiconductor Crystals

2.2.1 Sample Growth

Semiconductor compound crystals are grown on site by Molecular Beam Epitaxy (MBE) onto semi-insulating GaAs wafers under ultra-high vacuum (UHV) conditions. The underlying GaAs substrate first needs to have the surface oxide removed. This is done by heating the substrate to about 600 °C with an arsenic flux. A buffer layer of GaAs is then grown on top of the oxide free substrate on which is grown the GaNAs semiconductor crystal. The buffer layer is necessary to cover the roughened condition of the original surface from which the oxide was thermally removed.

Epitaxial growth of the III-V semiconductor compounds by MBE is carried out under group-V rich conditions. The larger vapour pressure of these elements places excess group-V atoms on the surface available during growth. For this reason the growth is controlled by the amount of the group-III available. The diffusion length of the group-III atoms along the surface is determined by the substrate temperature, growth rate, and step density. Higher substrate temperatures allow for greater diffusion, and leads to smoother surfaces. Bulk GaAs samples are grown with substrate temperatures in the range 400 °C to 620 °C. The best samples are grown at the higher end of this range. Using growth temperatures below this range leads to films that are non-stoichiometric, with excess As incorporated into Ga sites or interstitially degrading the material properties[5]. The Ga/As flux ratio is kept slightly greater than 1 during growth, this allows for a 2×4 reconstruction. In this reconstruction the surface unit cell lattice parameter is twice that of the bulk along $[01\overline{1}]$ and four times as long along [011].

Nitrogen Incorporation

The growth of $\operatorname{GaN}_x \operatorname{As}_{1-x}$ requires conditions different from those used to grow simple GaAs. An RF plasma source developed by Adamcyk[6] produces the nitrogen atoms for the growth process. More or less nitrogen is present in the chamber by raising or lowering the flux by changing input pressure to the plasma source. As was stated, the growth rate is limited by the arrival of the group-III atoms. Furthermore the amount of N incorporation is inversely proportional to the growth rate[5] for constant substrate temperature. Surface desorption of nitrogen has an activation energy of 2.1 eV[5], so for a substrate temperature greater than approximately 550 °C very little nitrogen is found in the crystals[6]. There exists also some competition between group-V elements, N and As, for incorporation in $\operatorname{GaN}_x \operatorname{As}_{1-x}$. It is therefore advantageous to have a low As flux during growth to allow for more nitrogen incorporation. A simple empirical relation exists between the nitrogen concentration, [N], and the fluxes[6]:

$$[N] = \frac{F_N}{F_{As}} \tag{2.9}$$

Where F indicates the flux of the subscripted element. Nitrogen incorporation is slightly more sensitive to the As flux for higher growth temperatures[6]. Samples are also grown either with or without bismuth used as a surfactant. The effect of the Bi surfactant on nitrogen incorporation and material properties is still under investigation.



F	GaN _x As _{1-x} GaAs Buffer Layer	300nm 300nm	GaAs GaAs Buffer Layer	300nm 10nm QW 300nm
a)	GaAs Substrate	350 um b)	GaAs Substrate	350 um

Figure 2.3: Cross-sections of a) bulk GaN_xAs_{1-x} sample and b) a single quantum well sample

Nitrogen content varied from 0% to 0.67% in the samples studied here. To date, samples with concentrations as high as 4% have been grown on site. It is possible to grown crystals with higher nitrogen concentrations, however cracks and dislocations form above the critical thicknesses[4]. Thus, samples need be grown thinner to prevent these defects. Fig. 2.3 shows the structural cross-sections of the crystals investigated in this thesis.

2.2.2 Band Gap Bowing

When growing alloyed semiconductors, it is important to know how the band gap of the material is affected by the concentrations of the various elements. Both the band gap and the lattice constant are changed as the composition of the material changes. As more and more Al is added to $Al_xGa_{1-x}As$, with x varying from 0 (pure GaAs) to 1 (pure AlAs), the band gap and lattice constant both increase. The band gap as a function of lattice constant is shown pictorially in fig. 2.4, with the above example shown with a dashed line. Insofar as the band gap of an alloyed material is concerned the variation of the band gap with composition can be approximated by a simple parabolic function[13].

$$E_g^{AB}(x) = x E_g^B + (1-x) E_g^A - bx(1-x)$$
(2.10)



Figure 2.4: Band gap as a function of lattice parameter for various semiconductor compounds

Superscripts A and B designate the constituents of the alloy, x is the composition, and the constant b is known as the bowing parameter. For GaN_xAs_{1-x} , A is GaAs and B is GaN; $E_{GaN} = 3.4$ eV and $E_{GaAs} = 1.412$ eV. Typically the bowing parameter takes on values of only a fraction of an eV for most III-V alloys. GaNAs on the other hand, has been discovered to have an large anomalous bowing parameter[16]. for GaN_xAs_{1-x} the bowing parameter has been fit to the following equation:

$$b = b_a + b_1 e^{\frac{x}{0.26\%}} + b_2 e^{\frac{x}{3.3\%}} \tag{2.11}$$

This bowing results in the band gap being related to the lattice parameter by the curve shown by the dotted line in fig. 2.4. Note that for a range of nitrogen incorporation, the alloy has a negative band gap and therefore acts as a metal.

