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QUANTUM WELL ABOVE-BARRIER STATES AND SHORT WAVELENGTH INTERSUBBAND TRANSITIONS IN InGaAs/AlGaAs QUANTUM WELLS

A DISSERTATION
SUBMITTED TO THE DEPARTMENT OF APPLIED PHYSICS
AND THE COMMITTEE ON GRADUATE STUDIES
OF STANFORD UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

Baegin Sung
August 1998
I certify that I have read this dissertation and that in my opinion it is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Abstract

Nonlinear optical (NLO) frequency conversion based on quantum well (QW) intersubband transitions (ISBTs) has been widely studied because QW ISBTs exhibit extremely large optical nonlinearities produced by the resonant features with large dipole moments. Since the transition energy is limited by the conduction band offset, ISBTs have been limited to wavelengths longer than 4 μm in most QWs. This limitation excludes room temperature operating semiconductor diode lasers as the pump sources for the desired NLO process. QW ISBTs resonant to high power diode laser wavelengths in the range of 1.55 - 2.0 μm would open the possibility to realize a compact, low cost, room temperature operating mid-infrared light source by integrating intersubband QWs with diode lasers on the same substrate. Such a light source has many potential applications, including remote pollution monitoring, identification of chemical and biological agents, chemical process control, thermal imaging, laser radar, and medical diagnosis.

This dissertation describes investigation of short wavelength ISBTs and related physics. Two approaches have been pursued to obtain large ISBT energies: 1) creating quasi-bound states above the barrier energy, and 2) constructing deep InGaAs/AlGaAs QWs. Unbound above-barrier states are confined by λ/4—Bragg-mirrors to achieve large transition energies. The first demonstration of control of quasi-bound states by electron mirrors is described. Growth of highly strained InGaAs/AlGaAs QWs on GaAs is studied to achieve larger transition energies from bound and quasi-bound states. The largest ISBT energy on a GaAs substrate, 780 meV (1.59 μm), is reported. Electron dynamics in subbands are also studied by short-pulse pump-probe experiments and absorption saturation measurements to resolve the upper state lifetime in both bound and quasi-bound
states. These are important parameters for the design and performance of devices, such as the quantum cascade laser based upon ISBTs.
Acknowledgments

First of all, I would like to thank my Heavenly Father who has “Immanuel”ed throughout my life for His amazing grace and love. I can never thank Him enough for everything He has done for me.

Looking back all those years I have spent at Stanford, I found I owe many thanks to many people. First, I would like to thank my advisor Prof. Jim “Coach” Harris for providing excellent guidance and environment. I have benefited from not only his depth of technical knowledge of semiconductor physics and engineering but also his personal advice and encouragement especially when I was depressed.

I would also like to thank Prof. Marty Fejer for all his help and guidance. I was lucky to have his advice and insights into quantum well intersubband physics, nonlinear optics, and experimental techniques available to me.

I would like to thank Prof. Walter Harrison for reading my thesis and giving valuable advice on the theoretical parts. Many thanks also go to the other members of my orals committee, Prof. Sebastian Doniach and Prof. Robert Feigelson.

I was fortunate to closely work with many talented researchers. Gary Woods helped me enormously in optical measurements and pump-probe experiments. His knowledge about intersubband transitions have been really helpful to me. Herman Chui and Eric Martinet taught me experimental and theoretical stuffs about intersubband transitions at the initial stage of my study. Michael Procter, Chris Evert, and Renan Milo have also
provided much assistance in various experiments. I would also like to appreciate the collaboration with Konstantin Vodopyanov in optical absorption saturation measurements.

Many thanks also go to the Harris group comrades. I would especially like to thank the MBE gurus, especially Herman Chui, Mike Larson, Glenn Solomon, Dave Miller, and Fred Sugihwo for their hard work to keep the both MBE systems running. I am also grateful to Alan Massengale, Sam-Dong Kim, and Heon Lee for their help and friendship. Especially, Alan did go extra miles with me in preparing my oral defense. I really appreciate his help. I would also like to thank Prof. Schwettman and his students and staff who have generously provided us with their free electron laser facilities.

I would also like to thank Gail Chun-Creech and Lu Miao in the Solid State Laboratory and Paula Perron in the Applied Physics Department for their generous help in all sorts of administrative matters.

I am also greatly indebted to New Community Baptist Church members for their love and fellowship in Jesus Christ. I would like to thank Korean physicists at Stanford, Sang-Il Park, Kookrin Char, Seungoh Ryu, Changyoung Kim, Chulhong Park, Jungsang Kim, and Sanghyun Oh for the useful discussions and fun time we have had together.

This work would not be possible without the tremendous support of my family. My greatest gratitude goes to my parents for their loving support throughout my graduate education. My brothers have always showed their trust to me which encourages me a lot. Finally, I can never adequately express my gratitude to my wife, Hyunjeong, and two daughters, Yoojin (Christine) and Yoojung (Katherine) for their being with me. They have been the greatest source of my joy and strength over the last five years. I thank God for them.
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Chapter I. Introduction

One of the major advances in semiconductor technology over the past 25 years has been the hetero-epitaxial growth of complex multi-layered structures and the energy band engineering it has enabled for optical and optoelectronic devices. One of the main features of these structures is the quantum wells that are created by layers of different bandgaps and the resulting quantized levels in the wells. Such a quantum well structure is shown in Figure I.1. Optical transitions can occur between these quantized levels\(^1\), just as between the valence and conduction bands. Such transitions are known as intersubband transitions.

This dissertation is devoted to investigation of large-energy intersubband transitions (ISBTs), quasi-bound states and related intersubband physics in semiconductor quantum wells (QWs), such as a carrier lifetime in excited states and optical absorption saturation. This chapter presents the motivation and organization of this dissertation.

---

Figure I.1. A quantum well structure with two bound and one quasi-bound states. The bound states are confined to the well region by the potential barriers and the quasi-bound state by Bragg reflection from the "electron mirror" layers on both sides of the well.
I.1. Motivation

The mid-infrared (MIR) region is a spectrally rich region with many molecular species providing “fingerprint” absorptions by which they can be identified. Figure I.2 illustrates infrared absorption regions of several gases and chemicals as well as several potential MIR light sources in these wavelengths. These materials have vibrational and rotational absorption resonance bands in the atmospheric windows at 3 - 5 μm and 8 - 12 μm ranges.\textsuperscript{2,3} Thus compact, tunable and room temperature laser sources at these wavelengths should greatly facilitate the detection of these substances which are important for environmental pollution control, semiconductor materials processing and medical diagnosis of disease such as diabetes. Lasers whose outputs are in the transparency window of the atmosphere could also be utilized for laser radar and thermal imaging.\textsuperscript{4}

In reality, the existing laser technology at these wavelengths has been quite limited especially when one requires non-cryogenic operation. The CO\textsubscript{2} laser has been a powerful tunable source between 9.2 - 10.8 μm wavelengths for several decades, but it is too expensive and far too big to be used in a compact form. The most desirable light source for these applications would be semiconductor diode lasers, which are now being widely used in high volume applications, such as CD players, bar code scanners and fiber optics communication. However most conventional semiconductor lasers based on InGaAs material are limited to wavelengths shorter than 2 μm because their output wavelength is determined by the bandgap of the active layer material. There has been extensive research to realize long wavelength semiconductor lasers based on narrow bandgap materials, such as InGaAlSb and Pb-salt, but so far these lasers require cryogenic cooling for operation beyond 4 μm.\textsuperscript{5} As the bandgap narrows to get long wavelength output, the laser gain is
severely degraded by undesirable thermally activated processes, such as Auger recombination.\(^5\)

![Infrared spectrum of available mid-IR laser sources, spectroscopic absorption bands of chemical compounds and two atmospheric windows useful for active imaging and transmission.](image)

**Figure I.2.** Infrared spectrum of available mid-IR laser sources, spectroscopic absorption bands of chemical compounds and two atmospheric windows useful for active imaging and transmission.
In contrast to the “bipolar” diode lasers which are based on radiative electron-hole recombination described above, an “unipolar” semiconductor laser, called the quantum cascade laser, was invented in 1994 and it has developed very rapidly.\textsuperscript{7} Unipolar means that the laser operation involves only one type of charge carriers, electrons. The stimulated emission results from the electron ISBTs in the conduction band of a QW, which is the same mechanism studied in this thesis. Quantum cascade lasers have demonstrated tailored output wavelengths between 4 and 11 $\mu$m in InGaAs/InAlAs QWs on InP substrates. However the performance gets worse as the output wavelength increases even though the quantum cascade laser is much less affected by thermally activated non-radiative processes than the bipolar laser diodes.\textsuperscript{8} True cw operation at room temperature has not been achieved yet. However, considering it is still in its early developing stage, it has quite a reasonable chance to overcome all the shortcomings that it now has and become a mature technology like today’s semiconductor laser diodes.

