Investigation of laser cooling in semiconductors

by

Babak Imangholi

M.S., Kerman University, Kerman-IRAN, 2000
B.S., Sharif University of Technology, Tehran-IRAN, 1997

DISSERTATION

Submitted in Partial Fulfillment of the Requirements for the Degree of

Doctor of Philosophy
Optical Science & Engineering

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Dedication

This dissertation is dedicated to my parents.
Acknowledgments

I am very proud that I have spent six years of my educational life working under Professor Sheik-Bahae’s research group here at UNM. The time was full of learning and experiencing. I am sincerely appreciating Professor Sheik-Bahae and Professor Epstein for their scientific support and advise throughout my academic years at UNM. Fulfilling this project without their scientific support and encouragement would not have been possible.

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ABSTRACT OF DISSERTATION

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Abstract

The physics and engineering issues associated with laser cooling of bulk semiconductors are experimentally investigated. This research addresses the key concepts of internal and external quantum efficiency in a semiconductor laser cooler. The former describes how optical excitations at the semiconductor band-edge recombine radiatively and the latter is a measure of how well recombination radiation is removed from the cooling device. The quantum efficiency of a GaAs device is affected by optical absorption, device processing and geometry, and background temperature. The technique of differential luminescence thermometry (DLT) was developed to provide a real-time, non-contact temperature measurement of semiconductors with an unprecedented accuracy of $< 100 \mu^oK$. Using DLT, a record external quantum efficiency of 99% has been obtained with a GaAs laser cooler held at $100^oK$. The knowledge gained in the research described here is essential for the realization of net laser cooling in semiconductors.
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## Glossary

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<thead>
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>Al</td>
<td>Aluminum</td>
</tr>
<tr>
<td>AlAs</td>
<td>Aluminum arsenide</td>
</tr>
<tr>
<td>BRF</td>
<td>Birefringence filter</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge couple device</td>
</tr>
<tr>
<td>CW</td>
<td>Continues wave</td>
</tr>
<tr>
<td>DLT</td>
<td>Differential luminescence thermometry</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>EQE</td>
<td>External quantum efficiency</td>
</tr>
<tr>
<td>EXE</td>
<td>Extraction efficiency</td>
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<tr>
<td>FTIR</td>
<td>Fourier transform infra red</td>
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<tr>
<td>GaAlAs</td>
<td>Gallium aluminum arsenide</td>
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<tr>
<td>GaAs</td>
<td>Gallium arsenide</td>
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<tr>
<td>HMDS</td>
<td>Hexamethyldisilane</td>
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<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
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# Glossary

<table>
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<th>Abbreviation</th>
<th>Full Form</th>
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<tr>
<td>GaInP</td>
<td>Gallium indium phosphate</td>
</tr>
<tr>
<td>IQE</td>
<td>Internal quantum efficiency</td>
</tr>
<tr>
<td>PLE</td>
<td>Photoluminescence excitation</td>
</tr>
<tr>
<td>MPE</td>
<td>Multiphonon emission</td>
</tr>
<tr>
<td>MPL-E</td>
<td>Modified photoluminescence excitation</td>
</tr>
<tr>
<td>PMT</td>
<td>Photo multiplier tube</td>
</tr>
<tr>
<td>RE – doped</td>
<td>rare-earth doped</td>
</tr>
<tr>
<td>SB – E</td>
<td>Sheik-Bahae and Epstein</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silicon dioxide</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>TPA</td>
<td>Two photon absorption</td>
</tr>
<tr>
<td>T.E</td>
<td>Thermo-electric</td>
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<tr>
<td>ZnS</td>
<td>Zinc Sulfide</td>
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<td>ZnSe</td>
<td>Zinc Selenide</td>
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Chapter 1

Introduction

1.1 Overview

Laser cooling of solids is the process of lowering the temperature of a condensed matter system by illuminating it with laser light. The plausibility of this phenomenon was predicted by Pringsheim in 1929, more than 30 years before the laser was invented [1]. Another 35 years passed before suitable sample quality was available to allow the first experimental demonstration of net laser cooling by Richard Epstein and co-workers at Los Alamos National Laboratories in 1995 [2].

The essential principle of radiative cooling is that the thermal energy of a material is carried away by luminescence photons. A necessary condition for laser-induced cooling is that the system be excited at a wavelength longer than the mean luminescence wavelength ($\lambda_f$). This condition is known as anti-Stokes luminescence.

To achieve laser cooling, thermal energy must be removed from the system in the three-step process illustrated in Fig. 1.1. The cooling cycle proceeds as follows: i) a pump photon with energy less than the mean luminescence energy ($h\nu$) is absorbed
to create excited electrons, ii) the optically excited electrons gain additional thermal energy from the lattice through phonon absorption and equilibrate with lattice, and iii) excited electrons return to ground state by emitting photons with an average mean photon energy \( (h\nu_f) \) that is higher than the pump photon \( (h\nu) \). If the excitations decay primarily by photon emission and these luminescence photons are efficiently removed from the sample without heating it, net cooling can occur.

Figure 1.1: Left) The laser cooling cycle in a solid. Cold electrons are generated in the excited manifold \( |2\rangle \) using photons with energy \( h\nu \). Electrons absorb lattice energy and redistribute it in the two manifolds. Electrons return to ground state via photon emission at \( h\nu_f \), which carries away thermal energy of lattice. (Right) Absorption and emission of a typical two level system. Pump laser wavelengths longer than mean luminescence wavelength \( (\lambda_f) \) must be used to achieve cooling.

An all solid-state laser cooling system is of great interest for a wide variety of applications because it is compact, vibrationless, reliable, long-lived, efficient, and produces minimal radiation compared to conventional refrigeration concepts. In addition, no refrigeration fluids (freon gases or liquid cryogens, for example) are involved.
Chapter 1. Introduction

Thermo-electric (TE) coolers based on the Peltier effect are the most relevant competing technology to laser cooling. While TE coolers possess most of the engineering advantages of laser coolers, their ultimate absolute temperature is limited. Multi-stage TE coolers have not been pushed lower than $\sim 150$ K, which is already in the temperature range of state-of-the-art laser cooled glasses [3]. The design of TE coolers trades off absolute temperature for cooling power. In contrast, laser cooled glass can achieve temperatures comparable to a multi-stage TE cooler in a single stage [4, 5]. The estimated cooling power obtained at various temperatures for TE coolers and a Yb$^{3+}$:ZBLAN laser cooler is compared in Fig. 1.2.

Figure 1.2: Calculated performance comparison of a Yb$^{3+}$:ZBLAN laser cooler and thermo-electric cooler technology [4, 5].

Pringsheim’s prediction was initially rejected by some scientists as contrary to the second law of thermodynamics; Landau proved its principle in 1946 [6]. He established the entropy lost by the sample is compensated by an increase in the entropy of the fluorescence light, which loses monochromaticity, phase coherence, and directionality. Kastler suggested that rare-earth doped (RE-doped) crystals might provide a medium for solid-state cooling using anti-Stokes emission [7]. Net laser cooling remained elusive until 1995, however, due to material purity issues.
Chapter 1. Introduction

The pioneering experiments at Los Alamos used a polished, high purity glass sample doped with ytterbium (Yb) atoms. The cooling process occurs in the Yb atomic system, which removes thermal energy from the glass host to achieve net cooling of the sample. Since then cooling in Yb has been observed in different host glass materials such as fluorochloride glass (Yb$^{3+}$:CNBZn), and fluoride glass (Yb$^{3+}$:BIG) by Fernandez et al [8]. Although other RE-doped systems have exhibited net cooling, Yb$^{3+}$:ZBLAN glass currently holds the record for the greatest temperature reduction below ambient in a laser cooling experiment: $\Delta T \approx 100K$ [3]. Laser cooling has also been observed in different crystals such as: Yb$^{3+}$:KGd(WO$_4$)$_2$ [9], Yb$^{3+}$:YAG [10], Yb$^{3+}$:Y$_2$SO$_5$ [10], and Yb$^{3+}$:KPb$_2$Cl$_5$ [11]. Crystals offer advantages over glass materials such as high thermal conductivity, improved ruggedness, potentially larger absorption cross sections and, in some crystals, low thermal emissivity.

Shortly after the Los Alamos work was published, cooling was reported in dye solutions [12]. This experiment has been the focus of some controversy and problems have been encountered in attempts to reproduce it. In 2000, Hoyt et al obtained net cooling in thulium-doped glass (Tm$^{3+}$:ZBLAN) at about twice the laser wavelength of the Yb experiment [13]. This work was important because it confirmed energy gap scaling predictions, led to a record amount of cooling power (i.e. heat lift), and a temperature decrease of 26 K from room temperature [14]. Cooling by an amount of 1.5 K has been observed in a Tm$^{+3}$-doped BaY$_2$F$_8$ crystal by Patterson et al [15].

The ultimate efficiency of a laser cooler is its ‘quantum-limit’ cooling efficiency, determined by referring to Fig. 1.1. The cooling efficiency is the ratio of the removed thermal quantum to the pump photon energy:

$$\eta_{qc} = \frac{h\nu_f - h\nu}{h\nu} = \frac{\lambda - \lambda_f}{\lambda_f}. \quad (1.1)$$

where $\lambda_f = c/\nu_f$. This is obtained assuming all the fluorescence light is dumped in a heat sink and thus wasted. If, however, the escaping light is captured by a pho-
tovoltaic device to recycle this energy, the ultimate cooling efficiency can approach the Carnot limit [16].

Equation 1.1 indicates the cooling efficiency can be made arbitrary large by selecting $h \nu \ll h \nu_f$ (i.e. $\lambda \gg \lambda_f$). Practical considerations, however, dictate that $\Delta h \nu = h \nu_f - h \nu$ be of the order of the thermal energy $k_B T$. This is imposed, as will be discussed in more detail later, by vanishing optical absorption as $h \nu \ll h \nu_f$ as well as the presence of parasitic background absorption. The quantum cooling efficiency is then approximated by a more practical limit:

$$\eta_{qc} \approx \frac{k_B T}{E_{gap}}.$$  (1.2)

where the approximation $h \nu_f \sim E_{gap}$ has been made.

There are additional complications that reduce the cooling efficiency of a real device below that defined in Eq. 1.2. Some of the optical excitations decay via non-radiative or heat-producing channels. Internal quantum efficiency is defined as the ratio of the radiative recombination to the sum of the radiative plus non-radiative recombination:

$$\eta_{int} = \frac{W_r}{W_r + W_{nr}}.$$  (1.3)

Not all the luminescing photons escape from the cooling device; this is quantified with an extraction or escape efficiency coefficient $\eta_e$. This defines the external quantum efficiency $\eta_{ext}$, in which $\eta_e$ modifies the internal efficiency as follows:

$$\eta_{ext} = \frac{\eta_e W_r}{\eta_e W_r + W_{nr}} \approx \eta_{int} \frac{1}{\eta_e}.$$  (1.4)

In an ideal system, both the internal and external quantum efficiency are unity. This condition can never be achieved in practice, hence deleterious heating of the
sample occurs. If the internal and external quantum efficiency are not well managed, this heating can overwhelm the laser cooling process.

Accounting for the external quantum efficiency, the cooling efficiency is modified as follows (derivation will be given in Chapter 2):

\[ \eta_c = \eta_{ext} \frac{\nu_f}{\nu} - 1 \]  

(1.5)

An important operational consideration is that all the incident laser power may not be absorbed in the desired state. This is of primary importance for laser cooling of glasses. The presence of background absorption leads to a resonance absorption efficiency, defined as

\[ \eta_{abs} = \frac{\alpha(\nu)}{\alpha(\nu) + \alpha_b} \]  

(1.6)

where \( \alpha(\nu) \) is the resonant absorption and \( \alpha_b \) is the parasitic background absorption of pump light. When the situation of non-ideal absorption exists \( (\eta_{abs} < 1) \), the cooling efficiency is further modified to:

\[ \eta_c = \eta_{abs} \eta_{ext} \frac{\nu_f}{\nu} - 1. \]  

(1.7)

The derivation of Eq. 1.7 will be given in Chapter 2. Net cooling is attained with the condition: \( \eta_c > 0 \). Taking \( h\nu_f - h\nu \approx k_B T \), this leads to

\[ \eta_{abs} \eta_{ext} > 1 - \frac{k_B T}{E_{\text{gap}}}. \]  

(1.8)

For a material with energy gap of \( \sim 1 \) eV at room temperature, absorption efficiency and external quantum efficiency must be managed properly to achieve \( \eta_{abs} \eta_{ext} > 97.5\% \) if laser cooling is to be realized. According to Eq. 1.2, the cooling
efficiency of smaller energy gap materials is higher. This simple scaling relation has been verified experimentally in a comparative study of Tm- and Yb-doped ZBLAN [13].

The ultimate efficiency of an optical cooling device is limited by temperature (see Eq. 1.2). This is a manifestation of absorption narrowing that is a consequence of depleted phonon populations. In RE-doped glasses and crystals, optical transitions occur between manifolds of states (see Fig. 1.1). The population of electrons within each manifold is determined by the Boltzmann distribution under a local thermal equilibrium assumption [17]. As the temperature drops, the population of higher states in the ground manifold $|1\rangle$ drops (see Fig. 1.1). The electron supply for the laser cooling process comes from lower energy states in the ground manifold $|1\rangle$. As $\nu$ approaches $\nu_f$ in RE-doped materials, $\eta_{qc}$ approaches zero. This ground state “condensation” limits the ultimate cooling of Yb to $\sim 100$ K [5].

Laser cooling of semiconductors is very attractive because absolute temperatures far lower than the RE-doped glass system can be reasonably expected. The reason for this is discussed in the following section. In addition, semiconductor laser cooling offers the exciting possibility of a “refrigerator on a chip”. This means the cooling system could be integrated with, for example, a high performance opto-electronic device such as an infrared sensor.

No reliable report of net laser cooling in semiconductors exists at the time this dissertation is written. The physics issues and engineering obstacles associated with laser cooling of semiconductors are studied here in a detailed experimental investigation. It is concluded that realization of laser cooling in semiconductors is now largely an engineering problem. Once these challenges are overcome, laser cooling in direct bandgap semiconductors such as GaAs will be possible.
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1.2 Laser cooling of semiconductors

Semiconductor laser cooling has three primary advantages when compared to RE-doped systems: i) semiconductors have higher excitation density per unit volume leading to greater cooling power, ii) advanced growth and fabrication technology exists allowing for integration with optoelectronic components, and iii) achieving temperatures as low as $\sim 10$ K may be possible.

RE-doped glasses and crystals do not have reasonable expectations for reaching temperatures on the order of 10 K. The limitation, as discussed earlier, is imposed by Boltzmann statistics that govern the electron distribution in the ground state manifold. In contrast, electrons in semiconductors obey Fermi-Dirac statistics in a continuum of states. Fermi-Dirac statistics ensure that a large supply of ground-state electrons are available for optical excitation, even at absolute zero. This means that, in principle, there is no fundamental physical limitation affecting the laser cooling cycle of a direct bandgap semiconductor at very low temperatures.

A direct bandgap in semiconductor materials means that the minimum of the conduction band lies directly above the maximum of the valence band in momentum space. In a direct bandgap semiconductor, electrons in the conduction-band can combine directly with holes in the valence band while conserving momentum without any phonon mediations. The energy of the recombination across the bandgap will be emitted in the form of a photon of light. This radiative recombination is called luminescence in semiconductors. In indirect bandgap semiconductors such as crystalline silicon, the conduction band minimum and valence band maximum are not located at the same point in momentum space; a direct transition across the bandgap does not conserve momentum and is forbidden. Recombination occurs with the mediation of a third body, such as a phonon or a crystallographic defect, which allows for conservation of momentum. These recombinations will often release the bandgap
energy in the form of phonons and thus do not emit light. As such, light emission from indirect semiconductors is very inefficient and weak. The laser cooling process is only feasible in direct bandgap semiconductors where radiative recombination is efficient.

In principle, any direct-gap semiconductor that exhibits anti-Stokes luminescence has potential for laser cooling. There are other complicating issues, however, that quickly narrow the list of candidate materials. The various design tradeoffs will be discussed at length in this dissertation. Important considerations include the availability of mature fabrication technology to maximize internal quantum efficiency, bandgap energy compatibility with high power laser sources, and the deleterious effects of Auger recombination that increases at smaller bandgap energy. With these and other considerations in mind, the UNM research effort has been directed exclusively at high quality, bulk GaAs. An experimental spectrum of anti-Stokes luminescence in GaAs is shown in Fig. 1.3

![Figure 1.3: Anti-Stokes luminescence of GaAs at 295 K. The sharp spike is from the pump laser.](image-url)

Observing anti-Stokes luminescence with a semiconductor by itself is not an indication of laser cooling. The fundamental condition required by Eq. 1.8 must also
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be satisfied. Laser cooling of semiconductors must deal with efficiency issues that are more severe compared to transparent glasses and crystals. Great care must be expended to maximize the external quantum efficiency. To achieve this, one requires an extremely small amount of non-radiative recombination to maximize the internal quantum efficiency and a highly efficient method to remove the luminescence photons.

To address the former problem, GaAs heterostructures have been developed by our collaborators at the National Renewable Energy Laboratory (NREL). The heterostructures employ surface passivation to reduce the primary non-radiative recombination pathway that exists there. Record amounts of internal and external quantum efficiency have been measured at UNM, a result that has implications for the operation of high performance solar cells [18].

The much higher index of refraction encountered in semiconductors \((n \sim 3)\) compared to transparent crystals and glass \((n \sim 1.5)\) means that a greater amount of luminescence is trapped in semiconductors. Laser cooling requires that luminescence be removed from the illuminated material to air or vacuum \((n = 1)\). Snell’s Law dictates that total internal reflection will occur for a range of incidence angles when light attempts to propagate across a high- to low-index interface. The larger the index mismatch, the smaller the escape cone for light rays propagating in the material. This is a similar problem in light emitting diodes (LED’s) [19]. The light extraction efficiency is \(\eta_e \sim 2\%\) for a slab of a bare GaAs (see Chapter 4). In Tm\textsuperscript{3+}:ZBLAN, \(\eta_e\) corresponds to \(\sim 74\%\) [20].

1.2.1 Historical development

The first attempt to cool GaAs with laser light used a dome lens scheme for luminescence removal as reported by Gauck et al [21] (1996). They placed a passivated GaAs
heterostructure between a flat piece of sapphire and a transparent ZnSe dome lens. The entire assembly was clamped using copper wires to achieve an optical interface between the sample and dome. Their laser cooling experiment was pumped with a tuneable Ti:sapphire laser. Although no net cooling was attained, they observed reduced heating when the laser was tuned below the mean luminescence wavelength while maintaining the same excitation density. This was the first experimental evidence indicating that laser cooling of a semiconductor was possible. An external quantum efficiency of $\eta_{ext} \sim 96\%$ was deduced for their device.

Gfroerer et al. [22, 23] (1998) attempted laser cooling with the semiconducting alloy InGaAs using a Si dome lens and also an InP parabolic reflector. Even though the luminescence extraction efficiency is $\sim 2 \times$ greater than the GaAs/ZnSe system, the measured external quantum efficiencies were only $\sim 43\%$ with a Si dome lens and 63% for a InP parabolic reflector, i.e. considerably less than Gauck et al. This was attributed to a much larger rate of non-radiative Auger recombination that impaired the internal quantum efficiency and hence degraded $\eta_{ext}$ [24].

Finkeissen et al. [25] (1999) claimed to observe local laser cooling in three double heterostructure GaAs/AlGaAs quantum wells held at a nominal temperature of 40 K. This experiment has been critically re-examined, however, and their interpretation has been found to be flawed for reasons relating to light management, cooling power, luminescence extraction, and complications in their method of non-contact temperature measurement. An analysis of this experiment is presented in chapter 6.

Lin et al. [26](2004) were interested in thermo-photovoltaic process. This is direct energy conversion from heat differentials to electricity via photons. A basic thermophotovoltaic system consists of a thermal emitter and a photovoltaic diode. The principle of the thermo-photovoltaic process is similar as anti-Stokes light cooling.

1. Lin et al. aimed to demonstrate cooling of a GaAs thin film by photoluminescence.

\[1\text{In thermophotovoltaics (TPV) an emitter is heated up to a high temperature and emits}\]
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instead of electroluminescence, primarily to avoid heating at the electrical junctions. An external quantum efficiency of 96% was measured for an undoped planar sample on a transparent substrate using the dome lens light extraction scheme.

There have been theoretical investigations on laser cooling with semiconductors. Oraevsky [27] (1996) and Rivlin et al [28] (1997), considered the cooling of a semiconductor crystal via anti-Stokes luminescence. They estimated the optimum carrier density and the lowest attainable temperature. Malshukov et al [29] (2001), suggested combining the ideas of laser cooling and thermionic cooling. They proposed an opto-thermionic cooling process and investigated cooling caused by light emission from a quantum well embedded into a semiconductor p-n junction. Rayner et al [30] (2003), reviewed progress on laser cooling of solids and discussed candidate materials for laser cooling including gases, dyes, crystals, semiconductors, and iron-doped glasses.

Sheik-Bahae and Epstein [31] (2004), theoretically investigated laser cooling based on photon absorption and recombination processes in semiconductors. They considered the critical issues of luminescence trapping and red-shifting which had not been taken into account previously. They comprehensively discussed experimental conditions needed to attain net cooling in GaAs.

Huang et al [32, 33, 34](2004-2005) introduced a nonlocal energy-balance equation for the optical absorption, photoluminescence, and inelastic electron-phonon scattering, which determines the electron and hole temperatures for any given lattice temperature. They found laser cooling to be more efficient for large bandgap materials, a weaker laser field, and a high initial lattice temperature. They proposed a four-step laser cooling model for AlGaAs/GaAs semiconductor quantum wells. They also proposed a successive four-step model for spatially selective laser cooling infrared light. Above bandgap photons can then be converted into power by photovoltaic cells at room temperature.
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of carriers in undoped semiconductor quantum wells. Apostolova et al [35] (2005) theoretically investigated laser cooling of wide-band-gap semiconductors. A generalized nonlocal energy-balance method showed that the wide-gap semiconductor AlN could be cooled via nonlinear three-photon absorption from a low power cw He-Ne laser. High-order nonlinear excitation of a semiconductor is highly inefficient even with a powerful pulsed laser, so this prediction must be viewed with considerable skepticism.

Zhang et al and Yu et al [36, 37] (2006) theoretically investigated cooling via electroluminescence. Electrons can be excited from the valence band to the conduction band in a semiconductor p-n junction with an applied bias. The principle of anti-Stokes electroluminescence refrigeration is the same as laser cooling. Electroluminescence cooling, however, has an additional complication not present in laser cooling: ohmic heating must be reduced below the cooling power. This is a formidable problem.

1.3 Summary: Key results and insights

In this dissertation, the prospects for laser cooling in GaAs are theoretically and experimentally investigated. The various engineering obstacles are identified and solutions to overcome them are described. A detailed description of experiments to examine the various issues involved in laser cooling of GaAs are presented.

In Chapter 2, the cooling process in bulk intrinsic direct bandgap semiconductors is investigated theoretically. The external quantum efficiency (EQE) and cooling condition are derived based on recombination processes and geometry-dependent luminescence extraction efficiency. In Chapter 3, the construction and characteristics of a cw Ti:sapphire laser are discussed. This Ti:sapphire laser is used as a pump source in cooling experiments with GaAs. Chapter 4 discusses and compares differ-
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ent light extraction schemes. Chapter 5 is dedicated to semiconductor engineering and device fabrication for laser cooling experiments. The characterization of semiconductor parameters and laser cooling experiments with GaAs are presented in Chapter 6. The non-radiative recombination coefficient is theoretically and experimentally investigated as well as the effect of epitaxial lift-off and processing. A comprehensive study of laser cooling and EQE measurements at different temperatures are presented. A new non-contact, high resolution temperature measurement scheme is developed and implemented. The concluding chapter summarizes the results and outlines future experiments that should allow the observation of net laser cooling in GaAs.
Chapter 2

Foundations of laser cooling in semiconductors

In this chapter the model of laser cooling is discussed. This model incorporates optical absorption, electron-hole pair recombination, and band structure.

Optical transitions in atoms such as rare earth-doped materials occur between discrete levels. Semiconductors are characterized by continuous bands. The study of optical processes in semiconductors usually requires some knowledge of the band structure. In general, a complete description of the energy states of electrons and ions is obtained by solving the Schrödinger equation for each individual particle. The optical transitions relevant for laser cooling in semiconductors (absorption and luminescence) involve electrons in an energy interval that is a small fraction of an eV both in the conduction band (CB) and the valence bands (VB) [38]. It is sufficient to understand the band structure within a few $k_B T$ of the band extrema, thereby allowing perturbation methods to be used. Bloch’s theorem states that electrons in a periodic potential have wave functions and energies that are periodic in wave vector up to a constant phase between neighboring reciprocal lattice vectors. The $k.p$
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perturbation theory is based on Bloch wavefunction in a periodic potential around the extrema. The wave function can be described mathematically by \( \Psi(r) = e^{i \mathbf{k} \cdot \mathbf{r}} u(r) \) where the function \( u(r) \) is periodic over the crystal lattice. Near the band edges the Schrödinger equation for electrons can be solved using \( k.p \) perturbation to give a simple effective mass picture. In essence, conduction electrons behave as if they are in the free space except their masses are modified from the bare electron mass. The mathematical formalism and a comprehensive discussion of \( k.p \) theory can be found in semiconductor textbooks [38, 39]. Near zone center, there are four primary energy bands of a direct bandgap semiconductor as shown in Fig. 2.1.

![E-k relation](image)

Figure 2.1: E-k (Energy vs wave vector) relation for the four most important bands in a direct bandgap semiconductor. There is a single conduction band (CB) and three valence bands (VB): heavy-hole (hh), light-hole (lh), and split-off (so). The CB and VB minima are separated by the bandgap energy \( E_g \).

Electrons move in the conduction band with the effective mass \( m_{ce} \). The effective mass is different than the bare mass due to the Coulomb potential felt by electrons in a solid [39]. In the valence bands, the displacement of electrons in the lattice looks like positive ions (holes) moving in the opposite direction of bound electrons with
effective masses $m_{hh}$, $m_{lh}$, and $m_{so}$. The dispersion relations are:

$$E_{c} = E_g + \frac{\hbar^2 k^2}{2m_{ce}},$$  \hspace{1cm} (2.1)

and

$$E_{hh} = -\frac{\hbar^2 k^2}{2m_{hh}}, E_{lh} = -\frac{\hbar^2 k^2}{2m_{lh}}, E_{so} = -\Delta - \frac{\hbar^2 k^2}{2m_{so}},$$  \hspace{1cm} (2.2)

where $E = 0$ is taken as the top of the valence band. The bandgap energy, $E_g$ is the energy difference between the top of the valence band and the bottom of the conduction band. The energy $\Delta$ is the difference between the top of the $hh$ and $lh$ bands and the top of the $so$ band. The optical transitions of interest in laser cooling occur between the conduction band and lowest energy valence bands.

In the laser cooling process, electrons are excited from top of the valence band ($hh$ and $lh$) to the bottom of the conduction band (see Fig. 2.1). The excited electron distribution is initially colder than the lattice. Photo-carriers interact with the lattice and on average absorb net lattice energy and they warm up to the lattice temperature. This causes the e-h Fermi-Dirac distributions to acquire a higher temperature. The e-h recombine by either: i) emitting photons or ii) recombining non-radiatively by giving up their energy as heat to the lattice. In this chapter, a mathematical description of these different recombination processes is presented. The electron-lattice interaction is one of the fundamental steps in the laser cooling process. In the next section, the electron-lattice interaction is introduced briefly.

### 2.1 Electron scattering by lattice.

The Bloch electrons in a crystalline semiconductor suffer collisions with various imperfections and have their wave vector changed from an initial value $k$ to a final
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value $k'$. There are various mechanisms for scattering; for example, the presence of a localized impurity ion produces a Coulomb potential that can scatter an electron, changing its wave vector and energy. One of the most important scattering mechanisms is the electron-lattice interaction, which is responsible for carrier relaxation in the conduction and the valence bands. Electrons and holes can both absorb and emit phonons, which are the quanta of lattice vibrations. To model laser cooling, it is necessary to have an understanding of electron-lattice scattering and how the scattering probabilities are calculated. Although a detailed mathematical description of this interaction is beyond the scope of this dissertation, an outline of basic physics will be presented.

An electron moving in a rigid periodic crystal potential with no applied force is not scattered by the atoms of the crystal. When a force from the lattice is applied to an electron, its acceleration can be described by Newton’s law where the perfect periodic crystal potential is taken into account by an effective mass. This perturbation is referred to as a scattering potential $\Delta U(r)$ where $r$ is the distance between the ions in the lattice and the electron. The source of such a potential is the lattice vibration. This potential describes vibrations in the lattice in different directions. Distortions of the lattice disrupt the periodicity of the potential, giving rise to a time-dependent perturbation. The lattice scattering potential can be divided into two general categories: i) Deformation potential scattering in which short range distortions of the lattice cause changes in potential due to mechanical stress. This potential is the most important scattering mechanism in undoped group IV semiconductors with no ionic molecules, such as Si and Ge; ii) Polar scattering occurs in materials where distortions cause a disruption of local electrical neutrality. This type of scattering is observed in III-V and II-VI semiconductors such as GaAs and ZnS. The mathematical formalism of deformation potential scattering and polar scattering can be found in advanced semiconductor textbooks [40, 41].
In order to understand and formulate the scattering rates, an understanding of lattice vibrations is required. The quantum of lattice vibration is a phonon. For simplicity, consider a one dimensional atomic chain. If the vibration mode is along the atomic chain, the phonon of this mode is longitudinal phonon. If the vibration mode is perpendicular to the atomic chain, the mode is transverse. In a mono-atomic chain, energy and momentum transfer from one primitive cell\(^1\) to another. If there is more than one atom per primitive cell, the spectrum shows additional high frequency features. These features are due to atomic vibrations within the primitive cell. Vibrational modes divide into two sets of eigenvalues. The higher energy modes are optical phonons; both longitudinal (LO) and transverse (TO) optical phonons exist. The lower energy phonon modes are defined over many primitive cells and are called acoustic; longitudinal acoustic (LA) and transverse acoustic (TA) phonons are formed depending on the orientation of the propagation direction to the vibrational coordinate. The phonon energy (or frequency) dispersion curve for a diatomic one-dimensional lattice chain is shown in Fig. 2.2.

\[\text{Optical branch}\]
\[\text{Acoustical branch}\]
\[1\text{st Brillouin zone}\]

Figure 2.2: Phonon dispersion curve in a diatomic one-dimensional lattice chain [40].

In non-polar crystals such as Si and Ge, electron scattering with the lattice is

\(^{1}\text{the primitive cell is a minimum unit whereby a single lattice point of a structure has translational symmetry. A lattice can be characterized by the geometry of its primitive cell.}\)
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mediated by the deformation potential for acoustic and optical phonons [42]. In polar crystalline materials such as GaAs, carrier scattering is dominated by the oscillating electric field caused by the polarization of the ions in the unit cell. Scattering with TO phonons is negligible because the macroscopic electric field due to the TO mode vanishes [43]. Hence the electron-lattice and hole-lattice interactions are largely due to the scattering of carriers with LO phonons. As is shown in Fig. 2.2, the frequency or energy of LO phonons does not change significantly across phonon momentum space.

In the laser cooling process, electrons are excited from the top of the valence band to the bottom of the conduction band. The next step in the cycle requires photo-electrons and photo-holes to absorb phonons. The temperature-dependent phonon absorption rate can be approximated as [38]:

\[ W_{\text{phonon}} = W_{\text{LO}} + W_{\text{LA}} \approx \frac{\gamma_{\text{LO}}}{\exp(\frac{\hbar \omega_{\text{LO}}}{k_B T}) - 1} + \gamma_0 T, \]  

(2.3)

where \( W_{\text{LO}} \) and \( W_{\text{LA}} \) are scattering rates for optical and acoustic phonons, respectively and \( \hbar \omega_{\text{LO}} \) is the LO phonon energy. The constant coefficients \( \gamma_0 \) and \( \gamma_{\text{LO}} \) ignore the the temperature-dependence of the carrier distributions and other factors such as screening and Pauli blocking [38]. The key message of Eq. 2.3 is that LO phonon absorption becomes disabled at sufficiently small temperatures; weaker acoustic phonon absorption is then required to maintain the laser cooling cycle. Because phonon absorption is key component of laser cooling, the efficiency of the process is reduced at lower temperature.

In GaAs, the LO phonon energy \( \hbar \omega_{\text{LO}} \approx 36 \text{meV} \). At room temperature for carriers near the band edge, \( \gamma_{\text{LO}} \approx 10^{13} \text{sec}^{-1} \) and \( \gamma_{\text{LA}} \approx 10^8 \text{sec}^{-1}K^{-1} \) [38, 44]. LO phonon absorption drops dramatically at lower temperatures. Acoustic phonon scattering \( W_{\text{LA}} \) becomes comparable to \( W_{\text{LO}} \) at about 50 K.
The phonon scattering timescale is of the order of hundreds of femtoseconds to a few picoseconds [38, 44, 45]. In a cw laser cooling experiment, phonon scattering can be assumed to occur instantaneously except at very low temperatures. In this temperature regime where only acoustic phonon absorption is operative, radiative recombination is also much stronger suggesting that efficient laser cooling may not be possible. To overcome this problem, quantum confined structures (i.e. quantum wells) may provide sufficiently enhanced acoustic phonon absorption compared to a bulk (3D) device [31].

2.2 Generation and recombination processes in intrinsic direct bandgap semiconductors.

In laser cooling of a direct bandgap semiconductor, electrons are excited from top of the valence band to the bottom of the conduction band leaving free holes in the valence band. This process is called e-h pair generation. The excited carriers thermalize with the lattice via phonon scattering and redistribute in the bands. The e-h pairs can recombine radiatively via photon emission. The photocarriers can also lose their energy to the lattice via phonon emission and recombine non-radiatively. At steady state for a given temperature, the e-h population density $N$ can be obtained by balancing the optical generation rate $G$ with the radiative ($W_r$) and non-radiative ($W_{nr}$) recombination rates as follows

$$\frac{dN}{dt} = 0 = G - W_{nr} - W_r . \quad (2.4)$$

where $G = \frac{\alpha(\nu,N)I}{h\nu}$, $I$ is the laser irradiance at frequency $\nu$, and $\alpha(\nu,N)$ is the carrier density dependent band-to-band absorption coefficient.
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In practice, not all the luminescing photons escape from the semiconductor material. This is due to the refractive index mismatch at the semiconductor-vacuum interface. Propagating from a high index semiconductor ($n \sim 3$) to vacuum ($n = 1$) leads to a substantial amount of total internal reflection and hence luminescence trapping (This subject will be discussed in detail in Chapter 4). Luminescence trapping is quantified with an extraction or escape efficiency coefficient $\eta_e$. The radiative recombination that escapes the sample is $\eta_e W_r$ and the trapped luminescence is $(1 - \eta_e) W_r$. Trapped light is re-absorbed causing additional e-h generation. Although, a fraction of luminescence may be absorbed by impurities, in high quality samples (such as samples in laser cooling) this amount is negligible. The sum of the carrier generation and loss processes modifies Eq. 2.4 as follows

$$\frac{dN}{dt} = 0 = \frac{\alpha(\nu, N) I}{h\nu} + (1 - \eta_e) W_r - W_{nr} - W_r.$$ (2.5)

which simplifies to

$$\frac{dN}{dt} = 0 = \frac{\alpha(\nu, N) I}{h\nu} - W_{nr} - \eta_e W_r.$$ (2.6)

The key conclusion in Eq. 2.6 is the net luminescence reduction from $W_r$ to $\eta_e W_r$; since absorption is weakest near the band edge, the net effect of trapping and re-radiation of light is a red-shift of the luminescence spectrum. This process is therefore detrimental to the laser cooling efficiency.