2.3 Temperature Dependence of the Band Gap

To derive the temperature dependence of the photoluminescence, it is important to first know how the band gap changes with temperature. This shift in the relative positions of the conduction and valence bands is due to two main mechanisms: 1) a change in the lattice parameter with temperature and 2) a temperature dependent electron-lattice interaction. The former gives rise to a linear temperature dependence for high temperatures, contributing only a fraction to the total shift in band gap in this temperature regime. At low temperatures the thermal expansion becomes a non-linear function of temperature. The latter effect, due to electron-phonon interaction, is the major contributor to the shift seen in the band gap. It has been shown that this leads to the following temperature dependence:

$$\Delta E_q \propto T^2, \quad for \ T \ll \theta_D$$
 (2.12a)

$$\Delta E_q \propto T, \quad for \quad T \gg \theta_D$$
 (2.12b)

A fit based on the above dependencies gives that for a given temperature, the band gap of a material, $E_g(T)$, can be given by:

$$E_g(T) = E_g(0) - \frac{\gamma T^2}{T + \beta}$$
 (2.13)

The above empirical formula is known as the Varshni expression[18], $E_g(0)$ is the T=0 K band gap energy, and γ and β are constants for the material. The constant β is related to the Debye temperature, θ_D . Table 2.2 gives the parameters for GaAs and GaN. Chapter 2. Background

	$\gamma, \frac{meV}{K}$	β , K	θ_D, K	
GaAs	0.5408	204	344	
GaN	.939	722	614	

Table 2.2: Varshni fit parameters from literature, GaAs[15] and GaN[17], as well as θ_D

An expression with a more obvious physical significance can be used, proportional to the Bose-Einstein occupation of a single phonon mode[19].

$$E_g(T) = a - b\left(1 + \frac{2}{e^{\frac{\Theta_B}{T}} - 1}\right)$$
 (2.14)

Where Θ_B is the average frequency for both optical and acoustic phonons, b represents the strength of the electron-phonon interaction, and (a-b) gives the band gap at T=0 K.

2.4 Photoluminescence

Photoluminescence spectroscopy is a non-destructive, contactless method of investigating the electronic structure of a material. Light incident on a sample, typically a laser or some other intense light source of a fixed wavelength, optically excites the electrons. As an electron falls back into the lower energy states, some of its energy is released in the form of radiation. This is in turn collected by a detector to be analyzed. The spectrum of the emitted photons contains information about the electronic structure of the material. The process of relaxing back to the lower energy bands is called recombination.





As the material returns to equilibrium, recombination processes affect the amount of luminescence. It should be noted that de-excitation can result from several different recombination processes. Shown in fig. 2.5 are photon and phonon emission, as well as the Auger effect. Emission of photons of energy at the conduction band edge, $\hbar\nu_1$, are more likely to occur than emission of photons with higher energy, $\hbar\nu_2$. The higher energy photons are a result of thermal excitation above the band minimum, giving rise to a tail in the photoluminescence spectra, proportional to k_BT . Phonons are emitted when the decaying electron interacts with the surrounding atoms and excites a vibrational mode in the lattice. Phonon emission is typically associated with defects or impurities in the material which tend to give states inside the band gap. Both photon and phonon emission are unavoidable recombination processes, they are a result of the existence of energy bands. The Auger

Chapter 2. Background

effect is a result of an electron-electron interaction, the recombining electron gives its energy up to another electron in either the valence (not shown) or conduction band. Electron-electron collisions will occur more frequently for larger carrier concentrations. The efficiency of the photoluminescence of a material depends on the lifetimes of the excited state with respect to both radiative and non-radiative recombination processes. In practice, the efficiency of the radiative recombination processes can be quite low if there are competing non-radiative processes.

The strongest radiative transition in semiconductors is the one where an electron falls back into the valence band from the conduction band. The energy difference between the two bands is known as the band gap, E_{q} . PL experiments therefore, permit a direct measure of the band gap of a semiconducting material. At the same time the emission spectrum gives information about impurity levels, the presence of defects, recombination mechanisms, and material quality. Non-radiative recombination is associated with localized defect levels, which are themselves associated with poor material quality or impurities. Therefore, a material grown under certain conditions can be compared with a similar material grown under slightly different condition to test the effect of growth conditions on the overall material quality. Also, changing the sample temperature during PL measurements can give more information on the recombination processes than simple room temperature or constant temperature experiments. First of all, there is a large increase in efficiency of the luminescence at lower temperature. Furthermore, practical use may be made of the knowledge of how the band gap shifts with temperature to produce a variable wavelength source. On the other hand, the lack of a shift could be useful in the production of highly temperature stable devices.

Chapter 3

System Design and Operation

Previously there existed no set-up to perform low and variable temperature experiments to characterize the semiconducting crystals grown on site. The following chapter discusses the design of such a device. Emphasis was placed on creating a system that was simple, efficient, and able to do a number of different experiments. It was therefore necessary to consider optical access for photoluminescence, taking into account any extra heating caused by the viewports, size constraints imposed by the available magnet set-up for Hall measurements, and most importantly the ability to control temperature over a large range, 10 K to greater than 300 K.

3.1 CTI Model 350P CryoCooler System

The cryogenic cooling system was built up from an existing CTI model 350P closed cycle helium refrigerator, originally used as a cryopump. It consists of three main parts: a compressor, drive unit, and the displacer unit, inside of which are the regenerators. Shown in fig. 3.1 is a schematic of the system, along with a more detailed view of the displacer unit. Considerable time was spent by the author, with help from J. MacKenzie, repairing/replacing several components of the refrigerator unit before the system

Chapter 3. System Design and Operation

was operational. The displacer is comprised of a coiled mesh (regenerator) of high heat capacity material wrapped in a phenolic shell. Gas that enters the cylinder first passes through the regenerator in the lower portion of the displacer, out into the open space above and then into, through and back out of the second element of the displacer. The large specific heat of the regenerators allows them to hold the temperature of the last cycle, thus the gas is cooled to the temperatures of the respective cold stages. A pair of seals, O-rings, prevents the cooled gas from escaping back through the cylinder outside of the regenerators. The advantage of such a set-up is that it allows more freedom in the design of a interfacing apparatus, particularity with respect to size and accessibility, otherwise unavailable when using conventional liquid helium as a coolant (i.e. dip probes or flow cryostats). Another consideration for low temperature application is cost of the coolant. In the closed cycle set-up, little or no helium is lost during a typical run of the experiment.