An alternative approach to direct MIR laser sources is nonlinear optics (NLO) which has been a versatile tool to produce coherent light sources at wavelengths where no direct laser source is available. When coherent optical beams, like lasers, propagate through a nonlinear optical medium, additional coherent radiation is generated via nonlinear interaction between the input beams and the material. The frequency of the generated light is determined by the corresponding nonlinear polarization of the material atoms or molecules caused by the input optical fields. Although there are variety of nonlinear optical processes that take place in a NLO material, the nonlinear fields are usually relatively weak unless the input fields are very strong. The advent of high power coherent light sources, such as the laser, has made the NLO phenomena of practical interest to obtain coherent light at new frequencies. Efficiency of this NLO frequency conversion process is governed by optical and material parameters, such as the intensity of the input beams, a nonlinear optical property of the material called the nonlinear susceptibility, and phase velocity matching
conditions between the input and generated beams. The advantage of nonlinear optics is that the efficiency is not spoiled by thermal effects and thus the operation is usually at room temperature or higher where the proper phase matching condition is satisfied. Of course, the material should be transparent to both input and generated beams and the input intensity should be below saturation and optical damage threshold to achieve a useful amount of output. As we will see in the next chapter, QW intersubband transitions (ISBTs) have many desirable features for NLO applications by having a huge nonlinear susceptibility, which was first observed by M. M. Fejer, et. al. in 1989.⁹

![Figure I.3. Schematic of Difference Frequency Generation (DFG).](image)

Among many kinds of nonlinear optical processes, difference frequency generation (DFG) offers a means to generate longer wavelength outputs using shorter wavelengths inputs (frequency down conversion). DFG uses two input beams which interact with a NLO medium to generate a third beam at the difference frequency of the two inputs, as illustrated in Figure I.3. In 1994, H. C. Chui et. al.¹⁰ demonstrated that QW ISBTs yield very large nonlinear susceptibility for difference frequency generation of MIR light around 10 µm using two near-infrared (NIR) input beams around 2 µm. This opens the possibility of MIR generation by mixing the output of two laser diodes in a semiconductor material which could lead to an integrated compact MIR source. In order to realize this possibility in a practical device, however, many problems must be resolved, such as larger intersubband energy, optimized linewidth, high saturation intensity, phase matching, etc. For example,
in order to match the output wavelengths of readily available high-power diode lasers\textsuperscript{11}, ISBT energy needs to be up to 800 meV. The work described in this dissertation addresses some of these issues and contributes a deeper understanding for the QW ISBTs. The main focuses among many issues are: large energy or short wavelength ISBTs, QW above-barrier states, intersubband lifetime and saturation behavior.

We have taken two approaches to achieve high intersubband energies: first, constructing deep QWs from InGaAs / AlGaAs heterostructures and second, creating confined states above the QW barrier potential, which are called "quasi-bound" (QB) states, as illustrated in Figure I.1.

InGaAs / AlGaAs QWs offer very large conduction band offsets between the well and barrier materials, which concomitantly provides large intersubband energies. Epitaxial growth of InGaAs / AlGaAs heterostructures on GaAs substrates has been limited to indium content below 30 % because of lattice mismatch between InGaAs and AlGaAs layers until S. M. Lord, et. al.\textsuperscript{12} showed that a linearly graded indium InGaAs buffer layer greatly relieves the strain in subsequent pseudomorphic layers and leads to good quality epitaxial layers with high indium content. H. C. Chui, et. al.\textsuperscript{13} adopted this technique to obtain ISBT energies as large as 580 meV (2.1 \(\mu\)m). In this thesis, optimized growth of InGaAs / AlGaAs QWs was used on linearly graded InGaAs buffers to achieve large energy ISBTs. This growth and quantum well design will be discussed and large energy ISBTs of 780 meV (1.59 \(\mu\)m) were demonstrated.

So far, all the descriptions of subband states and transitions between them are bound states which are confined by the barrier potential. A different kind of confined state, called "quasi-bound" state will also be investigated in this thesis. The quasi-bound state is
different from the conventional bound state in that it is located at energies higher than the barrier energy but confined or spatially localized by Bragg reflection from barriers of a periodic superlattice structure outside of the quantum well. Because they are above the barrier potential, they offer higher ISBT energies, along with other distinct features due to the different confinement mechanism. The transitions to quasi-bound states are also investigated with respect to intersubband absorption, lifetime and saturation, and they are compared with transitions between the ordinary bound states. Pump-probe experiments and saturation measurements are performed on various QW samples with bound and quasi-bound states in order to investigate carrier relaxation behavior of these states.

I.2. Overview of the dissertation

The organization of this dissertation is as follows. Chapter II introduces background information to provide a foundation to understand the work presented in later chapters. Chapter III describes detailed theoretical and experimental work on QW above-barrier and quasi-bound states and ISBTs to these states. Chapter IV describes short-wavelength or high-energy ISBTs in InGaAs / AlGaAs QWs. In Chapter V, pump-probe experiments and saturation measurements will be presented to investigate intersubband lifetimes and carrier relaxation in bound and quasi-bound states. Finally, a summary and suggestions for future work are presented in Chapter VI to conclude this dissertation.
Chapter II. Background

This chapter presents background theory related to quantum wells (QWs) and intersubband transitions (ISBTs), which facilitates understanding the subjects described in the succeeding chapters.

II.1. Quantum wells

All work described in this thesis is related to optical transitions and carrier relaxation between subband states in semiconductor QWs. A QW is a semiconductor structure composed of a thin layer of narrow bandgap material sandwiched between two wide bandgap materials as illustrated in Figure II.1. Such a structure renders a potential profile like a well in the conduction and valence bands. The narrow bandgap layer is called a well and the wide bandgap layer the barrier. Because the well region is the lowest energy state for both electrons and holes, they are confined to the well layer by the potential barrier. If the thickness of the well layer is on the order of 100 Å which is comparable to the electron de Broglie wavelength in the well, the wave property of the electron state strongly manifests itself, forcing the electron (hole) motion normal to the layer plane to be quantized into discrete energy levels. On the other hand, the electron (hole) motion in the layer plane sees only the normal crystalline periodic potential, which can be approximated as free particle motion. This gives rise to energy dispersion curves (bands) starting at each discrete energy which are quadratic with respect to in-plane k-vectors, k,. These energy bands are called “subbands”. In this thesis, we will only be concerned with subbands in the conduction band. Equivalent, although more complex physics applies to the valence band because of its degeneracy, and extensive research has also been done on the valence subbands.\textsuperscript{14}
Figure II.1. Schematic of QW layer structure and subbands. (a) Layer structure consisting of alternating wide (barrier) and narrow (well) bandgap materials. (b) Conduction ($E_C$) and valence ($E_V$) band edges of a QW showing the quantized wavefunctions and minimum subband energies. (c) Schematic of subband dispersion in conduction and valence bands for transverse $k_t$.

Modern crystal growth techniques, such as molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD), make it possible to fabricate quantum well structures with mono-layer ($\approx 2.8 \text{ Å}$) level accuracy. Most QWs are composed of III-V semiconductors, that is alloys formed of combination of column III (Al, Ga, or In) cation and column V (N, P, As, or Sb) anion atoms. Properties of these semiconductors vary significantly depending on the constituent materials. Some important properties are the
crystal structure, lattice constant, bandgap, effective mass of electron, and refractive index. The III-V semiconductors usually crystallize in a zincblende (cubic) structure, although III-nitrides also occur in a wurtzite (hexagonal) structure. In most cases, III-V semiconductors composed of lighter elements have smaller lattice constants, larger bandgaps, heavier electron effective masses, and lower refractive indices. For example, GaAs has a smaller lattice constant, larger bandgap, heavier effective mass, and lower refractive index than InAs. Likewise for GaP compared to GaAs. However, there are exceptions, such as AlAs, having a slightly larger lattice constant than GaAs and a larger refractive index than AlSb. One very important merit of the III-V semiconductors is the possibility of alloying the binary semiconductors to yield ternary or quarternary materials with desired properties. For instance, adjusting composition of each constituent material in complicated alloys, such as \( \text{In}_x\text{Al}_y\text{Ga}_{1-x-y}\text{As}_{1-z}\text{P}_z \), achieves a desirable combination of a lattice constant, bandgap and refractive index for diode laser structures.