In the following sections we describe the absorption coefficient $\alpha(\nu, N)$, radiative recombination $W_r$, and non-radiative recombination $W_{nr}$. These terms allow an estimation of the e-h pair density $N$ that ultimately leads to laser cooling power.
2.2.1 Absorption coefficient in intrinsic direct bandgap semiconductors.

Fundamental absorption in a semiconductor takes place when photons with energies greater than the valence-conduction bandgap energy are absorbed. This results in the generation of an e-h pair for each absorbed photon. The transition rate $W_{abs}$ for an electron initially in state $E_a$ to the state $E_b$ by absorption of a photon is given by Fermi’s golden rule (i.e. time-dependent perturbation theory):

$$W_{abs} = \frac{2\pi}{\hbar} |H_{ab}|^2 \delta(E_a - E_b). \quad (2.7)$$

The perturbation Hamiltonian for $H_{ab}$ is due to the incident electromagnetic wave [38, 39]. The direct-absorption coefficient $^2$ for a bulk semiconductor can be derived as [39]:

$$\alpha_{h\nu} = \frac{C_0}{\hbar \nu} \int \rho_r(E) \delta_\Gamma(E + E_g - h\nu) dE, \quad (2.8)$$

where $C_0$ is a constant that includes the electron mass and dielectric constant [39]. The function $\rho_r(E)$ is the joint density of states for the conduction- and valence-bands. The $\delta_\Gamma$ term in Eq. 2.8 describes the phenomenological linewidth broadening of the transition. Linewidth broadening is caused by different scattering mechanisms, as will be discussed later in this section.

Under the assumption of no broadening, $\delta_\Gamma$ is Dirac’s $\delta$ function and Eq. 2.8 simplifies to

$$\alpha_{h\nu} = \frac{C_0}{\hbar \nu} \rho_r(h\nu - E_g). \quad (2.9)$$

$^2$does not involve phonon momentum [39]
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The energy dispersion of the conduction and valence bands for the simple parabolic case is given by Eqs. 2.1 and 2.2. The allowed photon energies for direct transitions from the hh valence band to the conduction band can be written as:

\[
\hbar \nu = E_c - E_v = E_g + \frac{\hbar k^2}{2m_r},
\]

where \(m_r = \frac{m_{ce}m_{hh}}{m_{ce} + m_{hh}}\) is the reduced e-h effective mass. The density of states is the number of electronic states in a band per unit energy per unit volume of the material. In a bulk semiconductor, the total number of states per unit volume can be derived from the density of states following Refs. [38, 39]:

\[
\int \rho(E) dE = \int \frac{k^2}{\pi^2} dk.
\]

By substituting \(k\) from Eq. 2.10 in Eq. 2.11, the density of states for a parabolic band structure can be written as:

\[
\rho_r(h\nu - E_g) = \left(\frac{4\pi}{\hbar^3}\right)(2m_r)^{1.5}(h\nu - E_g)^{1/2}.
\]

From \(k \cdot p\) theory the reduced mass \(m_r\) can be expressed in terms of the bandgap energy \(E_g\) and the energy-momentum matrix element \(E_P\) \(^3[39, 38]\):

\[
\frac{m_r}{m_0} = \frac{E_g}{E_P}
\]

where \(m_0\) is the bare electron mass.

The band-to-band resonant absorption in a parabolic structure can be derived from Eqs. 2.13, 2.12 and 2.9 to be

\[
\alpha_0(\nu) = \kappa \frac{E_g}{h\nu} (h\nu - E_g)^{1/2},
\]

\(^3\)The \(E_p = \frac{2m_a P^2}{\hbar^2}\) where \(P\) is the matrix element of the momentum operator between the conduction and the valence band [39]. In GaAs \(E_p \approx 28.8 eV\) [46].
where $\kappa \approx 10^4 \text{cm}^{-1}(\text{eV})^{-1/2}$ is a constant coefficient. Additionally near the band edge, $\frac{E_g}{h\nu} \sim 1$ and Eq. 2.14 modifies to

$$\alpha_0(\nu) = \kappa (h\nu - E_g)^{1/2},$$  \hspace{0.5cm} (2.15)

At low e-h population in the conduction band, the absorption coefficient in a parabolic band structure is described by Eq. 2.15. When a large population density of e-h are generated, the absorption coefficient can no longer be represented by Eq. 2.15. In this case the probability of finding a bound electron in the valence band and a vacancy in the conduction band should be taken into account. Considering these probabilities, Eq. 2.15 modifies to [38, 39]:

$$\alpha(\nu, N) = \alpha_0(\nu)(f_{ev} - f_{ec}) .$$  \hspace{0.5cm} (2.16)

The terms $f_{ev}$ and $f_{ec}$ are Fermi-Dirac probabilities for the electrons in the valence and conduction bands respectively:

$$f_{ev}(E) = \frac{1}{\exp\left(\frac{E - F_e}{k_B T}\right) + 1},$$  \hspace{0.5cm} (2.17)

and

$$f_{ec}(E) = \frac{1}{\exp\left(\frac{E - F_h}{k_B T}\right) + 1},$$  \hspace{0.5cm} (2.18)

where $F_e$ and $F_h$ are quasi-Fermi energies.

The absorption $\alpha(\nu, N)$ depends on population density $N$ through the Fermi energy levels $F_e$ and $F_h$. At low e-h population density, $F_e \approx F_h \approx \frac{E_g}{2}$ and $f_{ev} \approx 1$ and $f_{ec} \approx 0$ [38, 39]. At low e-h population density, the absorption coefficient is density-independent. At high levels of optical pumping, band filling occurs and
Figure 2.3: Theoretical and experimental absorption coefficient in GaAs. Theory is the solid line and experiment is the plotted points. The data represents GaAs absorption at $T = 300K$ and population density of $N < 10^{14} cm^{-3}$.

$(f_{cv} - f_{cc})$ approaches zero. This absorption saturation is due to the Pauli exclusion principle.

The presence of band tailing in semiconductors is important in the laser cooling process. The theoretical absorption coefficient (Eq. 2.15) and experimental absorption coefficient \(^4\) in GaAs at very low e-h population density are shown in Fig. 2.3. As discussed in Chapter 1, increasing the quantum efficiency $\eta_q$ by decreasing the incident photon energy is possible. It means the photon energy for e-h excitation can be moved into the absorption tail. Absorption drops rapidly below the bandgap energy although there is non-negligible background absorption. Understanding absorption in the band tail helps to estimate cooling efficiency ($\eta_q$), absorption efficiency ($\eta_{abs}$), and a suitable cooling wavelength regime. The theoretical absorption coefficient does not explain the presence of band-tailing, although it indicates the presence of the band edge. In deriving the absorption coefficient, it is assumed carriers in parabolic bands have sharp and well defined energy and momentum. It is also assumed e-h pairs are free (in the effective mass picture) and there is no Coulomb attraction between them.

\(^4\)The absorption data is obtained from luminescence data, using reciprocity. Luminescence and absorption are related through reciprocity as will be discussed in this chapter.
There are different phenomena that can explain presence of band tailing in semiconductors: a) the Franz-Keldysh effect, b) excitonic effects, and c) the presence of mid-gap levels due to impurities and imperfections in crystal structure. These are discussed below.

a) Franz-Keldysh effect. The Franz-Keldysh effect is a change in optical absorption of a semiconductor when an electric field is applied \[40\]. This is the result of wave function tunnelling into the bandgap due to presence of a sufficiently large electrical field. This field may be due to presence of unintentionally doped ionic impurities. A detailed discussion of the Hamiltonian and mathematical formalism of the Franz-Keldysh effect can be found in Reference \[40\].

b) Excitons: Electron-hole pairs are attracted due to the Coulomb force. An exciton results from the Coulomb binding of the electron with a hole; as a result, the exciton (e-h pair) has slightly less energy than the unbound free electron and hole. The wave function of the bound state is hydrogenic although the binding energy is much smaller and its size is much bigger than a hydrogen atom. This is due to the screening of the Coulomb potential by other carriers and the lighter effective masses. The exciton energy slightly extends into the classically-forbidden bandgap. The wave function and energy of the excitons can be determined by perturbation theory, ignoring the Coulomb attraction between other exciton pairs \[38, 40\]. The total energy of exciton may be written as \[40\]:

\[
E(K) = E_n + \frac{\hbar^2 K^2}{2m_r} \tag{2.19}
\]

\[
E_n = 13.6\left(\frac{1}{n}\right)^2 \left(\frac{m_r}{m\epsilon_r^2}\right) \quad (eV)
\]

where \(K\) is the center of mass wave vector for the e-h pair or exciton, \(m_r\) is their reduced mass, and \(\epsilon_r\) is the dielectric constant of the semiconductor. The parameter
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$n$ is the principle quantum number of the hydrogenic energy level. The exciton states can not be drawn in the semiconductor energy band diagram. It is customary, however, to define the conduction band edge as the continuum state ($n=\infty$). Using Eq. 2.19, the energy level diagram for the excitons is shown in Fig. 2.4.

![Figure 2.4: Energy (E) versus center of mass wavevector (K) relations for excitons. The hatched region indicates continuum states. [38].](image)

The ground state of the crystal is at the origin, having $E = 0$ and $K = 0$. The excited states are the two particle excited states (e-h) or excitonic states. In the Fig. 2.4 the discrete exciton levels ($n = 1, 2, 3, ...$) are shown separated from the continuum states indicated by the hatched region. When excitons are excited below the band edge (small values of $n$) the Coulomb interaction between the e-h pair is very strong and the excitons are bound. If excitons are excited closer to the band edge (larger values of $n$) the Coulomb interaction between e-h pairs tends to be much smaller. In this case, e-h pairs or excitons are considered to be free. Semiconductor absorption may thus be analyzed in two different regimes: absorption of bound excitonic states (below the band edge) and the absorption of free excitonic states (near and above the band edge) [38]. The ideal excitonic absorption spectra for transitions to discrete levels (bound excitons) and to continuum states (free excitons) are shown in Fig. 2.5

If one includes only excitonic effects to model absorption, the spectra is predicted to contain a series of lines as shown in Fig. 2.5. The experimental data in Fig. 2.6
Figure 2.5: The ideal excitonic absorption spectra for transitions to discrete levels (vertical lines) and to continuum states (continuous curve). The dashed curve is interband absorption, neglecting the Coulomb interaction between e-h pairs [38].

shows a considerably different result. There is a broadening of the exciton absorption lines due to scattering with LA and LO phonons as discussed in previous section. In general, the temperature-dependent linewidth of excitonic absorption may be written as:

\[
\Gamma(T) = \Gamma_{\text{LA}}(T) + \Gamma_{\text{LO}}(T),
\]

(2.20)

where \(\Gamma_{\text{LA}}(T)\) is the broadening term due to scattering of excitons with LA phonons and \(\Gamma_{\text{LO}}(T)\) is the broadening term due to scattering of excitons with LO phonons.
In GaAs at room temperature $\Gamma_{LA}(T) \approx 0.19\text{meV}$ and $\Gamma_{LO}(T) \approx 20\text{meV}$. Usually the width of discrete lines is such that they merge with the continuum state. The broadening width $\Gamma$ is temperature-dependent and only in pure semiconductors at low temperatures can excitonic peaks be distinguished (see Fig. 2.6).

Excitons can also scatter with lattice imperfections leading to additional band tailing [38]. Including the broadening due to imperfections ($\Gamma_0$), Eq. 2.20 can be written as:

$$\Gamma(T) = \Gamma_0 + \Gamma_{LA}(T) + \Gamma_{LO}(T),$$

The value of $\Gamma_0$ is different from sample to sample.

In very pure, intrinsic semiconductors the excitonic absorption model fits the experiment data. Detailed analysis of semiconductors absorption considering excitonic effects can be found in Reference [47]. Advanced models involve numerical calculation such as found in the paper of Lowenau et al [48] and a recent publication by our collaborator at the University of Arizona [49].

c) Unintentionally doped impurities. The presence of small amounts of impurities during crystal growth is inevitable. These impurities can create intermediate or mid-gap states and contribute to band tailing. Absorption can occur from either the valence band or an un-ionized acceptor to donor states or the conduction band. In Chapter 6, transitions from acceptor levels to the conduction band in GaAs will be discussed.

One can consider all the different broadening effects ($\Gamma$) and theoretically model the absorption coefficient in one semiconductor. Although this model may characterize the absorption coefficient for one sample, it is not likely to predict band tailing for another sample. This is largely due to the type and level of unintentionally doped impurities and imperfections from sample to sample.
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To estimate the excited e-h population density and consequently cooling power in the laser cooling experiment, a simple quantitative model that accounts for absorption tailing is sufficient. The band tailing effect can be taken into account in Eq. 2.16 by substituting a phenomenological broadening function for $\Gamma$ [47]:

$$\alpha(\nu, N) = \left\{ f_{ev} - f_{ec} \right\} \int_{E_g}^{\infty} \kappa(h\nu - E_g)^{1/2} \frac{Sech\left(\frac{E - h\nu}{\Gamma}\right)}{\pi \Gamma} dE$$

(2.22)

where $\Gamma$ represents the broadening width [47].

The theoretical absorption (taking into account linewidth broadening of Eq. 2.22) and experimental data are shown in Fig. 2.7. The broadening width $\Gamma$ is adjusted to fit theory to experiment. The chosen value for $\Gamma$ may not be suitable to fit absorption data for a different GaAs sample.

![Figure 2.7](image-url)

Figure 2.7: Theoretical and experimental absorption coefficient in GaAs. Theory is the solid line and experiment is the plotted points. The data represents GaAs absorption at $T=300K$ and population density of $N < 10^{14} cm^{-3}$. In the absorption model, band tailing is taken into account through Eq. 2.22 considering $\Gamma \sim 12 \text{meV}$. This value corresponds to a line broadening of 5 nm.

In summary, the effects of saturation and band tailing have been discussed. An absorption model which includes the band tailing effect was introduced. In the next section, the radiative recombination process will be discussed.
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### 2.2.2 Radiative recombination process in direct bandgap semiconductors.

Radiative recombination is one of the three essential steps of the laser cooling cycle. Strong e-h recombination via photon emission is required in order to extract thermal lattice energy. The rate of radiative recombination ($W_r$) is proportional to the product of the electron density ($n$) in the conduction band times the holes density ($p$) in the valence band. Under steady state conditions the bimolecular rate of band-to-band radiative recombination is given by [39]:

$$W_r = B \, np$$  \hspace{1cm} (2.23)

where $B$ is the radiative recombination coefficient. The electron density in the conduction band and the hole density in the valence band can be written as

$$n = n_0 + \Delta n$$
$$p = p_0 + \Delta p$$  \hspace{1cm} (2.24)

where $n_0$ and $p_0$ are the quiescent populations of electrons and holes due to thermal generation or doping. The terms $\Delta n$ and $\Delta p$ account for optical excitation. For the case of $\Delta n > n_0$ and $\Delta p > p_0$ that occurs in laser cooling, $n = \Delta n$ and $p = \Delta p$. In intrinsic semiconductors, simplification occurs by writing $n = p = N$ where $N$ is the optically induced e-h population density. The radiative recombination rate can be re-written as [39]:

$$W_r = B \, N^2.$$  \hspace{1cm} (2.25)
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The excess e-h population lifetime \( \tau_r \) under steady state conditions is defined as the ratio of excess population density to the radiative decay rate [39]:

\[
\tau_r = \frac{N}{W_r} = \frac{1}{B \, N} \quad \text{(2.26)}
\]

The constant coefficient \( B \) is obtained from a spectral integration of the spontaneous emission rate. The spontaneous emission rate \( R(\nu) \) can be derived from the optical absorption process by using the principle of detailed balance under thermal equilibrium. This reciprocity relationship between the spontaneous emission rate and absorption rate was first derived by van Roosbroeck and Shockley [38]. This relationship states that the rate of optical generation of electron-hole pairs is equal to the rate of radiative recombination under thermal equilibrium. In this condition, the semiconductor is in a radiation balance with a black body source, i.e. the rate of spontaneous emission at a frequency \( \nu \) is equal to the rate of black body radiation absorbed. The spontaneous emission rate or luminescence spectral density rate can be derived as [38]:

\[
R(\nu) = \frac{\alpha_0(\nu) \, (h\nu)^2}{\pi^2 \hbar^3 (c/n)^2 \left[ \exp(h\nu/k_BT) - 1 \right]} \quad \text{(2.27)}
\]

Luminescence data obtained by applying the van Roosbroeck-Shockley relation (Eq. 2.27) to absorption is compared to luminescence data for GaAs in Fig. 2.8. In Eq. 2.27, linewidth broadening is taken into account through the absorption coefficient from Eq. 2.22.

The van Roosbroeck-Shockley relationship is established at low e-h population density in thermal equilibrium. In the case of high e-h population density at steady

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\(^5\)The principle of detailed balance relates the probabilities of forward and backward processes [50]
Figure 2.8: Luminescence spectrum predicted by the van Roosbroeck-Shockley relationship (solid line) and luminescence data from experiment (dotted line) for GaAs at $T = 300 \, \text{K}$ and population density of $N < 10^{14} \, \text{cm}^{-3}$. Linewidth broadening is taken into account through the absorption coefficient in the van Roosbroeck-Shockley relationship.

In state conditions, the relationship is modified as follows [38]:

$$R(\nu) = \frac{\alpha_0(\nu) (h\nu)^2}{\pi^2 \hbar^2 (c/n)^2 [\exp(h\nu - (F_e - F_h)/k_B T) - 1]}.$$  \hspace{1cm} (2.28)

where the quasi-Fermi levels $F_e$, $F_h$ account for the optical excitation.

The radiative recombination coefficient $B$ is derived by integrating over the luminescence spectral density [38]:

$$BN^2 = \int R(\nu)d\nu \approx \beta E_g \frac{N^2 T^{3/2}}{2}.$$ \hspace{1cm} (2.29)

In Eq. 2.29, $\beta$ is a constant coefficient allowing $B$ to be conveniently re-written as:

$$B(T) = B_0 \left(\frac{300}{T}\right)^{3/2},$$ \hspace{1cm} (2.30)

where $T$ is in Kelvin and $B_0$ is the radiative recombination coefficient at $T_0 = 300K$. Eq. 2.30 clearly shows that the radiative recombination coefficient increases at lower
temperatures, which has important implications for laser cooling that will be discussed later in this chapter. The values of $B$ at room temperature for different direct bandgap semiconductors are shown in Fig. 2.9.

Figure 2.9: Radiative recombination coefficient measured for different direct bandgap semiconductors at $T = 300K$ [24]

As is shown in in Fig. 2.9 and Eq. 2.29 the radiative recombination coefficient is of the same order of magnitude for all direct bandgap semiconductors. There is a trend of increasing recombination with bandgap energy. The coefficient $B$ is usually measured via photoluminescence decay, which is density-dependent [24]. This accounts for the large data scatter shown in Fig. 2.9.

In summary, the radiative recombination rate $W_r$ in direct bandgap semiconductors has been discussed and formulated. The rate is temperature dependent, increasing at lower temperatures. In the next section, the non-radiative recombination process is presented.
2.2.3 Defect related non-radiative recombination process in semiconductors.

Realization of long recombination lifetimes in semiconductors is important for the efficient operation of solar cells, light emitting diodes, and heterojunction bipolar transistors [51, 52, 53]. The study of non-radiative recombination in GaAs reported here is motivated by laser cooling as discussed in Chapter 1 and later in this chapter. In laser cooling, optical excitations near the bandgap energy decay with high efficiency in the form of blue-shifted radiation. Non-radiative decay paths prevent a portion of the optical excitations from recombining radiatively and create deleterious heating. The non-radiative process is discussed next.

Non-radiative recombination at an impurity or defect occurs in two steps. First, an electron in the conduction band is captured into a bound state (e.g. trap center). Second, the bound electron recombines with a hole in the valence band. During these two transitions, an energy equal to the energy gap (1.42 eV for GaAs at $T = 300$ K [54]) must be dissipated. An equivalent process can occur in the valence band with holes. Energy is dissipated by multi-phonon emission (MPE) [55, 56, 57]. The Auger effect will be discussed later in this chapter.

Cascade capture is a third non-radiative recombination mechanism [58]. An electron loses energy by dropping through a series of closely spaced levels, emitting one phonon during each transition. This mechanism is known as thermalization by donors $^6$ and acceptors $^7$ [58]. It is possible even at low temperatures. The cascade process cannot explain non-radiative capture into deep levels or mid-gap states because point defects normally only have a single deep level within the forbidden gap

$^6$Donor atoms are introduced into a semiconductor to generate free electron via thermal ionization. Donor atoms must have one more valence electron than the host semiconductor. In GaAs these are S, Se, Sn, Si, and C

$^7$Acceptor atom must have one less valence electron than the host semiconductor.
that is far from the band edges [59, 60, 55, 56, 57]. At room temperature, cascade capture of a carrier into shallow levels will be followed by rapid emission of the carrier back into the band. Separation of states by more than an optical-phonon energy prevents cascade capture into the ground state [57].

Localized trap states or point defects may be created by deep-level impurities (e.g. transition metals or normal metals such as Fe, Ni, Co, W, or An) or by radiation and process-induced defects such as vacancies \(^8\), interstitials \(^9\), anti-sites \(^{10}\), defects and their complexes, dislocations, and grain boundaries\(^{11}\) [42, 54, 50] [56, 57, 42]. Trap states can be located in the bulk or at surfaces. The nature of the defects causing non-radiative recombination in the bulk and surface or interfaces are different.

**Non-radiative processes in the bulk: Shockley-Read-Hall**

Bulk non-radiative recombination process in semiconductors is typically described by the Shockley-Read-Hall model [59, 60]. The mathematical formulation presented here is based on point defects with a single deep-level within the forbidden gap; this single deep level is far from the band edges [59, 60, 55, 56, 57] \(^{12}\).

The energy band diagram for the bulk non-radiative recombination process known as Shockley-Read-Hall process is shown in Fig.2.10. A localized mid-gap trap may be neutral or charged. In Fig. 2.10 an electron is captured by a neutral trap via multi-phonon emission. In Fig. 2.10 B a charged trap state provides an electron to

---

\(^8\) A vacancy is a missing atom in single crystal lattice; also known as Schottky defect

\(^9\) Interstitials are atoms or ions of a non-metal occupying holes between metal atoms or ions in a crystal lattice

\(^{10}\) Anti-sites are atoms of a semiconductor crystal situated incorrectly in the crystalline structure, e.g. a Ga atom located on an As site in GaAs.

\(^{11}\) Grain boundaries are the preferred location for the appearance new phases. Certain deterioration, such as cracking and caustic embrittlement occur almost exclusively at grain boundaries.

\(^{12}\) Point defects are usually associated with a single mid-gap state [59, 60, 55, 56, 57]
Figure 2.10: The energy band diagram for the Shockley-Read-Hall model. The localized trap energy level $E_t$ can be below or above Fermi energy level.

the conduction band via multi-phonon absorption. In Fig. 2.10 C a hole is captured from the valence band by phonon emission and in Fig. 2.10 D phonon absorption causes a hole to appear in the valence band. A single localized trap can capture only one type of a carrier at a time.

The rate equation describing the Shockley-Read-Hall model can be derived from the four recombination process shown in Fig. 2.10. It is assumed the semiconductor is nondegenerate and the density of trap states is small compared to the majority carrier density. The probability of a trap state (located at $E_t$ energy level in the forbidden gap) to be occupied by an electron in thermal equilibrium is given by Fermi-Dirac statistics:

$$f_t = 1 / (1 + \exp ((E_t - E_f) / k_B T)).$$

The rate of electron capture is a function of the density of conduction electrons $n$, electron capture cross section $c_n$ (cm$^3$/sec), and density of the empty traps. The rate of electron emission depends only on the density of traps being filled by the electrons; under steady-state conditions, the net rate of electron capture per unit
volume can be written as [59]:

\[ U_n = c_n N_t n (1 - f_t) - c_n N_t n_1 f_t \]  

(2.31)

where \( N_t \) is the density of traps (cm\(^{-3}\)), \( n_1 = n_0 \exp \left( \frac{(E_t - E_f)}{kT} \right) \) is the electron density at the mid-gap trap center, and \( n_0 \) denotes the thermally excited electron density in the conduction band. The first term on the right hand side of Eq. 2.31 represents the electron capture probability per unit time per unit volume (cm\(^{-3}\)/s). The second term is the electron emission probability per unit time per unit volume.

In a similar way, the net rate of hole capture per unit volume can be written as [59]:

\[ U_p = c_p N_t p_1 f_t - c_p N_t p (1 - f_t) \]  

(2.32)

where \( c_p \) is the hole capture coefficient (cm\(^{-3}\)/s), \( p_1 = p_0 \exp \left( \frac{(E_t - E_f)}{kT} \right) \) represents the hole density in the mid-gap trap center at thermal equilibrium condition, and \( p_0 \) is the thermally excited hole density in the valence band. The interpretation of this equation is identical to Eq. 2.31.

For simplification, it is assumed that the rates of electron and hole capture via single mid-gap recombination centers are approximately equal and thus the excess carrier density in the conduction and the valence bands at steady state are equal (\( \Delta n \approx \Delta p \)). This is a very reasonable approximation particularly in high quality samples with very low point defect density. The simplified expression for the net rate of non-radiative recombination rates is then:

\[ U = U_n = U_p = \frac{(np - n_1^2)}{\tau_{po}(n + n_1) + \tau_{no}(p + p_1)} \]  

(2.33)

where \( \tau_{po} = 1/c_p N_t \) and \( \tau_{no} = 1/c_n N_t \).
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With knowledge of the non-radiative rates, the net non-radiative recombination lifetime in the bulk can be defined as:

\[
\tau_{0B} = \frac{\Delta n}{\Delta p} = \frac{\Delta n}{U_n} + \frac{\Delta p}{U_p} = \frac{\tau_{po}(n_0 + n_1 + \Delta n)}{n_0 + p_0 + \Delta n} + \frac{\tau_{no}(p_0 + p_1 + \Delta p)}{p_0 + n_0 + \Delta p},
\]

(2.34)

When the excess carrier density is larger than thermally excited e-h carriers (as is the case in laser cooling), further simplification occurs: \(\tau_{0B} \approx \tau_{no} + \tau_{po}\). It is assumed that material properties (i.e. energy band diagram in a heterostructure device) do not change at large carrier density. The heterostructures used in this work (see Chapter 6) are unintentionally doped with p-type impurities. In this case, the non-radiative recombination coefficient \(A\) can be derived as:

\[
A_{0B} = \frac{1}{\tau_{0B}} = c_p N_t,
\]

(2.35)

where it is assumed the density of traps are low so that a small amount of excess carriers saturates the trap states. Eq. 2.35 shows that the non-radiative recombination coefficient depends on the density and character of the trap as defined by the coefficient \(c_p = \sigma_p < v_h >\) [42, 57]. The term \(\sigma_p\) is the hole capture cross section, which is a measure of the probability of capturing carriers and depends on the nature of the point defect. The mean thermal velocity for the holes is \(< v_{th} > = 3k_B T/m^*_h\) [42, 57], where \(m^*_h\) denotes the effective mass of the holes.

Lang and Henry [56, 57] investigated non-radiative recombination and capture at defects via MPE in both n-type and p-type GaAs and GaP. They have shown defects in GaAs are due to deep-level impurities from Cu, Fe, Mn, Cr, O as well as radiation. Not all of the capture cross sections in GaAs and GaP can be attributed to MPE. There is evidence of electron capture by single phonon emission at oxygen defects and single phonon hole capture by Fe and Cr in p-GaAs. Their work did establish that MPE capture is the most common and efficient process occurring in
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GaAs and GaP. They determined that the capture cross sections have a universal temperature behavior and fit the data with the expression $\sigma = \sigma_\infty \exp (-E_a/k_B T)$ for $100 \text{ K} < T < 500 \text{ K}$. For the deep-level impurities, $\sigma_\infty$ and $E_a$ are in the range $4 \times 10^{16} < \sigma_\infty < 1 \times 10^{14} \text{ cm}^2$ and $0 \text{ eV} < E_a < 0.56 \text{ eV}$ [56, 57]. The values of $\sigma_\infty$ and $E_a$ are determined by the type of impurity and its unique capturing behavior in the host material. Following Lang and Henry [57], the MPE theory is briefly discussed next.

![Diagram illustrating non-radiative capture](image)

**Figure 2.11:** Diagram illustrating how non-radiative capture of an electron takes place. The equilibrium positions of the lattice coordinate and the energy level, before and after capture, are indicated by the dashed lines. The shaded regions within the energy gap indicate how the energy of the level changes as the lattice vibrates. The smaller arrows represent the amplitudes of the thermal vibrations, before and after capture of an electron. The large arrow represents the amplitude of the lattice vibrations about the new equilibrium position, immediately after capture [57].

Non-radiative capture takes place because the energy of a deep-level impurity strongly depends on the positions of the atoms comprising the defect and its neighbors in the lattice [57]. As the lattice vibrates, the mid-gap energy level moves up and down in the energy gap. A diagram illustrating a simple model of the electron-lattice interaction is shown in Fig. 2.11. For simplicity the lattice is represented by a single coordinate. Consider the non-radiative capture of an electron. Prior to
capture, the equilibrium position of the mid-gap level is in the upper half of the gap. For sufficiently large vibrations the mid-gap level, an impurity state can cross (or nearly cross) into the conduction band and capture an electron. After capture of the electron the lattice near the defect relaxes in such a way as to lower the equilibrium position of the mid-gap level in the energy gap. Immediately after capture of the electron the lattice is displaced far from the new equilibrium position and there will be a violent lattice vibration at the defect. The vibration will rapidly damp down to the amplitude of thermal vibrations after a small number of vibrational periods. During the damping, the localized energy propagates away from the defect as lattice phonons. This justifies calling this process non-radiative capture by multi-phonon emission (MPE)[57]. A mathematical model describing MPE is beyond the scope of this dissertation. A comprehensive discussion can be found in the classic paper of Lang and Henry [57].

Lang and Henry [57] derived a unique, temperature-dependent capture cross section and used it to analyze their experimental data. The non-radiative recombination coefficient can be written as [61]:

\[ A_{0B}(T) = N_t \left( \frac{3k_B T}{m^*} \right) \sigma_\infty \exp\left( -\frac{E_a}{k_B T} \right) \approx A_{0B}(300K) \exp\left( -\frac{E_a}{k_B T} \right), \tag{2.36} \]

In Eq. 2.36, \( E_a \) is the lattice energy or activation energy \(^{13}\), which is the energy required for a state to cross into the conduction or valence band [57].

In high quality semiconductors having negligible deep-level defects in the bulk, large interface-to-volume ratios, or with dimensions small compared to the carrier diffusion length, interface effects dominate SRH recombination. This non-radiative surface recombination (i.e. surface SRH) is discussed next.

\(^{13}\)Lang and Henry write this as \( E_\infty \) [57]
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**Non-radiative recombination processes at interfaces**

The sudden termination of the periodic semiconductor structure at a surfaces creates dangling bonds: discrete or continuous energy states within the bandgap. A thin natural oxide layer is often easily formed on a freshly cleaved or chemically polished semiconductor surface when it is exposed to air. The lattice mismatch in the crystallographic structure at the semiconductor-oxide interface does not in general eliminate defects or dangling bonds. Fig. 2.12 illustrates the energy band diagram for an oxide-semiconductor interface having surface states in the bandgap of the semiconductor.

![Diagram illustrating oxide-semiconductor states and air (surrounding environment). The density of fast states (semiconductor-oxide interface) is usually much lower than the density of slow states (air-oxide) [42].](image)

In general, there are two types of surface states that are commonly observed: slow and fast surface states (see Fig. 2.12). The density of slow states is usually much higher than the density of fast states. The fast states are created either by termination of the periodic bulk lattice structure to create dangling bonds or by a lattice mismatch and defects at the oxide-semiconductor interface. These surface states are in intimate electrical contact with the bulk semiconductor and can reach a state of
equilibrium within a relatively short period of time (of the order of microseconds or less [42, 62]) and thus are referred to as the fast surface states.

The slow states exist inside the thin oxide layer near the air-oxide interface. This type of surface state may be formed by either chemisorbed ambient ions or defects in the oxide region (e.g. sodium ions or pin holes in an SiO$_2$ layer [42, 62]). Carriers moving from the oxide to bulk semiconductor either have to overcome the potential barrier due to the large energy gap of the oxide (usually located in UV region, [42, 62]) or tunnel through the oxide layer. Such charge transport involves a large time constant, typically of the order of seconds or more, and hence these states are usually called slow states.

The density of slow and fast states can be decreased by passivating the surface with another latticed matched semiconductor. A layer of single crystal semiconductor of different chemical composition but the same lattice constant changes the energy gap at the interface. In this way, the density of fast and slow states becomes negligible, although there will be new recombination states at interface with air. It will be shown in Chapter 6 that a layer as thin as 30 nm is enough to passivate the active GaAs layer.

In planar structures, the interface-to-volume dependence of SRH recombination can be separated from other interface phenomena via the recombination velocity $S$ [63, 61, 64]. The interface recombination rate is defined as $A_s = (S/d)$, where $d$ is the thickness of the active layer. The thickness $d$ appears in the equation because e-h carriers in the layer must travel a distance $d/2$ on average to reach to the interfaces [63, 61]. In thicker samples, $A_s$ will be smaller. When two interfaces are present, as in a double heterostructure, the contributions from both surfaces are combined: $S$ is replaced by $S_1 + S_2$ ($= 2S$ for equivalent interfaces). Because $S$ is independent of carrier density and layer thickness, it is straightforward to compare interface recombination in a variety of materials. $S$ depends strongly on the nature
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of the interface. For example, $S$ is of the order of $10^7$ cm/s at the interface of GaAs-air, whereas high-quality GaAs\GaInP interfaces can have $S < 10$ cm/s [53]. In the case that the semiconductor is passivated and the density of point defects is low, the surface non-radiative coefficient can be expressed by the simple Shockley-Read-Hall model presented earlier. In this case, the bulk capture cross section and bulk defect density are substituted with the surface capture cross section and surface defect density [42, 61]. The temperature-dependence of surface non-radiative recombination coefficient for a double heterostructure can be written as [61]:

$$A_s(T) = \frac{1}{\tau_s(T)} = \frac{S_0 \exp (-E_a/k_B T)}{2d} \ , \quad (2.37)$$

where $S_0$ is the interface recombination velocity at room temperature.