3.1.1 Closed Cycle Refrigeration

Cooling of the two low temperature stages is done by successively compressing and expanding helium gas. High pressure gas enters the cylinder from the compressor passing through the displacer and regenerators via the inlet valve, fig. 3.2a. Shown in fig 3.1 is a cross-section of the displacer unit. Gas entering through the inlet valve passes into the first component of the displacer through openings on its bottom face. It is then cooled by passing through the regenerator before exiting and moving on to the next unit. This unit cools the gas further on its way to the inner surface of the second cold



Figure 3.1: Model 350P CTI Cryocooler, and cross-section of the displacer unit

stage. Any gas that does not move into the second unit remains behind to cool the first cold stage. The gas then leaves by the same path through the displacer and out by the escape valve. The system of valves is timed with the movement of the displacer unit. When the gas enters the cylinder the displacer is on its way down nearing the bottom of its cycle (define bottom as fully retracted), the gas passes through the regenerators inside the two units of the displacer into the spaces left between the displacer and the cooling stages. As the gas passes through the regenerators it is cooled to a temperature slightly warmer than the temperature achieved by the previously expanded gas, warmed due to the heat load on the system. The inlet valve closes as the displacer reaches the bottom of its cycle, fig. 3.2b. On the subsequent up stroke the gas is compressed, fig. 3.2c. The escape valve opens during the up stroke and the gas is allowed to expand to the low pressure line of the compressor, cooling the regenerators as it leaves, fig. 3.2d.



Figure 3.2: Cryocooler displacer unit cycle

Cylinder Specifications

Outside of the cylinder there are three interfacing surfaces, the lower flange at room temperature and the two cooling stages. These are connected by an alloy of low thermal conductivity, most likely stainless steel or a similar material. The stages themselves are made from a material of high thermal conductivity and specific heat, for uniformity and stability of temperature in the cooling stage. The vacuum chamber is mounted to the lower flange. Surface area on the inner side of the chamber was kept to a minimum to keep radiative heating from the chamber low. The first cooling stage is used for mounting the heat shield, and a discussion of its function will follow in section 3.2.2. This stage operates at a temperature of approximately $60 \text{ K} \rightarrow 77 \text{ K}$. The uppermost cooling stage holds the sample mount components, and typical temperatures range from 6 K to 10 K. The final temperature of either stage depends on the heat load imposed by the attached apparatus. Cooling time for the second stage, as quoted by the operation manual, is approximately 45 minutes and plus an additional 7-8 minutes per kilogram of load attached to the second stage[21].

3.2 Heating and Cooling Considerations

Before the design was finalized all possible heat sources and thermal links in the set-up had to be taken into consideration. The system to be designed called for the ability to cool to low temperatures. Initially the goal was to achieve a minimum of 10 K-15 K, and to reach room temperature, 300 K, with a great deal of control at all temperatures in between. First and foremost, the thermal link from the cold head and the sample had to be set. Discussion on its design of the thermal link will follow in section 3.3.1. The temperature controller available in the lab presently is limited to a maximum output of 3 W, thus the link was designed to remove much less than this at room temperature. With the main issues covered, other sources of heat had to dealt with; mechanical heating from the vibration caused by the displacer in the cylinder, heat conducted along electrical leads to the sample, and heating from the excitation laser used for PL measurements, radiative heating from the inner surface of the vacuum chamber, and radiation through

and from the optical viewports.

3.2.1 Sources of Heat

i) Mechanical Heating

Significant heating can occur as a result of an experiment otherwise thermally isolated, being mechanically coupled to structure which is itself vibrating. As the displacer cycles the helium coolant to and from the cooling stages, some minor heating can occur at the sample stage. Typically, heat linput from mechanical vibrations are only a serious problem for liquid helium temperatures, 4.2 K and below. However, some consideration should be given to this issue beause of the relatively large vibrations of the cryocooler. The compressor can be set to run the drive unit in one of two modes, 50 Hz and 60 Hz. The former was chosen as the displacer runs at a lower frequency in this case approximately 1 Hz, compared with 1.2 Hz for the latter. The amount of heat input from a vibrating system is directly proportional to the frequency of the vibration, the effect being less at higher temperatures. Such heating should not prove to be problematic for the temperatures achieved with the cryocooler. Any other vibrations of the cryostat caused by outside sources are kept to minimum by having it securely anchored to a large aluminum plate.

ii) Electrical Leads

Thin brass wires are used for the electrical leads in the system. They extend from the electrical feed through in the chamber, at room temperature,

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to the sample, at a minimum temperature 6 K. Brass is used since as an alloy, the thermal conductivity is significantly lower than that of a pure metal. All the wires are insulated and in addition run inside small teflon tubing for safety; as a result it is very difficult to properly thermally anchor the leads to a heat sink to prevent heat input along the wire due to the extremely poor thermal link across the teflon. However, a worst case scenario calculation, using equation 2.8, with the greatest possible temperature gradient $T_1 =$ 300 K to $T_2 = 6$ K yielded the total heat flow along the leads to be on the order of 10 mW.