Among many QW structures composed of a variety of alloy and binary materials, GaAs / Al\(_x\)Ga\(_{1-x}\)As is the most commonly used QW materials system because the two materials have almost identical lattice constants and GaAs substrates are readily available. One of the drawbacks of the GaAs / AlGaAs QW for engineering ISBT is that the ISBT energies are limited to mid-infrared wavelengths. Indium can be introduced into the well layer to increase the bandgap difference between the well and barrier layers, which in turn increases the QW depth and ISBT energies as shown in Figure II.2. In\(_{0.5}\)Ga\(_{0.5}\)As yields a well depth 400 meV deeper than GaAs. However, there is a problem with growing In\(_y\)Ga\(_{1-y}\)As / Al\(_x\)Ga\(_{1-x}\)As QW samples. Because of the different lattice constants of the two materials: InGaAs has a larger lattice constant than GaAs, strain develops and if the InGaAs layer is thick enough, dislocations are generated to relieve the strain. Dislocations are very deleterious in GaAs, causing carrier trapping, lifetime shortening and linewidth broadening. We employed a special growth technique for InGaAs / AlGaAs QW samples
using a linearly graded InGaAs buffer layer in order to overcome this type of lattice mismatch problem.\textsuperscript{12} This technique will be fully described in Chapter IV.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Conduction band diagrams of GaAs / AlGaAs and InGaAs / AlGaAs QWs. The well depth and intersubband energy increase by introducing indium into the well layer.}
\end{figure}

\section*{II.2. Quantum well growth techniques}

Single crystal thin films of III-V semiconductors can be grown by many techniques, including LPE (liquid phase epitaxy), MOCVD (metal-organic chemical vapor deposition), and MBE (molecular beam epitaxy). MBE and MOCVD are mostly used for growing QW samples. All growths of the QW samples in this work were grown using the MBE technique. The advantages of MBE are accurate control of layer thickness and abrupt heterojunction interface which are very crucial to model the QWs correctly. MBE also offers low substrate temperature during the crystal growth which is advantageous for growing strained layers, such as InGaAs on GaAs, because the critical layer thickness increases at lower temperatures. The MBE machine we used for sample growth was a Varian Gen II system which was loaded with various source materials: column III (Al, Ga, In), column V (As), n-type dopant (Si), and p-type dopant (Be). The source materials were contained in crucibles which were inserted into furnaces. The source materials are sublimated at a rate controlled by the temperature of the furnaces and deposited on a
substrate. The chamber needs to be under ultra-high vacuum (UHV), around $10^{-10}$ torr, to ensure ballistic deposition and formation of high purity films. The substrate is mounted on a holder which rotates to maintain deposition uniformity and is heated to 400 - 700 °C during the growth. The substrate temperature is one of the most critical parameters for lattice mismatched growth because it affects surface mobility of the constituents and the degree of strain that can be accommodated. There are shutters in front of the crucibles of each source material, which block or clear the paths of evaporated materials to the substrate. The composition and thickness of deposited films are controlled by the shutter action. For instance, in order to grow an AlGaAs layer of a certain thickness, shutters of Al, Ga, and As are kept open simultaneously for some time which was determined from the growth rate of the layer or the fluxes of evaporated materials for the layer. The composition of the ternary material layer is determined by the relative growth rate of each binary material. Thus, if the growth rate of GaAs were three times higher than that of AlAs, the alloy would be $\text{Al}_{0.25}\text{Ga}_{0.75}\text{As}$.

II.3. Quantum well eigenstates

Electrons confined in a QW are assigned to quantized energy states called eigenstates due to the quantum effect. The property of the eigenstates is fundamental to the properties of the ISBTs we will discuss in later chapters. We will first discuss in this section the mathematical model for the eigenstates.

II.3.1. Effective mass approximation

A rigorous treatment of electron states in a crystal is a complicated process requiring a band calculation yielding the conduction band, light hole band, heavy hole band, and split-off band.\textsuperscript{15,16} In this thesis, we will only be concerned with electrons in the
conduction band, thus we use an approximation based upon a single-band effective Hamiltonian. It is written as

\[ H = -\frac{\hbar^2}{2m^*} \vec{\nabla} \cdot \frac{1}{m^*} \vec{\nabla} + V \tag{II.1} \]

where \( m^* \) is the electron effective mass accounting for the effect of the periodic lattice potential and \( V \) is the macroscopic potential which is the quantum well confining potential, \( V_{QW} \), in our case. In a bulk crystal, the full electron wavefunction at \( k \) point in the Brillouin zone has the general Bloch form.

\[ \Psi_k(\vec{r}) = u_k(\vec{r})e^{i\vec{k} \cdot \vec{r}} \tag{II.2} \]

where \( u_k(\vec{r}) \) is the periodic Bloch function with the same periodicity as the crystal lattice and \( e^{i\vec{k} \cdot \vec{r}} \) is a slowly varying envelope when \( \vec{k} \) has a small value near the zone center. The confining potential of a QW in the \( z \)-direction, \( V_{QW}(z) \) (assuming that the well and barrier layers are parallel to the \( x \)-\( y \) plane) leads to rewriting the envelope function and Equation II.2 as

\[ \Psi_k(\vec{r}) = u_k(\vec{r})e^{i\vec{k}_t \cdot \vec{r}_t} \chi(z) \tag{II.3} \]

where \( \vec{k}_t \) and \( \vec{r}_t \) are transverse components in the \( x \)-\( y \) plane of \( \vec{k} \) and \( \vec{r} \). Further simplification comes from the envelope function approximation\(^{15}\) which assumes that the Bloch functions in the well and barrier are the same at the interface\(^{17}\), and do not change over a small range of \( k \) near the zone center: \( u_k(\vec{r}) = u_0(\vec{r}) \). With these approximations, the Hamiltonian (II.1) applies to the wavefunction (II.3) and gives a Schrödinger equation given by
\[ \left( -\frac{\hbar^2}{2m^*}(z) \frac{d}{dz} + \frac{\hbar^2k_z^2}{2m^*}(z) + V_{QW}(z) \right) \chi_n(z) = E_n(k_t) \cdot \chi_n(z) \quad (II.4) \]

The boundary condition requires that \( \chi_n(z) \) and \( \frac{1}{m^*(z)} \frac{d}{dz} \chi_n(z) \) be continuous at the interface.\(^8\) Strictly speaking, Equation II.4 has to be solved at each \( k_t \) to obtain \( E_n(k_t) \) and \( \chi_n(z) \), but assuming the effective mass in the well is constant and the effective mass mismatch between the layers is small, we obtain the parabolic subband dispersion relation,

\[ E_n(k_t) = E_n(k_t = 0) + \frac{\hbar^2k_z^2}{2m^*_{\text{well}}} \quad (II.5) \]

**II.3.2. Band nonparabolicity**

Band nonparabolicity could be rigorously included using tight-binding theory (Harrison, W. A., “Elementary Electronic Structures,” to be published), but we have followed other approaches. The above Schrödinger equation (II.4) assumes a constant effective mass in the well. Without the QW confining potential, Equation II.4 yields a quadratic dispersion relation in the \( z \) direction given by

\[ E(k_z, k_t = 0) = \frac{\hbar^2k_z^2}{2m_0^*} \quad (II.6) \]

where \( m_0^* \) is the effective mass of an electron at the conduction band edge. This simple model, however, becomes inaccurate when \( k \) is far from the zone center, that is the electron energy is higher than the conduction band edge by a few hundred meV. It is then necessary to consider nonparabolicity of the band due to higher order term in \( k \). In this dissertation, the nonparabolic band dispersion is modeled using the so-called “approximate two-band”
\( \vec{k} \cdot \vec{p} \) model which is carried out to the fourth power in \( k \) and modifies the quadratic relation in Equation II.6 as

\[
E(k_z, k_z' = 0) = \frac{\hbar^2 k_z^2}{2m_0} \left( 1 + \frac{\alpha \hbar^2 k_z^2}{E_g 2m_0} \right)
\]  

(II.7)

where \( \alpha \) is the nonparabolicity factor and \( E_g \) is the bandgap of the material. \( \alpha \) is -0.82 for GaAs and -0.86 for In\(_{0.5}\)Ga\(_{0.5}\)As\(^2\). This nonparabolic band dispersion is depicted as “Quartic 1” in Figure II.3 along with the parabolic and other nonparabolic models for In\(_{0.5}\)Ga\(_{0.5}\)As, which has \( E_g = 0.755 \text{ eV} \) and \( m_0^* = 0.034m_0 \) where \( m_0 \) is the free electron mass. As seen in Figure II.3, a problem with Equation II.7 is that it yields an infinite effective mass when the energy reaches a maximum value of about 200 meV. Thus it is not an adequate model for subband energies higher than the maximum energy. This problem can be corrected by using a quadratic dispersion with an energy dependent effective mass described by\(^2\)

\[
m^*(E) = \frac{m_0^*}{1 + \alpha E / E_g}.
\]