In summary, the non-radiative recombination rate $W_{nr}$ in Eq. 2.6 can be written as

$$W_{nr} = \frac{N}{\tau_{nr}(T)} = A(T) N \ , \quad (2.38)$$

where $A(T)$ is the temperature-dependent non-radiative recombination coefficient in the bulk or surface. As the temperature decreases, lattice vibrations and consequently the capture cross section will decrease. The temperature dependence of non-radiative recombination impacts laser cooling of semiconductors at low temperatures (discussed later in this chapter). Material quality, crystal growth conditions, and processing play key roles in reducing defect assisted recombination. This recombination is not a fundamental property of the material. In the next section, the non-radiative Auger process in direct bandgap semiconductors is investigated.
2.2.4 Non-radiative Auger process in direct bandgap semiconductors.

Auger recombination is a fundamental process of the semiconductor material. It is a band-to-band, three-particle scattering process that involves either: i) an e-e collision in the conduction band and recombination with a hole in the valence band or ii) a h-h collision in the valence band followed by recombination with an electron in the conduction band. Three distinct paths are shown in Fig. 2.13: CCCH, CHHS, CHHL, where letter C stands for conduction electron, H for heavy-hole, L for light-hole and S for split-off hole. In CCCH, two electrons in the conduction band and one hole in the heavy hole band are involved. In CHHS, one electron in the conduction band, one hole in the heavy hole band, and one hole in the split off band interact. In CHHL, one electron from the conduction band and two holes in the heavy hole band scatter.

A collision occurs between two carriers in the same band (e-e or h-h): energy from the recombining carrier is transferred to the remaining carrier (see Fig. 2.13). Note that both energy and momentum must be conserved to complete the scattering event. The excited or hot carrier will quickly thermalize with the lattice via phonon emission.
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and generate heat. The Auger recombination process in semiconductors can either be direct or phonon-assisted; both have been widely investigated in semiconductors [65, 66]. The CCCH and CHHS are believed to be the two dominant processes [67].

The net rate of Auger recombination in steady-state can be written as [38]:

$$R_A = C_e(n^2 p - n_0^2 p_0) + C_p(np^2 - n_0 p_0^2).$$  \hspace{1cm} (2.39)

where $C_e$ and $C_p$ denote the non-radiative Auger recombination coefficients for electrons and holes, respectively. These coefficient are independent of carrier density. Using the identical assumptions of the previous section, the non-radiative Auger recombination rate can be written as:

$$R_A = (C_e + C_p)N^3 = CN^3.$$  \hspace{1cm} (2.40)

where $C$ is the aggregate Auger non-radiative coefficient. The Auger lifetime can be derived from the excess e-h population lifetime definition ($\tau$) discussed in Section 2.2.2:

$$\tau_A = \frac{N}{R_A} = \frac{1}{CN^2}.$$  \hspace{1cm} (2.41)

The direct Auger non-radiative coefficient $C$ can be estimated from the inverse Auger process, namely, impact ionization \(^{14}\). In thermal equilibrium, the rate at which carriers are destroyed via Auger recombination is equal to the generation rate of impact ionization, averaged over the Boltzmann distribution. The Auger coefficient $C_p$ and $C_e$ for CCCH and CHHS can be written as [68]:

$$C_{e,p}(T) \approx C_{e0,p0}\exp\left[-\frac{E_a}{k_B T}\right],$$  \hspace{1cm} (2.42)

\(^{14}\)Impact ionization is the generation of e-h pairs due to collisions of high kinetic energy charge carriers [42].
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where $E_a = \alpha E_g$ is an activation or threshold energy that is usually greater than the bandgap energy $E_g$, i.e. $\alpha > 1$. For the CCCH process, $\alpha$ includes the electron mass and the heavy-hole mass. For the CHHS process, $\alpha$ includes the electron mass, heavy-hole mass, split-off mass, and split-off energy [69]. Momentum conservation in Auger recombination involves band structure, which gives rise to the activation energy [70]. In phonon-assisted Auger recombination, conservation of momentum is fulfilled by phonon scattering for both CCCH and CHHS. As a consequence, the influence of the band structure is less important in phonon-assisted Auger recombination. This indirect Auger recombination is much weaker than the direct process [66, 69, 70].

As is shown in Eq. 2.42, the Auger coefficient decreases exponentially as the temperature is lowered. This has important consequences for laser cooling process as will be discussed in details later in this chapter.

![Figure 2.14: Auger coefficient in different direct-band-gap semiconductors, $T = 300K$ [24]](image)

The values of $C$ at room temperature for different direct bandgap semiconductors are shown in Fig. 2.14. The Auger process is usually determined through the density-dependent photoluminescence decay lifetime $\tau_A$ [24]. The scatter in the data is due to uncertainty in the population density $N$. It can be seen that the Auger recombination
coefficient increases exponentially with decreasing bandgap energy. This agrees with the model described by Eq. 2.42 and the corresponding physical picture: a smaller bandgap means that the remaining carrier must absorb less energy in the collision.

2.3 Laser cooling model

The rate equation for excess population density $N$ in a direct bandgap semiconductor in the absence of external electric field (Eq. 2.6) can be written based on balance between photocarrier generation and recombination:

$$\frac{dN(r,t)}{dt} = 0 = \frac{\alpha(\nu, N(r,t))I}{h\nu} - AN(r,t) - \eta_e BN^2(r,t) - CN^3(r,t) + D_a \nabla^2 N(r,t).$$

The last term on the right-hand side is included to account for the carrier diffusion with $D_a$ the ambipolar diffusion coefficient [39]. If the population density is not spatially uniform, diffusion can be important. In the experiments described in this dissertation, it is assumed that the semiconductor samples are sufficiently thin so that longitudinal non-uniformity can be neglected. It is also understood that e-h pairs are generated by a spatially uniform (top-hat) laser beam, an assumption that is justified later in this chapter.

Ignoring diffusion and considering e-h generation via top-hat laser illumination, Eq. 2.43 simplifies to:

$$\frac{dN}{dt} = 0 = \frac{\alpha(\nu, N)I}{h\nu} - AN - \eta_e BN^2 - CN^3$$

(2.44)
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where the four terms on the right-hand side describe generation, non-radiative recombination via traps and defects, radiative recombination, and Auger recombination, respectively. In the next section we investigate the laser cooling power density and cooling efficiency considering population density described by Eq. 2.44.

### 2.3.1 Cooling power density and cooling efficiency in direct bandgap semiconductors

The net steady-state optical power density in a laser cooling experiment is the difference between the absorbed laser power and the rate of heat removal:

\[
P_{net} = P_{abs} - P_{lum} ,
\]

(2.45)

where \(P_{abs}\) is the total absorbed laser power density \((W/cm^3)\) and \(P_{lum}\) is the total escaped luminescence power density. Both \(P_{abs}\) and \(P_{lum}\) can be formulated based on the absorption coefficient, radiative recombination rate, and non-radiative recombination rates. For the absorbed power density,

\[
P_{abs} = \alpha (\nu, N) I + \alpha_b I + \alpha_{fca} I ,
\]

(2.46)

The first term in the right-hand side of Eq. 2.46 describes resonant band-to-band absorption; the second and third terms account for background and free carrier absorption, respectively. Direct absorption near the band edge supplies the photo-carriers for laser cooling. Background absorption and free carrier absorption create undesired heating.

The source of background absorption may not necessarily exist in the active cooling layer. There are other components of the device that are illuminated by and absorb optical radiation. Background absorption may exist in the passivation layers
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For the moment, free carrier absorption is ignored, an assumption justified later in this section. Then $P_{abs}$ simplifies to

$$P_{abs} = (\alpha(\nu, N) + \alpha_b)I.$$  (2.47)

$P_{abs}$ can be written in terms of population density $N$, since $N$ and $I$ are related through Eq. 2.44. This gives:

$$I = \frac{h\nu}{\alpha(\nu, N)} (AN - \eta_f BN^2 - CN^3).$$  (2.48)

Substituting laser irradiance $I$ into Eq. 2.47 and rearranging, $P_{net}$ is written in terms of density $N$ as:

$$P_{abs} = (ANh\nu + \eta_f BN^2 h\nu + CN^3 h\nu)(1 + \frac{\alpha_b}{\alpha(\nu, N)}).$$  (2.49)

In a direct bandgap semiconductor, $P_{lum}$ can be written as

$$P_{lum} = \eta_f h\tilde{\nu}_f BN^2.$$  (2.50)

$P_{lum}$ in Eq. 2.50, describes the escaped luminescence power from the semiconductor with average or mean frequency $\tilde{\nu}_f$, which is in general different from $\nu_f$. The geometry-dependent mean luminescence frequency $\tilde{\nu}_f$ is defined as [21, 28, 31]:

$$\tilde{\nu}_f = \frac{\int \nu S(\nu) R(\nu) d\nu}{\int S(\nu) R(\nu) d\nu}.$$  (2.51)

Here $R(\nu)$ is the luminescence spectral density rate discussed in the previous section in connection with Eq. 2.27. $S(\nu)$ is the geometry-dependent escape probability that has a value less than one. This term arises due to trapping and absorption of luminescence (see Fig. 2.15).

15Passivation layers sandwich the cooling GaAs layer to decrease non-radiative recombination at the surface. Details will be presented in Chapter 6

16The dome lens is used to enhance the luminescence extraction efficiency, a technique used in LED’s. Further discussion is in Chapter 4
Figure 2.15: GaAs absorption and luminescence at $T = 300K$. Absorption is calculated from luminescence using the Van-Roosbrock-Shockley relationship of Eq. 2.27.

The geometry-dependent escape probability scales as $e^{-\alpha(\nu)l_a}$, where $l_a$ is semiconductor thickness. Absorption is weakest near the band edge (see Fig. 2.15), so the effect of trapping, absorption, and re-radiation of luminescence is a net red-shift of the spectrum. In the limit of perfect external efficiency $(S(\nu) = 1)$, the luminescence is not red-shifted: $\tilde{\nu}_f = \nu_f$ [31].

The net power density (Eq. 2.45) can be written based on carrier density as:

$$P_{net} = P_{abs} - P_{lum} = (AN\hbar\nu + CN^3\hbar\nu) \left(1 + \frac{\alpha_b}{\alpha(\nu, N)}\right) + \eta_e BN^2 \left(1 + \frac{\alpha_b}{\alpha(\nu, N)}\right) h\nu - h\tilde{\nu}_f.$$

As discussed earlier, the background absorption source is not necessarily presents in the active cooling area. In order to take into account the length of absorption, we substitute absorption with absorbance and re-arrange Eq. 2.52 as follows:
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\[ P_{\text{net}} = Nh\nu \{ A(1 + \frac{\alpha_b l_b}{\alpha(\nu, N) l_a}) + \eta_e BN((1 + \frac{\alpha_b l_b}{\alpha(\nu, N) l_a}) - \frac{\tilde{\nu}_f}{\nu}) + C(1 + \frac{\alpha_b l_b}{\alpha(\nu, N) l_b})N^2 \} \]  

where \( l_a \) is the thickness of the active cooling layer and \( l_b \) is the thickness of the element in the device with the largest background absorption (e.g. dome lens or passivation layers). Eq. 2.53 can be solved analytically to determine a favorable carrier density \( N \) for cooling.

In Chapter 1 laser cooling efficiency was introduced based on the cooling cycle shown in Fig. 1.1. For a practical cooling device, external quantum efficiency \( \eta_{\text{ext}} \) and absorption efficiency \( \eta_{\text{abs}} \) should be taken into account. Here, derivations of \( \eta_{\text{ext}} \) and \( \eta_{\text{abs}} \) are presented.

The cooling efficiency of a semiconductor or RE-doped glass is determined by the ratio of the net cooling power density \((-P_{\text{net}} \text{ in Eq. 2.53})\) to the total absorbed laser power density \((P_{\text{abs}} \text{ of Eq. 2.49})\):

\[ \eta_c = \frac{-P_{\text{net}}}{P_{\text{abs}}} = \frac{-Nh\nu \{ A(1 + \frac{\alpha_b l_b}{\alpha(\nu, N) l_a}) + \eta_e BN((1 + \frac{\alpha_b l_b}{\alpha(\nu, N) l_a}) - \frac{\tilde{\nu}_f}{\nu}) + C(1 + \frac{\alpha_b l_b}{\alpha(\nu, N) l_b})N^2 \}}{(ANh\nu + \eta_e BN^2 h\nu + C\nu^3 h\nu)(1 + \frac{\alpha_b}{\alpha(\nu, N)})}. \]  

Rearranging Eq. 2.54 yields:

\[ \eta_c = \{ \frac{\eta_e BN^2}{AN + \eta_e BN^2 + C\nu^3} \} \times \{ \frac{\alpha(\nu, N) l_a}{\alpha(\nu, N) l_a + \alpha_b l_b} \} \times \frac{\tilde{\nu}_f}{\nu} - 1. \]  

\[ \text{(2.55)} \]
where the first bracket in the right hand side defines the external quantum efficiency:

$$
\eta_{\text{ext}} = \frac{\eta_e BN^2}{AN + \eta_e BN^2 + CN^3}.
$$

(2.56)

The term $\eta_{\text{ext}}$ quantifies how much of the e-h recombination is via the desired photoluminescence emission path and also the fraction of luminescence escaping from the cooling device. The external quantum efficiency can be cast in terms of the internal quantum efficiency ($\eta_{\text{int}}$):

$$
\eta_{\text{ext}} = \frac{\eta_e}{\eta_{\text{int}} + 1} \approx \left( \frac{BN^2}{AN + BN^2 + CN^3} \right)^{1/\eta_e} = \eta_{\text{int}}^{1/\eta_e}.
$$

(2.57)

where the binomial expansion is used to make the approximation with the realistic assumption that $\frac{1}{\eta_{\text{int}}} \approx 1$. The $\eta_{\text{int}}$ quantifies how much of the e-h recombination is via photoluminescence emission. And $1/\eta_e$ is approximately denotes the number of luminescence recycling before it has a chance to couple out of the material.

The second bracketed term in Eq. 2.55 is defined as the absorption efficiency:

$$
\eta_{\text{abs}} = \frac{\alpha(\nu, N) l_a}{\alpha(\nu, N) l_a + \alpha_b l_b},
$$

(2.58)

which quantifies how much of the total laser absorption is due to the desired band-to-band resonant absorption; note that $\alpha_b$ accounts for deleterious background absorption.

The cooling efficiency ($\eta_c$) of Eq. 2.55 can be re-written in terms of $\eta_{\text{ext}}$ and $\eta_{\text{abs}}$:

$$
\eta_c = \eta_{\text{ext}} \times \eta_{\text{abs}} \times \frac{\tilde{\nu}_f}{\nu} - 1.
$$

(2.59)

Earlier in this section, free carrier absorption was ignored. Here, the effect of free carrier absorption on $P_{\text{net}}$ and $\eta_{\text{ext}}$ is estimated. The free carrier absorption in
Eq. 2.46 is a source of heating in the active cooling layer. Free carries in the valence and conduction bands can interact with photons and make a transition to higher states within the bands (see Fig. 2.16).

Figure 2.16: Intraband and interband free carrier absorption in a typical direct bandgap semiconductor. The indirect intra conduction band absorption is denoted by D. The three vertical inter-valence-band free carrier absorption involves transitions from lh-hh (A), so-to-lh (B) and so-hh (C).

Free carrier absorption is wavelength-dependent [54] and important for photons with energies less than semiconductor bandgap energy [71]. Inter-conduction band absorption \(^{17}\) is negligible for laser cooling wavelengths in GaAs (\(e.g. \alpha = 10^{-19} cm^{-1}\) for \(N \sim 10^{18} cm^{-3}\)) [72]. The indirect intra-conduction band transition requires an additional scattering event to conserve momentum. The change in momentum can be provided by the absorption or emission of a phonon or scattering with an ionized impurities. The dominant mode of scattering depends on temperature, the polar potential, and impurity concentration. Free carrier absorption is often written with a cross section \(\sigma_{fca}\) [38, 54, 42]:

\[
\alpha_{fca} = \sigma_{fca} N .
\]

\(^{17}\)i.e. from the \(\Gamma\)-valley to higher level conduction bands [72]
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The power density absorption due to free carrier absorption is $\sigma_{fca}NI$. In a steady-state laser cooling experiment, it is reasonable to approximate the absorbed laser power to be balanced by the escaped luminescence. Eq. 2.48 defines the laser irradiance as: $I \approx \frac{h\nu}{\alpha(\nu, N)} \eta_e BN^2$. This approximation defines the free carrier absorption power density $P_{fca}$ as:

$$P_{fca} = \left( \frac{\eta_e B\sigma_{fca}}{\alpha(\nu, N)} \right) h\nu N^3.$$  \hspace{0.5cm} (2.61)

Note that $P_{fca}$ scales as $N^3$, which is the same as Auger recombination contribution to Eq. 2.53. This means the Auger recombination rate is effectively changed to a modified term $C'$:

$$C' \approx C(1 + \frac{\alpha_b}{\alpha}) + \frac{\eta_e B\sigma_{fca}}{\alpha}.$$  \hspace{0.5cm} (2.62)

The effect of free carrier absorption on external quantum efficiency Eq. 2.56 can be approximated by replacing $C$ with $C'$ and setting $\alpha_b$ to 0.

In the next section, the power density and e-h population density $N$ for cooling are estimated for GaAs. The effect of free carrier absorption and minimum external quantum efficiency are determined.

2.3.2 Cooling condition and numerical estimates

The condition $P_{net} = 0$ occurs when cooling and heating are in balance. Eq. 2.53 shows $P_{net}$ as a second order polynomial in $N$, so the roots define the range of carrier densities for which cooling is possible: $N_1 - N_2$. This means that any population density $N$ satisfying $N_1 < N < N_2$ results in $P_{net} < 0$ and net cooling. Generating an e-h population density less than $N_1$ makes bulk and surface non-radiative recombination prevalent. On the other hand, generating carrier densities larger than $N_2$
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makes non-radiative Auger dominant. Only in a range of densities between \( N_1 \) and \( N_2 \) in which radiative recombination is dominant can net laser cooling be expected. Eq. 2.53 can be solved analytically to determine these concentrations:

\[
N_{1,2} = \sqrt{\frac{A_0}{C'}}[1 \mp \sqrt{1 - \frac{A}{A_0}}], \tag{2.63}
\]

where \( A_0 \) is defined as break-even non-radiative recombination rate:

\[
A_0 = \frac{1}{\tau_{0nr}} = \frac{\eta_e - \frac{\alpha_l B^2}{\alpha(\nu)I_a} \eta_c}{4C'} \tag{2.64}
\]

The coefficient \( A_0 \) sets the maximum acceptable non-radiative recombination rate for to achieve the heating-cooling balance condition. The minimum non-radiative lifetime is \( \tau_0 = 1/A_0 \). Note that the coefficient \( A_0 \) includes the radiative, Auger, and background absorption coefficients, extraction efficiency and quantum cooling efficiency. Radiative and Auger processes are fundamental properties of the semiconductor, while \( \eta_c \) and \( \tau_{nr} \) are engineering issues. If \( \eta_c \) and \( \tau_{nr} \) are managed properly, cooling is possible (see Chapters 4, 5 and 6). Enhancing extraction efficiency \( \eta_e \) is a long-time problem in LED engineering; different light extraction schemes have been employed to increase \( \eta_e \) [21]. Long non-radiative lifetime is a goal in high performance solar cells and sophisticated crystal growth techniques have been developed to address it [18]. A calculation of \( \eta_e \) is presented in Chapter 4) along with measurements of \( \tau_{nr} \). This allows estimates for the cooling window, break-even condition, and net cooling power density.

A GaAs samples with 0.75 µm thickness \(^{18}\) is measured to have \( \tau_{nr} = 1/A \approx 25 \mu sec \) (see Chapter 6). A ray-trace calculation using a dome lens as a light extraction scheme (see Chapter 4) is estimated to have an extraction efficiency of \( \eta_e \approx 14\% \) (see \(^{18}\)Extraction efficiency and non-radiative lifetime are thickness dependent. See Chapters 4 and 6.

\[18\]
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Chapter 4). Reported values for the radiative coefficient $B$ vary from $2 \times 10^{-10}$ to $7 \times 10^{-10} \text{cm}^3/\text{s}$ [24]. The range of measured Auger coefficients $C$ varies from $1 \times 10^{-30}$ to $7 \times 10^{-30} \text{cm}^6/\text{s}$ [24]. Here, room temperature mean values of $B = 5 \times 10^{-10} \text{cm}^3/\text{s}$ and $C = 4 \times 10^{-30} \text{cm}^6/\text{s}$ are used.

To make an initial estimate, parasitic background absorption is ignored. The effect of free carrier absorption can be included by modifying the Auger coefficient from $C$ to $C'$ in Eq. 2.60. The coefficient $C'$ can be estimated by considering the absorption coefficient at the laser cooling wavelength. In a practical cooler $h \tilde{\nu} - h\nu$ will be of the order of the thermal energy $k_B T$, which means the free carrier absorption cross section $\sigma_{fca} \approx 10^{-20} \text{cm}^2$ [72]. The measured mean luminescence of a GaAs device (0.75\text{$\mu$m} GaAs heterostructure bonded to a dome lens of ZnS; see chapter 6) is $\approx 860 \text{nm}$ (see Eq. 2.51), which sets the pump laser wavelength at $\approx 875 \text{nm}$. At this wavelength, the absorption coefficient of GaAs is $\alpha(\nu) \approx 2000 \text{cm}^{-1}$.

From Eq. 2.60, $C'$ is

$$C' \approx C + \frac{B \sigma_{fca}}{\alpha(\nu, N)} \approx 4 \times 10^{-30} + 2 \times 10^{-33} \approx C.$$ \hspace{1cm} (2.65)

This is valid for the condition $h\nu = h\nu_f - 2k_B T$ at $T=300 \text{K}$ corresponding to $\lambda = 890 \text{nm}$ and $\alpha(\nu) \approx 100 \text{cm}^{-1}$. This shows that free-carrier absorption is not a major limitation in the laser cooling experiment. It can be safely ignored to make the following estimates.

Eq. 2.63 indicates the desired e-h population density (cooling window) for GaAs is:

$$N_2 \sim 10^{19} > N > N_1 \sim 10^{15} \text{cm}^{-3}.$$  

The break-even non-radiative lifetime ($\tau_0$) as a function of the luminescence extraction efficiency ($\eta_e$) in bulk GaAs at 300K is plotted in Fig. 2.17. This calculated lifetime delineates the cooling zone and heating zone (shaded area). In bare GaAs
the luminescence extraction efficiency is calculated to be \( \approx 2\% \) (see Chapter 4). As is shown in Fig. 2.17, the minimum non-radiative lifetime to reach the cooling zone in bare GaAs is 450 \( \mu s \). When a dome lens is used the extraction efficiency improves to \( \eta_e \approx 14\% \), which reduces the minimum non-radiative lifetime to less than 10 \( \mu s \). Background absorption in the semiconductor device increases the minimum required non-radiative lifetime. Lowering the starting temperature in a laser cooling experiment has the desirable effect of weakening non-radiative processes and increasing radiative recombination. The effect of temperature will be discussed later in this chapter.

![Diagram showing the break-even non-radiative lifetime as a function of the luminescence extraction efficiency in bulk GaAs at 300K.](image)

Figure 2.17: The break-even non-radiative lifetime as a function of the luminescence extraction efficiency in bulk GaAs at 300K. This calculated lifetime delineates the cooling zone and heating zone (shaded area). A bare GaAs wafer \( (\eta_e \approx 2\%) \) requires a minimum non-radiative lifetime of 450 \( \mu s \). With a dome lens \( (\eta_e \approx 14\%) \), the minimum non-radiative lifetime drops to less than 10 \( \mu s \).

The net power density \( P_{net} \) is a direct measure of a device’s ability to cool. For a GaAs sample with thickness 0.75 \( \mu m \) \( P_{net} \) is plotted vs laser wavelength for different carrier densities (Fig. 2.18). Background absorption in the device is taken to be \( \sim 10^{-4} cm^{-1} \) (see Chapter 4). At room temperature, the mean luminescence of GaAs is found to be 860 nm (refer to Eq. 2.51).
As shown in Fig. 2.18, the cooling or heating power density is carrier density dependent. The absorption coefficient given by Eq. 2.22 is used to make this plot. The effect of band-filling is taken into account with the Fermi-Dirac factor. This is used to estimate the cooling/heating power density vs wavelength at different e-h population densities. A more sophisticated model that includes an absorption coefficient influenced by excitonic correlations and Coulomb screening has been developed by Sheik-Bahae et al [73].

An alternate approach to study the break-even condition and estimate a suitable e-h population density range is to use the cooling efficiency defined in Eq. 2.59. The advantage here is that external quantum efficiency (\(\eta_{ext}\)) is related to cooling efficiency (\(\eta_c\)) in a straightforward manner. This allows direct measurement of (\(\eta_{ext}\)) in a cooling experiment (see cChapter 4).
Net cooling occurs when $\eta_c > 0$ or $\eta_{abs} \eta_{ext} \frac{h \tilde{\nu}_f}{h \nu} - 1 > 0$. Rearranging this equation gives:

$$\eta_{abs} \eta_{ext} > \frac{h \nu}{h \tilde{\nu}_f}.$$  \hfill (2.66)

A practical cooler will have the removed energy quantum $h \tilde{\nu}_f - h \nu$ of the order of the thermal energy $k_B T$. Applying this to Eq. 2.66 leads to the following estimate:

$$\eta_{abs} \eta_{ext} > 1 - \frac{k_B T}{E_{gap}}.$$  \hfill (2.67)

The external quantum efficiency $\eta_{ext}$ required to achieve net cooling is derived from Eq. 2.67:

$$\eta_{ext} > \frac{(1 - \frac{k_B T}{E_{gap}})}{\eta_{abs}} \approx 1 - \frac{k_B T}{E_{gap}} + \frac{\alpha_b}{\alpha(N, \nu)}. \hfill (2.68)$$

In GaAs with negligible background absorption, $\eta_{ext}$ has to be larger than 98% to achieve net cooling at room temperature. The external quantum efficiency $\eta_{ext}$ vs density $N$ is plotted in Fig. 2.19 for a typical GaAs cooling device. Curve (2) corresponds to GaAs cooling device with non-radiative recombination lifetime of $\tau_{nr} = 1/A = 25 \mu s$ and curve(1) corresponds to $\tau_{nr} = 1/A = 2.5 \mu s$. The best $\eta_{ext}$ measured so far for a GaAs\GaInP heterostructure bonded to a ZnSe dome lens is 96% at room temperature [21, 26].

In a semiconductor cooling device, the optimum density $N_{opt}$ for maximizing $\eta_{ext}$ (Eq. 2.56) can be determined as follows:

$$\frac{d \eta_{ext}}{dN} = 0 \rightarrow N_{opt} = \sqrt{\frac{A}{C}}.$$  \hfill (2.69)
This density \( N_{\text{opt}} \) maximizes the cooling power density \( P_{\text{net}} \) (see Fig. 2.18). At this optimum population density \( N_{\text{opt}} \), \( \eta_{\text{ext}} \) is found to be:

\[
\eta_{\text{ext}}(N_{\text{opt}}) \approx 1 - 2\sqrt{\frac{AC}{\eta_e B}}. \tag{2.70}
\]

From Eq. 2.66 at optimum carrier density, the break-even condition enforced by Eq. 2.64 is achieved:

\[
\eta_{\text{ext}}(N_{\text{opt}}) \approx 1 - 2\frac{\sqrt{AC}}{\eta_e B} > \frac{-\eta_{\text{qc}}}{\eta_{\text{abs}}} \approx -\eta_{\text{qc}} + \frac{\alpha_b}{\alpha(N, \nu)}.
\tag{2.71}
\]

Rearranging Eq. 2.71 yields:

\[
A < \frac{[\eta_{\text{qc}} - \frac{\alpha_b}{\alpha(N, \nu)}] (\eta_e B)^2}{4C} \tag{2.72}
\]

Figure 2.19: External quantum efficiency \( \eta_{\text{ext}} \) vs population density \( N \) for GaAs bonded to ZnS/ZnSe. Curve (2) assumes a non-radiative lifetime of \( \tau_{\text{nr}} = 1/A = 25\,\mu\text{s} \) and curve (1) corresponds to \( \tau_{\text{nr}} = 1/A = 2.5\,\mu\text{s} \). The extraction efficiency \( \eta_e = 14\% \) is taken from a numerical calculation for GaAs bonded to a ZnS or ZnSe dome lens. The population density defining the cooling window \( N_1 - N_2 \) and \( N_{\text{opt}} \) are also shown (see Eqs. 2.63 and 2.69).
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\[ A < A_0, \]

where \( A_0 \) was defined earlier as the maximum acceptable non-radiative recombination rate to achieve net cooling.

The value of the linear non-radiative recombination coefficient, \( A \), can vary drastically from sample to sample. In the case of large non-radiative recombination coefficient and/or low extraction efficiency and/or large background absorption, it is not possible to achieve net cooling. These problems can be addressed starting a laser cooling experiment at temperatures below 300 K. Radiative recombination increases at low temperatures and the non-radiative recombination processes slow down. As a result, \( \eta_{ext} \) can increase to a point that net cooling is feasible. The theoretical investigation of laser cooling at low temperatures will be discussed next. The experimental result will be presented later in Chapter 6.

2.3.3 Spatial effect, carrier diffusion effect and spatial averaging

In the previous section, it was assumed that photo-carriers are generated with a spatially uniform (i.e. top-hat) laser beam profile; the effect of carrier diffusion length is assumed to be negligible. These assumptions allowed a derivation of cooling power, cooling efficiency, and the break-even condition. In this section, a non-uniform laser beam profile is considered i.e. the Gaussian TEM\(_{00} \) mode. The effect of carrier diffusion is also estimated.

I) The effect of a nonuniform (Gaussian) beam profile

A top-hat uniform beam and Gaussian beam are assumed to generate e-h pairs within the same area. The top-hat beam illuminates an area of \( \pi r_0^2 \), where \( r_0 \) is the beam
radius. For the Gaussian profile, the irradiance is $I(r) = I_0 \exp \left( -2r^2 / w_0^2 \right)$ where $w_0 = r_0 / \sqrt{2}$.

The average cooling efficiency for both beam profiles is defined following Eq. 2.54 except $P_{\text{net}}$ and $P_{\text{total}}$ are replaced by their spatially-averaged values. To make an initial estimate, parasitic background absorption and carrier density-dependent absorption are ignored. The spatially-averaged cooling efficiency is:

$$\langle \eta_c \rangle = \frac{\int P_{\text{net}} ds}{\int P_{\text{abs}} ds} = \left[ \frac{\int \eta_e B N^2 ds}{\int (A N + \eta_e B N^2 + C N^3)ds} \right] \times \frac{\tilde{v}_f}{\nu} - 1 \tag{2.73}$$

where $ds$ is the surface integral increment. The averaged external quantum efficiency $\langle \eta_{\text{ext}} \rangle$ is defined as:

$$\langle \eta_{\text{ext}} \rangle = \frac{\int \eta_e B N^2 ds}{\int (A N + \eta_e B N^2 + C N^3)ds} \ . \tag{2.74}$$

The e-h carrier density $N(r)$ is derived from carrier density equation (Eq. 2.44. This equation relates photocarrier density $N(r)$ to the laser intensity $I(r)$ via different e-h recombination processes and the density-dependent absorption coefficient. To make an initial estimate, the absorption is assumed to be constant: $\alpha(\nu, N(r)) \approx \alpha(\nu)$. At steady state condition, the external quantum efficiency simplifies to:

$$\langle \eta_{\text{ext}} \rangle = \frac{\int \eta_e B N^2 ds}{\int (A N + \eta_e B N^2 + C N^3)ds} \ . \tag{2.75}$$

The e-h carrier density $N(r)$ is derived from carrier density equation (Eq. 2.44. This equation relates photocarrier density $N(r)$ to the laser intensity $I(r)$ via different e-h recombination processes and the density-dependent absorption coefficient. To make an initial estimate, the absorption is assumed to be constant: $\alpha(\nu, N(r)) \approx \alpha(\nu)$. At steady state condition, the external quantum efficiency simplifies to:

$$\langle \eta_{\text{ext}} \rangle = \frac{\eta_e B h \nu \int N^2(r)ds}{\int \alpha(r)I(r)ds} \ . \tag{2.76}$$
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The carrier density $N(r)$ can be determined by obtaining the appropriate root of the third order polynomial shown in Eq. 2.44.

In the previous section, $\eta_c$, $\eta_{ext}$, and $P_{net}$ were estimated for GaAs. The spatially-averaged external quantum efficiency in GaAs for a uniform and Gaussian beam profile is plotted vs incident absorbed power in Fig. 2.20. Previously used values of $A = 40000 \text{ sec}^{-1}$, $B = 4.5 \times 10^{-10} \text{ cm}^{-3}$, $C = 4 \times 10^{-30} \text{ cm}^{-6}$, and $\eta_e = 14\%$ are assumed. The absorption coefficient at the cooling photon energy (i.e. for a pump photon $h\nu = h\tilde{\nu}_f - k_BT \approx 1.4 \text{ eV at } T = 300K$) is $\alpha(\nu) \sim 1000 \text{ cm}^{-1}$ [74]. The laser illuminates a sample with thickness of 1$\mu$m within an area of radius of $r_0 = 100\mu$m.

![Figure 2.20: Calculated external quantum efficiency for a top-hat beam (solid line) and Gaussian beam (dotted-line) plotted vs absorbed laser power. Peak external quantum efficiencies are $\eta_{ext} = 0.98746$ and $\eta_{ext} = 0.98635$, respectively. The absorbed power at maximum $\eta_{ext}$ is 0.575 mW and 1.55 mW, respectively, assuming a beam radius of 100$\mu$m.](image)

Fig. 2.20 shows the averaged external quantum efficiency for a top-hat beam is slightly larger than the Gaussian beam profile. Additionally, the maximum value

\[\text{The semiconductor samples studied here are thin enough that the photo-carriers are generated uniformly within the excited volume}\]
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of $\eta_{ext}$ occurs at higher incident power for a Gaussian beam. A varying spatial
distribution causes non-uniform recombination rates.

Note that for a typical GaAs sample with $\tau_{nr} = 20$–$30$ µsec and $\eta_e \sim 12$–$15$
(see Chapters 4 and 6), changing the power of a Gaussian pump beam by 2–3 times
causes only a minor change in $\eta_{ext}$. The reader is reminded that this calculation
ignores parasitic background absorption.

The average cooling efficiency $\langle \eta_c \rangle$ can be estimated based on $\langle \eta_{ext} \rangle$. Using
Eq. 2.59:

$$\langle \eta_c \rangle = \tilde{\nu} f \langle \eta_{ext} \rangle - 1 \approx \left( 1 + \frac{k_B T}{E_g} \right) \langle \eta_{ext} \rangle - 1,$$  \hspace{1cm} (2.77)

where the approximation $h\tilde{\nu} f \approx E_g$ is made.