Another source of heat input associated with the connecting electrical leads is resistive losses in the wires, which gives rise to a heat input $\dot{Q} = I^2 R$. A typical current used for resistivity and Hall measurements is on the order of μ A's, and the corresponding heating is on the order of few nW

iii) Photoluminescence Excitation Laser

A 1046 nm laser source pulsed at 200 Hz, frequency doubled with roughly 10% efficiency to 523 nm is used to excite the sample for photoluminescence measurements, giving a total of $3 \rightarrow 5$ mW incident on the sample. The amount of heat input from the excitation laser is too small to be noticeable to the performance of the cryostat or to affect the average temperature of the sample. However, some thought had to be put toward how this heat input affects the sample temperature locally. A simple calculation of the local heating of the sample at the site of the beam gave the maximum temperature rise induced by the laser to be approximately 10 mK. This should not

affect the sample characteristics dramatically and is less than the accuracy warranted by the experiments being performed, and we can therefore ignore this effect.

v) Radiative Heating

By and large, the most problematic source of heat is due to the radiation of the materials present inside the vacuum chamber, included the interior walls of the chamber itself and the optical viewports.

A perfect black body may be defined as any body which absorbs all radiation falling upon it, and for such a body the absorptivity and emissivity are 1. The total radiant heat energy emitted by a black body per second per unit area is given by:

$$E = \sigma T^4 \tag{3.1}$$

Where σ is Stefan's constant, having an experimental value of $5.67 \times 10^{-8} \frac{W}{m^2 K^4}$. When any two surfaces of different emissivities, ε_1 and ε_2 , are exposed to one another the total amount of heat energy transferred from the higher temperature surface can be expressed as:

$$\dot{Q} = \sigma A (T_1^4 - T_2^4) \frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2 - \varepsilon_1 \varepsilon_2}$$
(3.2)

Most metals have low emissivities, $0.01 \rightarrow 0.6$, depending on the quality of the surface, and non-metallic materials can approximate to black bodies having emissivities of 0.9[20] or higher.

Some intelligent guess work is required when estimating the radiant heat from the surfaces, both for surface condition and approximating actual radia-
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Material	Emissivity
Copper	$0.02 \text{ (polished)} \rightarrow 0.6 \text{ (highly oxidized)}$
Aluminum	$0.05 \text{ (polished)} \rightarrow 0.31 \text{ (highly oxidized)}$
Quartz	0.9

Table 3.1: Emissivity values for the materials located inside the vacuum chamber[12]

tive surface area impinging on the sample mount. For the calculations of the amount of radiant heat the area of the inside of the chamber as seen by the sample mount can roughly estimated to be comprised of 75% quartz and 25% aluminum. The sample mount itself is approximated by a copper surface with total exposed area of 100 cm². In the worst case, $\varepsilon_{Quartz} = 0.9$, $\varepsilon_{Al} = 0.31$, and $\varepsilon_{Cu} = 0.6$. The calculation states that approximately 2.2 W of thermal radiation flows into the sample mount; for the best case $\varepsilon_{Quartz} = 0.9$, $\varepsilon_{Al} = 0.05$, and $\varepsilon_{Cu} = 0.02$, approximately 0.1 W is found. For this reason it was necessary to consider an intermediate thermal shield, and this is the topic of the next section. Radiation other than that emitted from the internal surfaces, such as radiation from the environment passing in through the viewports, was considered insignificant in comparison.

3.2.2 Heat Shield

As illustrated above the sample stage requires heat shielding between it and the inner walls of the chamber and the viewports, in order to achieve the desired low temperatures. A simple design for the heat shielding was developed consisting of a length of copper tubing capped and surrounding the sample mount anchored to the first cold stage. The first cold stage operates at approximately $T = 60 \text{ K} \rightarrow 77 \text{ K}$. Keeping in mind the need for optical access to the sample, two shields were designed; one with optical access, the other without. The amount of heat radiated to the sample from the shielding, $T_{shielding} = 77 \text{ K}$, in place was 17 mW for the worse case $(\varepsilon_{Cu} = 0.6)$ and 0.4 mW for best case, $(\varepsilon_{Cu} = 0.02)$.

For optical access, three holes were included in the design, two smaller holes (0.45") 180° to the sides of the sample meant for input/output of the PL laser and one larger hole (0.75") in front for both laser input/output and the PL output. When the sample was first cooled with no modification to the thermal link, the lowest temperature achieved was 65 K. Modifications to the thermal link, described later in section 3.3.1, were made in order to compensate for the extra radiation passing through these holes.

3.2.3 Modeling the Sample Mount

In order to have an idea of how the system would perform a number of small simulations were run modeling the cooling and re-heating of the sample stage. Any system of heat sinks, sources, and thermal links can be modeled by an equivalent electric circuit[22]: resistors for thermal links, capacitors for heat sinks, and power supplies for heat sources. Temperature of the components in a thermal system reacts to changes in the flow of heat energy much in the same way the elements of an DC electric circuit do for changes of voltage. Shown diagrammatically in fig 3.3 is the equivalent circuit for



the cryostat sample stage where the capacitor, C, is derived from the specific

Figure 3.3: Electric circuit model of sample mount.

heat capacity of the copper sample stage and heater block, the resistor, R, is related to the inverse of the thermal conductance along the stainless steel tubing, and the current souce, I, is equivalent to the input heat from the heater. The cold head acts as a ground for the thermal circuit, with the following equations relating the equivalent components:

$$C = mC_v(T) \tag{3.3a}$$

$$R = (T - T_{base})^{-1} G^{-1}$$
(3.3b)

$$G = \frac{A}{l} (T - T_{base})^{-1} \int_{T_{base}}^{T} \kappa(T') dT' \qquad (3.3c)$$

Where the thermal conductivity of stainless steel can be closely approximated by:

$$\kappa(T) = -0.47127 + 0.1428T - 5.1049 \times 10^{-5}T^2 + 6.5181 \times 10^{-7}T^3 \quad (3.4)$$