(II.8)

This energy dependent effective mass includes the quartic term of Equation II.7 in itself through the energy dependence. As compared to measurements, this model (“Quartic2”) accurately predicts subband energies in most GaAs / AlGaAs QWs within 10 % error. However, the effective mass from this dispersion also approaches infinity as \( E \) increases since \( \alpha \) is negative. As a result, the calculation using this model yields values somewhat lower than measurements above 500 meV for In\(_{0.5}\)Ga\(_{0.5}\)As / AlGaAs QWs. This imposes difficulties in predicting subband energies in narrow InGaAs / AlGaAs QWs where upper states are often located as high as 1 eV above the conduction band edge. H. C. Chui, et.
al.\textsuperscript{13} extracted an empirical model to solve this problem and still retain the simple quadratic form with an effective mass. He noticed that the $E$ vs. $k$ curves calculated for InAs and GaAs using a pseudopotential method\textsuperscript{22} or Kane model\textsuperscript{15} were nearly linear for energies high above the band edge. Thus by expressing $m^*(E)$ as a function of $E$, the quadratic expression $E(k_z, k_t = 0) = \hbar^2 k_z^2 / 2m^*(E)$ was linearized for energies higher than some energy $E_p$ above the conduction band edge ("Quartic3" in Figure II.3). $E_p$ was set to 400 meV for In$_{0.5}$Ga$_{0.5}$As. We use this model to calculate subband energies higher than $E_p$ because it agrees well with experimental values for high ISBT energies in narrow InGaAs / AlGaAs QWs.

Figure II.3. Energy band dispersion In$_{0.5}$Ga$_{0.5}$As for various non-parabolic models described in the text.
II.3.3. Numerical method

In order to obtain eigenenergies and eigenstates, Equation II.4 is solved numerically for \( k_z = 0 \) using the following transfer matrix algorithm. First, consider an arbitrary shape of QW consisting of \( N \) layers, as shown in Figure II.4. We seek a wavefunction of the following form in the \( j \)-th layer.

\[
\chi(z) = A_j e^{k_j z} + B_j e^{-k_j z}, \quad z_j \leq z < z_{j+1}
\]  

(II.9)

with complex \( A_j, B_j, k_j \) and \( j = 1, 2, \ldots, N \). Inserting Equation II.9 in Equation II.4 gives

\[
k_j = \frac{1}{\hbar} \sqrt{2m_j^*(V_j - E)}
\]

(II.10)

where \( m_j^* \) is the energy dependent effective mass discussed in the previous section.

Enforcing the boundary conditions about \( \chi(z) \) and \( \frac{1}{m^*} \frac{d\chi(z)}{dz} \) at the interface between the \( j \)-th and \( (j+1) \)-th layers yields

\[\text{Figure II.4. Schematic diagram of the conduction band edge of an arbitrary shaped QW.}\]
\begin{equation}
\begin{pmatrix}
A_j \\
B_j
\end{pmatrix} = M_j \begin{pmatrix}
A_{j+1} \\
B_{j+1}
\end{pmatrix}
\tag{II.11}
\end{equation}

where \( M_j = \frac{1}{2} \begin{pmatrix}
\alpha_j^+ e^{z_j(k_{j+1} - k_j)} & \alpha_j^- e^{-z_j(k_{j+1} + k_j)} \\
\alpha_j^+ e^{-z_j(k_{j+1} - k_j)} & \alpha_j^- e^{z_j(k_{j+1} + k_j)}
\end{pmatrix} \) and \( \alpha_j^\pm = \frac{m_{j+1}^* k_j \pm m_j^* k_{j+1}}{m_{j+1}^* k_j} \).

Cascading these transfer matrices from N-th layer back to the 1st layer, we can obtain
\[
\begin{pmatrix}
A_1 \\
B_1
\end{pmatrix} \text{ from } \begin{pmatrix}
A_N \\
B_N
\end{pmatrix}
\text{ by}
\begin{equation}
\begin{pmatrix}
A_1 \\
B_1
\end{pmatrix} = M_1 \cdot M_2 \cdots M_{N-1} \begin{pmatrix}
A_N \\
B_N
\end{pmatrix}
\tag{II.12}
\end{equation}
\]

Now, we impose constraints on \( \begin{pmatrix}
A_1 \\
B_1
\end{pmatrix} \) and \( \begin{pmatrix}
A_N \\
B_N
\end{pmatrix} \): in the left and right semi-infinite layers, \( B_1 \) and \( A_N \) should vanish to keep the wavefunction from exponentially diverging. Thus we start with \( A_N = 0, B_N = 1 \) and then the eigenenergies are given as the values that make \( B_1 = 0 \). The wavefunction at each eigenenergy is obtained from Equation II.9.

\textbf{II.4. Intersubband transitions}

An intersubband transition (ISBT) is an optical transition between two subbands. From the effective mass approximation in Section II.3.1, we have a quadratic subband dispersion represented by Equation II.5. Since the subbands are parallel to each other, the intersubband energy between two subbands is independent of the in-plane wavevector \( k_r \). In this parabolic subband approximation, the joint density of states for ISBTs is a delta-function centered at each intersubband energy given by
\[ \rho_J(E) = \sum_{m<n} \frac{m^*}{\pi \hbar^2} \delta(E - E_{mn}) \]  

This expression indicates atomic like resonant transitions peaked at each intersubband energy. Although the joint density of states and the transition linewidth broaden in reality for various reasons, the ISBTs still retain their inherent resonant features and exhibit narrow linewidths. This is not the case for the interband transitions between the valence and conduction bands, for which the opposite curvature of the subbands gives rise to a stepwise joint density of states as shown in Figure II.5.

Figure II.5. Schematic illustration of intersubband and interband transitions. Shown on the right is the density of states of the two types of transitions.

The other significant characteristic of the ISBT is a large dipole matrix element which results in a strong transition strength and hence absorption. This results from the large spatial extent of the envelope wavefunctions of subband states in the QW, which is typically \( \sim 100 \) Å. With the effective mass approximation, dipole moments are obtained from the envelope functions given by
\[ z_{mn} = \langle \psi_m | z | \psi_n \rangle = \langle \chi_m | z | \chi_n \rangle \]  \hspace{1cm} (II.14)

where we assume unity overlap of the Bloch wavefunctions \(^{24}\). Note that the above equation yields a nonzero integral only for light polarized along the growth z-direction (TM-polarized) because the envelope wavefunctions are functions of \( z \) and orthogonal to each other. Light polarized in the xy-plane of the QW (TE-polarized) will not cause any ISBT to this level of single band effective mass approximation. Although more exact calculations predict small TE-active ISBTs \(^{25}\), none of the samples we studied for this dissertation have exhibited significant TE absorption. Equation II.14 also indicates that ISBTs in symmetric QWs are forbidden \( (z_{mn} = 0) \) between subbands with the same parity of envelope functions because it makes the integrand in Equation II.14 an odd function of \( z \). For example, ISBTs between the first and third subbands are forbidden \( (z_{13} = 0) \) in a symmetric QW because the envelope functions for both subbands are of even parity.

We can analytically calculate the wavefunctions (envelope), eigenenergies and thus the dipole moments for an infinite well of width \( L \) for which

\[ \chi_n = \sqrt{2} \frac{\sin \left( \frac{n \pi z}{L} \right)}{\sqrt{L}}, \quad E_n = \frac{\hbar^2 \pi^2}{2m^* L^2} n^2 \]  \hspace{1cm} (II.15)

and

\[ |z_{m,n}| = \frac{8}{\pi^2} \frac{mn}{\left( m^2 - n^2 \right)^2} L \]  \hspace{1cm} (II.16)

where \( m \) and \( n \) should be indexes of two states with opposite parities: for example, \( z_{12} = 0.18L \). A typical QW width is on the order of 100 Å and thus the dipole moment is tens of Å as compared to atomic or molecular dipole moments of a few Å. The strength of an optical transition is often expressed by the oscillator strength, defined by \(^{26}\)
\[ f_{mn} = \frac{2mE_{mn}}{R^2} |z_{mn}|^2 \] (II.17)

where \( m \) is the free electron mass. For the infinite well discussed above, we find that
\[ f_{12} = 0.96 \frac{m^*}{m} = 15 \] for GaAs \((m^* = 0.065m)\). This is a very large oscillator strength considering that the typical atomic oscillator strength is close to unity. This large enhancement of the oscillator strength of the QW ISBT is due to the small effective mass of electrons in the semiconductor and quantum confinement.