An estimate for $\eta_{ext}$ can be made assuming an asymmetric Gaussian beam with
ellipticity of two. Within the numerical accuracy, no difference between symmetric
and asymmetric Gaussian beam profile is found.

In conclusion, the required laser pump power increases with a Gaussian beam
(i.e. TEM\(_{00}\)), while the change to $\eta_{ext}$, $\eta_c$, and $P_{net}$ is negligible. When a Gaussian
beam is employed, however, it may not possible to generate an optimum e-h popu-
lation density at a low temperature as a result of absorption saturation.

II) The effect of e-h carrier diffusion

To this point, the density balance equation has been used while ignoring carrier
diffusion. In the absence of an external electric field, the density equation can be
generalized to:
\[
\frac{dN(r,t)}{dt} = 0 = \frac{\alpha(\nu, N(r,t))}{h\nu} I - AN(r,t) - \eta eBN^2(r,t) - CN^3(r,t) + D_a \nabla^2 N(r,t),
\]

where the last term in the right hand side accounts for carrier diffusion with the ambipolar diffusion coefficient \(D_a\) \cite{39, 62}. If the photocarrier density is not uniform such as occurs when the laser spot is much smaller than the sample area, diffusion can be important \(^{20}\).

The electron-hole diffusion length \((L_{e-h})\) can be estimated and compared to laser beam diameter. The diffusion length is the mean distance that carriers travel before recombining. It is related to ambipolar diffusion coefficient \(D_a\) and recombination lifetime \(\tau\) as \(L_{e-h} = \sqrt{D_a\tau}\) \cite{62}. Diffusion coefficient is dominated by electrons since their mass is much smaller than the holes and hence their mobility is higher. This leads to the approximation \(D_a \approx D_e\). The diffusion coefficient is related to mobility via Einstein relation \(D_e = \mu_e k_B T / e\) where \(\mu_e\) is the electron mobility and \(e\) is the electronic charge \cite{62}. The recombination lifetime depends on carrier density \(N\). In an efficient laser cooling experiment, the recombination lifetime is dominated by the radiative process. Carrier densities are of the order of \(\sim 10^{17} \text{ cm}^{-3}\), which makes the radiative lifetime \(\tau = 1/BN \approx 2 \times 10^{-8} \text{ sec}\) at room temperature. At lower temperatures this lifetime decreases (discussed previously). The electron mobility in GaAs with impurity level of \(10^{14} - 10^{15} \text{ cm}^{-3}\) (i.e. consistent with our samples) is reported to be \(\sim 8500 \text{ cm}^2\text{V}^{-1}\text{sec}^{-1}\) \cite{62}. The electron diffusion coefficient found from the Einstein relation is \(D_a \approx 260 \text{ cm}^2\text{sec}^{-1}\), which makes the average diffusion length approximately \(L_{e-h} \sim 20\mu\text{m}\). This means that for a laser beam with a

\(^{20}\)The inhomogeneity discussed here involves the transverse dimensions; carriers uniformly fill the heterostructure depth.
footprint much larger than diffusion length (e.g. 100 × 100 μm²), the effect of carrier diffusion can be neglected.

Diffusion does, however, set a limit on minimum laser power for very tight focusing. Focusing to a vanishingly small area will still result in an effective beam footprint dictated by photocarrier diffusion. The calculation shown in Fig. 2.20 assumed a beam radius of 100 μm resulting in an optimum absorbed laser power of 1 mW. In the limit where focusing is much tighter than the diffusion length, the interaction diameter is \( L \sim 20 \) μm leading to a corresponding reduction of beam irradiance and a minimum absorbed pump power of 160 μW.

### 2.4 Prospect of laser cooling at low temperatures.

In this section, the laser cooling condition and external quantum efficiency are studied at temperatures below 300 K. The temperature-dependence of the various processes are shown to be of critical importance.

As the temperature decreases below 300 K, non-radiative interface recombination becomes less efficient. This is a direct result of the multi-phonon emission theory (MPE) discussed previously. Radiative recombination, on the other hand, increases at lower temperatures. This is the direct result of increasing e-h momentum confinement in the conduction and valence bands. The bimolecular e-h radiative recombination coefficient is given by Eq. 2.30: \( B(T) = B_0 \left(\frac{300}{T}\right)^{3/2} \), where \( T \) is in Kelvin.

The Auger non-radiative process also decreases with temperature, again due to e-h confinement. Auger scattering requires that momentum be conserved; large momentum exchange is more difficult to achieve at lower temperature, giving rise to the following temperature-dependent coefficient in Eq. 2.42 such as:
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\[ C(T) = C_0 \exp(-\alpha E_g / k_B T), \]
where \( \alpha E_g \) is the threshold or activation energy for the Auger process.

Time-resolved spectroscopy and luminescence measurements reveal that the heterostructures used in this work are slightly p-type (see Chapter 6), which means CHHS Auger recombination is the dominant path [67]. A measurement of the Auger coefficient vs temperature in p-GaAs has been made by Takashima [67]. This data is fit with an empirical formula (Eq. 2.42):

\[ C(T) = C_0 \exp \left[ \beta \left( 1 - \frac{300k}{T} \right) \right], \]  
(2.78)

where \( \beta = 2.24 \) [67] and \( 1 \times 10^{-30} < C_0 < 7 \times 10^{-30} \text{cm}^6 / \text{s} \) [24] is the Auger coefficient at \( T = 300 \text{ K} \).

A reduction in the interface and Auger non-radiative processes and an increase in the radiative rate are exactly the desired conditions for attaining laser cooling. The break-even lifetime was derived in Eq. 2.64 and reproduced here: \( A_0 = \left[ \eta_{qc} - \alpha_b l_b / \alpha(n) l_a \right]^2 (\eta_e B)^2 / 4C' \). The break-even lifetime vs temperature can be written as:

\[ \frac{\eta_e^2}{A_0} = \tau_0 \left( \frac{T}{300K} \right) \exp \left( \beta \left( 1 - \frac{300K}{T} \right) \right), \]  
(2.79)

which is derived from the known temperature scaling of radiative and Auger recombination, ignoring background absorption, and using the approximation \( \eta_{qc} \approx 1 - k_B T / E_g \). This defines a characteristic lifetime \( \tau_0 \) in Eq. 2.79:

\[ \tau_0 = \frac{4C_0 B_0^2}{E_g^2} \left( \frac{E_g}{0.026} \right)^2 \]  
(2.80)

where \( B_0, C_0, \) and \( E_g \) are the radiative coefficient, Auger coefficient, and bandgap energy (eV), respectively, at 300 K \(^{21}\). For GaAs, the value of \( \tau_0 \) is in the range 100

\(^{21}\) \( E_g \) changes by an amount 1.52–1.43 eV for \( T = 0–300 \text{ K} \). This is much smaller than \( \left( \frac{T}{300K} \right) \exp \left( \beta \left( 1 - \frac{300K}{T} \right) \right) \)
ns < \tau_0 < 1 \text{ ms} \) due to the uncertainty in \( B_0 \) and \( C_0 \) \([24]\). The calculated break-even lifetime vs temperature for a 1 \( \mu \text{m} \) sample bonded to a ZnS dome is shown by the solid curve in Fig. 2.21. Non-radiative lifetimes above the solid curve are conducive to net cooling; heating occurs below the curve (shaded region).

![Figure 2.21: Break-even condition vs temperature for 1.0 \( \mu \text{m} \) GaAs sample. The solid curve is the calculated minimum non-radiative lifetime (1/\( A_0 \)) required to attain net cooling (\( \tau_0 = 500 \text{ ns} \) and \( \eta_e = 10\% \)). The shaded (unshaded) region corresponds to net heating (cooling). The dashed curve is the measured surface non-radiative lifetime of unetched GaAs\GaInP. Dotted curve is measured non-radiative lifetime after processing.](image)

As will be discussed in Chapter 6, lift-off processing and bonding (see Chapter 5) degrade the non-radiative lifetime. The measured recombination velocity parameters and temperature scaling of \( S \) allow calculation of the non-radiative lifetimes for both unprocessed (dashed curve) and processed (dotted curve) samples. As is shown in Fig. 2.21, laser cooling should be possible even in processed samples at \( T < 250 \text{ K} \).

The material-dependent break-even external quantum efficiency for cooling was derived in Eq. 2.71 as \( \eta_{\text{ext}}(N_{\text{opt}}) \approx 1 - 2\sqrt{AC_0}/\eta_eB_0 > 1 - kT/E_g \) where the background absorption is assumed to be negligible. When temperature is included, the break-even external quantum efficiency at optimum carrier density becomes:
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\[
\eta_{\text{ext}}^{\text{opt}}(T) = 0 = 1 - 2\sqrt{AC_0 \over \eta_e B_0} \left[ \left( {T \over 300} \right)^{3/2} \exp \left\{ {1 \over 2} \left( {E_a \over 0.026} + \beta \right) \left( 1 - {300 \over T} \right) \right\} \right] > 1 - {k_B T \over E_g(T)}
\]  

(2.81)

which is derived from the known temperature scaling of radiative, Auger, and non-radiative recombination coefficients and using the approximation \( \eta_{\text{qc}} \approx 1 - k_B T / E_g(T) \approx 1 - k_B T / E_g(300) \) \(^2\). The value of \( A = 1/27 \mu s \) with \( E_a = 0.018 \) eV is measured for a 1 \( \mu m \) GaAs\GaInP sample (see Chapter 6). Using \( A = 1/27 \mu s \), the value of \( 1 - 2\sqrt{AC_0 / \eta_e B_0} \) varies between 0.9%–0.99% due to uncertainty in \( B_0 \) and \( C_0 \) [24] where \( \eta_e \approx 10\% \) in 1\( \mu m \) GaAs attached to ZnS is considered in the estimate (see Table 4.2)). A value of \( \eta_{\text{ext}} = 96\% \) has been measured several times for a \( d \approx 1 \mu m \) GaAs\GaInP at room temperature [21, 26, 73] (see also Chapter 6).

Figure 2.22: External quantum efficiency vs temperature is plotted at optimum carrier density. The heating and cooling region are indicated by gray and white color, respectively.

Taking \( d = 1 \, \mu m \), the external quantum efficiency vs temperature at optimum carrier density is plotted in Fig. 2.22. The plot shows that cooling can be achieved

\(^2\)The temperature dependence of \( E_g \) is negligible compared to \( k_B T \)
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below 200 K for a processed sample having 96% external quantum efficiency at room
temperature; in this calculation it is assumed the trap density does not change at
lower temperature and different carrier densities. An issue of concern not addressed
here is the role of Pauli band-blocking and bleaching of inter-band absorption, espe-
cially at low temperatures.

The optimum carrier density required to maximize \( \eta_{\text{ext}} \) is also temperature de-
pendent as a result of the temperature-dependent recombination coefficient. The
optimum carrier density was derived previously as \( N_{\text{opt}} = \sqrt{A/C_0} \) (see Eq. 2.69). The
temperature dependence of the optimum carrier density can be written as:

\[
N_{\text{opt}} = \sqrt{\frac{A}{C_0}} \exp \left( \frac{1}{2} \left( \frac{E_a}{0.026} - \beta \right) \left( 1 - \frac{300}{T} \right) \right) \tag{2.82}
\]

which is derived from the known temperature scaling of Auger and non-radiative
recombination coefficients. The optimum carrier density, boundary-carrier density
to attain cooling (i.e. \( N_1 \) and \( N_2 \) defined in Eq. 2.69), and the maximum attainable
carrier density limited by band-blocking at \( \sim k_B T \) above mean luminescence (this
occurs when the difference in the quasi-Fermi levels \( \{f_{ev} - f_{ec}\} \approx 0 \) are plotted in
Fig. 2.23.

In plotting Fig. 2.23, it is assumed the \( d = 1 \mu m \) sample of GaAs\GaInP has a
non-radiative lifetime of 27 \( \mu s \) at 300 K and \( E_a = 0.018 \) eV as discussed previously.
The average of reported values are used to set \( B_0 = 5 \times 10^{-10} \text{cm}^{-3} \text{sec}^{-1} \) and \( C_0 =
4 \times 10^{-10} \text{cm}^{-6} \text{sec}^{-1} \) [24]. The carrier density \( N_{\text{Max}} \) where bleaching of the interband
absorption occurs is estimated by taking the quasi-Fermi levels as \( E_{FC} \approx E_C \approx 1.42\)
eV and \( E_{FV} \approx E_V \approx 0 \) eV in Eq. 6.2 and \( n_0(T) \approx p_0(T) \approx N_{\text{Max}}(T) \) condition [39].
The shaded area denotes the cooling carrier density window. The maximum carrier
density in the cooling window is limited by Pauli band-blocking. The density \( N_{\text{opt}} \)
for typical high quality samples \(^{23}\) can be compared with \( N_{\text{Max}}(T) \). An optimum

\(^{23}\)Almost all the GaAs\GaInP samples studied here demonstrate a non-radiative lifetime
density $N_{opt}$ should be achievable down to 77K. Below 77 K, $\eta_{ext}$ approaches unity even for $N = N_{Max} < N_{opt}$. This result can be understood since the non-radiative terms $A$ and $C$ tend to zero at $T < 77$ K.

$\eta_{ext}(T)$ at optimum and bleaching carrier densities are plotted in Fig. 2.24.

In plotting $\eta_{ext}^{N_{Max}}(T)$, value of $\eta_{ext} = 96\%$ is taken at room temperature as discussed earlier. This is the external quantum efficiency that has been measured and reported for $d \approx 1 \mu m$ sample of GaAs/GaInP at room temperature [21, 26, 73].

All samples used here are slightly unintentionally p-doped due to a small concentration of residual carbon or zinc in crystal growth reactor. The presence of an acceptor background can cease the cooling cycle at low temperatures ($< 77$ K); it is > 20 $\mu s$ (see Chapter 6)

24It is assumed that a long non-radiative lifetime is maintained at low temperatures for all carrier densities (see Chapter 6)
Figure 2.24: External quantum efficiency vs temperature is plotted at bleaching $N_{\text{max}}$ and optimal $N_{\text{opt}}$ carrier densities. Below 77K for typical high quality samples $\eta_{\text{ext}}$ remains one even at $N = N_{\text{Max}} < N_{\text{opt}}$ (see Fig. 2.23).

due to freeze-out of the acceptors and opening of new path for bimolecular recombination from the conduction band to acceptor level (see Fig. 6.11). Electrons at acceptor level then recombine with holes at valence band non-radiatively, returning thermal energy to the lattice via phonon emission. The net effect is red shifting of the luminescence. This is the same problem occurs in rare earth doped glasses as discussed in Chapter 1. To achieve net cooling at low temperatures ($T \sim 10K$)[31], very pure samples is required.

## 2.5 Investigation of laser cooling in different direct bandgap semiconductors

The laser cooling analysis presented in the previous section is general and applies to all direct-band-gap semiconductors. Comparing recombination coefficients $A$, $B$ and $C$ in different types of direct-band-gap semiconductors help select the best candidates...
for laser cooling experiments. The non-radiative recombination coefficient $A$ strongly depends on the quality of crystal growth and processing. The radiative rate $B$ and Auger coefficient $C$ are fundamental properties of a particular semiconductor. Note that the radiative recombination coefficient $B$ is roughly the same for all direct bandgap semiconductors (see Fig. 2.9)

As the direct band-gap energy decreases, cooling efficiency increases. The Auger recombination coefficient $C$, in turn, increases exponentially with decreasing bandgap energy (see Fig. 2.14). The dominance of the Auger term causes $\eta_{ext}$ to decrease drastically in small bandgap semiconductors [23]. As is shown in Fig. 2.14, Auger recombination is the critical limiting factor for small bandgap semiconductor in a laser cooling application. Crystal growth technology for wide gap semiconductors is not yet mature leading to unacceptably high background absorption and non-radiative recombination as required by by Eq. 2.71. A high power tunable laser source in a wavelength region compatible with the semiconductor bandgap energy is also needed.

A GaAs layer passivated with GaInP provides a manageable non-radiative recombination rate and moderate Auger non-radiative coefficient and is at the present time the best candidate for laser cooling with a widely available Ti:sapphire laser pump. Narrow gap semiconductors may have promise for laser cooling at very low starting temperatures.
Chapter 3

Pump laser: Ti:Sapphire laser system

In the laser cooling experiment, pump photons with energies below the mean luminescence energy generate e-h pairs in the conduction band. A tunable, cw Ti:Sapphire laser with appropriate optical components is used for the laser cooling experiment with GaAs. The bandgap energy of GaAs is temperature dependent as will be discussed in Chapter 6. As temperature changes in the range $10^{-400} K$, the bandgap energy of GaAs varies as $1.38 - 1.52 eV$ [54]. A cw Ti:Sapphire laser tuneable over the wavelength range 800–950 nm produces pump photons of energy $1.3 - 1.6 eV$. In this solid state laser system, titanium ($Ti^{3+}$) doped into the transparent Sapphire crystal ($Al_2O_3$) is responsible for stimulated emission.

In order to create population inversion, $Ti^{3+}$ ions are usually pumped with intense laser light [17]. Pump light can be obtained from argon lasers (514.5 nm) or frequency-doubled $Nd : YAG$, $Nd : YLF$, and $Nd : YVO$ lasers (527–532 nm). The Ti:Sapphire laser can be tuned between 660–1180 nm [17] (see Fig. 3.1). In our experiment, an 8-Watt intracavity-doubled neodymium: vanadate ($Nd : YVO$) laser.
(Verdi-V8, Coherent Inc.) is used as a pump source at $\lambda = 532\text{nm}$. 

The Ti:Sapphire laser used in this dissertation work operates from 770–950 nm in the continuous (cw) mode. In order to cover this wide range of wavelengths, two sets of optical mirrors are used in the resonator. The optical mirror sets are coated and optimized for a lasing range of 800 nm–890 nm and 850–920 nm. Laser output can be obtained outside these ranges (770–800 nm and 920–950 nm) but power is low and output is unstable at the extremes. This Ti:Sapphire laser is also used for absorption measurements in dome lens material (see Chapters 4 and 6). 

A schematic diagram of the asymmetric gamma-cavity is shown in Fig. 3.2. The two curved mirrors MR$_1$ and MR$_2$ (R=10 cm) and flat mirror BM are dielectric coated to be highly reflective (HR) between 800–920 nm and anti-reflection (AR) coated at the pump wavelength of 532 nm. The output coupler mirror OCM is a flat surface with $\approx 95\%$ reflectivity in the range 800–920 nm.

The two curved mirrors MR$_1$ and MR$_2$ are tilted horizontally by about 22.5° to compensate for astigmatism created by the Brewster angle cut Sapphire crystal [17].
Chapter 3. Pump laser: Ti:Sapphire laser system

Figure 3.2: Schematic diagram of the cw Ti:Sapphire laser used in the experiments with critical distances shown.

Brewster angle surfaces prevent intra-cavity Fresnel reflection loss. A 10 cm focal length lens focuses the pump laser light into the Sapphire crystal. This lens provides mode matching between pump and Ti:Sapphire laser beams. Critical distances such as crystal position, distance between mirrors MR$_1$ to MR$_2$, and position of the focusing lens are estimated based on calculations [17]. Distances and alignment are fine tuned during lasing operation to produce maximum output power. Laser output is always p-polarized due to the Brewster-cut Sapphire crystal.

The operating laser wavelength is selected based on the gain and loss of the cavity. In its simplest configuration, the laser wavelength is neither stable nor tunable. In order to select a fixed wavelength, a birefringent wave plate is placed at Brewster angle inside the cavity. The combination of wave plate and Brewster cut Ti:Sapphire crystal form a birefringent filter that provides the desired tuning. Birefringent filters are useful in a number of applications including tuning of synchronously pumped optical parametric oscillators, tuning dye and Ti:Sapphire lasers, and for line-narrowing in solid-state lasers [75, 76, 77].
An optically anisotropic birefringent medium such as quartz wave plate creates a relative delay between ordinary and extraordinary rays aligned along the fast and slow axes of the crystal. The birefringent plate is a linear retarder, with the crystal axis parallel to the faces of the plate. It is used for line-narrowing by selectively tuning a desired wavelength and creating reflection losses at other wavelengths. In the laser described in this chapter, the quarter wave plate is placed at the Brewster angle. The crystal can be rotated around its axis to achieve full wave retardation at the wavelength of interest. The selected wavelength will contain only p-polarization and thus will experience no reflection loss. Other wavelengths will necessarily have some s-polarization, leading to reflection losses at the Ti:Sapphire crystal. Wavelength resolution is dictated by the wave plate thickness. A zero-order wave plate is used to achieve maximum tuning bandwidth [78]. The Ti:Sapphire laser output wavelength is tunable within the resolution of an Ocean-Optics USB-4000 spectrometer $\pm 0.3\text{nm}$. This is more than enough selectivity for laser cooling experiments since the wavelength difference corresponding to $k_B T$ (average energy gained from lattice) is $\Delta \lambda \approx 5 - 15\text{nm}$ for absolute temperatures in the range 100-300 K. A photograph of the laser setup is shown in Fig. 3.3.

The laser output is a slightly elliptical beam with diameters of $d_x = 1.8\text{mm}$ and $d_y = 1.6\text{mm}$. The ellipticity is due to astigmatism in the Brewster cut crystal, which is not completely compensated by tilting mirrors $MR_1$ and $MR_2$. Complete removal of astigmatism causes an unacceptable loss of laser power. The Ti:Sapphire laser operates in TEM$_{00}$ mode. The wavelength-dependent output power for 8-Watt pumping is plotted in Fig. 3.4.
Chapter 3.  *Pump laser: Ti:Sapphire laser system*

Figure 3.3: Photograph of the cw Ti:Sapphire pump laser. The beam path is shown in red. An electronic shutter is used inside the laser cavity to gate-off lasing for a few msec. Time-gating laser output helps with temperature measurement of GaAs using the DLT technique (see Chapter 6).

Figure 3.4: Power output of the Ti:Sapphire laser plotted vs wavelength for two different sets of mirrors.
Chapter 4

Luminescence extraction in semiconductors

4.1 Introduction

Laser cooling in semiconductors requires that the dominant path of electron-hole (e-h) recombination is via luminescence emission. This condition by itself is not enough to cool the device since a large portion of the luminescence is trapped. The luminescence must be removed from the sample to complete cooling cycle. Snell’s Law dictates that total internal reflection occurs for a range of incidence angles when light attempts to propagate across a high-to-low index interface (see Fig. 4.1). The larger the index mismatch, the smaller the escape cone for light rays propagating in the high index material. In a thin slab of GaAs with refractive index of \( n = 3.6 \) [74] a 16° cone angle exists for light escaping to air or vacuum (\( n = 1 \)). For a slab of a material with refractive index \( n \) in vacuum, the ratio of extracted optical power to the total generated optical power is (assuming no multiple reflections or interference): \( \eta_e \approx 3(1 - (1 - 1/n^2)^{1/2}) \), [19]. The light extraction efficiency for glasses
Chapter 4. Luminescence extraction in semiconductors

(n ≈ 1.5) is, \( \eta_e \approx 76\% \). A thin slab semiconductor has light primarily escaping from just two surfaces; in this case, \( \eta_e \approx (1 - (1 - 1/n^2)^{1/2}) \) corresponding to \( \eta_e \approx 4\% \) for GaAs. When luminescence occurs primarily around the bandgap energy, material absorption should be accounted in determining \( \eta_e \). Including absorption at the mean luminescence wavelength \( \alpha \) gives \( \eta_e \sim (1 - (1 - 1/n^2)^{1/2}) \exp(-\alpha l_a) \) where \( l_a \) is the thickness of the device in Fig. 4.1 (see Chapter 2).

![Figure 4.1: Illustration of luminescence trapping in a thin slab semiconductor.](image)

The absorption coefficient of GaAs at the mean luminescence wavelength (\( \lambda \sim 860\,nm, T = 300K \)) is \( \sim 8000\,cm^{-1} \) [74]. A 1\( \mu \)m thick GaAs sample produces \( \eta_e \sim 2\% \). This extraction efficiency is about thirty times less than the rare earth-doped glass [20].

Extracting luminescence from semiconductor devices is an ongoing challenge in the design of light emitting diodes (LEDs)\(^1\). There are different techniques to enhance luminescence extraction in LED’s and these solutions can in principle be applied to laser cooling. In the laser cooling experiment, however, there are additional design issues. If the background parasitic absorption is not managed properly, the absorption efficiency \( \eta_{abs} \) will decrease drastically. Such concerns are addressed in this chapter.

\(^1\)A light-emitting diode (LED) is a direct bandgap semiconductor device that emits light around its bandgap energy.
4.2 Short overview in light extraction schemes in LED’s

High efficiency light-emitting diodes (LEDs) are needed for many applications such as displays, printers, short-haul communications, and optoelectronic computer interconnects. There is a large difference between the internal and external quantum efficiencies of a commercial LEDs. The internal quantum yield of good quality III-V double heterostructures can exceed 99% [21, 26, 79]. These ordinary LEDs, however, have an overall efficiency that is only a few percent due to luminescence trapping. A luminescence photon can follow three different paths: i) it can enter the surface escape cone and leave the device, ii) it can suffer parasitic optical absorption and get converted to heat, or iii) it can be reabsorbed in the active layer and experience reincarnation as a photon in some new, random direction. In bare GaAs, for example, the photons have a 2% probability of finding the escape cone. For a high internal quantum efficiency layer with low parasitic absorption, the external quantum efficiency is derived as $\eta_{ext} \approx \eta_{int}^{1/\eta_e}$ (see Eq. 2.57). In the case of low parasitic absorption and high internal quantum efficiency, the number of recycling round trips is $N \approx 1/\eta_e$ [21]. The internal quantum efficiency $\eta_{int}$ is close to but smaller than unity in real devices; therefore in the realistic device optimizing the extraction efficiency is crucial for obtaining high $\eta_{ext}$. A number of schemes have been developed to address this problem: i) hemisphere dome [80], ii) surface texturing [52] and iii) photonic bandgaps (PBG) [81]. Each approach will be briefly discussed.

4.2.1 Hemispherical dome lens

In this approach, the semiconductor heterostructure is placed at the center of the planar face of a dome lens (see Fig. 4.2). The refractive index of the lens should be as
Chapter 4. Luminescence extraction in semiconductors

close as possible to the semiconductor (i.e. nearly index-matched) and the material should not have appreciable absorption at the luminescence wavelengths.

![Dome Lens Concept](image)

Figure 4.2: Illustration of the dome lens concept widely used in LED design. The lens material has refractive index $n_{dome}$ close to the semiconductor $n$. Drawing not to scale.

Luminescence outcoupling improves by about a factor of 10 compared to a bare interface. Fresnel reflection on the round surface can be almost completely eliminated with anti-reflection coating; this increases the efficiency slightly (Fig. 4.2). Neglecting absorption, the light extraction efficiency at a GaAs surface can be improved from $\eta_e \approx 2\%$ for a vacuum interface to $\eta_e \approx 20\%$ using a dome lens made of ZnSe ($n \approx 2.5$ [74]).

4.2.2 Surface texturing

Devices that have a very high internal quantum efficiency and low parasitic absorption may benefit from surface texturing [52]. Upon encountering a textured interface, photons are scattered randomly, which breaks the chain of the continued total internal reflections that occurs at a planar surface (see Fig. 4.3). If parasitic absorption is negligible, the geometrical light extraction efficiency can be improved.

Texturing is limited to thin semiconductor devices because of resonant and parasitic absorption. The trade-off between geometrical extraction efficiency and thickness will be presented later in this chapter.
4.2.3 Photonic-bandgap (PBG)

Spontaneous emission arises from the intricate interplay between a radiating system and its surrounding environment. A prominent example of this interplay can be seen in a photonic crystal, where spontaneous emission can be enhanced, attenuated, or even suppressed by changing the density of electromagnetic states at the transition frequency, or by changing the orbital angular momentum of the emitted photon [82]. The ability to control spontaneous emission could have profound consequences on many optoelectronics devices. Confinement of light to small volumes has important implications for optical emission properties: it changes the probability of spontaneous emission from atoms, allowing both enhancement and inhibition. Therefore a thin slab of two-dimensional photonic crystal (< λ/n) can be used to alter drastically the radiation pattern of spontaneous emission. More specifically, by eliminating all guided modes at the transition frequencies, spontaneous emission can be coupled entirely to free space modes, resulting in a greatly enhanced light extraction efficiency. Such structures might provide a solution to the long-standing problem of poor light extraction from high refractive-index semiconductors in light-emitting diodes [83].

Surface texturing and photonic crystals light may improve light extraction efficiency compared to the dome lens approach. Texturing is only suitable for thin layer devices. The trade-off here is that non-radiative surface recombination (A) becomes more important as the device thickness decreases (See Chapter 2). In addition, the
cooling power density will be lower in thinner semiconductors. In the research presented here, the conventional dome lens approach is used [21, 26] (See Chapter 6).

The primary disadvantage of hemispherical lenses in LEDs is the cost of producing a high refractive index dome. This problem may be partially overcome by using nearly indexed matched plastic epoxy [84] or growing another semiconductor with a hemispherical shape on top of LED [84, 85]. The situation is more complicated in laser cooling since parasitic absorption can lead to deleterious heating. The next section presents measurements of the absorption coefficient of different high refractive index dome materials.

There is a promising alternative method to dome lens approach based on coupling of evanescent waves. This approach will also be discussed later in this chapter.

### 4.3 Light extraction scheme using hemispherical lens

As discussed in Chapters 1 and 2, one of the major obstacles in laser cooling of semiconductors is luminescence trapping. Luminescence trapping occurs due to the refractive index mismatch at the escaping interface. Luminescence trapping can partially overcome by placing the cooling device at the center of nearly index-matched hemispherical (i.e. dome) lens. Efficient coupling exists at the interface, luminescence enters the dome, and finally leaves the dome at close to normal incidence at the curved surface. Fresnel reflection there can be prevented by applying an anti-reflection coating as shown in Fig. 4.4.

The dome lens should have very low parasitic absorption to prevent deleterious

---

2A thin layer may be pumped at the edge to increase cooling power density
heating; this minimum background absorption can be estimated. In Chapter 2, it was shown that \( \eta_c = \eta_{\text{ext}} \eta_{\text{abs}} > 1 - k_B T / E_g \) to achieve net cooling (See Eq. 2.67). The external quantum efficiency is estimated as \( \eta_{\text{ext}} \approx 1 \), leading to \( \eta_{\text{abs}} \approx 1 - k_B T E_g \) at which point cooling and heating are in balance. Using \( \eta_{\text{abs}} = \alpha_b l_b / (\alpha_b l_b + \alpha(\nu, N) l_a) \) from Eq. 2.58:

\[
\alpha_b l_b < \frac{k_B T}{E_g} \times \alpha(\nu) l_a
\]

where the approximation \( \alpha(\nu, N) \approx \alpha(\nu) \) is made.

In GaAs, \( E_g = 1.42eV \) [54] and \( \alpha(\nu) \approx 500 - 1000 cm^{-1} \) [74] in the vicinity of the cooling photon energy at 300 K. For a device with a 1 \( \mu \)m thickness, \( \alpha_b l_b \) must be less than 0.001 to satisfy the break-even condition. If a dome lens with radius of 1 cm is used, the lens material should have absorption coefficient of \( \alpha_b < 0.001 cm^{-1} \).

In the next section, different wide-gap materials are evaluated for suitability as dome lenses: ZnS (Cleartran), ZnSe, TiO\(_2\), and GaP. Although there are many semiconductors with larger energy gaps compared to GaAs, the presence of uncontrolled
imperities leads to a small but measurable amount of background absorption in the near infrared. This absorption can be quantified.

4.3.1 Parasitic absorption in dome lens: measurement and analysis

This section describes a thermal Z-scan technique to measure the absorption coefficient in a number of large bandgap semiconductors [86]. There are other sensitive techniques for measuring small absorption coefficients such as cavity-ring-down spectroscopy \(^3\) [87] and photothermal deflection [88]. The Z-scan technique [86] has superior sensitivity, ease of calibration, and is a non-contact, local absorption measurement. A two color Z-scan detects thermally induced refractive index changes as a result of absorption with little sensitivity to background noise [86]. Additionally, since it is an opto-thermal technique, this approach is most suitable for this laser cooling application. The experimental schematic is depicted in Fig. 4.5.

Pump light from a tunable, near-infrared CW Ti:sapphire laser,(see Chapter 3), is modulated with a mechanical chopper to allow lock-in detection. A thermal lens is created due to the Gaussian spatial profile of the pump and temperature-dependent index of refraction of the material. The probe beam is a low power, continuous He-Ne laser (\(< 1 \text{ mW} ; \lambda = 633 \text{ nm}\)) aligned collinearly with the pump beam. Pump and probe beams are focused with the same lens to a spot sizes of \(w_0 = 16 \pm 3\mu m\) and \(40 \pm 3\mu m\), respectively. Visible probe light monitors the differential refractive index change induced by the near-infrared pump laser. The sample is translated along the optical axis (i.e., the Z-axis), which causes a variation of the pump irradiation.

\(^3\)In cavity ring down, a laser pulse is trapped in a highly reflective (typically \(R > 99.9\%\)) detection cavity. The intensity of the trapped pulse will decreases by a fixed percentage during each round trip within the cell due to both absorption by the medium within the cell and reflectivity losses. This technique is different than calorimetric techniques.
The sample is mounted at Brewster’s angel to prevent Fabry-Perot fringing. Changes in the probe beam divergence are monitored by a detector placed behind a partially obscuring aperture in the far-field. The size of the aperture is set for $\approx 10\%$ transmission of the He-Ne probe beam [89].