The amount of power, P_1 , flowing from point T (\equiv temperature of the sample stage), to ground is equal to the negative of the power, P_2 , across the

capacitor.

$$P_1 = -P_2 \tag{3.5a}$$

$$P_1 = mC_v(T)\frac{dT}{dt}$$
(3.5b)

$$P_2 = \frac{A}{l} \int_{T_{base}}^{T} \kappa(T') dT' \qquad (3.5c)$$

To find the temperature, T, at any given time, t, we simply need to solve the differential equation:

$$\frac{dT}{dt} = \frac{A}{l} \frac{1}{mC_v(T)} \int_{T_{base}}^T \kappa(T') dT'$$
(3.6)

An analytical solution was unattainable due to the complex nature of the right hand side of the equation 3.6. It was therefore easiest to allow an iterative computer simulation to solve it. Codes were written, with much help from A. Ballestad, to calculate the cooling curves for several different ratios of area to length. Shown in fig. 3.4 are the cooling curves for two of the thermal bridges currently in use. Both cases are shown with the extra radiation from the optical access in the heat shield. Without the optical access a base temperature of 6 K is reached in the model.

It was discovered that the added heat load due to the openings in the heat shield, along with the upper limit on the power output by the heater constrained the range of attainable temperatures. For certain ratios of A to l the system is unable to reheat the sample to room temperature. Table 3.2 shows the lower and upper temperature limits and the corresponding ratio. In order to have the maximum possible temperature range, two set-ups are needed. The ratio of 3.278×10^{-4} m allows for a minimum temperature of

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Figure 3.4: Model of the cooling of the sample stage for both thermal links, solid line $\frac{A}{l} = 4.233 \times 10^{-4}$ m, dashed line $\frac{A}{l} = 3.35 \times 10^{-3}$ m

65 K and a max of higher than 300 K. A second arrangement with a ratio of 3.35×10^{-3} m allows sufficient overlap and a minimum temperature of 25 K.

3.3 Sample Mount

3.3.1 Thermal Bridge

At the heart of the design of the cryostat is the thermal bridge between the coldhead and the sample stage. The amount of heat that can travel from the sample stage and the cold stage is governed by the thermal conductivity, $\kappa(T)$ (see equation 3.4,) of the stainless steel tubing that runs between them. The ends of the stainless steel tubing are soldered to copper interfacing pieces. These can be assumed to be temperature boundary points, T_{sample}

Low Temperature (K)	Upper limit (K)	l (inches)
25	200	0.35"
40	300	1.18"
65	300+	2.15"

Table 3.2: Temperature ranges of various thermal links made from $\frac{1}{8}$ " O.D.stainless steel tubing, wall thickness 0.040"

and $T_{coldhead}$. The heat that travels along any solid under the influence of a temperature gradient is given by equation 2.7. Since the temperature controller being used has a maximum output of 3W, the thermal bridge was designed to have a maximum heat flow of 1 W for $T_2 = 300$ K and $T_1 = 6$ K. Using equation 2.8 a ratio of area to length of the compatible bridge can be found, in this case $\frac{A}{l} = 3.378 \times 10^{-4}$ m. This was accomplished using 0.375" outer diameter stainless steel tubing, of thickness 0.040", and having a length of 3.1".

Modification for PL

As previously mentionned, the ratio of area to length had to be re-calculated, to remove the extra heat load from the radiation passing through the optical ports in the heat shield. This was simply done by shortening the thermal bridge from 3.1" to 0.35". See table 3.2 for the upper and lower bounds of temperature imposed by these ratios. A copper clamp is used to accommodate this. By having it well thermally anchored to the cold head and thermal bridge, it shortens the effective thermal link. It is possible to increase the



Figure 3.5: Cryostat sample stage

upper temperature bound by simply having a temperature controller of a larger output power. However the cooling power of the cold heads would then have to be taken into consideration, see diagrams in appendix B. The cooling power of the second stage is a function of both its own operating temperature and the operating temperature of the first cold stage. In other words if too large a heat load is applied, the base temperature of the coldhead will be compromised.

3.3.2 Heater Block and Sample Stage

Heating is accomplished by means of a 33 Ω resistor inside a copper cylinder of sufficient thermal mass as to allow for stability in temperature in the

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sample stage. The resistor is placed in the center of a hollowed portion of the cylinder, held in place, electrically insulated, and well thermally linked to the copper by sapphire laden époxy. Thermal expansion of the epoxy is well matched to that of the copper, It is expected that the thermal cycling will eventually cause a break down in the epoxy, or in its connection to the copper. Any such defect, cracks or separation from the copper surface, will dramatically effect the performance of the heating stage. The heater block is thermally linked to the top end of the thermal bridge with a thin layer of indium, and by a thermally conductive compound to the sample stage.

Crystals are mounted on the sample stage, the top most component of the entire sample mount, held in place by the aforementioned thermal compound. The stage has a 600 μ m thick wafer of oxidized silicon on its face with 8 electrical contact pads, and again the thermal compound is used to thermally link the pieces. The contact pads were grown by E-beam evapouration, first a thin layer, 30nm, of chromium is wetted to the surface and then 200nm of gold is grown. This electrical contact wafer is unnecessary when PL measurements are being performed. During PL the crystals are simply placed on a small piece of copper shim, which is itself placed on the face of the sample stage.