II.5. Linear susceptibility and absorption

II.5.1. Linear susceptibility

Considering the resonant feature of the ISBTs discussed above, the linear susceptibility of a QW with \( n \) subbands is represented by

\[ \chi^{(1)}(\omega) = \frac{e^2 N_{\text{eff}}}{\varepsilon_0} \sum_n \frac{|z_{ln}|^2}{(\hbar \omega - E_{ln} + i\Gamma_{ln})} \] (II.18)

where \( N_{\text{eff}} \) is an effective three-dimensional average electron density of the QW and \( \Gamma_{ln} \) is a half-width at half-maximum (HWHM) linewidth of the 1-n transition. Here, we assumed all electrons reside in the first (ground) subband. The absorption coefficient is derived from the imaginary part of the linear susceptibility given by

\[ \alpha(\omega) = -\frac{\omega}{c_0 n} \text{Im} \left[ \chi^{(1)}(\omega) \right] \sin^2(\theta_{\text{int}}) \] (II.19)

where \( c_0 \) is the speed of light in vacuum, \( n \) is the average index of refraction over the QW period and \( \theta_{\text{int}} \) is the angle of incidence from the surface normal inside the sample.
II.5.2. Absorption measurement

Intersubband energies, dipole moments and oscillator strengths are experimentally determined from intersubband absorption measurements performed in a Fourier transform infrared (FTIR) spectrometer.\textsuperscript{21} We used two sample geometries for the absorption measurements: Brewster's angle incidence single pass and normal incidence multi-bounce geometries (Figure II.6). In any case, incident light should be TM-polarized (E-field in the plane of incidence or H-field parallel to QW layers) according to the polarization selection rule of ISBTs. Brewster's angle geometry minimizes the reflection loss of TM-polarized light at the surface when light is incident at Brewster's angle, defined by

$$\theta_B = \tan^{-1}(n) \quad (\text{II.20})$$

For GaAs, $\theta_B = 73^\circ$ and $\theta_{\text{int}} = 17^\circ$ around $\lambda = 10 \, \mu\text{m}$ with $n = 3.27$. Thus the $z$-component of the electric field is small ($E_z \approx \sin\theta_{\text{int}}$) in this sample geometry and so is the absorption strength because it is proportional to $E_z^2$. The multi-bounce geometry, in which light is incident normal to a 45$^\circ$-polished side facet and undergoes multiple total internal reflections at the top and bottom sample surfaces, significantly increases the absorption strength for two reasons: enhanced $E_z$ and multiple passes through the sample. Compared to the Brewster's angle single pass measurement, the absorption strength increases by the factor of $\sin^2(45^\circ)/\sin^2(17^\circ) = 5.85$ times the number of bounces which is typically 10 - 12 for the samples used in these measurements. Thus the multi-bounce measurement yields much stronger absorption peaks than the Brewster's angle measurement and is useful to observe ISBTs in a sample with small oscillator strength.
Figure II.6. Sample geometries for absorption measurements. (a) Brewster's angle incidence single pass geometry. (b) normal incidence multiple pass geometry. (c) $E_x$-field distribution in a standing wave seen by MQWs.

FTIR absorption spectra is usually recorded in absorbance units, which are defined by

$$\text{Abs}(\omega) = -\log_{10} T(\omega) = \frac{\alpha(\omega) \ell}{\ln 10}$$  \hspace{1cm} (II.21)

where $\alpha(\omega)$ is the absorption coefficient defined by Equation II.19 and $\ell$ is the path length of light through the MQW layers. The area under the absorption peak corresponding to the i-j transition is directly related to the integrated absorption fraction (IAF) defined by\(^\text{34}\)

$$\text{IAF} = \int \alpha(\omega) \ell \text{d}E$$

$$= \frac{\pi e^2 \sigma_{\text{eff}} |E_{ij}|^2 |Z_{ij}|^2}{\varepsilon_0 \hbar c n} \frac{\sin^2 \theta_{\text{int}}}{\cos \theta_{\text{int}}}$$  \hspace{1cm} (II.22)
The term $\sin^2 \theta_{\text{int}} / \cos \theta_{\text{int}}$ exists because the coupling between the electric field and the dipole transition is proportional to $|E_z|^2 = |E|^2 \sin^2 \theta_{\text{int}}$ and the path length is proportional to $1 / \cos \theta_{\text{int}}$. For the Brewster's angle incidence, we get $\sin^2 \theta_{\text{int}} / \cos \theta_{\text{int}} = 1 / n \sqrt{1 + n^2}$ from Equation II.20. For the multi-bounce measurement, we should multiply Equation II.22 by the number of light passes through the epilayers and we must also consider the standing wave effect caused by the total internal reflection as shown in Figure II.6(c). The standing wave results from the interference between the incident and reflected light at the semiconductor-air interface. By considering the boundary conditions on reflection, assuming an angle of incidence of 45° and refractive index of $n = 3.27$, the phase shift between these two beams was calculated to be 168°. This corresponds to almost complete phase reversal on reflection and produces a node in the intensity of the perpendicular field component, $E_z$, very close to the semiconductor-air interface. The acting optical field intensity varies with position according to

$$E_z^2(z) = 4E_{z0}^2 \sin^2 k_z z$$

where $E_{z0}$ is the amplitude of the perpendicular field component of the traveling wave and $k_z$ is the perpendicular component of optical wavevector, $k$. Then the period, $\Delta z$, of the standing wave intensity is given as $\Delta z = \pi / k_z = \lambda / 2 n \cos \theta_{\text{int}}$. The QW intersubband absorption, $A$, per bounce should be calculated by integrating Equation II.23 over the MQW thickness, $d$, which is given by

$$A \propto \int_0^d 4E_{z0}^2 \sin^2 k_z zdz.$$
If the MQW layer thickness is large enough compared to Δz or is an integer number of Δz, the average of the acting field, Equation II.23, over the MQW layers is close to or equal to 2E₉₀² and the absorption per bounce, Equation II.24, is equal to the integration of the traveling wave for a round trip given by

\[ A \propto \int_0^{2d} E_{20}^2 dz = 2dE_{20}^2 \quad (II.25) \]

Thus in this case, the interference has essentially no effect on the linear absorption. However, if the MQW layer thickness is small or the measurement depends on the local field intensity, not on the integration or average over the MQW layer, the standing wave effect makes a significant difference and the position dependent field intensity, Equation II.23, must be used for the absorption calculation. For example, the standing wave effect significantly affects the effective saturation intensity of the QW intersubband absorption, which we will discuss in Chapter V.

II.6. QW ISBTs as a nonlinear optical medium

II.6.1. Nonlinear optical interaction

When a high intensity electromagnetic field propagates in a dielectric medium, nonlinear susceptibilities of the material should be considered to account for the response of the material to the field. This is represented in the induced polarization of the medium;²⁹

\[ \vec{P} = \varepsilon_0 \left[ \chi^{(1)} \cdot \vec{E} + \chi^{(2)} \cdot \vec{E} \vec{E} + \chi^{(3)} \cdot \vec{E} \vec{E} \vec{E} + \ldots \right]. \quad (II.26) \]
\( \chi^{(1)} \) is the linear susceptibility accounting for the absorption and refraction of the field in the material. \( \chi^{(2)} \) and \( \chi^{(3)} \) are the second and third order nonlinear susceptibilities causing a number of nonlinear interactions in the medium with the electromagnetic field. We are especially interested here in \( \chi^{(2)} \), which gives rise to nonlinear optical frequency conversion processes, such as second harmonic generation (SHG) and difference frequency generation (DFG). For SHG with undepleted pump power and no loss, the generated SH intensity \( I_{2\omega} \) is related to the pump intensity \( I_\omega \) as

\[
I_{2\omega} \propto L_{\text{eff}}^2 |\chi^{(2)}|^2 I_\omega^2
\]  

(II.27)

here \( L_{\text{eff}} = L \frac{\sin(\Delta k L/2)}{\Delta k L/2} \) is the effective interaction length reduced by the phase-matching term \( \Delta k = k_{2\omega} - 2k_\omega \) where \( k_{2\omega} \) and \( k_\omega \) are the wavevectors of the second harmonic (2\( \omega \)) and fundamental (\( \omega \)) fields. From the above equation, we can see that efficient SHG (and similarly, DFG) requires three conditions: a NLO medium with a large \( \chi^{(2)} \), high pump intensity \( (I_\omega) \), and a large effective interaction length \( (L_{\text{eff}}) \) which results from both a large interaction length \( (L) \) and phase-matching \( (\Delta k = 0) \).