The two-color technique gives better sensitivity than a single beam Z-scan where there can be spatial distortion and measurement noise associated with surface imperfections. This occurs because a single laser beam encounters non-uniformities as its spatial profile changes during sample translation. Background subtraction can reduce this, but a non-ideal surface still limits the measurement accuracy. An excite-probe arrangement with lock-in detection can provide a greatly enhanced signal-to-noise ratio [86]. We are able to measure transmittance changes of $0.01\%$ corresponding to an absorbance resolution of $\alpha \sim 10^{-7} \, cm^{-1}$ in ZnS [90].
This is the same approach as in Ref. [90] except the present experiment is steady state. The time scale of the measurement is long enough to establish a constant thermal lens. For the materials studied here, the steady-state time scale at the focal point of the probe is on the order of 1 ms. It depends on the heat diffusion time and spot size of the probe beam. The appropriate time scale to reach steady state is determined by monitoring the time response of the signal. This limits the maximum chopping frequency, which is kept at 30 Hz. The far-field aperture in front of the detector is set much smaller than the probe beam diameter. Although the pump and probe are collinear they do not focus at the same point due to chromatic aberration of the lens. This is a mode-mismatched Z-scan setup [90]. The normalized transmittance is:

\[
\frac{T(z) - T_0}{T_0} = \Phi_0 \arctan \left[ \frac{2 m(z)v(z)}{1+m(z)+v(z)^2} \right],
\]

where the coefficient \(m(z)\) denotes the ratio of probe to pump beam areas (assumed to be Gaussian profiles), \(v(z)\) is a measure of the displacement of the sample from the probe beam waist, and \(T_0\) is the transmission in the absence of pump light. The dimensionless coefficient \(\Phi_0\) depends on material parameters as follows:

\[
\Phi_0 = \frac{P_{\text{excite}}}{\kappa \lambda_{\text{prob}}} L \left[ \frac{dn}{dT} + (n - 1) \frac{1}{L} \frac{dL}{dT} \right].
\]

Here \(P_{\text{excite}}\) is the excitation beam power, \(\lambda_{\text{probe}}\) is the probe beam wavelength, \(L\) is the sample length at Brewster’s angle, \(\kappa\) denotes the thermal conductivity, \(\frac{dn}{dT}\) is the thermo-optic coefficient, and \(\frac{1}{L} \frac{dL}{dT}\) represents the coefficient of thermal expansion. The linear absorption coefficient \(\alpha\) is extracted in the data fitting procedure. The Gaussian beam parameters of the pump and probe light are obtained independently using a Si beam profiler (Coherent Inc.). The Gaussian beam parameters of the pump and probe affect the shape of the Z-scan fit through the factors \(m(z)\) and \(v(z)\).
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The sample is translated $\Delta Z = 3.5$ cm through the focus of the pump beam (focal length: 15 cm). The excite-probe experiment is calibrated using a cuvette containing a 0.5% of solution (by mass) of CuSO$_4$ in nano-pure H$_2$O. The dilution is chosen to ensure that thermal lensing is entirely due to CuSO$_4$. Background absorption of H$_2$O and the cuvette are accounted for in the data analysis. The deduced absorption coefficient of CuSO$_4$ is $0.446$ cm$^{-1}$ at $\lambda = 850$ nm, which is in excellent agreement with the value obtained in an independent measurement using an FTIR spectrometer ($0.449$ cm$^{-1}$).

Z-scan data for a solution of 0.5% (by mass) of CuSO$_4$ in nano-pure H$_2$O is shown in Fig. 4.6 at an excitation pump wavelength of 840 nm. The solid line is the fitted curve. Reading left-to-right, the data displays a positive differential transmission followed by a valley. This is the signature of self-defocusing associated with a thermally induced change to the refractive index. This self-defocusing usually appears in liquids such as water due to negative thermal expansion.

![Z-scan data for CuSO$_4$ in nano-pure H$_2$O](image)

Figure 4.6: Pump-probe Z-scan signal of CuSO$_4$ in nano-pure H$_2$O. Solid line is theory and plotted points are data.

Z-scan data for the four materials, GaP, TiO$_2$, ZnSe and ZnS are shown in Fig. 4.7 at an excitation pump wavelength of 840 nm. The solid lines are fitted curves. Reading left to right, all the data display a negative differential transmission followed
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by a peak. This is the signature of self-focusing associated with a thermally induced change to the refractive index in solid materials. The data set for GaP has a very high signal-to-noise ratio, but shows some deviation from the calculated curve at displacements far from $z = 0$. We attribute this to aberrations introduced by the pump focusing lens that prevent realization of an ideal Gaussian beam.

![Figure 4.7: Absorption coefficient of GaP, TiO$_2$, ZnSe and ZnS.](image)

The excite beam power is kept low for high absorption material to stay in the range of validity of the first-order induced thermal lens approximation [89]. Material parameters relevant for our analysis are shown in Table 4.1.

The tabulated information is primarily obtained from the manufacturers. Extracted linear absorption coefficients in the wavelength range $840−900$nm are displayed in Fig. 4.8

TiO$_2$ is known to have birefringence in the near-infrared [91], but the Z-scan measurement used here is unable to detect changes in the response when the sample is rotated on its azimuth. The ZnSe data are corrected for the presence of two-photon
Table 4.1: Material parameters used in the analysis of Z-scan signal. Samples are acquired from Lambda Precision Optics (ZnS, ZnSe); Crystallod (TiO$_2$); MTI (GaP).

absorption (TPA). This nonlinear optical phenomenon can occur via two different physical pathways: i) absorption of two photons from the Ti:sapphire pump laser (degenerate TPA) and/or ii) absorption of one near-infrared photon from the Ti:sapphire laser and one visible photon from the HeNe probe laser (non-degenerate TPA). The very low probe power of our experiment and the mode-mismatch condition make the second process negligible. Degenerate TPA, however, can become comparable to the linear absorption at sufficiently high irradiance. This can be accounted for by writing an irradiance-dependent absorption coefficient

$$\alpha(I_{\text{excite}}, z) = \alpha + \frac{I}{2} \beta I_{\text{excite}}(z),$$

(4.4)

where $\beta$ is the degenerate TPA coefficient, and $I_{\text{excite}}$ is the on-axis pump intensity at a given position ($z$). A geometric factor of $\frac{1}{2}$ accounts for a spatially averaged Gaussian pump beam. Linear absorption is separated from nonlinear absorption using the following procedure: The sample is translated to the position of maximum differential probe transmission (i.e., the point of peak signal). The pump irradiance is then varied to generate the data shown in Fig. 4.9. Deviations from a linear response (solid line) indicate the presence of degenerate TPA. When the far-field aperture is removed, the Z-scan signal will reveal only nonlinear absorption. This so-called open aperture data is then subtracted from data taken with a partially transmitting
Figure 4.8: Z-scan signal of GaP, TiO$_2$, ZnSe and ZnS. Solid line is theory and doted symbol represents data

aperture to extract the thermal-refraction signal. The Z-scan data shown in Fig. 4.7 are corrected for nonlinear absorption in this way.

Figure 4.9: The Peak values of the Z-scan signal for different pump power in a ZnSe crystal. Dotted line represents model fitting including degenerate two photon absorption of pump photons. Solid line is a linear extrapolation of the low irradiance data.

Two-photon absorption is a third-order nonlinear optical process; observation of
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this effect normally requires large optical electric fields associated with pulsed, high irradiance laser beams. Detection of TPA with only cw beams is an indication of the high sensitivity of the excite-probe technique. The dotted line in Fig. 4.9 represents a calculation that includes both linear absorption and degenerate TPA. The data is fit using a TPA coefficient of $\beta = 3.2 \text{cm/GW}$. A value of 3.5 cm/GW was obtained previously at $\lambda = 780 \text{ nm}$ by using high power, ultrashort laser pulses [92]. A calculation based on a 3-band model of a semiconductor (light- and heavy-hole valence bands and a conduction band) yields 2.1 and 3.95 cm/GW at wavelengths of 850 and 780 nm, respectively [93]. No evidence of TPA is seen in the other materials. TiO$_2$ and ZnS are not two-photon resonant at Ti:sapphire laser wavelengths. The large background absorption prevents observation of TPA in GaP. The first report of TPA using cw lasers was an indirect measurement involving the magneto-photoconductivity of InSb [94]. The present experiment is believed to be the first direct observation of nonlinear transmission of a cw laser beam induced by TPA [95].

4.4 Luminescence modelling and light extraction efficiency in GaAs/ZnS and GaAs/ZnSe

4.4.1 Introduction

Semiconductor luminescence generally occurs over a continuum of wavelengths, with the mean luminescence wavelength defined as follows (refer to Chapter 2):

$$\lambda_f = \frac{\int \lambda S(\lambda) R(\lambda) d\lambda}{\int S(\lambda) R(\lambda) d\lambda},$$

(4.5)

where $R(\lambda)$ is the luminescence spectral density and $S(\lambda)$ is the geometry-dependent escape probability. The value of $S(\lambda)$ is less than unity due to luminescence trapping and absorption (see Fig. 2.15). The net effect of trapping, absorption, and
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Re-radiation of light is a red-shift in the luminescence spectrum (discussed in Chapter 2).

The escape probability $S(\lambda)$ is wavelength-dependent [96] because the absorption is wavelength dependent (see Fig. 2.15). The averaged $S(\lambda)$ over the entire luminescence spectrum can be determined as follow

$$\eta_e = \frac{\int S(\lambda)R(\lambda)d\lambda}{\int R(\lambda)d\lambda},$$

(4.6)

In the limit $S(\lambda) = 1$ the mean luminescence wavelength is $\bar{\lambda}_f = \lambda_f$, where $\lambda_f$ is the ‘internal’ mean luminescence wavelength, (i.e. ignoring photon recycling [31]). The different light extraction schemes to improve geometry-dependent escape probability were all briefly discussed earlier in this chapter.

Asbeck [96] determined the theoretical geometrical escape probability $S(\nu)$ and therefore the averaged geometry light extraction efficiency ($\eta_e$). He assumed a semiconductor having negligible parasitic absorption and determined $\eta_e$ for different thicknesses of GaAs\AlGaAs double heterostructures. Reincarnation of photons via luminescence trapping, re-absorption, and re-emission were taken into account by simply modifying the radiative recombination coefficient from $B$ to $\eta_e B$ in the carrier density equation, (i.e. Eq. 2.44 discussed in Chapter 2). This compact modification is relevant for low parasitic absorption devices used in laser cooling. Asbeck’s photon gas model uses solid-angle averaging of the photon energy, absorption coefficient, and luminescence spectrum, while ignoring Fabry-Perot effects and re-creation of photons. For strong parasitic absorption, replacing $B$ by $\eta_e B$ is not valid because the luminescence spectrum becomes sufficiently distorted.

Yablonovitch et al [97, 98] modified the photon gas model to account for parasitic absorption in LEDs. Their statistical model averages over internal angle, polarization, thickness, wavelength, and incorporates surface roughness. Reincarnation of
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... photons is included via resonant re-absorption and re-emission by introducing internal and external quantum efficiencies. Fuji et al [99] used texturing suggested by Yablonovitch et al and they were able to experimentally double the 4% light extraction efficiency of light-emitting multilayer GaN quantum wells via texturing.

Sheik-Bahae and Epstein [31] suggested two possible heterostructure designs to improve the light extraction efficiency of a laser cooling device bonded to a dome lens. Structure I has both surfaces polished, which limits the radiation escape cone because of total internal reflection; Structure II has one textured surface to statistically randomize the photon trajectories. A photon gas model is used to calculate the extraction efficiency $\eta_e$ while ignoring Fabry-Perot effects. The refractive index of the passivating GaInP layers was taken to be the same as GaAs. Their calculation reveals that texturing becomes efficient when the thickness is below 0.5$\mu$m because of the decreasing importance of resonance absorption in the active layer (see Fig. 4.10).

![Figure 4.10: Calculated extraction efficiency for two GaAs heterostructures. Structure I (solid curve) has two polished surfaces; Structure II (dashed curve) has one polished and one textured surface. The polished surface is bonded to a ZnS dome lens. After Ref. [31].](image)

A luminescence red-shift occurs as a result of photon recycling in the material. The amount of red shifting in the averaged mean luminescence is shown for the devices considered by Sheik-Bahae and Epstein [31] in Fig. 4.11.
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Calculating the geometrical extraction efficiency based on the photon gas model is a cumbersome computational task. Special care is required for interfaces or non-planar geometrical shapes. Ray-tracing software is available for analysis using the Monte Carlo method. Light extraction calculations using ray tracing software have been compared to results of the photon gas model by Hylton [100] and Boroditsky [101]. Here, ZEMAX software [102] is used to model the calculate light extraction efficiency of laser cooling devices.

4.4.2 Luminescence extraction efficiency: computer modelling

The GaAs/GaInP double heterostructure is attractive due to its promising long non-radiative lifetime (see Chapter 6). A schematic of the GaAs/GaInP double heterostructure is shown in Fig. 4.12.

Light extraction is analyzed using the ZEMAX software package. The program launches and tracks a large number of random optical rays from the GaAs layer. New rays are created by reflection and refraction at interfaces. Tracking of individual rays
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Figure 4.12: A schematic of a GaAs double heterostructure. Devices have varying layer thicknesses as shown.

continues until the ray either disappears due to absorption or leaves the device. The number of rays and their polarization are user controllable. A schematic drawing of luminescence rays in a GaAs\GaInP double heterostructure wafer bonded to dome is shown in Fig. 4.13

Figure 4.13: A schematic of a GaAs heterostructure bonded to a hemispherical lens. Random rays are launched by ZEMAX in the GaAs layer. The curved side of the dome can have an anti-reflection coating as in a real device.

A typical device consists of a heterostructure formed into a 1 mm disk bonded to a 5 mm dome (see Chapter 5). To simulate the luminescence, a volume cylinder light source with size $100\mu m \times 100\mu m \times$ thickness is placed in the GaAs layer. Rays that enter the dome couple to vacuum without loss because they are normally incident on the AR coated dome surface. Two hemispherical detectors count the escaped luminescence photons (see Fig 4.14).
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![Ray tracing simulation for a GaAs heterostructure bonded to a hemisphere. Random rays are launched by ZEMAX inside the GaAs layer. Rays disappear due to absorption or by reaching one of two detectors. For simplicity, one detector is located inside the dome lens to avoid complications from modeling the AR coated surface.](image)

The luminescence power source is arbitrarily set to 1 Watt. The program parameters are adjusted to follow each ray energy until the power drops to 0.001% or the ray reaches the detector. It is assumed dome lens has negligible parasitic absorption (as measured and discussed in previous section) and Fabry-Perot effects are ignored. If a photon is trapped as a result of total internal reflection, it is considered to be absorbed and lost. The refractive index of GaAs, GaInP, ZnS and ZnSe are set at 3.64, 3.1, 2.31, and 2.51, respectively [74] at the mean luminescence wavelength $\lambda \sim 860nm$ [21] and $T = 295$ K. The absorption coefficient of GaAs is taken to be $\sim 8000cm^{-1}$ [74]. Trial-and-error shows that $10^5$ rays and 0.001% power drop are sufficient to converge the simulation. The calculated extraction efficiency is the ratio of the summed detector power to the launched luminescence power.

The values of $\eta_e$ values determined by ZEMAX are presented in Table 4.2 for GaAs thicknesses within the range of $0.5 \mu m \leq d \leq 2 \mu m$. This thickness range has been determined to be the optimum range for laser cooling experiments [21, 26] (will
be discussed later). The calculation error bar is ±0.2%. The luminescence pattern recorded on the two spherical detectors shown in Fig. 4.14 is displayed in Fig. 4.15.

<table>
<thead>
<tr>
<th>Semiconductor material</th>
<th>Thickness (µm)</th>
<th>Dome material</th>
<th>Extraction efficiency (EXE) %</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Air</td>
<td>2.4</td>
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</tr>
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</table>

Table 4.2: Calculated $\eta_e$ for GaAs on different substrates. The case of a GaAs double heterostructure on GaAs dome (zero absorption) represents perfect index matching. The AlAs layer is thicker than a wavelength.

A second set of simulations involves a dome lens that is not AR coated. The calculated $\eta_e$ values for this case are presented in Table 4.3. A slightly lower $\eta_e$ is due to Fresnel reflections back into the GaAs layer where they can be absorbed.

To determine the role of passivation layers, $\eta_e$ is modelled for only a bare GaAs layer bonded to dome lens with an AR coating. The $\eta_e$ values for this case are
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Figure 4.15: Contour plots of the recorded luminescence in the spherical detectors.

presented in Table 4.4. Within the calculation accuracy, the computed $\eta_e$ values for bare GaAs are slightly lower compared to a heterostructure GaAs\GaInP device.

The extraction efficiency calculated by ray tracing in ZEMAX depend on values of refractive index and absorption coefficient in the material. In a real device, the absorption coefficient may decrease due to saturation. The light extraction efficiency is not expected to change with temperature since absorption and luminescence shift in tandem (see Fig. 2.6). The temperature-dependent index change of ZnS and ZnSe is negligible [74]. In the next section, three other possible light extraction schemes are explored.
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<table>
<thead>
<tr>
<th>Semiconductor material</th>
<th>Thickness ((\mu m))</th>
<th>Dome material</th>
<th>Extraction efficiency (EXE) %</th>
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</thead>
<tbody>
<tr>
<td>GaAs/GaInP</td>
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</tr>
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</tr>
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<td>ZnSe</td>
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<td>GaAs/GaInP</td>
<td>1/0.5</td>
<td>ZnSe</td>
<td>10.4</td>
</tr>
<tr>
<td>GaAs/GaInP</td>
<td>2/0.5</td>
<td>ZnSe</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Table 4.3: Calculated \(\eta_e\) for GaAs on different dome lens materials. No AR coating is on the dome lenses.

<table>
<thead>
<tr>
<th>Semiconductor material</th>
<th>Thickness ((\mu m))</th>
<th>Dome material</th>
<th>Extraction efficiency (EXE) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>0.5</td>
<td>ZnS</td>
<td>12</td>
</tr>
<tr>
<td>GaAs</td>
<td>1</td>
<td>ZnS</td>
<td>8.7</td>
</tr>
<tr>
<td>GaAs</td>
<td>2</td>
<td>ZnS</td>
<td>5.2</td>
</tr>
<tr>
<td>GaAs</td>
<td>0.5</td>
<td>ZnSe</td>
<td>14.8</td>
</tr>
<tr>
<td>GaAs</td>
<td>1</td>
<td>ZnSe</td>
<td>10.6</td>
</tr>
<tr>
<td>GaAs</td>
<td>2</td>
<td>ZnSe</td>
<td>6.4</td>
</tr>
</tbody>
</table>

Table 4.4: Calculated \(\eta_e\) for GaAs on different dome lens materials. No GaInP passivation layer is present.

4.4.3 Optimum GaAs thickness for laser cooling experiment

The external quantum efficiency was discussed in Chapter 2. In the external quantum efficiency, Eq. 2.70, both the non-radiative lifetime \(1/A(d)\) and luminescence extraction efficiency \(\eta_e(d)\) are thickness \(d\) dependent. The optimum cooling condition occurs for a sample thickness maximizing \(\eta_{ext}\) (see Eq. 2.70).

Using Table 4.2, the extraction efficiency of ZnS and ZnSe vs thickness \(0 \leq d \leq \)
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3 \mu m) can be approximated with a single exponential:

$$\eta_e(d) \approx \eta_e(0) \exp(-\alpha_{eff} \times d),$$

(4.7)

where $\eta_e(0) \approx 18.5\%$ and $\alpha_{eff} \approx 0.6(\mu m)^{-1}$ in GaAs bonded to ZnS and $\eta_e(0) \approx 23\%$ and $\alpha_{eff} \approx 0.6(\mu m)^{-1}$ for GaAs bonded to ZnSe.

In Eq. 4.7, $\eta_e(0)$ represents the geometrical light extraction efficiency of a sample attached to a dome lens in the absence of resonant absorption. The term $\exp(-\alpha_{eff} \times d)$ in Eq. 4.7 accounts for the GaAs absorption: $\alpha_{eff} \approx 0.6(\mu m)^{-1}$ at 300 K.

Using the thickness-dependent surface non-radiative coefficient $A(d) = 2S/d$ (see Eq. 2.36) the optimized value of $\eta_{ext}$ is derived to be $0.5 < d = 1/(2\alpha_{eff}) \approx 0.75 < 1 \mu m$ in GaAs bonded to ZnS and ZnSe. In this calculation it is assumed that interface activation energy or surface recombination velocity ($S$) remains the same (see Fig. 4.16). In plotting Fig. Fig. 4.16 averaged value of $B = 5 \times 10^{-10} cms^{-1}$, $A = 250 \times 10^{-3} s^{-1}$ and $C = 4 \times 10^{-30} cm^2 s^{-1}$ are considered for GaAs.

![Figure 4.16](image)

**Figure 4.16:** Optimum value of ($\eta_{ext}(d)$) in ZnS and ZnSe. The maximum external quantum efficiency occurs for a thickness $0.5 < d \approx 0.75 < 1 \mu m$ for both ZnS and ZnSe.
4.5 Exploring micro-domes arrays and texturing

In this section, different approaches for improving $\eta_e$ are investigated. One possibility is semiconducting micro-domes grown on top of the luminescing layer [84, 85]. A candidate dome lens material should satisfy the condition of Eq. 4.1. There are many materials with higher refractive index and bandgap energy compared to GaAs, but the amount of background absorption makes them unsuitable for laser cooling. If the size of the dome decreases significantly (radius of the order of 1 $\mu$m), however, absorption will be minimal. An array of such small radius micro-domes can be considered for luminescence removal.

Photo-lithographic technology is available to fabricate a variety of 3D micro-features including domes [103]. For laser cooling of GaAs based heterostructures, a thicker GaInP passivation layer can be grown to include these micro-domes. A schematic of this concept is shown in Fig. 4.17.

![Conceptual illustration of micro-dome array fabricated in the GaInP passivation layer via photo-lithography.](image)

Light extraction is modeled using the ZEMAX ray-tracing software. Analysis shows a GaInP micro-dome array improves $\eta_e$ by only $0.2 - 0.5\%$ for domes of radius 5-10 $\mu$m compare to a planar surface. The majority of the luminescence is trapped in the structure due to the presence of whispering gallery modes. These trapped propagation modes are often encountered in structures with index greater than the surrounding medium. Light undergoes total internal reflection at the volume surface, eventually undergoing absorption and the generation of heat. Other micro-features
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(i.e. pyramids and cylinders) have been simulated, producing essentially the same result. It is concluded that the presence of trapped whispering gallery modes make micro-structure arrays ineffective for light removal in semiconductor laser cooling. In conclusion, due to the present of whispering gallery modes the micro-features are not an efficient way to extract luminescence. This may not, however, be the case for some LED designs [84, 85].

Another idea taken from LED engineering is surface texturing [52]. The main idea behind this technique is to statistically randomize luminescence ray trajectories to reduce total internal reflection. A schematic of a textured device is shown in Fig. 4.18

![Figure 4.18: A schematic of a textured GaAs double heterostructure.](image)

Sheik-Bahae and Epstein [31] calculated $\eta_e$ in a cooling device with a single dome lens to compare texturing to a polished surface (refer to discussion of Fig. 4.10). ZEMAX software is used to simulate a double heterostructure GaAs\GaInP device that is textured on one side and flat on the other. No dome lens is present (see Fig. 4.18). The ZEMAX simulation shows that texturing improves $\eta_e$ by about 0.2% for 1 $\mu$m, which is at the calculation accuracy. Texturing increases the efficiency in thin samples $\leq 0.2$ $\mu$m. For these thicknesses, the light extraction efficiency of a bare heterostructure becomes comparable with a 1 $\mu$m layer of GaAs bonded to a ZnS or ZnSe dome lens.

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4.6 Evanescent wave coupling and light extraction in nano-gap device

In the condition of total internal reflection, an evanescent wave exists in the medium with lower refractive index [104]. The tunnelling depth of the evanescent wave depends on the relative refractive indices of the two media and on the wavelength light [78, 104]. Evanescent wave coupling can be exploited to enhance the luminescence extraction [105].

If a mis-matched interface (e.g. GaAs and vacuum) is placed in close proximity to an absorber, evanescent wave coupling to the absorber is possible. The separation distance must be less than the wavelength of light for efficient coupling. The absorber must have a refractive index comparable to the index of the luminescing layer. Silicon is an excellent candidate for the absorber since its refractive index is close to GaAs, it has weak luminescence because it is an indirect semiconductor, and its luminescence is not absorbed by GaAs [106].

Epstein et al [105] proposed that a nanogap could be registered using a two-dimensional array of narrow posts. The anticipated post spacing could be as large as several hundred microns and their height would be less than 100 nm. Minimizing the number of posts is essential to form a thermal barrier at the interface. A schematic is shown in Fig. 4.19. The fabrication of such a device is presented in Future works chapter.

![Figure 4.19: Schematic of a nano-gap in a laser cooling application.](image-url)
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The calculation of $\eta_e$ vs gap distance is shown in Fig. 4.20\(^4\). The absorbing medium is Si with higher refractive index of $n_3 \approx 3.63 - 0.0025\,i$. For simplicity, this calculation does not include absorption in GaAs. The extraction efficiency of a nano-gap can exceed a ZnSe dome at gap separations of less than about 40 nm.

Absorption in GaAs is included in the calculation presented in Fig. 4.21 by multiplying the results in Fig. 4.20 by a factor of $\exp(\alpha\,l_a)$, where $\alpha \sim 8000\,cm^{-1}$ [74] at the mean luminescence wavelength $\lambda_{\text{mean}} \sim 860\,nm$ [21] and $l_a = 1\,\mu m$ is GaAs thickness. This calculation confirms that light extraction via nano-gap is a viable approach for gap spacings below 40 nm.

In summary, different light extraction schemes for laser cooling of semiconductors have been analyzed. The absorption coefficient of different dome lens materials is measured and ZnS and ZnSe are found to be the most suitable due to the very low absorption coefficients ($\sim 10^{-4}\,cm^{-1}$). The dome lens approach is the best approach for laser cooling at this time because the concept is established. Other light extraction schemes used in LED design are efficient provided the structures they are bonded to are sufficiently thin.

\(^4\)This calculation was done by M.P. Hasselbeck
Figure 4.21: Results in Fig.4.20 modified to account for absorption in GaAs.)
Chapter 5

Device design and fabrication

In this chapter the fabrication of GaAs\GaInP heterostructure devices for the laser cooling experiments is presented. The discussion includes passivation of GaAs, processing, epitaxial lift-off, and epilayer wafer bonding to a dome lens.

5.1 Double heterostructure design: GaAs\GaInP and GaAs\AlGaAs

This dissertation has stressed the crucial rule of non-radiative recombination process in laser cooling of semiconductors. As introduced previously, the non-radiative recombination process can be in the bulk or at the interfaces and surfaces. Bulk non-radiative recombination strongly depends on the quality of crystal growth and presence of impurities. Recently, crystal growth technology and quality of the materials has improved to a level where Shockley-Read-Hall non-radiative recombination in the bulk is negligible.

Non-radiative recombination due to the presence of surface states is, in contrast,
very efficient. The most effective way to decrease surface recombination is to passivate all surfaces with another lattice-matched semiconductor. This produces an energy barrier at the surface interface while maintaining the same crystallographic structure. Carriers are confined within the active layer and dangling bonds associated with the surface are essentially eliminated. This is a very common design method in advanced LED and laser diode engineering.

In GaAs there are two common passivation approaches: GaAs \( (E_g = 1.42 \text{ eV at } T = 300 \text{ K } [46]) \) can be passivated with \( Al_{0.3}Ga_{0.7}As \) \( (E_g = 1.85 \text{ eV at } T = 300 \text{ K } [46]) \) or \( Ga_{0.5}In_{0.5}P \) \( (E_g = 1.85 \text{ eV } T = 300 \text{ K } [46]) \). Heterostructures of GaAs\AlGaAs used in this research are grown by Molecular Beam Epitaxy (MBE) in the facility of Dr. J.L. Reno at Sandia National Laboratories and Dr. A. Stintz at the Center for High Technology Materials at UNM. GaAs\GaInP is grown by Dr. S. Kurtz at the National Renewable Energy Laboratory using Metal-Organic Chemical Vapor Deposition (MOCVD).

The optimum GaAs thickness (active layer) is chosen to maximize cooling efficiency and therefore cooling power. The cooling efficiency \( (\eta_c) \) is a function of light extraction efficiency \( (\eta_e) \) and the non-radiative recombination process \( (A) \). It was shown that \( \eta_e \) and the non-radiative recombination coefficient (Chapter 2, 4) are both thickness-dependent. Knowledge of \( A \) and \( \eta_e \) define the optimum active layer thickness for laser cooling as 0.5–1 \( \mu \text{m} \) (see Chapter 4). A very thin passivation layer \( (\sim 30 \text{ nm}; \text{Chapter 6}) \) is sufficient to neutralize the dangling surface bonds. Thicker passivation layers will strengthen the double heterostructure for epitaxial lift-off and wafer bonding. A schematic of a GaAs double heterostructure grown on a substrate of n-doped GaAs is shown in Fig. 5.1. Note that a thin \( (50 \text{ nm}) \) latticed-matched AlAs release layer is added to facilitate epitaxial lift-off.
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Figure 5.1: A schematic of a GaAs double heterostructure before epitaxial lift-off.

5.2 Device fabrication

The GaAs double heterostructure must be separated from its parent substrate before it can be bonded to hemisphere dome lens (see Fig. 5.1). Epitaxial lift-off takes place by applying 49% HF acid to selectively etch the AlAs layer. The reaction of HF with GaAs and Ga$_{0.5}$In$_{0.5}$P is limited at room temperature; a few nm native oxide layer formed on the surface may be etched [107, 108]. Passivation layers of Al$_{0.3}$Ga$_{0.7}$As have extremely slow chemical reaction rates with HF solution at T $\leq$ 300 K, which is insignificant on the time scale of the lift-off [109].

The double heterostructure layer in the laser cooling devices is very thin ($<$ 3 $\mu$m), hence the device aspect ratio affects the integrity of the lift-off process. If care is not taken, the device can shatter. Shattered pieces are unsuitable for laser cooling because mechanical stress, micro-cracks, and dislocations increase the non-radiative recombination rate (see Chapter 6).

The GaAs double heterostructures are removed from the substrate in the form of circular disks. The disk diameter is chosen considering the following: i) it must be larger than the laser pump spot size plus the carrier diffusion length. This is necessary to keep the photo-carriers far away from the non-passivated edges on the
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circumference \(^1\); ii) The diameter must be small enough to maintain rigidity to bending and twisting during handling; iii) The disk must have sufficient flexibility for wafer bonding to the flat face of a dome lens. In addition, a disk-shaped sample does not have any stressed edges to initiate the formation of cracks, bends, or twists. Note that a symmetrical shape is not used by Yablonovitch et al [110] in order to allow epitaxial lift-off using black wax. The epitaxial lift-off process used here has been refined to facilitate direct bonding on the dome lens.

Nominal dimensions for a cooling device are: dome lens radius of 5 mm, pump beam diameter of \( w_0 \sim 100\mu m \), and GaAs double heterostructure thickness of \( \sim 1.5-3\mu m \). Different heterostructure diameters are systematically investigated using standard contact mask photolithography techniques [111] and epitaxial lift-off. For a 1\( \mu m \) thick heterostructure, lift-off and Van der Waals bonding to a dome lens without shattering or creating micro-cracks can be accomplished up to a maximum disk diameter of 0.7 mm. At 2\( \mu m \) thickness, the disk diameter increases to a maximum of 1.2 mm.

The following steps describe the process of sample fabrication. Processing is performed in a cleanroom environment primarily to avoid trapping particles in between the double heterostructure and dome lens. The Center of High Technology Material (CHTM) cleanroom includes different sections with 100-1000 ratings \(^2\). The fabrication described here is performed in a Class 100 surrounding. The cleaning solvents used are acetone, methanol, isopropanol, and deionized (DI) water \(^3\). These solvents are semiconductor grade and leave the least amount of residue. In order of decreasing

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1Passivating the exposed narrow edges requires complicated additional growth and processing.
2Cleanroom class is defined as number of particles 0.5 micrometer and larger per cubic foot of air; e.g. A Class 10 cleanroom has a maximum of 10 particles per ft\(^3\).
3DI water is ultra-pure water used in semiconductor manufacturing. It is produced by removing all ions of dissolved minerals using reverse osmosis and ion-exchange. DI water is also be free from bacteria, organics, and dissolved oxygen. Purity is determined from resistivity; a target resistivity is 18 M\( \Omega \) cm.
purity, the cleaning agents rank as follows: deionized water, isopropanol, methanol, and acetone [112]. All washing processes start with acetone and finish with a DI water rinse. The photolithography techniques used to create the disk-shaped heterostructures can be found in standard textbooks (e.g. [111]). Literature from AZ Electronic Materials provide recipes and properties for photoresist materials [113].

Processing steps: cleaning, patterning, etching, lift-off, and bonding

Cleaning. A quarter-wafer (see Fig. 5.2) of double heterostructure GaAs is cleaned in sequence with acetone, methanol, isopropanol, and DI water. A clean microscope slide is used to apply wax to the wafer on the double heterostructure side. Clear wax prevents scratches during handling and bonding of the dust from sample during the cleaving process. The wax melts at 70 C and dissolves easily in acetone.

Dicing. The double heterostructure wafer is cut into $6 \times 6$ mm pieces using a cleaving saw. The size of the samples is chosen to be provide an edge that is 1 mm larger than photolithography area (see Fig. 5.2).

Surface morphology. GaAs\GaInP heterostructures grown by MOCVD contain oval defects at the surface (see Fig. 5.3). The oval (elliptical) form is found to depend on growth kinetics and orientation. These defects appear as hillocks or faceted growth around nucleation centers. Their typical density varies between 10–
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$10^5 \text{ cm}^2$ depending on the cleanliness of the substrate and growth reactor, growth rate, and epilayer thickness as discussed by Van de Ven *et al* [114] and Sarov *et al* [115]. Scanning electron microscopy (SEM) images of oval defects are shown in Fig. 5.4.

![SEM micrograph of oval defects](image)

Figure 5.3: Photographs of a MOCVD grown GaAs/GaInP sample. The oval defects can be clearly identified by their dark hillock shapes. Their size can be as large as $\sim 40 \mu\text{m}$ (major axis).

Figure 5.4: (A) SEM micrograph of oval defects on a GaAs/GaInP sample. (B) is a magnification of (A).
Energy dispersive X-ray spectroscopy (EDXS) confirms that the elemental composition of the oval defects is the same as the double heterostructure (see Fig. 5.5). EDXS is a standard procedure for identifying and quantifying the elemental composition of sample areas. The characteristic X-rays are produced when a material is bombarded with electrons in an electron beam instrument (e.g. SEM). Detection of these X-rays can be accomplished by an energy dispersive spectrometer.

Figure 5.5: EDS of oval defects on GaAs/GaInP sample (lower right hand corner of image). The EDS confirms the elemental composition of the oval defects to be the same as the double heterostructure. The white box indicates the analysis area.

Considering the size and elemental composition of these oval defects, it is conjectured that they are produced due to unfavorable crystal growth conditions in the MOCVD reactor. The MOCVD machine uses metal-organic compounds as source materials in relatively high pressure growth conditiona ($\sim 10^{-3}$ Torr). It is possi-

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$^4$Dr Elshan Akhadov at the Center for Integrated Nanotechnologies (CINT) took the SEM pictures and performed the EDS analysis.
Oval defects may cause problems in laser cooling experiments. A local measurement with a near-field microscope shows much shorter lifetime compared to clean parts of sample (see Chapter 6). In addition, oval defects can inhibit uniform bonding of the heterostructure to a ZnS and ZnSe dome lens; this will negatively affect light extraction from the heterostructure. The problem can be circumvented by choosing defect-free areas of the sample or choosing samples with defects sufficiently far removed from the laser-illuminated area. The oval defects occur almost uniformly on the sample with average density of five-to-eight defects per mm$^2$. Solving the oval defect problem is beyond the scope of this dissertation. Providing sample with less oval defect are subject of the future research.