3.4 Thermometry and Temperature Control

Fixed to the rear face of the sample mount is a diode thermometer, held stationary with a narrow band of copper shim, which is lined with thermal compound. The diode is positioned directly opposite the sample, and is well thermally connected to the sample mount in order to achieve the most accurate reading of the temperature as possible. Diode thermometry is based on the temperature dependence of the forward bias drop across the p-n junction. A constant current of 10μ A is run through a calibrated diode and its voltage measured. The forward bias voltage as a function of temperature is shown in fig. 3.6. Calibration was carried out inside a SQUID device for a temperature range of 6 K $\leq T \leq$ 300 K, with an overall accuracy of ± 0.25 K. Some thermal drift is to be expected in the diodes, therefore the diodes are required to be replaced from time to time. Diodes will be routinely checked against original calibration data for selected temperatures, T = 77 K and T = 273 K.



Υ¥,

Figure 3.6: Calibration curve of a silicon diode

In order to control the temperature of the sample stage the diode thermometer is connected a non-commercial temperature controller, manufactured by the departmental electronics shop at U.B.C. A reading from the diode is compared to a referenced voltage, corresponding to the voltage of the desired temperature, and the output of the heater is adjusted accordingly. The temperature controller uses proportional and derivative control feedback circuitry to adjust the heater output to the sample mount.

3.5 Vacuum Chamber

Everything is housed inside an aluminum vacuum chamber, equipped with the necessary electrical, optical, and vacuum feed throughs. The chamber is comprised of two pieces, an upper and a lower segment. The lower portion reaches up to just above the first cold stage. It was designed as a simple cylindrical chamber fixed with the necessary electrical and vacuum feed throughs. Another valve, also on the lower portion of the chamber, is used to let in dry nitrogen when rapid reheating of the cold stages is desired. An O-ring is used to maintain the vacuum seal between the base flange of the cryocooler cylinder, as well as between the sections of the chamber. The upper half of the chamber is designed to have as little inner surface area as possible, to lower radiative heating from the chamber to the cold stage and heat shield. Quartz was chosen for the optical viewports for its broad transmission spectrum. The viewports are positioned at the top of the of the upper portion of the chamber. The windows are 50.4mm in diameter, allowing for a maximum incident angle of 26° through the front window and a minimum incident angle of 64° through the side windows. Another set-up of the windows has been designed. These are smaller in size and inset into the chamber to be closer to the sample, and subtend approximately the same solid angle as the larger windows.

To pump the system down, a combination of a mechanical scroll pump and a molecular drag pump is used initially. However as the cold stages cool, predominately the second stage, the system begins to pump itself more effectively than the roughing pumps. At this point the rough pumps are valved off until the coldhead is to be reheated after the experiment is finished.

Chapter 4

Temperature Dependence of PL

4.1 Experimental Set-up

While the cryostat is outfitted to perform several different types of characterization experiments, only PL measurements will be discussed in the following chapter. As was described earlier in section 2.4, photoluminescence experiments are carried out by first optically exciting the electrons and then collecting the emitted photons from the recombination process. Shown in fig. 4.1 is the current optical set-up in use. Presently two lasers are used to excite the sample: a pulsed 523nm (green) laser and a continuous wave 633nm (red) helium-neon laser. Reasons for this will be given later on. Laser light from the green laser is first passed through a filter, f1, to remove any unwanted 1046 nm beam that does not get frequency doubled. The now filtered 523 nm beam is directed, as shown, to the sample by the system of mirrors, m1a and m2, and a prism. The red laser beam is directed to m2 and the prism by mirror m1b. Redirecting the beam to the sample with a small prism is done in order to block as little of the emitted photons as possible reaching the detector. To this end, the prism sits atop a thin steel rod of similar cross-sectional area, which blocks only a fraction of the emitted radiation. After the prism, the beam passes through the approximate



Figure 4.1: Schematic of the PL optical set-up

center of the collecting lens, L1, which is placed at its focal length away from the sample. Before hitting the sample the beam has to pass through a 2" diameter 0.25" thick quartz window. The relative positions and orientations of the mirrors and prism are adjusted so that any specularly reflected beam is returned to the laser.

Emitted photons are collected into a horizontal beam by a plano-convex lens, L1 (plane side to the sample), as wide as the lens face ($\simeq 2$ ", 50.4mm), and sent to the focusing lens, L2, also a plano-convex (plane side towards the detector). This lens focuses the beam of emitted radiation to the input coupler of the fiber bundle from the detector, which is placed at the focal point

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of the focusing lens. Positions of the lenses and fiber bundle are adjusted to maximize the signal received, a 3-axis stage is used to maneuver the fiber bundle. A reference sample of strong, well-known PL is used as a measure of the optical through-put, and to check the alignment of the fiber bundle. The current set-up has comparable measured intensities to those of the old PL set-up where the fiber bundle was placed very near, $\simeq 1cm$ from the sample. The fiber bundle is connected to an Acton Spectra Pro 300i spectrometer. Currently it is equipped with two gratings, 150 $\frac{g}{mm}$ (groves per millimeter), and 600 $\frac{g}{mm}$. Typically the lower $\frac{g}{mm}$ grating is used because it has a much wider wavelength range, this gives a resolution of approximately 1.1nm. An InGaAs linear photo diode array (PDA) is used in collection of the signal.