II.6.2. Second order susceptibility of QW ISBTs

The QW ISBTs yield a very large \( \chi^{(2)} \) due to the large dipole moments and narrow linewidths which were discussed in Section II.4. Treating the QW subbands as a n-level system, the second order susceptibility can be written as

26
\[
\chi^{(2)}(\omega = \omega_1 + \omega_2) = \frac{e^3 N_{\text{eff}}}{\varepsilon_0} \sum_{m,n} z_{1n} z_{nm} z_{m1} 
\left\{ \frac{1}{(\hbar \omega - E_{n1} - i\Gamma_{n1})} \left[ \frac{1}{(\hbar \omega_1 - E_{m1} - i\Gamma_{m1})} + \frac{1}{(\hbar \omega_2 - E_{m1} - i\Gamma_{m1})} \right] 
+ \frac{1}{(\hbar \omega + E_{n1} + i\Gamma_{n1})} \left[ \frac{1}{(\hbar \omega_1 + E_{m1} + i\Gamma_{m1})} + \frac{1}{(\hbar \omega_2 + E_{m1} + i\Gamma_{m1})} \right] 
- \frac{1}{(\hbar \omega + E_{nm} - i\Gamma_{nm})} \left[ \frac{1}{(\hbar \omega_1 - E_{n1} - i\Gamma_{n1})} + \frac{1}{(\hbar \omega_2 - E_{n1} - i\Gamma_{n1})} \right] 
- \frac{1}{(\hbar \omega + E_{nm} - i\Gamma_{nm})} \left[ \frac{1}{(\hbar \omega_1 + E_{m1} - i\Gamma_{m1})} + \frac{1}{(\hbar \omega_2 + E_{m1} - i\Gamma_{m1})} \right] \right\} \right\}
\]

(II.28)

This long equation reduces to a few dominant terms near a resonance. For example, around a double resonance condition for SHG (\( \omega_1 = \omega_2 = \omega \); \( \hbar \omega = E_{12} = E_{23} \) and \( 2\hbar \omega = E_{13} \)), only a single term is dominant:

\[
\chi^{(2)}(2\omega = \omega + \omega) = \frac{2e^3 N_{\text{eff}}}{\varepsilon_0} \frac{z_{12} z_{23} z_{31}}{(2\hbar \omega - E_{31} - i\Gamma_{31})(\hbar \omega - E_{21} - i\Gamma_{21})}.
\]

(II.29)

Note that Equation II.29 consists of a product of three dipole moments and a resonant denominator which is basically the product of two linewidths at resonance. Thus the large dipole moments and narrow linewidths of the QW ISBTs yield a large \( \chi^{(2)} \) at resonance.

Since the subband energies are determined by the QW design, the resonance condition can be satisfied by the QW design. This design freedom also provides opportunity to maximize the dipole moments and minimize the linewidths at given intersubband energies. Combining these advantages, an extremely large nonlinear susceptibility which is three orders of magnitude greater than that of typical NLO materials such as LiNbO\(_3\) has been observed from the QW ISBTs.\(^9, 30-32\) Despite the large value of \( \chi^{(2)} \) produced by QW ISBTs, their large dipole moment is also detrimental to the conversion efficiency because
the large dipole moment causes a large absorption loss of the fundamental and SH fields. It also reduces the saturation intensity, above which the absorbed optical power depletes the ground state population and bleaches the absorption significantly, thus decreasing the nonlinearity with intensity. Thus, although a high fundamental intensity \( I_{\omega} \) is advantageous for efficient SHG (Equation II.27), there is nothing to gain with high pump power beyond the saturation intensity, \( I_{\text{sat}} \) represented by\(^{26}\)

\[
I_{\text{sat}} = \frac{\hbar \omega}{2 \sigma \tau}
\]  

(II.30)

where \( \sigma \) is the absorption cross section proportional to the absorption coefficient and \( \tau \) is the upper state lifetime. The upper state lifetime and saturation behavior will be discussed in Chapter V.

II.6.3. Asymmetric QWs

Equation II.29 tells us that a QW should have a spatial asymmetry in the growth direction in order to have a nonvanishing \( \chi^{(3)} \) because \( z_{13} = 0 \) for a symmetric QW. Asymmetry can be introduced in a QW by several techniques as shown Figure II.7. An external electric field applied across a QW layer breaks the inversion symmetry. The first QW \( \chi^{(2)} \) was measured in a square QW under an electric field bias.\(^9\) Asymmetry can be built in a QW through an asymmetric growth structure such as a step QW or coupled QW. A step QW has two well layers with different material composition to produce a potential step. A coupled QW has a thin barrier between two unequal well layers so that the two wells are strongly coupled. Very large \( \chi^{(2)} \)'s have been measured from these asymmetrically grown QWs.\(^{30,33}\) Doping asymmetry, such as delta-doping, or a built-in field from strain can also be used to break the inversion symmetry.
Figure II.7. Conduction band diagrams for various asymmetric QWs. (a) External field-biased QW. (b) Step QW (c) Coupled QW.

Among these asymmetric QWs, the coupled QW is suitable for generating mid-infrared (MIR) light through DFG pumped by two near-infrared (NIR) input beams. Figure II.8 illustrates an example of generating 11 μm (112 meV) out of 1.55 μm (800 meV) and 1.8 μm (688 meV) in a doubly resonant coupled QW. If two narrow deep QWs are put together across a thin barrier, they form a coupled QW whose lower two states are produced by coupling of the ground state of each square QW and two higher states are also coupled states (bonding and anti-bonding) of the excited state of each QW.\(^3\) Then the two NIR inputs are resonant to the transitions from the two lower coupled states to one of the higher coupled states and the MIR output is resonant to the transition between the two lower coupled states, which makes the coupled QW a doubly resonant DFG medium.\(^9\) QW ISBTs resonant to those NIR wavelengths are not achievable with conventional QWs and requires very deep and narrow QWs which will be discussed in next two chapters.
Figure II.8. Construction of a coupled QW for DFG of mid-infrared using two near-infrared inputs. (a) Two square QWs approaching each other to form a coupled QW. (b) A coupled QW with a double resonance to generate 11 μm from 1.55 μm and 1.8 μm inputs.

II.6.4. Waveguide and quasi-phasematching

As stated earlier in this section, besides a large $\chi^{(2)}$, it is also important to maintain high optical intensities over long interaction lengths for efficient NLO frequency conversion. One technique is focusing light into a waveguide. Semiconductor thin films are very suitable to fabricate waveguide structures which consist of a high refractive index core material sandwiched between low refractive index cladding materials. Light is confined in the core region by total internal reflection, which maintains high optical intensities over long interaction lengths. One major drawback of III-V semiconductors for NLO applications, however, is the lack of birefringence. Birefringence offers different refractive index dispersion relation in a material for different polarizations. This provides the possibility to cancel the difference between the fundamental and SH refractive indices for SHG by having the fundamental and SH at the ordinary and extraordinary polarizations of the crystal. This means perfect phase-matching ($\Delta k = 0$ in Equation II.27) and the SH
power grows quadratically with interaction length. But this favorable condition is limited to very narrow angle and temperature ranges and is almost impossible to achieve in a waveguide geometry. Non-phase matching results in a small oscillating SH power (Figure II.9) due to the alternation of the power flow between the fundamental and SH waves caused by the phase slip. An alternative solution to this undesirable situation is to periodically modulate the sign or magnitude of the nonlinear coefficient, which is termed quasi-phasematching (QPM).\textsuperscript{35,36} For example, if the sign of the nonlinearity changes whenever the two waves become 180° out of phase, that is at every coherence length defined by

\[
L_c = \frac{\pi}{\Delta k} = \frac{\lambda}{4(n_{2\omega} - n_\omega)}
\] (II.31)

then the power transfer is unidirectional from the pump to the SH producing continuous growth of the harmonic wave (+/- QPM in Figure II.9). This QPM technique has been widely used in LiNbO\textsubscript{3} waveguides with periodically reversed sign of nonlinearity by ferroelectric domain polling\textsuperscript{37, 38}. The QPM can also be achieved by modulating the magnitude of nonlinearity: for example, 'turning off' the nonlinearity at every other \(L_c\) (on/off QPM). This QPM method can be readily achieved in an intersubband QW core by periodic proton bombardment which eliminates free electrons in the QW\textsuperscript{30}. On the contrast to these various QPM methods, it has also been proposed\textsuperscript{39} that SHG in a microcavity of a NLO material would not require any phase-matching procedure if the cavity is much smaller than \(L_c\) and the cavity has a sufficiently high finesse.
Figure II.9. Effects of (a) phase-matching, (b) +/- quasi-phase-matching, (c) on/off quasi-phase-matching and (d) non-phase-matching on the second harmonic power $P_{2\omega}$ with propagation distance.
Chapter III.