An Alpha-step surface profiler\footnote{The Alpha-step is a mechanical, stylus-based step profiler that can measure step height.} is used to analyze the surface roughness of the GaAs/GaInP double heterostructure and dome lens surface. The surface roughness of the heterostructure surface before lift-off is shown in Fig. 5.6.

The resolution of the profiler is $\pm 4$ nm for a single pass measurement. A roughness of less than 4 nm is obtained after a 10 scan average. This roughness is acceptable for wafer bonding\footnote{Oval defects with size less than 1µm are also abundant.}.

The height and size of individual oval defects are also measured using the Alpha-step (see Fig. 5.7). The largest defects have diameters in the range 30–50 µm and height between 10–20 µm\footnote{Oval defects with size less than 1µm are also abundant.}. Large dimension oval defects prevent full contact between the sample and the dome lens, inhibiting the efficient coupling of luminescence to the ambient.

**Photolithography.** Cleaved square pieces are ultrasonically cleaned in DI water.
using an ultrasonic cleaner. Samples are then separated from the clear wax with acetone. Additional ultrasonic cleaning was found to be detrimental because of the formation of micro-cracks and possible shattering. A second sequence of acetone, methanol, isopropanol, and DI water cleaning takes place followed by N$_2$ gas drying. The sample is baked on a hot-plate at not more than 90 C to evaporate any remaining water residue. Group III-V semiconductors are very hydrophobic $^7$ although it is possible water is held in native oxide. Water removal is critical before depositing photoresist on the surface because its presence can inhibit adhesion and uniformity [113]. Drying at more than 90 C is avoided to keep the native oxide diffusion length to less than a few nanometers [117, 118, 119]. The photolithography pattern is also baked at < 90 C. Native oxide is removed when the sample is exposed to HF for epitaxial lift-off along with a few mono-layers of exposed GaAs at the edge of the sample and passivation layers [117].

The sample is mounted on a spinner for photoresist coating. A few drops of

$^7$hydrophobic $\equiv$ water beads on the surface
hexamethyldisilane (HMDS) are sometimes applied to provide adhesion between the photoresist and surface\textsuperscript{8}. A procedure of ramping the spin velocity (nominally 500 rpm) up and down at 5 s intervals for 30 s is required to provide a very thin HMDS in this regard. A few drops of AZ-4620 type photoresist is then applied on the surface for patterning. Ramping the spin speed in the same way leads to a 5.6 µm thick layer of photoresist. The sample is baked on a 90 C hot plate for 90 s to dry the photoresist solvent (The reason for such a thick resist coating will be discussed later in this chapter). After photoresist coating the sample is exposed to ultraviolet (UV) radiation at \( \lambda \approx 405 \) nm through a positive photo-mask. The photo-mask has transparent holes to define individual samples after a 19 s exposure to high intensity UV light from a mercury lamp. The photo-mask is in near-contact with the surface. The mask is AR coated to reduce scattered UV light and better define the pattern edges.

\textsuperscript{8}HMDS has been found to provide very strong adhesion between photoresist and sample after ICP (will be discussed later). This adhesion makes cleaning of processed-photoresist very difficult. Therefore it is preferred to avoid HMDS if it is possible.
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Diluted AZ-400 developer (1/4 solution) is used to develop the photoresist and render disks on the sample surface. The exposed sample is dipped for 2 minutes into the diluted AZ-400 solution and then DI water for 1 minute. The process is repeated for 20–30 s if the disks are found to be not sharp and clear. When the disks are suitably defined, the sample is rinsed in DI water for 5 minutes. There are always areas where photoresist residue can be seen, especially near the edges where photoresist accumulates during spinning. The presence of this residue is found to be acceptable. Further development is detrimental as it thins and eventually removes photoresist defining the disks. The ideal result is sketched in Fig. 5.8.

![Figure 5.8](image)

**Figure 5.8:** Side view illustration depicting the photoresist pattern on the heterostructure.

**Etching.** The next step is vertical etching with an inductively coupled plasma (ICP) (see Fig. 5.9). The etching rate of AZ-4620 on photoresist is negligible compared to bare GaAs\GaInP and GaAs\AlGaAs. The main advantages of ICP etching over conventional cleaving and wet etching are that it is fracture-free, produces straight etches, has a highly controllable etching rate, higher reliability, repeatability, speed, ease of use, and safety.

The ICP etch rate for GaAs\GaInP and GaAs\AlGaAs is \( \sim 3 \, \mu m \) per 10 min. The rate depends on plasma power, gas flow, and pressure. An etching time of 12 minutes is sufficient to expose the AlAs release layer (see Fig. 5.1). It is necessary
to expose the AlAs edges for lift-off with HF acid. After ICP etching, the sample is cleaned of any additional photoresist using the same sequence of acetone, methanol, isopropanol, and DI water. It is found that the thicker photoresists are easier to remove. This is due to the heat insulation of thick photoresist that reduces baking during ICP etching and hence bonding at the interface. A 5.6 µm thick photoresist can be readily removed as a consequence. Small spots of photoresist can be removed with a GaAs\GaInP photoresist remover such as RR2 or RR4. It is important to remove all photoresist to reduce background parasitic absorption of cooling luminescence. Like oval defects, the presence of resist on the surface also prevents full contact bonding of the dome lens.

**Lift off.** Lift-off is accomplished by etching the AlAs layer with a 49.2% HF acid solution. The HF solution strongly reacts with AlAs to produce a water soluble salt AlF$_3$ and a toxic colorless gas AsH$_3$ [120]. Due to the weight of the released samples, they often fall back and re-attach to the substrate as shown in the photo of Fig. 5.10. This Van der Waals bond is very strong and prevents removal of the disk without destroying it. To overcome this problem, the still attached samples are adhered to a

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piece of teflon using black-wax and then dipped into the HF solution as illustrated in Fig. 5.11).

![Fig. 5.10: Disk heterostructures after horizontal etching of AlAs and lift-off in HF acid. These disks fell back to the substrate and bonded to it.]

Figure 5.11: To prevent the sample from re-attaching to the substrate upon lift-off, it is manipulated with an adhesive layer of black-wax and teflon.

The etching time for 1 mm disk is about 15 minutes at room temperature. After lift-off, the disk is washed by adding DI water in the etch container to achieve a pH of 7. At this point, the disks are ready for bonding to a dome lens. If the dome is coated with a hygroscopic AR coating, water is removed from the solution by adding isopropanol.
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An alternative technique demonstrated by Yablonovitch et al. [110] is to lift-off the samples (i.e. not the substrate) using black-wax. This method has been very successful for large size epilayers with minimum bends and twists. It is not well-suited for this work since the disks are too small and fragile for manipulation with black wax (see Chapter 6). In addition, the black-wax must be eventually removed with trichloroethylene solvent (TCE) that has a high boiling temperature of 87 °C. TCE is very hard to clean and always leaves a small but measurable amount of residue. Such residue is deleterious for luminescence absorption and bonding to the dome. Furthermore, a dome lens AR coating can be damage by a residual film of TCE.

5.2.1 Van der Waals wafer bonding

Overview

Direct wafer bonding technology has recently attracted significant attention since it is difficult and in some cases impossible to grow lattice-mismatched materials into structures. In direct crystal growth of mismatched materials, differences in the lattice structure/spacing can create dislocations and consequently very poor crystallinity. This is a primary problem in hetero-epitaxy systems such as GaAs grown on Si. In some cases fabricating devices in one material is required because monolithic integration is impossible. Diode lasers, modulators, detectors, and transistors for high speed data processing and transmission are examples in which such hybrid integration is performed [121].

For devices used in laser cooling, direct wafer bonding of GaAs\GaInP to ZnS and ZnSe dome lenses is of great interest. Unlike other material joining techniques

\[Hetero-epitaxy\ is\ an\ epitaxial\ deposition\ process\ in\ which\ the\ chemical\ composition\ of\ epi-material\ is\ different\ than\ the\ substrate\]
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like adhesive bonding [122] or bump bonding [123], wafer bonding can yield robust, atomically smooth, electrically conductive, and optically transparent interfaces.

Recently, tremendous progress has been made in both the fundamental understanding of the wafer bonding process and its optoelectronic device applications [121, 124, 125]. A typical wafer bonding process consists of surface preparation, placement of the substrates in contact with each other, followed by pressure or annealing, or a combination of the two. Crystallites in full contact can fuse together at high temperatures because of surface energy-induced migration [121]. Full contact is usually provided as a result of mechanical pressure; wafer fusion results after baking at high temperature [121]. Both pressure and heat should be avoided in wafer bonding of the GaAs/GaInP-dome lens interface. Pressure and heat can drastically reduce the non-radiative lifetime in GaAs/GaInP samples (see Chapter 6).

An alternative approach for wafer bonding has been successfully demonstrated by Yablonovitch et al [110, 126]. They used natural intermolecular surface forces (i.e. the Van der Waals force) to bond GaAs thin-films to Si, glass, sapphire, LiNbO$_3$, InP, and both GaAs and diamond substrates. This method is desirable for bonding GaAs/GaInP to ZnS and ZnSe dome lenses because heat treatment and external pressure are not involved.

The Van der Waals force arises from the polarization of molecules. Fixed or angle-averaged dipoles cause Keesom forces, rotation dipoles lead to Debye forces, and shifts in the electron cloud distribution result in London forces [127]. In Van der Waals bonding between sample and substrate, a polarizability of the two materials is necessary [127]. The polarization of a material can arise in two ways: a local field can distort the charge distribution and produce an induced dipole moment or the material may possess a permanent dipole moment [43].

If two materials are placed in close contact, Van der Waals forces may be efficient
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enough to hold them together. Yablonovitch [110] and Liau [125] used capillary forces to pull a wafer and substrate together. Liau [125] has shown mathematically and experimentally that surface tension can pull two wafers into uniform close contact. This is not easily achieved by mechanical pressing with rigid anvils.

The capillary or surface tension force between substrate and epilayer is provided by small amount of liquid solvent such as DI water, methanol, or isopropanol [110, 125]. The capillary force depends on hydrophobicity (hating water) or hydrophilicity (loving water) of the two materials. The hydrophilicity and hydrophobicity of a surface can be tested by dipping material in liquid and measuring the adhesion. Qualitatively, if liquid beads on a surface it is hydrophobic; otherwise it is hydrophilic. A liquid’s surface wetting characteristics (hydrophilicity) can be measured quantitatively by the contact angle of a drop of liquid placed on the surface of the material. The contact angle is the angle formed at the solid-liquid interface and the liquid-air interface [127]. This angle strongly depends on the cohesive forces between the molecules of a liquid and the adhesion forces due to surface tension between liquid and solid.

Wafer bonding uses a liquid solvent such as methanol, isopropanol, or DI water to attach epilayers to dome lens substrates. As in the techniques of Yablonovitch [110] and Liau [125], it is expected that as solvent evaporates from the edge of the epilayer on the dome lens, a capillary force will pull the epilayer and dome lens substrate together. It appears that surface tension (i.e. a cohesive force) pulls the liquid solvent out as it evaporates. If the interfacial energy of the epilayer-liquid and dome lens-liquid is smaller than the epilayer-dome lens, this force will not be enough to drive the liquid solvent from the interface [110, 127].

As the two surfaces (epilayer and the dome lens) get in the close proximity, a Van der Waals bond may be formed. This bond depends on the interfacial energy of the two materials. If the surface energy of the epilayer-air and the dome lens-air
substrate decreases as a result of Van der Waals bonding, the two materials can bond [110, 127]. Material polarizability is a necessary but not sufficient condition to attain Van der Waals bonding.

In the previous section, sample preparation steps prior to wafer bonding were discussed. The epitaxial lift-off process was refined by eliminating black-wax as suggested by Yablonovitch et al [110]. This refinement is important because it eliminates the TCE solvent and allows the possibility of direct bonding on dome lens (see next section).

**Bonding process**

The following steps are performed to directly wafer bond the epilayers of GaAs \GaInP and GaAs\AlGaAs heterostructures to ZnS and ZnSe dome lenses. An ultrasound bath cleans the ZnS and ZnSe dome lenses using acetone, methanol, and isopropanol. DI water is avoided since some of the AR coatings on the lenses are slightly hygroscopic \footnote{Communication from Lambda Precision Research}. A plasma cleaner removes possible organic residues from the ZnS and ZnSe domes [128]. The GaAs double heterostructure disks are suspended in isopropanol, then placed on soft cleanroom wiper tissues (class 1 particles). At this point, they are ready for wafer bonding. While the disk is still wet, the flat face of the dome is pressed gently on the disk. The weight of dome lens is enough to start the primary capillary force. Proper alignment begins immediately to center the disk. Liau et al use methanol since it has high capillary force and excellent wettability of hydrophobic semiconductors [125]. Isopropanol is used in this research to avoid possible water absorption in the lens coatings. Yablonovitch et al use DI water as the primary bonding agent. They use constant pressure (< 15 g/mm² to avoid bending the wax and cracking sample) to force the two surfaces to bond as the water evaporates [110]. This pressure is required in their process since black-
wax is not flexible enough for Van der Waals bonding. In the process used here, the heterostructure disks are sturdy enough to avoid bends and twists, yet flexible enough to facilitate Van der Waals bonding to the flat dome surface.

There are different ways to test wafer bonding quality [129, 110]. One of the simplest is to observe the sample at perpendicular and grazing angles through the dome lens [21]. A completely visible disk from 0 to 80 degrees incidence indicates a uniform bond.

Both ZnS and ZnSe are strongly hydrophobic in DI water; water easily beads on their surfaces. Methanol and isopropanol are able to wet both materials very well to provide the necessary capillary force. Wafer bonding has been successful and repeatable with ZnS using different solvents, but not so with ZnSe. Extended drying time up to 24 hours and added pressure via a homemade press (see Fig. 5.12) have not solved the problem.

The epilayer and ZnSe dome are squeezed between two well polished and flat quartz plates (roughness less than 10 nm and flatness less than 15 seconds). The press test has been performed with different liquid solvents and also in a dry condition. As pressure increases, the epilayer and dome lens make complete contact as can be observed by looking at sample at a sharp grazing angle. This was the motivation for using wires to attach the GaAs\GaInP sample to the ZnSe dome in experiments by Gauck et al [21](see Chapter 6). It is believed that the surface energy of epilayer-air and ZnSe-air are less than the epilayer-ZnSe interface 12. Wafer bonding seems rely on decreasing surface energy between the two materials before and after bonding. Surface energy quantifies the disruption of chemical bonds that occurs when a surface is created. Surfaces are energetically less favorable than the bulk material 13. It is obvious in a perfect vacuum and clean surfaces Van der Waals bonding always

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12 The native oxides in GaInP, ZnS, and ZnSe have not been removed
13 If this was not the case, there would be a driving force from inside to outside to create a new surface [127]
Chapter 5. Device design and fabrication

favorable.

Figure 5.12: An epilayer disk and ZnSe dome are squeezed together by placing them between two blank quartz plates having roughness less than 10 nm and flatness less than 15 seconds. The two quartz plate are pressed using a spring. A lens cleaning tissue (cleanroom class 1, thickness: $\sim 50 \, \mu m$) is placed between the epilayer disk and bottom quartz plate (not shown). The tissue fills empty space between the quartz plate and oval defects on the sample.

This ZnSe bonding problem may be overcome by coating a 10 nm layer of SiO$_2$ or TiO$_2$ on the ZnSe surface. Luminescence transmission through 10 nm of SiO$_2$ or TiO$_2$ is extremely high (see Fig. 4.20). A TiO$_2$ layer is preferred since it has higher refractive index and higher polarizability ($\epsilon \sim n^2$), which leads stronger Van der Waals bonding.

An Alpha-step of the flat face of a ZnS dome lens before and after bonding of GaAs\GaInP is shown in Fig. 5.13. In frame (A) the bare surface is measured; in frame (B) the heterostructure is measured in the same region of the face. The region exhibits the same morphology before and after bonding. Bonding is also investigated in the region around oval defects. An Alpha-step of an oval defect feature measured through GaAs\GaInP on ZnS is shown in Fig. 5.14. Oval defects in our samples have height larger than it is shown in Fig. 5.14. We think this oval defect is have been shattered during the bonding process.
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Figure 5.13: (A) morphology of ZnS dome lens flat surface before bonding heterostructure epilayer to it. (B) Same region after bonding the epilayer. The graphs are averaged over 10 scans and do not compare the exact same spot, although the same step near the origin is evident in both scans. The resolution is ± 2 nm for 10 averaged scans.

A photograph of bonded GaAs sample to ZnS dome is shown in Fig. 5.15.

The oval defects are indicated on the sample. The circle bright rings and scattered white features are due to camera and illuminating light used to take the picture.

Oval defects in the samples usually have a height of about 10–20 µm as discussed earlier. Depending on what side of the double heterostructure epilayer is bonded, oval defects can be oriented upwards or downwards. This means the oval defects may be sandwiched between the epilayer and dome lens, creating a tent effect and trapping solvent. This is similar to observations reported by Yablonovitch et al [110] and Schnitzer et al [130, 52] as a result of dust particles trapped between the epilayer and glass. Tent-like structures are visible under an optical microscope as a series of Newton rings. When subject to flash heating, these hydrated dust particles can produce blisters under the film. This prior work was not carried out in a cleanroom environment. Due to the dome lens shape, this problem is hard to study in laser cooling devices.
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![Morphology of GaAs\GaInP epilayer heterostructure bonded to ZnS dome showing oval defects.](image)

Figure 5.14: Morphology of GaAs\GaInP epilayer heterostructure bonded to ZnS dome showing oval defects.

![GaAs double heterostructure wafer bonded on a dome of ZnS. The oval defects are indicated on the sample. The circle bright rings and scattered white features are due to camera and illuminating light used for photography.](image)

Figure 5.15: GaAs double heterostructure wafer bonded on a dome of ZnS. The oval defects are indicated on the sample. The circle bright rings and scattered white features are due to camera and illuminating light used for photography.
Defect related non-radiative recombination was discussed in Chapter 6. Efficient passivation of a semiconductor surface decreases the density of dangling bonds, increasing the non-radiative recombination lifetime significantly. There are two lattice-matched semiconductors with large bandgaps that can be used to passivate GaAs for this work: $Ga_{0.5}In_{0.5}P$ ($E_g = 1.88$ eV at 300 K [46]) and $Al_{0.3}Ga_{0.7}As$ ($E_g = 1.88$ eV, $T = 300$ K [46]) (see Fig. 6.1). In the following section, the GaAs double heterostructures are characterized. The non-radiative recombination lifetime is measured before and after lift-off from the substrate.
Chapter 6. Device characterization

6.1.1 Time-resolved spectroscopy of GaAs/GaInP double heterostructures

GaAs heterostructure and experiment setup

There are different experimental techniques to characterize the non-radiative lifetime and identify defects. Methods include deep-level transient spectroscopy (DLTS) [42], surface photovoltage [42] (SPV), luminescence decay [61], and phase fluorometry [131]. Both DLTS and SPV are very powerful for characterizing the decay lifetime and nature of the defects. They are especially useful for materials with poor luminescence efficiency such as Si. The disadvantage of DLTS and SPV is that samples must be electrically biased [42]. For materials with efficient luminescence, passivated devices that cannot be made into a p-n junction, or where converting material into a p-n junction by doping them modifies the lifetime, alternate approaches are required. Time-resolved spectroscopy and phase fluorometry are very effective and
convenient techniques for this purpose. Time-resolved spectroscopy is used here since it is not possible to create a p-n junction in the cooling devices without significantly modifying the heterostructure.

In time-resolved spectroscopy, the non-radiative lifetime of a passivated heterostructure is measured via luminescence decay. The carrier density must be low enough that non-radiative recombination is dominant (i.e. $A \gg BN$) [63, 51, 53]. The heterostructure is optically pumped using a short pulse diode laser. Olson et al [51] performed a temperature-dependent study of recombination with GaAs. They found that GaInP passivation provides the longest non-radiative lifetimes and attributed this to the absence of oxygen-related defects at the interface. This work placed an upper limit on the interface recombination velocity $S < 1.5$ cm/s based on photoluminescence measurements at room temperature with the heterostructure attached to the substrate. In this section, measurements of photoluminescence decay in GaAs\GaInP and AlGaAs\GaAs before and after lift-off are discussed. The experiments are performed over a wide temperature range from 7 to 450 K, which allows the different recombination mechanisms to be clearly separated. It is found that GaAs\GaInP heterostructure gives the longest non-radiative lifetime, so it is the arrangement of choice for laser cooling experiments.

Two types of GaAs double heterostructures are measured. The first is GaAs \GaInP grown by atmospheric-pressure chemical vapor deposition using trimethylgallium, trimethylindium, arsine, phosphine, trimethylaluminum and disilane in a hydrogen carrier gas using GaAs substrates 1. The second is GaAs\AlGaAs is grown by molecular beam epitaxy (MBE) 2. Here the substrate is (001) semi-insulating GaAs. Native oxide is desorbed at 640 C followed by a GaAs buffer layer at 580 C. The temperature is then raised to 720 C to grow the remainder of the structure. The

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1Sample grown by Dr S. Kurtz at National Renewable Energy laboratory, Golden, Colorado.

2Dr A. Stintz at the Center for High Technology Materials, University of New Mexico
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beam-equivalent-pressure ratio of the group III elements to As$_2$ is approximately 1:15. Growth rates are 0.7 microns/hour for GaAs and 1 micron/hour for Al$_{0.3}$Ga$_{0.7}$As.

In the GaAs/GaInP heterostructures, the unintentionally p-doped GaAs active layers are clad with Si-doped GaInP. Si donor-doping modifies the energy-band alignment of the heterostructure as shown in Fig. 6.2 A.

![Energy band alignment of p-GaAs/n-GaInP](image)

Figure 6.2: Energy band alignment of p-GaAs/n-GaInP [132]. Vertical direction represents energy and horizontal directions represents position. (A) p-doped GaAs to $\sim 10^{15}$ cm$^{-3}$ and n-doped GaInP at $\sim 10^{17}$ cm$^{-3}$. (B) Energy band alignment assuming GaAs is insignificantly n-type compared to GaInP.

Once contact is made between GaAs and GaInP (e.g. during the crystal growth), the conduction and valence bands adjust in a manner to align the Fermi levels. This is due to charge displacement from the layer with higher concentration of electrons (lower concentration of holes) to the layer with lower electrons (higher concentration of holes) [132]. The band diagram of intrinsic GaAs/GaInP is shown in Fig. 6.2 A. The sign of the band discontinuity changes in B, where it is assumed GaAs is insignificantly less p-type than GaInP.

The GaAs samples used in this dissertation work are slightly p-type. If GaInP is not doped, it is also slightly p-type but with larger density than the GaAs active
layer. The band energy discontinuity at the interfaces in GaAs/GaInP acts as a trap for holes [64] (Fig. 6.2 B). Oda et al were able to improve current gain in InP/GaAs$_{0.51}$Sb$_{0.49}$/InP heterojunction bipolar transistors by addressing the band energy discontinuity [133]. Horikoshi et al observed photoluminescence quenching in GaAs/AlGaAs quantum-wells as a result of carrier tunnelling to the band edge discontinuity [134]. In this dissertation work, the hole-traps caused by the band discontinuity are reduced with a heavily n-doped ($\sim 10^{17}$ cm$^{-3}$) cladding layer as shown in Fig. 6.2 A.

The energy band band diagram in Fig. 6.2 A follows the Anderson model [132]. The plot assumes an electron affinity of $\chi_a \approx 4.07$ eV [135] and $\chi_a \approx 4.1$ eV [135] for GaAs and GaInP, respectively. Since the electron affinities of the clad and the active layer are different than at the heterojunction, an energy discontinuity in the conduction and valence bands appears. The Ga$_{0.5}$In$_{0.5}$P cladding is intentionally n-doped with Si. In this system, Si has a donor ionization energy of $E_D \approx 1.78$ meV [136]. The density of Si dopants in GaInP is $\sim 10^{17}$ cm$^{-3}$. The position of the Fermi levels with respect to valence band in GaInP and GaAs can be determined using the charge-neutrality equation [39]:

$$n_0 + N_A^- = p_0 + N_D^+$$  \hspace{1cm} (6.1)

where $N_A^-$ is ionized acceptor concentration and $N_D^+$ is the ionized donor concentration. $n_0$ and $p_0$ denote the density of thermally excited e-h pairs in the conduction and valence bands. The quantities $N_A^-$, $N_D^+$, $n_0$, and $p_0$ (in units of cm$^{-3}$) at thermal equilibrium are [39]:

$$N_A^- = \frac{N_A^0}{1 + g_A \exp\left(\frac{E_A - E_F}{k_BT}\right)}$$  \hspace{1cm} (6.2)
\[ N_D^+ = N_D^0 \left\{ 1 - \frac{1}{1 + \frac{1}{g_D} \exp\left[\frac{(E_D - E_F)}{k_B T}\right]} \right\} \]

\[ n_0 = 2.51 \times 10^{19} \left( \frac{m_e^* T}{m_0 300} \right)^{3/2} F_{1/2} \left( \frac{E_F - E_C}{k_B T} \right) \]

\[ p_0 = 2.51 \times 10^{19} \left( \frac{m_h^* T}{m_0 300} \right)^{3/2} F_{1/2} \left( \frac{E_V - E_F}{k_B T} \right) \]

where \( N_A^0 \) and \( N_D^0 \) are the density of acceptor and donor dopants, respectively. The ionization energies of the acceptors and donors \( E_A \) and \( E_D \) are taken with respect to the valence band energy level \( E_V = 0 \). \( m_e^* \) and \( m_h^* \) are the effective mass of electrons and holes in the conduction and valence bands, respectively, and \( m_0 \) is the bare electron mass. The terms \( g_A \) and \( g_D \) account for the ground state degeneracy of acceptor and donor levels \[39\]. \( F_{1/2}(x) \) is the textbook Fermi integral \[39\].

The time-integrated luminescence spectrum (see below) reveals the likely presence of carbon acceptors with ionization energy of \( E_A \approx 0.026 \) eV \[62\]. The effective mass of conduction electrons and holes in GaAs are 0.063 \( m_o \) and 0.51 \( m_o \), respectively \[39\]. For Ga\(_{0.5}\)In\(_{0.5}\)P, the effective mass of electrons and holes are 0.088 \( m_o \) and 0.7 \( m_o \), respectively \[135, 136\].

Fig. 6.2 displays the calculated conduction and valence band offsets \( \Delta C \sim 1 \) eV and \( \Delta V \sim 1.5 \) eV in this heterostructure. These values depend on the dopant density in GaInP and GaAs. The GaInP passivating layer is thick enough (> 0.5\( \mu m \)) that Fermi level pinning does not affect the band energy in the GaAs \(^3\). Band alignment at the interfaces is plotted qualitatively. Quantitative information on band discontinuities position can be obtained by solving Poisson’s equation \[132\].

At low e-h carrier densities (i.e. less than the amount of doping in the GaAs layer) the energy band diagram will look like that shown in Fig. 6.2 A. Note that holes are

\(^3\)In semiconductors, the presence of surface states in the bandgap is known to ”pin” the Fermi level position of the semiconductor. Surface states that are not positioned inside the bandgap have a different work function compared to the bulk. Pinning occurs within a short distance of the surface and depends on the interface material \[62, 132\].
effectively confined. At higher carrier density (i.e. at densities encountered in laser cooling) the band energy alignment shifts toward to that shown in Fig. 6.2 B as a result of excessive charge displacement \(^4\). Hence nature of defect related recombination is different in the different density regimes. Time-resolved spectroscopy and other techniques mentioned earlier can identify the non-radiative recombination rate at low carrier density. At high carrier density, bimolecular radiative recombination dominates non-radiative recombination making it more difficult to quantify. Since the non-radiative rate drives the internal and hence the external quantum efficiency \((\eta_{\text{ext}})\), the \(A\) coefficient can be obtained indirectly from \(\eta_{\text{ext}}\). The accuracy of this approach hinges on the uncertainty of the coefficients \(B\) and \(C\) (see Chapter 2).

Bandgap energy engineering and carrier confinement for laser cooling of semiconductors is an area of ongoing research. In this work, heterostructures with a band energy diagram shown in Fig. 6.2 A are used. This heterostructure has demonstrated a long non-radiative lifetime at both low and high carrier densities. This subject is discussed in more depth later in this chapter.

In time-resolved spectroscopy, e-h pairs are generated optically with a short laser pulse. The time rate of change of the optically excited e-h pair density \(N\) in a semiconductor sample with a negligible amount of unintentionally doped impurities is written as follows:

\[
\frac{dN}{dt} = G - AN - \eta_e BN(N + N_x) - \eta_e B_x NN_x^0 - CN^3, \tag{6.3}
\]

where \(G\) is the excitation rate, \(A\) is the non-radiative recombination coefficient for bulk and surface defects, \(B\) is the bandgap radiative recombination coefficient of GaAs, \(B_x\) is the coefficient for radiative recombination to the impurity level \((x\) denotes a donor \(D\) or acceptor \(A\) level) \([38]\), and the coefficient \(C\) accounts for the three-body Auger recombination process. \(N_x\) and \(N_x^0\) are the densities of ionized

\(^4\)An exact treatment requires solution of Poisson’s equation at each carrier density.
and unionized impurities, respectively, and $\eta_e$ is geometrical luminescence extraction efficiency as discussed previously (see for example, Table 4.2). These parameters are all temperature-dependent.

Eq. 6.3 describes carrier decay for timescales much longer than diffusion time [53]. The diffusion time $d^2/D_a$ can be estimated in our samples by assuming $d \sim 1 \mu m$ and $D_a \sim 260 \ cm^2 \ s^{-1}$ at $T = 300 \ K$ (see discussion in Chapter 2). The estimated diffusion time is in the range $10^{-12} - 10^{-11} \ s$. This means that a steady-state density profile is established instantaneously on the timescale of the luminescence decay in the high quality devices under study here ($\sim 10^{-6} \ s$). Bulk defect recombination via the Shockley-Read-Hall process is small compared to interface recombination, particularly with the high surface-to-volume ratio [53, 64, 63]. As discussed earlier, the non-radiative recombination rate at the interface is taken to be $A = 2S/d$, where $S$ is the recombination velocity and $d$ is the thickness of the bulk layer. The temperature-dependent recombination velocity (see Eq. 2.37) is taken as $S(T) = S_0 \exp(E_a/k_B T)$, where $E_a$ is the activation energy of the defect state. The luminescence signal is proportional to the radiative terms in Eq. 6.3 and gives a direct measure of the non-equilibrium carrier concentration.

A comparison is made of the photoluminescence between samples released from the substrate by etching the AlAs layer as described in detail in Chapter 5 (see Fig. 5.1) and those still attached. After lift-off, the sample is bonded to a ZnS slide to simulate a laser cooling device (see Fig. 5.15). Two different GaAs thicknesses: $d = 0.5 \ \mu m$ and $1.0 \ \mu m$ are studied.

A diode laser operating at $\lambda = 670 \ nm$ produces 30 pJ pulses of duration 5 ns that uniformly illuminate the sample with beam area of $\sim 1 \ cm^2$ at repetition rate of 20 KHz. The semiconductor heterostructure is attached to the cold-finger of a closed-cycle helium optical cryostat 5. A schematic of the experimental setup

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5 Janis Research
is shown in Fig. 6.3. A multi-alkali photomultiplier tube ⁶ detects time-resolved, spectrally-integrated luminescence via photon counting. An oscilloscope displays discrete pulses from the photomultiplier tube (PMT) corresponding to individual photons ⁷ [137]. A digital storage oscilloscope ⁸ averages waveforms containing discrete PMT pulses to create a decay signal. In this measurement, 10,000 individual signal waveforms are averaged. A single exponential fits the late-time signal (i.e. the minimum resolvable signal at the longest delay from the pump pulse) indicating that nonlinear (bimolecular and Auger) processes are insignificant at long enough delay (see Fig. 6.4).

Analyzing the late-time tail of the photoluminescence signal minimizes the influence of nonlinear bimolecular $BN^2$ and Auger $CN^3$ recombination of photo-carriers

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⁶Hamamatsu R937
⁷Although single photons are observed, this experiment is not the same as traditional single photon counting in which a discriminator is used. This approach is possible only if the decay is much longer than the PMT and oscilloscope response.
⁸Tektronix TDS 520
Figure 6.4: Time-resolved spectrally-integrated photoluminescence of an unprocessed sample, \((d = 1 \, \mu m)\). Data (points) are fitted with single exponential decay (dashed line) in the tail. The data is generated by averaging 10,000 individual photoluminescence signals.

in Eq. 6.3. Because the late-time signal is just above the noise, there is a range of linear fits possible in Fig. 6.4. Two different slopes define the error bars of this measurement.

It is possible to estimate the excited e-h density in the experiment. The absorption of GaAs at the pump laser wavelength is \(\sim 10^4 \, cm^{-1}\) [74], the pump pulse energy is \(< 1 \, nJ\), and the area of illumination is \(\sim 1 \, cm^2\). Immediately after the pump pulse, the photocarrier density is \(\alpha I \tau P / h\nu \sim 10^{14} \, cm^{-3}\) (see Chapter 2). A density of \(\sim 10^{14} \, cm^{-3}\) or less limits the recombination process to the linear, non-radiative regime.

Recombination in pure material goes as: \(dN/dt = -AN\) and \(P_{lum} \propto BN^2 \propto \exp(-2At)\). In samples with impurities, however, the luminescence signal is: \(P_{lum} \propto BNN_x + B_x N N_0\), which follows from Eq. 6.3. At low excitation in impure material:

\[
\frac{dN}{dt} \approx G - AN - \eta e BNN_x - \eta e B_x N N_0^0.
\] (6.4)
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The non-radiative coefficient \( A \) and linear radiative process from the conduction band to impurity levels \( \eta_e BN_x + \eta_e B_x N_0^x \) cannot be distinguished in this case. A complete temperature study is required to separate \( A \) and \( B \). Note that the decay lifetime is the reciprocal of these coefficients, i.e. \( 1/\tau = A + \eta_e BN_x + \eta_e B_x N_0^x \).

The temperature-dependent bimolecular radiative coefficient \( B \) was derived in Chapter 2. If the impurity type is a donor, radiative recombination occurs from the donor level to the valence band. Conversely, if the impurity is an acceptor the radiative recombination is from the conduction band to the acceptor level [38]. Small energy recombination from the conduction band to shallow donor levels and acceptor levels to the valence band (e.g. C and Zn impurities in GaAs) take place by cascade-phonon emission [38, 58]. As will be shown, the luminescence data demonstrates that the impurities in the passivated heterostructures studied here are acceptor-type. Following Basu [38], the radiative acceptor coefficient \( B_A(T) \) is:

\[
B_A(T) = B_A^0 \beta^{3/2} \int_0^\infty \frac{x^{1/2}}{(1 + x)^4} \exp(-\beta x) dx.
\]

where \( \beta = (m_A E_A/m_e k_B T) \) and \( m_A \) is the effective mass of acceptor. \( B_A^0 \) refers to the constant value of \( B_A(T) \) at a reference temperature \( T_0 \). As will be shown below, the data is fitted with \( B_A^0 \) at 7 K; at this temperature there is acceptor level freeze-out that allows recombination from the conduction band to the acceptor level to dominate.