4.2 Experimental Results

As the samples are cooled the energy of the emitted photons shifts to the blue as expected. Cooling also results in sharper peaks and an increase in intensity. Blue shifting of the band gap energy approximately follows the description given in section 2.3. The band gap corresponds to the energy of the peak in the photoluminescence. The increased intensity and decreased width is due to the decrease in the thermal linewidth with lower temperatures. Upon cooling further unexpected features begin to appear in the luminescence spectra. A second peak, and occasionally a third peak, is observed in the luminescence spectra when the pulsed laser source is used for photoexcitation. These additional low temperature peaks appear at slightly lower energy than the band gap of the samples. Therefore they will be hereafter referred to as in-gap peaks. The intensity of the in-gap peaks rises sharply as the samples are cooled below 125 K, as shown in fig. 4.2. Above 125 K the pulsed excited spectra shows only a long low energy tail. It was found that it was possible to observe emission from only the in-gap states by using a continuous wave (CW) excitation laser, as shown in fig. 4.3. A 633nm 5mW helium-neon laser was used for this purpose. The shape and intensity of the in-gap peaks vary for different concentrations of nitrogen and for different growth parameters. The in-gap spectra are shown in fig. 4.4 for the samples whose full spectra is shown in fig 4.2.

The fall off at high energy of the luminescence spectra for the pulsed pump is proportional to the Boltzmann distribution for the corresponding temperature. Lowering the temperature of the samples reduces the amount of thermal excitation to states above the conduction band minimum. This results in sharper, more intense peaks in the photoluminescence. The slope on the high energy side of the peak for the in-gap states also shows a similar temperature dependence. This suggests that electrons in these states reach thermal equilibrium with the conduction band before recombination occurs. It is assumed that the low energy slope of the peak of the in-gap photoluminescence is related to the fall off in the density of states towards mid gap.

The band gap energy of the samples tends to a constant value for temperatures below approximately 75 K, observed by a constant peak energy in the photoluminescence spectra. Fig. 4.5 shows the band gap energy of two samples as a function of temperature, along with a Varshni fit to the data. Similar results are observed for all samples regardless of growth pa-

Chapter 4. Temperature Dependence of PL

rameters. The transition temperature, where the low temperature energy limit is reached, coincides with the temperature for which the intensity of the in-gap states becomes significant: refer to fig. 4.2. Above the transition temperature, the band gap appears to have a nearly linear dependence on temperature. This anamalous behaviour has not been observed elsewhere in the literature for pressure dependent measurements[23]. Recall that the band gap energy also depends on the concentration of nitrogen, as described by equation 2.10. Fig. 4.6 shows the low temperature limit of the band gap energy as a function of nitrogen concentration, along with a fit for the expected band gap from equation 2.10 and 2.11. The fit lies above the measured values of the band gap. Also note that the slopes of the fit and the experimental data do not agree.

An increase in the overall intensity of the photoluminescence is measured when bismuth is used as a surfactant during the crystal growth process. It is also observed that some of the previously mentioned features of the photoluminescence spectra do not appear as strongly in samples where bismuth is used, as shown for example in fig. 4.7a. Several sets of samples were measured where the only change in the growth parameters was the introduction of bismuth. Note that the in-gap states photoluminescence also shows a small change with CW excitation (fig. 4.7b). Fig. 4.8 is the temperature dependence of the band gap for one set of paired samples. Note that no change is observed in the temperature dependence of the band gap with Bi surfactant. These particular samples happen to have similar concentrations of nitrogen. This is not easy to achieve since the amount of nitrogen incorporation depends on bismuth flux as well as other growth parameters[5].

N atoms on Ga	Energy, meV	N atoms in Chain	Energy, eV
2	-90	2	-90
3	-165	3	-270
4	-260	4	-400
		5	-480
· · · · · · · · · · · · · · · · · · ·		6	-500

 Table 4.1: Energies of nitrogen cluster states relative to conduction band

 minimum[24]

4.3 Evidence for Nitrogen Cluster States

It is believed the above mentioned features in the low temperature luminescence are due to the presence of randomly distributed nitrogen clusters and isolated nitrogen impurity states in the GaN_xAs_{1-x} crystals. Clusters in GaN_xAs_{1-x} consist of two or more nitrogen atoms in close proximity to one another within the lattice. This occurs when two or more nitrogen atoms are bonded to a single Ga centered tetrahedron or by simply having nitrogen atoms neighbouring or near other nitrogen atoms on different Ga centers. The neighbouring nitrogen atoms bonded to different Ga centers may have a linear arrangement, in which case they are referred to as chains. The assumption is made that the nitrogen is incorporated only substitutionally on As sites and not interstitially. The small amount of interstitial nitrogen present in the crystal maya also contribute to the in-gap states, but it is not known what the contribution is. Shown in table 4.1 are the theoretically calculated[24] energies for the cluster states (CS). The single nitrogen

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impurity produces a resonant state in the conduction band approximately 150 meV[24] above the conduction band minimum. These states have been shown to be highly localized around the impurity or cluster[24] and have much weaker pressure dependence than does the conduction band[25].

With the relatively high concentrations of nitrogen in the samples studied here, the localized states will produce a distribution of bound states below the conduction band minimum, which in turn gives the density of states as shown schematically in fig. 4.9. The electrons in the conduction band will be in thermal equilibrium with the cluster states to an energy depth, ε^* . This means states in the gap above ε^* will be populated according to a Boltzmann distribution. The threshold, ε^* , for thermal excitation corresponds to the deepest trap from which an electron can escape during its lifetime (i.e. before recombination occurs). This will be referred to as the kinetic limit model[26]. In this model, ε^* corresponds to a demarcation energy which separates the states which are in equilibrium with the band from those that are not. The population of the cluster states is kinetically limited and governed by progressive trapping-detrapping processes. In other words, electrons have a more difficult time finding the clusters states farther below the conduction band minimum, where the states are less dense. It is also possible that the cluster states give rise to a quasi-Fermi level just below the conduction band minimum [26]. This would happen if the pump intensity were sufficiently strong to completely fill the cluster states up to some level, ε_{fn} . Population of the states in this case is governed by the excitation intensity. Both models would have a distribution of occupied states similar to that shown in fig. 4.9.

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Further investigation is needed in order to be able to establish which model is the correct interpretation.