Intersubband transitions to above-barrier states

In this chapter, we discuss quantum well (QW) above-barrier states and intersubband transitions (ISBTs) to them. One can obtain higher ISBT energies from the above-barrier states than from the conventional bound states. The above-barrier states have different features from the bound states because they are not spatially confined by potential barriers. We will investigate the above-barrier states and ISBTs to them in GaAs/Al$_{0.3}$Ga$_{0.7}$As square QWs in this chapter. In next chapter, we will use the above-barrier states in deeper QWs to get higher ISBT energies. Intersubband lifetime and saturation behavior of the above-barrier states are dealt with in Chapter V.

III.1. Quantum well above-barrier and quasi-bound states

So far, we have discussed only bound QW states below the barrier potential. They have envelope wavefunctions $\chi_n(z)$ localized in the QW region at discrete eigenenergies $E_n$. An ISBT usually means a transition between two bound subband states. However, if the QW is narrow enough, there is only one bound state (ground state) and no upper bound state to which an electron in the ground state can be excited. In that case, electrons can still make transitions to the states above the potential barrier called above-barrier states. Electrons are allowed to have any energy above the barrier energy because above-barrier states are not confined in a localized region but extended over the barrier region. The wavefunctions of the above-barrier states are obtained similarly to the bound states: applying a plane wave solution with proper boundary conditions. Figure III.1 shows two wavefunctions at a given energy, E: right-going wave and left-going wave. For the right-going wave, the wavefunction $\chi_E(z)$ reads as\textsuperscript{40}
Figure III.1. Schematic of two wave solutions (right-going and left-going) for an above-barrier state.

\[
\chi^R_E(z) = \frac{A_1}{N} e^{ik_B z} + \frac{B_1}{N} e^{-ik_B z} \quad \text{for } z < -\frac{L_w}{2}
\]

\[
= \frac{A_2}{N} e^{ik_w z} + \frac{B_2}{N} e^{-ik_w z} \quad \text{for } -\frac{L_w}{2} \leq z \leq \frac{L_w}{2} \quad (III.1)
\]

\[
= \frac{1}{N} e^{ik_B z} \quad \text{for } z > \frac{L_w}{2}
\]

where \(k_B = \sqrt{2m_B^* (E - V)/\hbar^2}\) and \(k_w = \sqrt{2m_w^* E/\hbar^2}\) are the wavevectors in the barrier and well layers. \(A_{1,2}\) and \(B_{1,2}\) are obtained from Equation II.11. \(N\) is the normalization factor, which approximates to \(\sqrt{\left(1 + |A_2|^2 + |B_2|^2\right)L/2}\) for large \(L\). Similar equations apply for the left-going wavefunction \(\chi^L_E(z)\). Because the potential has an inversion symmetry, the two wavefunctions have the following relation.

\[
\chi^L_E(z) = \chi^R_E(-z) \quad (III.2)
\]

34
For bound states, the two states are not independent because \( \chi_E(-z) = \pm \chi_E(z) \) (a bound state definitely has even or odd parity), and thus there is no degeneracy. But for above-barrier states, \( \chi^R_E(z) \) and \( \chi^L_E(z) \) generally do not have a definite parity and are independent to each other. \( \chi^R_E(z) \) and \( \chi^L_E(z) \) can construct an even and odd functions when they are linearly combined:

\[
\chi^e_E(z) = \left( \chi^R_E(z) + \chi^L_E(z) \right) / \sqrt{2} \\
\chi^o_E(z) = \left( \chi^R_E(z) - \chi^L_E(z) \right) / \sqrt{2}
\]  

(III.3)

Thus above-barrier states have both wavefunctions of even and odd parities at the same energy whereas the bound states have a definite even or odd wavefunction. Figure III.2 shows both even and odd above-barrier wavefunctions.

![Figure III.2. Even and odd wavefunctions of an above-barrier state.](image)

In Equation III.1, non-zero \( B_1 \) means that a part of the incoming wave is reflected at the well-barrier boundary. However, at some particular energies where the QW width corresponds to an integer multiple of half wavelength of the electron state, the electron goes through the boundaries without reflection, which is called the transmission resonance.\(^{40}\)
Although the electron amplitude in the well layer is enhanced at the transmission resonance, the wavefunctions are still not localized in the well region. Using the wave property of the electron, however, the state at the transmission resonance can be localized in the well region by stacking quarter-wavelength ($\lambda/4$) layers on both sides of the well. These $\lambda/4$-stacks are an electronic analogy of optical distributed Bragg reflectors and cause constructive interference in the well region between partially reflected electron waves to create a localized state above the barrier energy called a “quasi-bound” state\textsuperscript{41-43}. In this sense, we call these stacked layers “electron mirrors”. The conditions for a quasi-bound state at the transmission resonance energy are

\begin{align}
  k_W L_{CW} &= n\pi \quad \text{(III.4a)} \\
  k_W L_W &= \frac{(2m-1)}{2} \pi \quad \text{(III.4b)}
\end{align}

![Diagram](image.png)

Figure III.3. Confinement of an above-barrier state at the transmission resonance by a series of $\lambda/4$-quantum well stacks.

36
\[ k_B L_B = \frac{(2m-1)}{2} \pi \]  

(III.4c)

where \( n, m \) are positive integers and \( k_W, k_B \) are the wave numbers in the well and barrier regions, respectively. \( L_{CW}, L_W, L_B \) are the widths of the central well, reflector well and reflector barrier, respectively as shown in Figure III.3.

### III.2. Kronig-Penney model of quasi-bound states

In the preceding section, we considered the quasi-bound state formed at the transmission resonance energy. This is a special case of quasi-bound states. They can be treated more generally with the Kronig-Penney model in which the electron mirror layers are considered as a superlattice which create minibands and minigaps due to the periodic potential.\(^{44}\)

Consider a QW structure which has semi-infinite superlattices on both sides of the well as electron mirrors (Figure III.4). The wavefunction at an energy greater than \( V_2 \) is written in each region of (I) right mirror, (II) center well, (III) left mirror as

\[
\begin{align*}
(I): \psi(z) &= \begin{cases} 
    c_n^I e^{ik_2^I (z-z_{n,2}^I)} + d_n^I e^{-ik_2^I (z-z_{n,2}^I)} & \text{for } z_{n,2}^I \leq z < z_{n,1}^I \\
    a_n^I e^{ik_1^I (z-z_{n,1}^I)} + b_n^I e^{-ik_1^I (z-z_{n,1}^I)} & \text{for } z_{n,1}^I \leq z < z_{n+1,2}^I 
\end{cases}
\end{align*}
\]

(III.5)

\[
\begin{align*}
(II): \psi(z) &= ae^{ik_3^I z} + be^{-ik_3^I z} & \text{for } 0 \leq z < d_3
\end{align*}
\]

\[
\begin{align*}
(III): \psi(z) &= \begin{cases} 
    c_n^{III} e^{ik_2^{III} (z-z_{n,2}^{III})} + d_n^{III} e^{-ik_2^{III} (z-z_{n,2}^{III})} & \text{for } z_{n,1}^{III} < z \leq z_{n,2}^{III} \\
    a_n^{III} e^{ik_1^{III} (z-z_{n,1}^{III})} + b_n^{III} e^{-ik_1^{III} (z-z_{n,1}^{III})} & \text{for } z_{n+1,2}^{III} < z \leq z_{n,1}^{III} 
\end{cases}
\end{align*}
\]
Figure III.4. A generic structure of a QW with superlattice mirror layers.

where $k_i$ is the electron wavenumber in each layer and $z_{n,1}^I = d_3 + (n - 1)L + d_2$, $z_{n,2}^I = d_3 + (n - 1)L$, $z_{n,1}^{III} = -(n - 1)L - d_2$, $z_{n,2}^{III} = -(n - 1)L$ with a positive integer $n$ are the boundary positions. $L$ is the superlattice period, $L = d_1 + d_2$. Using the boundary conditions on the wavefunction and its derivative in region I, each coefficient in Equation III.5 is related to previous coefficients through a transfer matrix given by

$$
\begin{pmatrix}
c_n^I \\
d_n^I
\end{pmatrix} =
\begin{pmatrix}
e^{i\delta_2 (\cos \delta_1 + i\xi_{\epsilon_1^2} \sin \delta_1)} & ie^{-i\delta_2 \xi_{\epsilon_1^2} \sin \delta_1} \\
-ie^{i\delta_2 \xi_{\epsilon_1^2} \sin \delta_1} & e^{-i\delta_2 (\cos \delta_1 - i\xi_{\epsilon_1^2} \sin \delta_1)}
\end{pmatrix}
\begin{pmatrix}
c_{n-1}^I \\
d_{n-1}^I
\end{pmatrix} \quad (III.6)
$$

where $\delta_i = k_i d_i$ and $\xi_{\epsilon_1^2} = \frac{1}{2} \left( \frac{m_i^* k_i}{m_i^* k_j} \pm \frac{m_j^* k_i}{m_j^* k_j} \right)$. According to the Bloch theorem, the periodic potential in region I forces the wavefunction to satisfy

$$
\begin{pmatrix}
c_n^I \\
d_n^I
\end{pmatrix} = e^{iKL}
\begin{pmatrix}
c_{n-1}^I \\
d_{n-1}^I
\end{pmatrix} \quad (III.7)
$$
Combining Equations III.6 and III.7 yields an equation known as the Kronig-Penney dispersion relation for a miniband and minigap.