Time-resolved decay measurement of GaAs/GaInP double heterostructures

The temperature-dependence of the photoluminescence lifetime before and after lift-off in GaAs/GaInP double heterostructures \( (d = 1 \ \mu m) \) are shown in Fig. 6.5. The late-time photoluminescence is scaled by the calculated extraction efficiency \( \eta_e \) to
account for different amounts of photon recycling that occur in the two device geometries (see Table 4.2).

Figure 6.5: Photoluminescence lifetime of GaAs/GaInP ($d = 1 \mu m$) double heterostructures before (closed circles) and after (triangles) lift-off. The dotted curve is theory ignoring interface recombination. Solid curve includes interface recombination. Inset top left: Schematic of unprocessed sample; Inset top-right: After lift-off and bonding to ZnS.

At temperatures $T \geq 250$ K, a decreased lifetime for the processed sample (triangles) indicates an increase of the non-radiative recombination rate. It is believed this is caused by defects introduced by the flexing of the non-rigid heterostructure upon release from the substrate (discussed in Chapter 5). In the temperature range 100–300 K, radiative recombination from the conduction to valence band governs the decay signal for both samples. Radiative recombination scales with temperature as $B = B_0 (T/300)^{-3/2}$ where $T$ is in Kelvin (see Chapter 2). The pronounced rise that occurs below 40 K for the unetched sample reflects the onset of impurity (i.e. acceptor) freeze-out in GaAs. The increase of photoluminescence lifetime is due to the disappearance of extrinsic holes in the valence band, which inhibits valence band recombination [138]. There is no low temperature data for the sample bonded to the ZnS slide because the slide insulates the cold finger from the sample, preventing it from reaching temperatures below 90 K. The presence of the impurity level is
confirmed with time-integrated, spectrally resolved photoluminescence data shown in Fig. 6.6.

![Figure 6.6: Time-integrated photoluminescence of an unprocessed GaAs\GaInP sample ($d = 1 \mu m$) demonstrating acceptor freeze-out at 30 K. The spectrum is taken at the same light intensity as used in time-resolved decay. To obtain enough signal, the spectrometer slit is open to give a resolution of ± 2.5 nm.](image)

For temperatures $T < 30$ K, the luminescence is dominated by conduction-to-acceptor recombination at $\lambda \approx 829$ nm, which is distinguishable from the bandgap wavelength of 818 nm. At higher temperatures, the acceptor peak disappears due to the increased electron population in this state. Only direct bandgap recombination ($\lambda \approx 824$ nm) is visible at 100 K; the blue shift in the luminescence spectrum is due to the temperature variation of the bandgap energy: $E_g(T) = 1.5216 - (8.871 \times 10^{-4}T^2)/(T + 572)$ (eV) [54]. The impurity peak corresponds to an ionization energy of $30 \pm 4$ meV, limited by the resolution of the spectrometer ($\Delta \lambda = \pm 2$ nm). The spectrum is taken at the same light intensity as used in time-resolved luminescence decay. The spectrometer slit is opened to provide sufficient light collection, leading to a spectral resolution of ± 2.5 nm. The freeze-out of impurities below 50 K is the signature of typical GaAs acceptors; donor activation energies are an order of magnitude smaller (see Fig. 6.7).
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The acceptors are likely carbon or zinc residue in the MOCVD chamber. The data are analyzed with a self-consistent model using the charge neutrality condition Eq. 6.1. An acceptor concentration $N_A^0 = 3.53 \times 10^{15} \text{ cm}^{-3}$ is derived in the temperature range of 60–300 K. The recombination velocity $S_0$ and interface defect activation energy $E_a$ are obtained using lifetime data for higher temperatures ($T > 300$ K). Conduction to acceptor radiative recombination is modeled as described in Eq. 6.5 to deduce $B_A(T) = 1.3 \pm 0.13 \times 10^{-10} \text{ cm}^3\text{s}^{-1}$ at 7 K (Fig. 6.5, dotted curve). The analysis (dotted line) cannot determine the interface recombination due to a negligible deviation from the data for $T \leq 300$ K. This means only a lower limit can be placed on the non-radiative lifetime of the unetched sample. This is not the case for the processed sample (triangles in Fig. 6.5) since a deviation from the model.

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9Dr. Sarah Kurtz, NREL, private communication
(dotted line) is evident. A modified model that accounts for fixed impurity density (solid line) is necessary. The extraction efficiency $\eta_e$ must be modified from the unprocessed device to account for the ZnS substrate. The best fit is obtained with $\eta_e \approx 12\%$, which is close to the value of 9\% determined in numerical ray tracing via ZEMAX (see Table 4.2). The non-radiative component is then found by subtracting the simple model (dotted line in Fig. 6.8) at each data point. The result is plotted in Fig. 6.8 with open circles. A linear fit to this data gives an activation energy of $E_a = 0.018 \pm 0.004$ eV, which is consistent with GaAs acceptors.

![Figure 6.8: Semi-log plot of the extracted surface recombination lifetime (circles). The fitted line corresponds to activation energy of $E_a = 0.018 \pm 0.004$ eV.](image)

Including interface recombination gives a fit to the data with $S_0 = 3.1 \pm 0.6$ cm/s and an activation energy of $E_a = 0.018 \pm 0.004$ eV for the processed sample (see solid curve in Fig. 6.5). The values measured for $S_0$ and $E_a$ correspond to a minimum non-radiative lifetime of $\sim 27\mu$s at room temperature. Although defect related non-radiative recombination is evident in the Fig. 6.5, the high temperature lifetime is primarily driven by radiative recombination.

Even though the non-radiative recombination process appears negligible for the unetched sample with thickness $d = 1 \mu$m, it is possible to estimate the non-radiative
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recombination. Comparison with before and after lift-off must be done with caution since the nature of the defects may not be the same. The activation energy is also assumed to be the same, i.e. $E_a = 18$ meV. The upper limit for the interface recombination velocity is then estimated to be $S_0 \approx 0.6$ cm/s. This is found by simply increasing $S_0$ until the model calculation (dashed line) deviates from the data in Fig. 6.5 at high temperatures. The value of $S_0 = 0.6$ cm/s corresponds to a lifetime of $d/2S \approx 80\mu s$ at room temperature.

The temperature-dependence of the photoluminescence lifetime before and after lift-off for a thinner layer of GaAs ($d = 0.5 \mu m$) in a GaAs\GaInP double heterostructure is shown in Fig. 6.9. The same procedure as discussed for the 1 $\mu$m sample is used to evaluate the non-radiative recombination velocity at the interface. The theoretical model indicates that acceptor impurities are present in the sample having ionization energy of 32 ± 4 meV, i.e. the same as the thicker sample. The data is best fit with $N_A \approx 3.8 \times 10^{15}$ cm$^{-3}$ and $B_A(T) \approx 1.42 \pm 0.15 \times 10^{-10}$ cm$^3$/s at 7 K, where surface recombination is ignored. The same model cannot be used
to describe the etched sample data because of the pronounced deviation that is evident. As before, the model is modified to include a fixed impurity density with an adjustable extraction efficiency \( \eta_e \) to account for the ZnS substrate. The model fits the data very well at low temperatures with \( \eta_e \sim 17\% \), which is close to the value of 12.7% calculated using ZEMAX (see Table 4.2). The non-radiative recombination contribution is obtained by subtracting the model fit from the data points to produce the results shown in Fig. 6.10. The linear fit has a slope corresponding to activation energy of \( E_a = 0.02 \pm 0.002 \) eV. The scattered data at lower temperatures are past the limit of measurement noise in the experiment and are ignored in the fitting procedure.

![Figure 6.10: Surface recombination lifetime of a 0.5 \( \mu \)m GaAs layer (circles). A linear fit (solid line) gives an activation energy of \( E_a = 0.02 \pm 0.002 \) eV. Data at lower temperatures is ignored in the linear fitting because the non-radiative lifetime is not measurable above the noise.](image)

Including interface recombination provides an estimate for the velocity of \( S_0 = 2.4 \pm 0.65 \) cm/s assuming an activation energy of \( E_a = 0.02 \pm 0.002 \) eV. The deduced values for \( S_0 \) and \( E_a \) correspond to a minimum non-radiative lifetime of approximately 16 \( \mu \)s at room temperature. An upper limit estimate for the interface recombination velocity before processing is \( S_0 \approx 2.1 \) cm/s, corresponding to a lifetime of...
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\( d/2S \approx 25 \, \mu s \) at room temperature.

The \( d = 0.5 \, \mu m \) sample exhibits qualitatively similar behavior as the thicker sample but is found to have an interface recombination lifetime that is 2–3 times smaller (see Fig. 6.9). This confirms the \( 1/d \) scaling of the surface recombination rate. It also confirms that the nature of the interface recombination is approximately the same in both samples after processing.

In the theoretical model described by Eq. 6.4, a combination of the terms \( \eta_e, B, \) and \( N^0_A \) appears. The uncertainty in reported values for \( B \) is relatively wide (see chapter 2), so a range of values \( \eta_e \) and \( N^0_A \) can be adjusted to fit the data. The product \( \eta_e N^0_A B \) is set by the error bar of the experiment. In the theoretical modeling, a value of \( B = 4 \times 10^{-10} \, cm^{-3}sec^{-1} \) has been set. It is believed that the extremely long non-radiative lifetimes measured in this dissertation work is a record at the time of this writing.

The temperature dependence of the time-integrated photoluminescence of GaAs\,\GaInP heterostructures is also investigated (see Fig. 6.11) by use of a closed-cycle helium cryostat. The heterostructure is optically excited with cw laser light at \( \lambda \approx 532 \, nm \) and irradiance of of \( \sim mW/cm^2 \). Photoluminescence is collected with a fiber and delivered to the monochrometer (\( \Delta \lambda = \pm 0.4 \, nm \)). The luminescence spectra from GaInP and GaAs are shown in Fig. 6.11. The grating and mirror efficiency in the monochromator have been corrected for in this plot.

The relatively wide luminescence spectrum in GaInP compared to GaAs is caused by the larger density of surface states in GaInP. Almost all the pump light (\( \lambda = 532 \, nm \)) is absorbed in the GaInP cladding layer; electrons generated in GaInP cannot fall into GaAs layer since they are well confined (see Fig. 6.2). There is no passivation at the GaInP/air surface, which means carriers can recombine there via multi-phonon emission. The presence of significant non-radiative surface recombination requires
a rapid diffusion of the photo-excited carriers to the non-passivated surface. The diffusion time in GaInP is estimated assuming the transport parameters of GaAs since values for Ga$_{0.5}$In$_{0.5}$P are unknown (see Chapter 2). Mobility in large bandgap semiconductors (e.g. GaAs and GaP) depend on the density of impurities [62]. The donor impurity density in GaInP is of the order of $10^{17}$ cm$^{-3}$ compared to $10^{15}$ cm$^{-3}$ for GaAs. The diffusion time for a 1 µm layer of GaInP can be roughly estimated to be in the range $10^{-10} - 10^{-9}$ s. This is comparable to the typical radiative lifetime in direct semiconductors where radiative recombination is the dominant process. Hence the poor luminescence intensity is due to carriers recombination at the non-passivated

Figure 6.11: Time-integrated photoluminescence of the GaAs\GaInP heterostructure vs temperature ($d = 1$ µm). The short wavelength photoluminescence originates in GaInP and longer wavelengths from GaAs. Luminescence of the sample is generated by pumping the sample with green cw laser at $\lambda = 532$ nm and light intensity of 5 mW/cm$^2$. The spectrometer resolution is $\Delta\lambda = \pm 0.4$ nm.
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GaInP lay.

The broad symmetric luminescence spectrum of GaInP at room temperature makes it very difficult to define a bandgap energy. As the temperature drops, the luminescence signal increases as a result of freeze-out in the surface states (refer to the MPE theory discussed earlier). The luminescence intensity of GaAs also increases at lower temperature, which is a direct consequence of favorable bimolecular recombination [38] as discussed in Chapter 2.

To investigate the minimum thickness for efficient passivation in GaAs, a 30 nm GaInP layer is grown on top of GaAs. Time-resolved luminescence shows that a long non-radiative lifetime is maintained even with very thin passivation. Thin passivation layers are important for the efficient luminescence extraction in nanogap devices (see Chapter 4).

Oval defects in GaAs heterostructures were discussed in Chapter 5. Time-resolved spectroscopy of a typical oval defect shows 200 ns decay lifetime measured with an atomic force microscope. This is much shorter than the clean areas of the surface. An oval defect is recognized by its rough hillock shape indicating poor local crystal growth [114, 115]. The fast luminescence decay is likely due to non-radiative recombination, although a temperature measurement is needed to isolate the cause.

6.1.2 Time-resolved spectroscopy of GaAs\AlGaAs double heterostructures

Another lattice-matched semiconductor for passivating GaAs is AlGaAs. A heterostructure of GaAs\AlGaAs grown by MBE was investigated by time-resolved spectroscopy. The measured lifetime vs temperature (7–295K) for a 1 μm GaAs

Measurement performed by Daniel Bender at UNM

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Figure 6.12: (A) Late-time lifetime determined by time-resolved spectroscopy of GaAs/AlGaAs double heterostructure vs temperature for $d = 1 \mu m$. The data demonstrates a strong non-radiative recombination down to 200 K. Below 200 K, the effect of non-radiative recombination decreases and radiative recombination due to ionized impurities dominates. The semi-log of data vs $1/k_B T$ in (B) clearly demonstrate the effective temperature range of non-radiative recombination process.

passivated with 0.75 $\mu m$ AlGaAs is shown in Fig. 6.12. A qualitative assessment of time-resolved photoluminescence at room temperature at above 200 K reveals strong non-radiative recombination in an unprocessed sample (see Fig. 6.12 A). The model fitting procedure shows $S_0 \approx 14000$ cm/s and an activation energy of $E_a \approx 0.095$ eV (see Fig. 6.12). The room temperature surface recombination velocity is determined to be $S(T) = S_0 \exp(E_a/k_B T) = 350$ cm/s. This surface recombination velocity is in the range of previously reported values observed in GaAs/AlGaAs by other research groups [53, 51, 139].

The large non-radiative recombination process is believed to be related to oxidation of Al in AlGaAs as previously reported by Ahrenkiel et al [53] and Olson et al [51]. Olson et al [51] compared the decay lifetimes of GaAs/AlGaAs
and GaAs\GaInP structures, both grown in an MOCVD reactor. They also found higher non-radiative recombination in GaAs\AlGaAs. Wolford et al [139] investigated GaAs\AlGaAs structure grown by organometallic vapor-phase epitaxy and MBE. The non-radiative recombination in the heterostructure was very high in both cases, with MBE giving the shortest lifetime. The conclusion is that the inherent GaAs\AlGaAs structure is inherently unsuitable for long non-radiative lifetimes. Devices based on GaAs\GaInP are evidently more suitable for laser cooling experiments.

6.2 External quantum efficiency

6.2.1 Introduction

The ultimate goal of any laser cooling experiment is to achieve a net temperature decrease below the ambient. To attain this, an understanding of the relevant design parameters is crucial. The cooling efficiency $\eta_c$ is a function of the external quantum efficiency ($\eta_{ext}$) and absorption efficiency ($\eta_{abs}$) as discussed in Chapter 2. In this section $\eta_c$ and $\eta_{ext}$ in GaAs\GaInP heterostructures is measured at room temperature and below. Different thicknesses of GaAs\GaInP bonded to a ZnS dome lens are also investigated to find the optimum thickness of the GaAs layer. A heterostructure/dome device is excited with laser light in the absorption tail, i.e. just at or slightly below the band gap energy of GaAs.

The cooling efficiency is the ratio of the cooling (or heating power) to the absorbed optical power. It is clear that this efficiency must be proportional to the temperature change (see Eq. 2.59):

$$\eta_c = \frac{P_{net}}{P_{abs}} = (\eta_{ext}\eta_{abs}\frac{\lambda}{\lambda_f} - 1) \propto \Delta T.$$  (6.6)
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Eq. 6.6 shows that the external quantum efficiency $\eta_{ext}$ can be deduced from the wavelength-dependent heating or cooling. This is possible provided the absorbed laser power $P_{abs}$ is known or at each pump wavelength. This is a key point because the absorption coefficient will vary dramatically at wavelengths near the band gap. One way around this problem is to keep the optically excited carrier density constant by keeping the luminescence power constant ($P_{lum} \propto BN^2$) at each wavelength. In this case:

$$\eta_{ext} = \frac{P_{lum}}{P_{abs}} = \frac{\eta_{lum}BN^2h\nu_f}{(AN + \eta_{lum}BN^2 + CN^3)h\nu} \rightarrow P_{abs} = \frac{P_{lum}}{\eta_{ext}} \tilde{\lambda_f}.$$  \hspace{1cm} (6.7)

Where $P_{lum}$ and $\eta_{ext}$ are constants. Substituting $P_{abs}$ from Eq. 6.7 into Eq. 6.6

$$\eta_e = \frac{P_{lum}}{\eta_{ext}} (\eta_{ext} \eta_{abs} - \frac{\tilde{\lambda_f}}{\lambda}) \propto \Delta T.$$  \hspace{1cm} (6.8)

This ensures that $P_{net}$ maintains the correct proportionality to the fractional heating $\Delta T$ following Eq. 6.6: A wavelength-dependent heating (ideally cooling) experiment will then provide direct information on the external quantum efficiency ($\eta_{ext}$).

Unlike the situation in rare-earth doped glasses, the external quantum efficiency in semiconductors strongly depends on carrier density. One must optimize $P_{net}$ as well as the carrier density at a range of pump wavelengths. This extra free parameter (i.e. photo-carrier density) makes optimization experiments in laser cooled semiconductors considerably more difficult compared to glass. In addition, $\eta_{abs}$ will be close to but always less than unity due to the presence of parasitic background absorption.

An alternate approach to measuring external quantum efficiency is widely used in the study of light-emitting diodes and solar cells [52, 140]. The ratio of absolute extracted luminescence to the optical pump is measured, which directly determines
$\eta_{abs}$ as shown in Eq. 2.59). Although this method is direct and convenient, significant errors are introduced because of the difficulty in collecting all the emitted luminescence as well as obtaining all the absorbed power. In devices with low background absorption and high external quantum efficiency such as used in the present experiments, the ratio $\eta_{ext} : \eta_{abs}$ approaches unity. The relative error in $(1-\eta_{ext} \eta_{abs})$ is large because this quantity is the difference of two nearly equal numbers.

A more accurate method to characterize $\eta_{ext}$ – and the approach applied in this dissertation work – was suggested by Gauck et al [21]. They used the complement of the radiative emission process: heating due to non-radiative recombination events (see Chapter 2). The net power density is proportional to fractional heating, so for devices with $\eta_{abs}(\lambda) \approx 1$, the coefficient $\eta_{ext}$ can be found by extrapolating fractional heating data to obtain the so-called zero crossing wavelength. This zero crossing wavelength $\lambda_{cross}$ is the wavelength where net cooling is identically zero, i.e. heating and cooling exactly cancel to make $\Delta T = 0$. In this case, Eq. 6.8 is set equal to zero to give:

$$\eta_{ext} = \frac{\tilde{\lambda}_f}{\lambda_{cross}},$$  \hspace{1cm} (6.9)

This approach has a range of validity that must be understood. The approximation $\eta_{abs}(\lambda) = 1$ is not valid at wavelengths much below the band gap because the absorption of the semiconductor tends to zero. Fractional heating data obtained for wavelengths far below the band gap must be ignored; $\lambda_{cross}$ is determined by extrapolating data at shorter wavelengths where absorption is high enough to justify $\eta_{abs}(\lambda) \approx 1$.

The first experimental attempt to obtain laser cooling with a GaAs\GaInP double heterostructure was reported by a group at the University of Colorado led by Prof. Eric Cornell [21]. A 0.5 µm thick and 0.5 mm diameter GaAs\GaInP was van de Waals bonded to a thin glass slide. The slide is mounted on a sapphire support.
structure and a hemispherical ZnSe lens is strapped to the structure by means of a copper wire harness \(^{11}\). The dome lens is used for luminescence extraction (see Chapter 4). The pressure exerted by the twisted wires establishes optical contact between GaAs\(\backslash\)GaInP and the dome (see Fig. 6.13).

Figure 6.13: Photograph of the University of Colorado laser cooling device. The black dot visible through the dome lens indicates the heterostructure is in optical contact with it. The diameter of the hemispherical lens is 7.6 mm [21].

The GaAs sample was illuminated with pump laser wavelengths above and below the band gap and the temperature measured with a thermistor. The carrier density generated in GaAs was kept constant at the different pump wavelengths. To accomplish this, the luminescence power, which is proportional to carrier density, was kept constant. Luminescence was monitored in a narrow spectral window above than band gap energy and sufficiently removed from the pump laser wavelength. The measured fractional heating vs laser photon energy is shown in Fig. 6.14. Although no net cooling was attained, they reported decreased heating in the sample for laser wavelengths below the mean luminescence wavelength of GaAs. A value of \(\eta_{ext} \sim 96\%\) was reported for their device.

Another laser cooling experiment at room temperature with GaAs\(\backslash\)GaInP and

\(^{11}\)The discussion in Chapter 5 stated that GaAs\(\backslash\)GaInP cannot van der Waals bond to ZnSe, which necessitates the force provided by wires.
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Figure 6.14: Fractional heating vs wavelength measured in a 0.5 $\mu$m thick GaAs in contact with ZnSe. The dashed vertical line denotes the center energy of the luminescent light, and the dashed horizontal line indicates the fractional heating at the center energy, which is the complement of the external efficiency [21].

GaAs\AlGaAs was conducted by Lin et al [26]. Their original motivation was to construct a thermo-photovoltaic device $^{12}$. Lin et al aimed to demonstrate cooling of a GaAs thin film by photoluminescence instead of electroluminescence, primarily to avoid heating at the electrical junctions. They conducted cooling experiments using different sample thicknesses and different dome lens materials. An integrating sphere measured absolute luminescence and absolute pump power to characterize $\eta_{ext}$. Although no net cooling was attained, they reported decreased heating in the sample for laser wavelengths below the mean luminescence wavelength of GaAs and a value of $\eta_{ext} \sim 96\%$ was reported [52, 140, 26]. They also found $\eta_{ext} \sim 96\%$ in GaAs\GaInP bonded to a ZnSe dome lens. Their experiments demonstrated that the optimum thickness for maximum $\eta_{ext} \sim 96\%$ was a 0.8 $\mu$m thick GaAs\GaInP heterostructure bonded to a ZnSe dome lens.

$^{12}$This is a direct energy conversion of thermal gradients to electrical currents via photons. A basic thermo-photovoltaic system consists of a thermal emitter and a photovoltaic diode. The principle of the thermo-photovoltaic device is the same as in anti-Stokes light cooling.
Here, the external quantum efficiency is measured by refining the approach of Gauck et al. Experiments to obtain net laser cooling and measure the external quantum efficiency are discussed next.

### 6.2.2 External quantum efficiency of GaAs\GaInP at room temperature

![A schematic of the laser cooling setup. Temperature is measured with a thermal camera.](image)

A schematic of the experimental setup to measure external quantum efficiency is shown in Fig. 6.15. There are important differences with respect to the experiments described in Ref. [21]. These include: i) epitaxial lift-off and direct wafer bonding of the heterostructure to a ZnS or ZnSe dome lens (see Chapter 5) to eliminate the wires and ii) a non-contact temperature measurement using a thermal camera. These key changes decrease parasitic background absorption of the luminescence and provide more sensitivity to temperature changes.

As is shown in Fig. 6.15, the GaAs/dome lens is mounted on two microscope cover slides (0.17 mm thick) to provide minimum thermal conduction the surround-
ing enclosure. An infrared-thermal camera is a non-contact method to monitor the temperature, eliminating the need for a thermocouple or a thermistor. The ZnS and ZnSe lenses are both transparent at thermal wavelengths in the mid-infrared [141]. The very low emissivity coefficients of ZnS and ZnSe make direct measurement of their temperature using a thermal camera very problematic. The advantage, however, is that thermal loading on them from the surrounding environment is negligible. To allow thermal camera measurement, a small piece of high grade, low OH-content quartz (dimension: $1 \times 1 \times 1$ mm) is attached to the dome lens using a miniscule amount of transparent epoxy $^{13}$. Quartz is not transparent in the deep IR providing the IR-camera with a high-contrast temperature probe. The vacuum chamber is isolated from its surroundings using a NaCl viewport. The NaCl window is highly transparent in deep IR and allows the thermal camera access to the device.

Following Gauck et al, the same carrier density is maintained as the pump wavelength is tuned. The carrier density is monitored via luminescence collected by an optical fiber and dispersed by a 1/4 meter grating monochrometer (see Fig. 6.15). This isolates the recombination radiation from the scattered pump light. A narrow spectral window in the luminescence is used, e.g. $820 \pm 0.5$ nm. The optical excitation density is kept constant by keeping this luminescence constant to within 4% at each wavelength [21]. The temperature-induced change of the radiative coefficient $B$ is small within the range of fractional heating $\Delta T$ and is ignored. The pump laser is modulated for lock-in detection of the luminescence.

An asymmetric duty cycle chopper wheel ($\sim 96\%$ On and $4\%$ Off with $f \sim 100$ Hz) is used to modulate the laser with a loss of only 4% of the power $^{14}$. The laser light is focused on the sample with an average beam spot size in the range $w_0 \approx 35 - 45 \, \mu$m. The laser spot size is determined by imaging the beam with the device removed via guiding mirrors and a beam profiler (see Chapter 3).

$^{13}$Duco Cement, Devcon Inc.
$^{14}$The usual chopper design is for 50% duty cycle.
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The experiment is performed in a vacuum chamber at a pressure $< 10^{-5}$ torr to minimize thermal contact with the surroundings. While this is ideal when the cooling condition is achieved, thermal runaway and device destruction is a danger when heating occurs. Thermal runaway happens because of the excellent isolation the device experiences. Runaway experiences positive feedback because as temperature increases, the GaAs band-gap energy decreases and optical absorption increases [54]. To prevent thermal runaway, device characterization is usually performed at atmospheric pressure. Air removes heat but does not alter the fundamental device characteristics (unlike wires, for example). Only the amount of fractional heating or cooling is reduced, but this does not prevent an accurate measurement of external quantum efficiency $\eta_{\text{ext}}$, for example.

Thermal camera performance and error analysis

A micro-bolometric thermal-camera from FLIR Systems (Model A40M) monitors temperature changes in the experiment. It has wavelength response range of 7.5–13 $\mu$m. The quartz thermal radiator is completely opaque within this wavelength range. The emissivity of quartz glass is taken to be $\varepsilon \approx 0.96$ for the purpose of calibration. The camera can be adjusted to account for background thermal radiation from the chamber \textsuperscript{15}. The camera can measure both absolute and relative temperature. It is equipped with a focusing lens with field-of-view: $34 \times 25$ mm at 80 mm, which is capable of resolving a point as small as $0.1 \times 0.1$ mm. The camera has a temperature resolution of $\pm 80$ mK and a display rate of 10 Hz. The resolution improves to $\pm 30$ mK with data averaging.

To test the response linearity, the displayed temperature of the quartz probe is compared to a calibrated thermocouple and found to match it with a resolution of $\pm 0.1$K. To eliminate the effect of lab temperature fluctuations, an identical quartz

\textsuperscript{15}Details are provided in the FLIR camera user’s manual
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probe is placed in the chamber close to cooling device so both are in the camera’s field-of-view. The temperature difference between the two quartz pieces is obtained this way (see Fig. 6.16).

![Figure 6.16: A photograph taken by A40M FLIR IR-camera depicting the GaAs/dome lens and reference (witness) quartz glass. Both are mounted on microscope cover slides.](image)

Results and analysis

The fractional heating vs wavelength is measured for 0.5, 0.75, 1, 1.5 and 2 µm thick GaAs/GaInP heterostructures bonded to ZnS dome lens and also for 1.5 µm thick GaAs/GaInP bonded to a ZnSe dome lens in room air. The fractional heating is measured at different carrier densities in an attempt to find the maximum value of η_{ext}. The fractional heating vs wavelength is shown in Fig. 6.17 for a 0.75 µm thick GaAs/GaInP sample bonded to ZnS dome lens. This thickness provides the highest $P_{net}$ at the optimum carrier density.

At long wavelengths, background absorption becomes severe and the temperature increases. To estimate the zero-crossing wavelength, long wavelength data is ignored and a linear fit of only the relevant data is attempted. By extrapolating data in the
Figure 6.17: Temperature change vs wavelength in 0.75 μm GaAs/GaInP at room temperature measured with a thermal camera. The solid curve is the theoretical fit of $\eta^\lambda$ to the data. Lines L-1 and L-2 attempt to fit the data in the linear regime to estimate $\eta_{\text{ext}}$ and its uncertainty.

In the linear region, it is found that $\lambda_{\text{cross}} \approx 889$ nm. The dashed lines L-1 and L-2 define the uncertainty in $\lambda_{\text{cross}}$.

To calculate the external quantum efficiency, it is required to know the mean luminescence wavelength. Laser scattering is strong at high carrier density, however, and saturates the spectrometer. The large difference between scattered laser power and luminescence power makes it very difficult to lower the power of laser without washing out the luminescence spectrum. It is also found that the luminescence shape changes as a function of collection angle, especially at grazing angles. The luminescence shape is affected primarily in the long wavelength tail where GaAs absorption is low. There is also an etalon effect due to the GaAs epilayer. The change in luminescence shape can modify the mean-luminescence value. It is essential to capture luminescence from all directions to minimize this problem. This is an area of ongoing research and setup optimization.

The mean luminescence data for different thickness GaAs heterostructure are
determined before bonding and attached to their substrate. The mean luminescence wavelengths for 0.5, 0.75, 1, 1.5 and 2 µm thick samples are very close (±2nm). The value is determined by the following calculation:

\[
\tilde{\lambda}_f = \frac{\int_0^{\infty} \lambda P_{\text{lum}}(\lambda)d\lambda}{\int_0^{\infty} P_{\text{lum}}(\lambda)d\lambda} \sim 860\text{nm},
\]

where \(P_{\text{lum}}(\lambda)\) is the luminescence spectrum. Using the above wavelength \(\lambda_f\) it is found that \(\eta_{\text{ext}}\) is 96.5 ± 0.5 % for 0.75 µm of GaAs\ GaInP bonded to a ZnS dome.

The effect of uncertainty in \(\lambda_f\) on \(\eta_{\text{ext}}\) can be estimated. A worst case estimate is \(\Delta\tilde{\lambda}_f = \pm 5\) nm giving \(\Delta\eta_{\text{ext}} = \Delta\tilde{\lambda}_f/\lambda_{\text{cross}} \approx \Delta\tilde{\lambda}_f/\tilde{\lambda}_f \sim 0.5\%\). This is similar to the uncertainty in previous experiments [21, 26].

The solid curve in Fig. 6.17 represents \(P_{\text{net}}(\lambda)\) (see Eq. 6.8) fitted to data considering wavelength-dependent pump absorption \(\eta_{\text{abs}}(\lambda)\). At short wavelengths, \(\eta_{\text{abs}}(\lambda) \approx 1\) and \(P_{\text{net}}(\lambda)\) traces a straight line. At longer wavelengths, \(\eta_{\text{abs}}(\lambda)\) weakens causing \(P_{\text{net}}(\lambda)\) to deviate from a straight lines. \(\eta_{\text{abs}}\) has contributions from \(\alpha_0(\lambda)I_{\text{GaAs}}\) [74]
and background absorption $\alpha_b l_b = 0.0005$. The latter number is the maximum value for which $P_{\text{net}}(\lambda)$ can be fitted for wavelengths longer than $\lambda = 880$ nm.

Absorption saturation is not be responsible for the deviation of the data from a straight line. The effect of absorption saturation even at a long pump wavelength of $\lambda = 890$ nm is estimated to have a negligible effect on $\eta_{abs}$. The absorption coefficient of GaAs at $\lambda = 890$ nm where $N \sim 10^{17} \text{cm}^{-3}$ is calculated to be

$$\alpha(890\text{nm}) = \alpha_0(890\text{nm}) \{f_c - f_v\} \approx 12 \text{ cm}^{-1}.$$ 

Therefore $\eta_{abs}(890\text{nm}) \approx 0.95$ is calculated assuming $\alpha_b l_b = 0.0005$. The data suggests that background absorption is wavelength dependent and is larger than flat pieces of ZnS crystals (see Chapter 4). The possible sources of background absorption are the ZnS dome, GaInP cladding (i.e. passivation layer), unintentional impurities in GaAs, and the quality of the interface between the heterostructure and dome. Reducing the background absorption is another area of ongoing research.

![Graph](image)

Figure 6.19: External quantum efficiency vs incident laser power for a 0.75 $\mu$m thick GaAs$\backslash$GaInP device bonded to a ZnS dome lens at room temperature.

The external quantum efficiency obtained at different incident laser powers ($N \propto P$) is plotted in Fig. 6.19. The carrier density dependence of $\eta_{ext}$ is clearly observed. A fractional heating measurement for 0.5, 1, and 2 $\mu$m GaAs$\backslash$GaInP devices bonded
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to ZnS dome and 1.5 µm GaAs\GaInP device bonded to ZnSe dome is shown in Fig. 6.20. The value of η_{ext} is derived by measuring the slope (and hence the extrapolated zero-crossing wavelength) for data taken at wavelengths where η_{abs} ≈ 1, i.e.
before it deviates from a straight line. The source of background absorption is still under investigation.

The ZnSe dome is coated with ∼ 10 nm SiO₂ to assist in van der Waals bonding

16The ZnSe dome is coated with ∼ 10 nm SiO₂ to assist in van der Waals bonding
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and 1.5 \( \mu m \) GaAs\GaInP bonded to ZnSe dome are determined to be: 95 \( \pm 0.6\% \),
96 \( \pm 0.5\% \), 91 \( \pm 1\% \), and 94 \( \pm 0.5\% \), respectively. The mean luminescence wavelength
of \( \bar{\lambda}_f \sim 860 \text{ nm} \) is the same for all thicknesses as discussed earlier. The results of \( \eta_{ext} \)
thickness optimization for GaAs\GaInP bonded to ZnS/ZnSe dome lens is plotted in Fig. 6.21.

![Graph showing external quantum efficiency \( \eta_{ext} \) vs GaAs thickness. The optimum thickness for laser cooling is between 0.5–1 \( \mu m \).](image)

Figure 6.21: External quantum efficiency \( \eta_{ext} \) for different GaAs thicknesses. The optimum thickness for laser cooling is between 0.5–1 \( \mu m \).

The difference in refractive indices of ZnS and ZnSe are assumed to be negligible (see Table 4.2). The optimum GaAs thickness for laser cooling is found to be in the range 0.5–1 \( \mu m \). This is in excellent agreement with the theoretical prediction in Chapter 4 (see Fig. 4.16) and other research groups [26]. As discussed in Chapter 4, at thicker samples the luminescence trapping decrease the external quantum efficiency; on the other hand at thinner samples the surface non-radiative recombination is preventing high external quantum efficiency. This later speculation can clearly observe in the external quantum efficiency measurement vs thickness.