Recombination from electrons in the cluster states that are not in thermal equilibrium into the band results in the second peak observed in the luminescence spectra. For the lower concentrations of nitrogen measured a third peak is also seen in the spectra, leading to the belief that certain cluster configurations are more likely to form in these crystals. The CW laser allows for long recombination lifetimes of the electrons through lower electron-hole pair density, therefore the excited electrons are able to thermalize deeper into the distribution of the in-gap states. This results in the spectra observed in fig. 4.3. For increasing temperature, electrons populating the cluster states are more likely to be thermally excited to the conduction band, leading toa less rapid variation of population with temperature.

The single nitrogen impurity state that lies inside the band at room temperature is expected to be less temperature dependent than is the CBM, based on their respective pressure dependencies[25]. Therefore, as the samples are cooled the CBM moves to higher energies approaching the energy of the impurity state. It is suspected that some of the nitrogen clusters states will move into the gap for decreasing temperature, since we expect the density of cluster states to be higher for higher energies. At low temperatures progressively smaller clusters (next nearest neighbour dimers for example) will appear in the band gap. The conduction band edge may become more nitrogen-like, and therefore less temperature dependent than the GaAs based conduction band. This may explain why the temperature dependence of the band gap of the GaN_xAs_{1-x} alloys are weaker than the GaAs parent material.

The measured differences in the photoluminescence of samples grown with and without bismuth leads to the conclusion that the introduction of bismuth during the growth of the GaN_xAs_{1-x} crystals reduces the number of nitrogen clusters present in the material. The increase in the intensity of the room temperature PL with bismuth[4] and other surfactants[7] has been previously been reported, but not explained. A reduction in the number of nitrogen clusters may be expected to reduce the number of non-radiative recombination centers.





Figure 4.2: Photoluminescence spectra of bulk GaN_xAs_{1-x} as a function of temperature for pulsed photoexcitation



Figure 4.3: Photoluminescence of GaN_xAs_{1-x} with pulsed and CW excitation lasers. The CW emission spectrum has been adjusted so that the low energy fall-offs match





Figure 4.4: Photoluminescence spectra of bulk GaN_xAs_{1-x} as a function of temperature for CW photoexcitation



Figure 4.5: Band gap Energy GaN_xAs_{1-x} as a function of temperature



Figure 4.6: Measured low temperature band gap for various nitrogen concentrations in GaN_xAs_{1-x} and expected fit



Figure 4.7: Comparison of the photoluminescence spectra of samples grown with and without bismuth. Pulsed excitation in a) and CW excitation in b)



Figure 4.8: Energy as a function of temperature for sample with and without bismuth. The error in the band gap energy is ± 0.002 eV for temperatures lower than 100 K



Figure 4.9: Sketch of the density-of-states for GaN_xAs_{1-x} . Also shown is the expected distribution of occupied for a) various threshold energies E^{*} relative to the conduction band minimum (CBM) and b) for increased temperature

Chapter 5

Conclusions

A closed cycle optical cryostat has been designed and implementationed. It has proven to be capable of achieving the desired low temperatures. While the system that has been developed performs as well as hoped, improvements can still be made. The addition of a sapphire window to the heat shield would allow for even lower temperatures to be reached during photoluminescence measurements. Other small modifications could be made to improve sample turn-over time. These would improve experimental productivity.

Photoluminescence investigations of GaN_xAs_{1-x} semiconducting crystals have shown evidence of in-gap states which we attribute to nitrogen clusters in the material. The clusters have been found to gives states with energies in the band gap near the minimum of the conduction band. It is believed that these cluster states are a direct cause of the loss of photoluminescence intensity observed with the incorporation of nitrogen. Use of bismuth as a surfactant, during the growth process of the samples reduces the density of the nitrogen clusters. The bismuth surfactant increases the intensity of the photoluminescence and decreases the relative intensity of the photoluminescence from the in-gap states. Further investigations are warranted in order to develop a more detailed understanding of the cluster states. Along

Chapter 5. Conclusions

with the emission spectra measured here, absorption spectroscopy would give an insight into the nature of the cluster states and the effect bismuth surfactant has on them. The addition of a tunable laser to the experimental set-up would allow for photoluminescence excitation (PLE) experiments to be carried out. As always, more samples should be investigated, especially samples with growth parameters different from those measured here. The effect of increased nitrogen content, the addition of indium and the use of other surfactants such as antimony, would also be of interest.

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Appendix A

Design Specifications of the System

In the following pages are found the design specifications for the cryostat. Shown below, fig. A.1, is a cut-away view of the entire set-up.



Figure A.1: Cryostat set-up designed for semi-conductor crystal characterization





Appendix A. Design Specifications of the System













Figure A.7: Assembled sample stage

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Appendix A. Design Specifications of the System



Figure A.9: Stainless steel thermal bridge







Appendix A. Design Specifications of the System

Figure A.11: Heater block



Figure A.12: Sample mount







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Figure A.15: Center piece of the heat shielding



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Figure A.17: Top most piece of the heat shielding modified for PL

Appendix A. Design Specifications of the System

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Appendix B

Cryocooler Cooling Capacity

For possible future consideration of upgrading the power input to the sample mount above the present value of 3 W, it will be necessary to consider the amount of cooling power capabilities of the cryostat. Shown in fig. B.1 as a function of both first and second stage temperature is the cooling power of the cryocooler set-up. Inputting more than the specified amount of thermal power to the cold stages will compromise the base operating temperature.





Figure 1.4 Typical refrigeration capacity of the Model 22C cryodyne cryocooler (50 Hz)

Figure B.1: Cooling capacities of the CTI cryocooler for both modes of operation