As theoretically studied in Chapter 2, a minimum \( \eta_{ext} \) of 98\% is predicted for net cooling at room temperature. The best values of \( \eta_{ext} \) reported at this time are all close to 96\% [21, 26, 73]. As temperature decreases, however, the situation
changes and there is a higher likelihood of achieving net cooling (see Chapter 2). Low temperature experiments are discussed next.

6.2.3 External quantum efficiency of GaAs\GaInP at low temperatures

Laser cooling of semiconductors at low temperatures is very promising since defect-induced non-radiative and Auger recombination decrease while radiative recombination becomes very efficient. The prospect of laser cooling at low temperatures is investigated theoretically in Chapter 2. In the following sections, experiments to study laser cooling at low temperature will be described.

6.2.4 Differential luminescence thermometry

One of the major challenges in laser cooling experiments, particularly at low temperatures, is having a suitable method for making fractional heating measurements. The specific challenge is obtaining temperature data, preferably with a non-contact technique. A thermal camera is convenient way to make non-contact temperature measurements. The principle drawback of the camera at low temperatures is that thermal wavelengths are red-shifted out of its sensitivity window [104] 17.

In this dissertation work, an alternative, very sensitive method of non-contact temperature measurement is developed that makes use of changes in material luminescence with temperature [142, 143]. This method is very suitable for semiconductors due to the band gap energy temperature dependence. Using luminescence as a high-sensitivity thermometer is an established technique in science and technology.

17 The majority of IR-thermal cameras are useful to about -20 C. Below this temperature, sensitivity is possible but it is cost-prohibitive.
Chapter 6. Device characterization

[142] [142, 143]. In this section, luminescence thermometry is refined and applied to semiconductors. At the time of this writing, this technique is believed to have superior sensitivity compared to other non-contact temperature probes for semiconductor experiments [142, 143].

Most semiconductors exhibit absolute shifts as well as changes to the spectral shape of their luminescence as a function of temperature. The shift is related to temperature dependence of the fundamental band-edge energy $E_g(T)$. The change in the luminescence shape is caused by broadening $\Gamma(T)$ as discussed in Chapter 2. These features are depicted in Fig. 6.22.

![Figure 6.22](image)

Figure 6.22: Luminescence of GaAs in the range 7–295 K. Excitation is with a 5 mW laser at a wavelength $\lambda=532$ nm far above the band gap.

As is evident from Fig. 6.22, there are significant changes to the luminescence of GaAs as a function of temperature. These can be exploited to build a non-contact differential thermometer. The luminescence of GaAs in a small temperature range
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between 200 and 201 K is shown in Fig. 6.23.

![Luminescence of GaAs at 200 K (solid line) and 201 K (dotted line).](image)

Figure 6.23: Luminescence of GaAs at 200 K (solid line) and 201 K (dotted line).

The luminescence signal by itself does not show significant differences with 1 degree temperature increments. When these two spectra are normalized and subtracted, however, a pronounced signal is produced as illustrated in Fig. 6.24.

![Differential luminescence signal in GaAs obtained by normalizing and subtracting luminescence spectra at 200 and 201 K.](image)

Figure 6.24: Differential luminescence signal in GaAs obtained by normalizing and subtracting luminescence spectra at 200 and 201 K.

The peak-to-valley height in the normalized differential luminescence signal can
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provide information about temperature changes. The new temperature data is subtracted from a reference spectrum. Reading left-to-right in the differential luminescence signal, a valley followed by a peak corresponds to heating and peak followed by a valley indicates cooling. This is due to the fact that the GaAs band gap energy blue shifts with decreasing temperature. This method of temperature measurement has been named Differential Luminescence Thermometry (DLT) and is a key tool for experiments on laser cooling of semiconductors.

A 1/4 meter long grating spectrometer \(^{18}\) is fit with a cooled CCD camera \(^{19}\) to capture luminescence data. The GaAs sample is excited by a weak cw diode laser \(\sim 20 \, \mu W\), \(\lambda = 785\,\text{nm}\), and \(w_0 \sim 0.5\,\text{mm}\). By exciting GaAs above the bandgap energy a non-thermal equilibrium emissivity is created. The luminescence is collected, dispersed, and imaged onto the CCD. The low power cw probe laser is coincident with with the main laser pump in the cooling experiment, but negligibly alters the photo-carrier density. The probe carrier density of \(10^{15}\, cm^{-3}\) is estimated for laser parameters of \(P \sim 20 \, \mu W\), \(\lambda = 785\,\text{nm}\), and \(w_0 \approx 0.5\,\text{mm}\). This should be compared to a typical pump carrier density of \(N_{opt} \sim 10^{17}\, cm^{-3}\) (see Chapter 2). The pump laser is gated off during the luminescence temperature measurement as will be discussed later in this chapter.

The linearity of the GaAs peak-to-valley DLT signal is investigated as a function of temperature. A GaAs disk/ZnS dome lens is mounted in the optical cryostat at a fixed temperature \(T_0\). A series of starting temperatures \(T_0 = 295\,\text{K}, 200\,\text{K},\) and \(100\,\text{K}\) are examined. Averaging, normalization, and subtraction are performed automatically and in real-time with a custom LabView program \(^{20}\). The spectrum at \(T_0\) defines the reference signal. The peak-to-valley difference signal for a 0.75 \(\mu m\) and 2 \(\mu m\) thick GaAs heterostructure bonded to a ZnS dome lens is plotted vs

\(^{18}\)Oriel Model MS257

\(^{19}\)Princeton Instruments Model TEA/CCD-1024-EM

\(^{20}\)Labview is from National Instruments Inc.
temperature change in Fig. 6.25.

![Graph showing temperature change vs peak-to-valley DLT signal for different temperatures.](image)

Figure 6.25: Peak-to-valley DLT signal ($\Delta P$) vs temperature change at 295 K, 200 K, 100 K for a 0.75 (bottom) and 2 µm thick (top) GaAs with a ZnS dome lens. The probe laser is a cw diode at $\lambda = 790$ nm, $P \sim 20 \mu W$, and $w_0 \sim 0.5$ mm.

As is shown in Fig. 6.25, the peak-to-valley DLT signal is linear with temperature change over a range of $\pm 10$ K, $\pm 6$ K, and $\pm 4$ K at 295 K, 200 K, and 100 K, respectively. As the temperature difference increases, the DLT linearity is reduced. The DLT sensitivity decreases outside the linear range, eventually becoming zero when the maximum possible difference of 200% is reached. The variation in slope for the different starting temperatures is likely due to impurity contributions to the band edge luminescence.

Because laser cooling experiments with GaAs involve small temperature changes, the linearity of DLT in this application is extremely high. For large temperature
differences ($\Delta T > 5$ K) band edge shifts alone are sufficient to track temperature changes. The onset of calibration nonlinearity depends on the luminescence shape. The sharper the luminescence shape ($\partial L_{\text{um}}(\lambda)$ 

\textit{partial}\(\lambda\)), the smaller is the linear calibration range (see Fig. 6.25).

### 6.2.5 Laser cooling experiments at low starting temperature

The first low temperature laser cooling experiment was reported by Finkeissen \textit{et al} [25]. They claimed to observe local laser cooling in a GaAs/AlGaAs heterostructure consisting of three quantum wells. The device was held at a nominal temperature of 40 K. This experiment has been critically re-examined, however, and the authors’ interpretation has been found to be flawed for reasons relating to light management, cooling power, luminescence extraction, and complications in their method of non-contact temperature measurement. An analysis of this experiment is discussed in Appendix.

For the experiments in this dissertation, a low starting temperature condition is provided by an optical cryostat \textsuperscript{21}. A cooling device is attached to the cryostat coldfinger at three contact points of cross-section $\sim 0.3 \times 0.3$ mm fabricated as part of a copper fixture (see Fig. 6.26). The thermodynamics of this device will be discussed later in this chapter.

In a fractional heating experiment using DLT to determine $\eta_{\text{ext}}$, the probe and pump lasers are different. A low power cw laser is defined as the ‘probe’ and provides a constant luminescence background for temperature measurements. Only this luminescence is present when a DLT spectrum is captured. A schematic of the experiment is shown in Fig. 6.27.

The cw probe laser operates at $\lambda \approx 780$ nm and $P \approx 20 \, \mu$W, as discussed in the  

\textsuperscript{21}Temperature controller made by Lakeshore Inc.
Previous section. Luminescence from the probe laser is collected with Spectrometer A that is equipped with cold CCD camera (see Fig. 6.27). Monochromator B monitors luminescence from the pump laser at a fixed wavelength ($\lambda \approx 820 \pm 1$ nm). A dual port fiber collects luminescence from pump and probe and delivers it to the proper spectrometer. The dual fiber is made of 300 individual 50 $\mu$m fibers. The fiber cross section is a $\sim 2$ mm circle on the collection side that divides into two separate delivery slits of dimension $\sim 10 \times 50$ $\mu$m.

In this experiment, the pump laser is briefly gated off ($\sim 20$ msec) while the probe luminescence is recorded by gating-on the CCD camera $\sim 1$ msec after the pump is blocked by a shutter. This delay is needed to allow photo-carriers from the pump to recombine; it is much longer than the recombination time in the samples, ($\tau \ll 0.1$ msec). A signal averaged from 500 luminescence spectra is normalized at its peak amplitude. The peak-to-valley DLT amplitude gives direct measure of the temperature change, as was discussed in the preceding section.

Time-gating of the laser and CCD are provided by two electro-mechanical shutters with opposite logic. The amount of delay between the two shutters, their opening

Figure 6.26: Photograph of a cooling device mounted on a home-made copper fixture attached to the coldfinger of a cryostat. The dark circle is an etched sample bonded to the planar face of a ZnS dome lens. The ZnS dome is attached to the fixture with Duco cement.
times, and period are all controlled with a digital time delay generator 22 and a custom Labview CCD controller. The maximum rate of data collection is limited to \( \sim 3 \) Hz due to the speed of the CCD controller. The minimum off time of the laser is limited by the shutter speed and data processing rate of the CCD controller 23 (\( \sim 20 \) ms). The laser shutter is located inside the Ti:sapphire laser cavity to completely eliminate lasing (i.e. not just block it) thereby avoiding possible leakage through the shutter blades (see Fig. 3.3).

All luminescence data has a resolution of \( \Delta \lambda \approx \pm 0.25 \) nm. This resolution is achieved with a 1/4 meter long spectrometer 24 with a 50 \( \mu \)m input fiber and

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22 Model DG535, Stanford Research Systems Inc.
23 The CCD controller operates at a minimum time gate of 5 ms
24 Oriel MS257
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26 µm CCD pixels. A high resolution spectrometer\textsuperscript{25} $\Delta \lambda \approx \pm 0.3$ nm records the wavelength of the cw Ti:sapphire pump laser in the range 850–960 nm. A photograph of the experimental setup is shown in Fig. 6.28

![Figure 6.28: A photograph of the low temperature experimental setup with a LN$_2$ optical cryostat.](image)

The pump laser is focused on the sample to a spot size of $w_0 \approx 35$-45 µm. The laser light is partially absorbed in the cooling sample with the leakage light transmitted through the 5 mm ZnS dome lens and scattered within the cryostat. Scattered laser light is found to produce a distinguishable temperature rise in the copper sample holder. To address the scattered laser problem, a home made silver waveguide is placed in the vicinity of the dome lens (see Fig. 6.29). The silver waveguide (10 mm diameter, 50 mm long) collects the laser light plus a large portion of the luminescence and removes it from the cryostat. The cryostat is accessed optically via two anti-reflection coated quartz windows (633 – 1064 nm). The cryostat is evacuated using a turbo-molecular pump to achieve a pressure $< 10^{-6}$ Torr.

One of the major obstacles in laser cooling experiments at low temperatures is maintaining a desired temperature without any conductive heat flow. Additionally,

\textsuperscript{25}Model HR400, Ocean Optics
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GaAs and ZnS are transparent in the deep infrared, which means a cooling device cannot be placed in the vicinity of a cold object. The most efficient and unambiguous way to perform a low temperature experiment is to investigate local cooling of the device.

Consider a heterostructure/dome lens device attached to a cold finger as is shown in Fig. 6.26. Any local heating or cooling will cause a change of the steady-state temperature $T_1$, which is different from cold finger temperature $T_0$. The temperature difference $T_1 - T_0$ depends on the size, thermal conductivity, and heat capacity of the ZnS dome suspended on the copper support fixture. This temperature difference can be estimated. The local temperature difference due to the pump laser can be written as:

$$\frac{\partial \Delta T}{\partial t} \approx -\frac{P_{\text{net}}}{C_v} - \frac{\Delta T}{\tau_{ac}} \approx -\eta e B N^2 (h\nu - h\nu_f) \frac{\Delta T}{C_v} - \frac{\Delta T}{\tau_{ac}}, \quad (6.11)$$

This is a one-dimensional estimate where the length of the object is the most relevant dimension in the thermal analysis, e.g. a long rod attached to a heat source.
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In Eq. 6.11, $C_v$ represents the specific heat capacity ($JK^{-1}cm^3$) and $\tau_{ac}$ can be regarded as the thermal accumulation time. The accumulation time $\tau_{ac}$ depends on the heat capacity, thermal conductivity, and the dimensions of the object: $\tau_{ac} = C_vL^2/\kappa$ [144] and $\kappa$ is the thermal conductivity. At steady state, $\Delta T$ can be derived as:

$$\frac{\Delta T}{T} \approx \frac{K_B\eta BA}{C_vC} \times \frac{\tau_{ac}}{\tau_s}$$

where the usual laser cooling approximation $h\nu - h\nu_f \approx k_BT$ is used along considering $N$ at optimum carrier density $N_{opt} = \sqrt{A/C}$. In Eq. 6.12, $\tau_s = C_vC/(K_B\eta BA)$ is the characteristic response time of the sample. A value of $\tau_s \sim 20$ s can be roughly estimated for $T = 300 – 100$ K using $C_v/\kappa \approx 10s/cm^2$ in ZnS or ZnSe (see Table 4.1). This gives $\tau_{ac} \approx 10 \times L^2$ s.

In the setup shown in Fig. 6.26, the minimum distance between the 1 mm diameter GaAs disk at the center and the cold copper fixture is 2 mm. Therefore $\Delta T/T \approx 0.02$ or $\Delta T \approx 2–6$ K can be measured between 100–300 K. This temperature can be measured easily with the DLT technique. The thermal accumulation time is much longer than the estimated value 0.4 s. This is not surprising since the dome lens is in contact with the cold finger at only three small points (see Fig. 6.26). Increasing the delay time to 1 s before collecting spectra for DLT did not show any difference compared to a 1 ms delay. Limitations in the CCD controller did not allow longer delays to be studied.

### 6.2.6 External quantum efficiency at low temperatures

Laser cooling experiments at room temperature using a thermal camera were discussed previously. The maximum and minimum external quantum efficiencies are
achieved with 0.75 and 2 \( \mu m \) GaAs layers, respectively. In this section, the external quantum efficiency of a 2 \( \mu m \) GaAs layer at low temperatures is presented.

A 2 \( \mu m \) GaAs\GaInP disk is lifted-off from the substrate and wafer bonded to a ZnS dome lens (see Chapter 5). The device is mounted to the cryostat cold-finger via the three point copper fixture shown in Fig. 6.26). Fractional heating is measured via differential luminescence thermometry to obtain the zero crossing wavelength as discussed previously (see Section 6.2.2). The optimum fractional heating data is achieved by maximizing the slope of the data to minimize the zero crossing wavelength at different carrier densities (see Section 6.2.2). Data at 295 K, 200 K and 100 K are shown in Fig. 6.30.

To calculate the external quantum efficiency, the mean luminescence wavelength is required. Luminescence spectra is captured with the CCD at close to normal incidence to minimize the etalon effect. Collecting luminescence at high carrier densities, however, saturates the spectrometer because scattered pump laser is within the luminescence spectrum. The mean luminescence data at high density is therefore estimated by using data obtained at low carrier density. The luminescence of 2 \( \mu m \) GaAs\GaInP heterostructures at low temperatures is shown in Fig. 6.31.

The spectrum is wider than the spectrometer width at room temperature and is slightly clipped. The effect of clipping is small because the signals are near the noise level. As discussed previously, the maximum error in \( \eta_{ext} \) is not more than 0.5 % resulting from a \( \pm 5 \) nm ambiguity in the mean luminescence wavelength. The 0.5% error is less than the measurement in high quality samples with large \( \eta_{ext} \) [21, 26].

In Fig. 6.31 (top frame), a pronounced extra peak is visible at \( \sim 840 \) nm due to the

\[27\] Both the Oriel/Princeton CCD and Ocean Optics spectrometer saturate. The 1/4 m Oriel spectrometer has one port that can be used as spectrometer or monochrometer. To avoid disturbing the sensitive DLT setup, the Oriel spectrometer is dedicated to DLT measurements.
presence of unintentionally doped acceptor impurities in the GaAs layer. As discussed previously, acceptor freeze-out occurs at around 50 K. It is enhanced by the larger geometrical light extraction efficiency at longer wavelengths. Absorption in this spectral region is very low and decreases at lower temperature. This luminescence has a larger extraction efficiency \( \eta_e \) compared to direct band gap recombination. The intensity of the acceptor peak varies from sample to sample, depending on the level of impurity dopant and light extraction efficiency (compare Fig. 6.31 to Fig. 6.30). The net effect is a red-shift of the mean luminescence wavelength. The background noise is attributed to random cosmic events that can be averaged out. The external quantum efficiency of a 2 \( \mu \)m GaAs sample bonded to a ZnS dome at different temperatures is presented in Table 6.1 and plotted in Fig. 6.32.

<table>
<thead>
<tr>
<th>T</th>
<th>( \eta_{ext} )</th>
<th>( \tilde{\lambda}_f )</th>
<th>( \lambda_c )</th>
<th>( \Delta T_{error} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>295K</td>
<td>96 ± 0.5 %</td>
<td>~866nm</td>
<td>~899nm</td>
<td>~0.12K</td>
</tr>
<tr>
<td>200K</td>
<td>97 ± 0.8%</td>
<td>~844nm</td>
<td>~868nm</td>
<td>~0.075K</td>
</tr>
<tr>
<td>100K</td>
<td>98.5 ± 0.5%</td>
<td>~832nm</td>
<td>~842.5nm</td>
<td>~0.12K</td>
</tr>
</tbody>
</table>

Table 6.1: Measured \( \eta_{ext} \) in 2 \( \mu \)m GaAs bonded to ZnS dome lens as a function of temperature.

An external quantum efficiency of 98.8 ± 0.5% at 100 K is enough to achieve net cooling. Large parasitic absorption prevents this from happening. The four possible sources of this deleterious background absorption are: the ZnS dome, the GaInP cladding layer, impurities in the GaAs, and/or quality of the interface between the heterostructure and dome lens. These engineering problems are areas for future work.
Figure 6.30: Fractional heating measurement in a 2 μm GaAs\GaInP heterostructure bonded to ZnS dome at low temperatures. The upper right corner is calibration of peak-to-valley vs temperature and used to convert \( \Delta P \) to temperature.
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Figure 6.31: Luminescence of a 2 µm GaAs device bonded to a ZnS dome at 295 K, 200 K, 150 K and 100 K. The extra peak on the right hand side of the luminescence is due to the presence of unintentionally doped acceptor impurities in the GaAs layer.
Figure 6.32: Plot of the same data shown in the above table.
Chapter 7

Conclusion and future works

Conclusions

The prospects for laser cooling in semiconductors have been investigated theoretically and experimentally. The fundamental issues for achieving net cooling have been addressed. These include light extraction efficiency, the critical importance of a long non-radiative lifetime, and the need for low background absorption.

Different light extraction schemes in semiconductor devices have been examined. A dome lens made from nearly index-matched low absorption material was found to be the most suitable approach for present laser cooling experiments. The background absorption coefficient in different high refractive index materials has been measured. ZnS and ZnSe are the best choices for GaAs cooling experiments because of their low absorption at the luminescence wavelengths ($\sim 10^{-4}$ cm$^{-1}$). The light extraction efficiency depends on the device geometry. Different thickness GaAs heterostructures in contact with ZnS and ZnSe domes have been modelled using random ray tracing. The optimum GaAs layer thickness has been theoretically determined to be 0.5-1 $\mu$m and this was confirmed experimentally.
Chapter 7. Conclusion and future works

GaAs\GaInP epilayers have been fabricated for laser cooling experiments. A procedure of epitaxial lift-off followed by direct van der Waals wafer bonding to a ZnS or ZnSe dome lens has been developed. Processing issues and the quality of the interface contact have been discussed.

Defect related non-radiative recombination in GaAs\GaInP and GaAs\AlGaAs have been investigated using time-resolved spectroscopy. A mathematical model has been developed to explain the experimental observations. A record-low surface recombination velocity ($< 0.6 \text{ cm/s}$) was measured in an unprocessed GaAs\GaInP sample. The effect of epitaxial lift-off and processing on defect related non-radiative lifetime has been measured and discussed.

Laser cooling experiments have been performed by extending and refining the previous work. A high sensitivity (temperature resolution: $< 100 \text{ mK}$), non-contact thermal measurement technique called Differential Luminescence Thermometry was developed and implemented for this purpose. Direct wafer bonding of GaAs\GaInP heterostructures on dome lenses has been used to minimize background parasitic absorption. External quantum efficiency in different devices has been measured at room temperature and below. The external quantum efficiency is maximum when the GaAs layer thickness is in the range 0.5-1 $\mu$m. A record external quantum efficiency of 99% has been obtained with a GaAs laser cooler held at 100 K. This result shows that there is no fundamental physical limitation preventing the realization of net laser cooling in a GaAs-based device. It is believed that when deleterious background absorption in the present device design is sufficiently reduced, net laser cooling will be observed for the first time.
Chapter 7. Conclusion and future works

Future work

The following are suggested as future directions for research on laser cooling of semiconductors:

I) Reducing parasitic absorption is currently an ongoing and active area of research. The simplicity of the heterostructure/dome lens design provides for a systematic investigation this problem. The four possible sources of parasitic absorption are: i) the dome lens, ii) the heterostructure/lens interface, iii) the GaInP passivating layer, and iv) impurities in the GaAs active layer.

II) The effect of doping in the passivation layer is another subject of great interest. The non-radiative interface recombination physics may be favorably altered if the passivating layer is doped p-type or n-type.

III) Removing cooling luminescence by the principle of frustrated total internal reflection at a vacuum nanogap is another idea of substantial promise. A device design based on the nanogap can improve the efficiency by: i) maintaining the long non-radiative lifetime that has been shown to degrade after lift-off and ii) enhancing the luminescence removal compared to the dome lens approach. Nanogap fabrication is described in the Appendix.
Appendix A

Analyzing the result and experiment conducted by Finkeissen et al

In 1999, a European consortium claimed to observe local laser cooling in a GaAs \AlGaAs heterostructure consisting of three quantum wells held at a nominal temperature of 40 K [25]. This experiment (schematic is sketched Fig. A.1) is critically re-examined here. The interpretation presented in Ref. [25] is found to be flawed for reasons relating to light management, cooling power, luminescence extraction, and complications in their method of non-contact temperature measurement.

The ratio of the luminescence intensities of two different magneto-exciton peaks is used as temperature indicator (reproduced in Fig. A.2. As the heterostructure is pumped with higher laser intensity, the ratio of luminescence intensity from the magneto-exiton lines hh(2s) to lh(1s) drops to about 0.8 of the value at low intensity pump. This is interpreted as local laser cooling by an amount \( \Delta T = -5 \) K.

A qualitative thermodynamic analysis of the setup immediately reveals a serious
Appendix A. Analyzing the result and experiment conducted by Finkeissen et al

flaw in the experiment. Because the quantum wells are so thin (9 nm each), the vast majority of the pump laser power is deposited in the thick (0.1 mm) GaAs substrate of the device. Essentially all the laser pump power will be converted to heat; the proximity of the substrate to the wells will swamp out any local cooling that may exist there. In addition, luminescence emanating from a cooling process in the quantum wells will be largely trapped by total internal reflection and absorbed in the substrate, which adds to the heat load on the wells.

The temperature gradient between quantum wells and the cryostat can be estimated. In Chapter 6, the temperature difference between the laser cooling region and cryostat cold finger was analyzed. Using the same approach for the ideal (albeit unrealistic) condition where GaAs substrate heating is ignored, it is found that the temperature difference between quantum well GaAs and cold finger is $\Delta T/T \approx 0.001$ or $\Delta T \approx 0.1$ K. This assumes a 0.1mm layer of GaAs acting as a thermal barrier between the quantum wells and cryostat coldfinger. Their deduced temperature decrease of $\Delta T = 5$ K does not appear to be possible in this setup.

The experiment may have produced magneto-exciton spectra that were affected by carrier density. The high carrier density could distort the published luminescence thermometry measurements in two ways: i) phonon absorption bottleneck and ii) ex-
FIG. 3. Up-converted luminescence at a bath temperature of 45 K in a magnetic field of 9 T for three different excitation powers: (a) 0.1, (b) 1, and (c) 10 mW. The excitation energy was at the hh(1s), marked by the arrow. Circles: intensities deduced from a Maxwell distribution yielding a temperature $T_L$ (error bars correspond to ±1.5 K).

Figure A.2: Magneto-exciton luminescence data taken from the report of Finkeissen et al [25].

citon screening. With these alternate explanations in mind, the experiment may have been incorrectly interpreted as an observation of local cooling in a semiconductor.

**Phonon bottleneck.** The phonon bottleneck is analyzed with a simple three-level energy band diagram for GaAs\AlGaAs quantum well shown Fig. A.3.

The rate equation between level $|2\rangle$ and level $|3\rangle$ can be written in steady-state as:
Appendix A. Analyzing the result and experiment conducted by Finkeisen et al

Figure A.3: Three-level model for excitation-relaxation rates in a quantum well.

\[ 0 = w_{23}N_2 - w_{32}N_3 - R_{31}N_3 \]  \hspace{1cm} (A.1)

\[ \rightarrow \frac{N_3}{N_2} = \frac{w_{23}}{w_{32} + R_{31}} = \frac{1}{\exp(\Delta E/k_B T) + R_{31}/w_{23}}. \]

The ratio \( N_3/N_2 \) can decrease by: i) a decrease of the temperature to increase \( \exp(\Delta E/k_B T) \) or ii) an increase in the ratio rates \( \rho = R_{31}/w_{23} \). The change of \( \rho \) to mimic the temperature change is:

\[ \partial \left( \frac{N_3}{N_2} \right) = \frac{\partial (N_3/N_2)}{\partial T} \Delta T = \frac{\partial (N_3/N_2)}{\partial \rho} \Delta \rho \]  \hspace{1cm} (A.2)

\[ \rightarrow \Delta \rho = -\frac{\Delta E \Delta T \exp(\Delta E/k_B T)}{k_B T^2}. \]

A temperature change of \( \Delta T = -5 \text{ K} \) at 50 K in Eq. A.2 requires \( \Delta \rho \approx 6.5 \) to mimic the temperature change and modify the ratio of \( N_3/N_2 \). An energy separation of \( \Delta E \approx 10 \text{ meV} \) is taken for the lh(1s) and lh(2s) magneto-excitons. To induce the claimed temperature drop, the incident laser power increased from 0.1 mW to 10
mW (corresponding to 4 W/cm$^2$). Using the fact that $R_{31} \propto \sqrt{I}$ provides an order of magnitude estimate of $w_{23} \sim 10^7$ sec$^{-1}$ due to a possible phonon bottleneck at high power. This rate appears to be excessively slow, but a microscopic analysis of energy relaxation and phonon reabsorption in a quantum well is required to determine if it is realistic.

**Screening of excitons.** Coulomb screening of the magneto-exciton binding potential can occur at sufficiently high photocarrier density. Larger radius excitons are more likely to be screened, which is consistent with the observed changes in the experimental peaks shown in Fig. A.2. The luminescence of three-dimensional excitons (i.e. an approximation to the confined magneto-excitons involved in the experiment) was modeled with Banyai-Koch theory [47]. The luminescence intensity of high energy (i.e. large radius) excitons drops as carrier density increases [145] (see Fig. A.4). The larger radius exciton peak (centered at 1.514 eV) disappears when the carrier density increases to $N = 7^{14}$ cm$^{-3}$. This means it is possible that the exciton spectra might change in the manner observed without a temperature decrease.
Appendix A. Analyzing the result and experiment conducted by Finkeissen et al

Figure A.4: Theoretical model of luminescence of 3-D excitons as a function of photocarrier density $N$ at 50 K. The high energy luminescence peak (centered at 1.514 eV) washes out as carrier density increases.
Appendix B

Nano-gap device fabrication

In Chapter 4, different light extraction schemes were discussed. Removing cooling luminescence by the principle of frustrated total internal reflection at a vacuum nanogap is an idea of substantial promise and considered briefly in this Appendix. A fabrication method for a nanogap cooling device is described.

The fabrication starts with a wafer of GaAs/GaInP double heterostructure grown on a GaAs substrate. A sacrificial layer of AlAs separates the substrate from the heterostructure. The wafer is cleaned and processed as described in Chapter 5. Photolithography is used to create posts in the photoresist. The posts serve to register the two surfaces and defines the width of the nanogap. An ICP machine etches the wafer vertically to produce posts in the GaInP passivation layer (see Fig. B.1). An excessively thick GaInP layer can be etched down to $\leq 30$ nm; the smaller the gap, the better the light extraction. Below 30 nm, however, begins to compromise surface passivation.

After cleaning off the photoresist, the wafer is coated with Al or SiO$_2$; these two materials etch readily in HF solution. The thickness of the new coating is exactly the same as the thickness of the desired nanogap. The directional nature of coating
Appendix B. Nano-gap device fabrication

Figure B.1: Schematic of a GaAs double heterostructure on which an array of posts have been etched in the passivation layer. These posts register the separation of the vacuum gap.

Prevents growth of the post diameter, which is a key advantage of this approach. Even better results may be achieved by growing an Al layer with an MBE machine. A thick Si or poor quality GaAs layer much larger than the post height can be coated with Al or SiO$_2$. Neither of these materials dissolve in HF. The new layer is thick enough to absorb all the luminescence from the cooling process; re-radiation is extremely weak.

For strength and handling, a thick layer of gold metal (up to few mm thickness) is placed on top of the Si or GaAs coating. This provides high structural strength for epitaxial lift-off. The device is dipped into 49% HF to selectively remove the Al or SiO$_2$ layer along with the sacrificial AlAs layer. The heterostructure along with the absorptive layer and support structure are released. The heterostructure remains attached to the absorptive layer via the GaInP posts. After this etching, a well defined nanogap exists between the GaAs\GaInP double heterostructure and the thick absorptive layer and its support structure. The nanogap provides optical coupling and high thermal isolation. A schematic of the final steps is shown in Fig. B.2.
Appendix B. Nano-gap device fabrication

Figure B.2: Schematic of the final processing steps in monolithic nanogap fabrication.
Appendix C

Signal processing in DLT measurement

The application of Differential Luminescence Thermometry (DLT) to laser cooling experiments was discussed in Chapter 6. More details are presented here.

The temperature resolution of DLT can be improved by filtering the noise using Fast Fourier Transform (FFT) numerical techniques. Sample DLT signals and corresponding Fourier spectra for temperature differences of 0 K, 1 K and 3 K at a nominal temperature of 200 K are plotted in Fig. C.1. For each of these DLT signals, the peak-valley height is linear with temperature change (see Fig. 6.25). The Fourier transforms have the same frequency distribution as shown in Fig. C.1). The signal for $\Delta T = 0$ K demonstrates the ultimate sensitivity for a given white noise level.

Best resolution is achieved with low pass filtering the Fourier signal from the frequency where white noise and DLT signal cross. Determining this point is subjective, but must be kept the same throughout the experiment. The resolution can be improved drastically by increasing the signal-to-noise ratio. Since normalized luminescence signal is used in the measurement, the stronger the signal the lower
Appendix C. Signal processing in DLT measurement

Figure C.1: DLT signals at 200 K for $\Delta T = 0$, 1, and 3 K (top frame). Corresponding FFT spectra are shown in the lower frame.

The probe laser power cannot be increased arbitrarily, however, because it must contribute a negligible photocarrier density compared to the pump. Further improvements to signal-to-noise can be achieved by data averaging and using a cooler CCD device. Note that probe laser heating of the sample creates a small, unimportant dc offset in the starting temperature.

The DLT signal from GaAs is modelled with the luminescence spectral density derived from the absorption coefficient obtained from the van Roosbroeck-Shockley relationship (see Chapter 2). This simple absorption coefficient based on a two-band model is relatively poor in predicting the slope of the peak-valley DLT signal vs temperature change. A more complicated model that accounts for excitons [47] provides a more accurate value for the absorption coefficient. An analysis of DLT
Appendix C. Signal processing in DLT measurement

based on this model ¹ are compared to experiment in Fig. C.2. The model describes the experiment very well, although it predicts sharper DLT signals at 100 K because it neglects band tailing in the GaAs (see Chapter 2).

![Figure C.2: Theoretical modelling and experimental DLT signals in GaAs. Data is collected using a grating monochromator.](image)

The temperature resolution achieved with DLT is $\sim 1.5$ mK, $\sim 0.078$ mK, and $\sim 0.050$ mK at $T_0 = 295$ K, 200 K, and 100 K, respectively using a 0.75 $\mu$m GaAs sample. These limits are derived from the noise observed in the wings of the DLT signal. Near the middle curve of DLT signal where the temperature is measured, the temperature resolution is 10 mK, 12 mK and 15 mK at these three temperatures (see Fig. C.3).

¹Calculations performed by Prof Mansoor Sheik-Bahae.
Appendix C. Signal processing in DLT measurement

Figure C.3: DLT signal from a sample at 200 K before filtering (light curve) and after filtering (dark curve). Fluctuations reflect the temperature stability of the cryostat.

The limit of resolution in the experiment is limited by the temperature instability of the cryostat and is not the ultimate accuracy of the DLT technique. In all DLT measurements used for this dissertation work, 500 individual signals are averaged. Temperature drift of the cryostat is built into this average. The cryostat temperature stability depends on the controller set-point and the type of fixture used to hold the heterostructure/dome lens in place. The noise varies on a day to day basis and must be accounted for.

The DLT signals of different GaAs samples are investigated to determine the consistency of the calibration factor. The luminescence of a 0.75 µm and 2 µm thick GaAs samples at 200 K is shown in Fig. C.4. The difference in the luminescence shapes directly affects calibration factor for the peak-to-valley DLT signal vs temperature change (see Fig. 6.25). Sample-to-sample variation for the same nominal thickness were also observed, although very small, likely depending on doping and probe laser power. Each sample has a unique calibration curve.
Appendix C. Signal processing in DLT measurement

Figure C.4: Normalized luminescence signals of two different GaAs samples (thickness: 0.75 µm and 2 µm) at 200K. The difference in spectral shapes affects the DLT calibration.
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