$$\cos(KL) = \cos\delta_1 \cos\delta_2 - \xi_{12}^{12} \sin\delta_1 \sin\delta_2 = D \quad \text{(III.8)}$$

If $|D| \leq 1$, $K$ is a real number and Equation III.8 gives the dispersion relation in a miniband (allowed states). If $|D| > 1$, $K$ should be a complex number which can be written by\(^1\)

$$K = \frac{m\pi}{L} \pm i\kappa \quad \text{(III.9)}$$

where $\kappa > 0$ and $m$ is an even integer for $D > 1$ and an odd integer for $D < -1$. With this complex $K$, Equation III.7 represents an exponentially decaying or growing state neither of which is physically allowed (minigap). Note that the quasi-bound state we are looking for is a state whose amplitude is localized in the well region and decays in the mirror region (I and III). Then we can write Equation III.7 as

$$\begin{pmatrix} c_n^l \\ d_n^l \end{pmatrix} = e^{-\kappa L} \begin{pmatrix} c_{n-1}^l \\ d_{n-1}^l \end{pmatrix} \quad \text{(III.10)}$$

Then Equations III.6 and III.10 lead to the following eigenstates

$$\begin{pmatrix} c_n^l \\ d_n^l \end{pmatrix} \propto \begin{pmatrix} ie^{-i\delta_2} \xi_{12}^{12} \sin\delta_1 \\ \pm e^{-\kappa L} - e^{i\delta_2} (\cos\delta_1 + i\xi_{12}^{12} \sin\delta_1) \end{pmatrix} \quad \text{(III.11)}$$
where + is for $D > 1$ and - for $D < 1$. Similarly the eigenstates in region (III) are given by

$$
\begin{pmatrix}
  c_{n}^{III} \\
  d_{n}^{III}
\end{pmatrix} =
\begin{pmatrix}
  \pm e^{-\kappa L} - e^{i\delta_{1}} (\cos \delta_{1} + i\xi_{-}^{12} \sin \delta_{1}) \\
  ie^{-i\delta_{2}} \xi_{-}^{12} \sin \delta_{1}
\end{pmatrix}
\begin{pmatrix}
  c_{1}^{I} \\
  d_{1}^{I}
\end{pmatrix}
\quad (\text{III.12})
$$

Then we impose the boundary conditions across the QW (region II) on Equations III.11 and III.12, which are represented by a transfer matrix as the following.

$$
\begin{pmatrix}
  c_{1}^{III} \\
  d_{1}^{III}
\end{pmatrix} =
\begin{pmatrix}
  \cos \delta_{3} - i\xi_{2}^{23} \sin \delta_{3} & i\xi_{2}^{23} \sin \delta_{3} \\
  -i\xi_{2}^{23} \sin \delta_{3} & \cos \delta_{3} + i\xi_{2}^{23} \sin \delta_{3}
\end{pmatrix}
\begin{pmatrix}
  c_{1}^{I} \\
  d_{1}^{I}
\end{pmatrix}
\quad (\text{III.13})
$$

Inserting Equations III.11 and III.12 in Equation III.13 yields the following equation which a quasi-bound state should satisfy.

$$
\tan \delta_{3} = \frac{\pm e^{-\kappa L} \cos \delta_{2} - \cos(2\delta_{2}) \cos \delta_{1} + \xi_{2}^{12} \sin(2\delta_{2}) \sin \delta_{1}}{\pm e^{-\kappa L} \xi_{2}^{23} \sin \delta_{2} - \xi_{2}^{12} \xi_{2}^{23} \sin \delta_{1} - \xi_{2}^{12} \xi_{2}^{23} \cos(2\delta_{2}) \sin \delta_{1} - \xi_{2}^{23} \sin(2\delta_{2}) \cos \delta_{1}}
\quad (\text{III.14})
$$

Equation III.14 can be numerically solved and Figure III.5 shows graphical solutions obtained by two equations given by

$$
\begin{align*}
\tan \delta_{3} &= \frac{\pm e^{-\kappa L} \cos \delta_{2} - \cos(2\delta_{2}) \cos \delta_{1} + \xi_{2}^{12} \sin(2\delta_{2}) \sin \delta_{1}}{\pm e^{-\kappa L} \xi_{2}^{23} \sin \delta_{2} - \xi_{2}^{12} \xi_{2}^{23} \sin \delta_{1} - \xi_{2}^{12} \xi_{2}^{23} \cos(2\delta_{2}) \sin \delta_{1} - \xi_{2}^{23} \sin(2\delta_{2}) \cos \delta_{1}} \\
&= y 
\quad (\text{III.14a})
\end{align*}
$$

$$
\begin{align*}
\tan \delta_{3} &= \frac{\pm e^{-\kappa L} \cos \delta_{2} - \cos(2\delta_{2}) \cos \delta_{1} + \xi_{2}^{12} \sin(2\delta_{2}) \sin \delta_{1}}{\pm e^{-\kappa L} \xi_{2}^{23} \sin \delta_{2} - \xi_{2}^{12} \xi_{2}^{23} \sin \delta_{1} - \xi_{2}^{12} \xi_{2}^{23} \cos(2\delta_{2}) \sin \delta_{1} - \xi_{2}^{23} \sin(2\delta_{2}) \cos \delta_{1}} \\
&= y 
\quad (\text{III.14b})
\end{align*}
$$

Quasi-bound states are formed at energies where Equation III.14 is satisfied or the two curves (Equations III.14a and III.14b) intersect. The $\lambda/4$-layer mirror stacks at the transmission resonance energy discussed in the previous section are a special case that satisfies Equation III.14 with $\delta_{1} = \delta_{2} = \frac{\pi}{2}$ and $\delta_{3} = \pi$. 

40
Figure III.5. Graphical solutions of Equation III.14. The broken lines are Equation III.14a and the solid lines are Equation III.14b. Quasi-bound state energies are obtained by the intersection of the two curves.

III.3. Bound to above-barrier intersubband transitions

With the theoretical background discussed in the previous two sections, we now describe investigations of optical transitions between bound and above-barrier states in real QW samples. Four samples were grown which consist of 50 GaAs / Al_{0.3}Ga_{0.7}As QWs with well widths of \( L_w = 80 \, \text{Å} \), 60 Å, 40 Å and 35 Å. All samples were uniformly doped n-type in the well layers with a sheet charge density of \( 4 \times 10^{11} \, \text{cm}^{-2} \) per QW. According to calculation, the 80 Å and 60 Å QW samples have two bound states and the 40 Å and 35 Å QW samples have only one bound state. Conduction band diagrams and calculated eigenenergies for these samples are presented in Figure III.6.

As discussed in Section II.4, the oscillator strength is a measure of the transition strength between two states. The oscillator strength defined in Equation II.17 was with respect to two discrete states. We now consider a differential oscillator strength between a ground state at \( E_1 \) (bound) and an upper state at \( E \) (bound or above-barrier) given by
Figure III.6. Bound and above-barrier states in GaAs / Al$_{0.3}$Ga$_{0.7}$As QW samples with various well widths.

\[
\frac{df(E_1, E)}{dE} = \frac{2m_e(E - E_1)}{\hbar^2} |\langle E|z|1\rangle|^2 D(E) \tag{III.15}
\]

where $D(E)$ is the density of states of the upper state at $E$ given by

\[
D(E) = \begin{cases} 
\sum_{i \geq i_1} \delta(E - E_i) & \text{for } E < V \\
\frac{L}{\pi \hbar \sqrt{m^*}} & \text{for } E > V 
\end{cases} \tag{III.16}
\]

Figure III.7(a) shows the differential oscillator strengths for the four samples. As expected from the density of states, the 80 Å and 60 Å QW samples have δ-function peaks at the 1-2 transition energy, $E_{12}$, of each sample. For the 60 Å sample, there are small oscillator strengths distributed above the ionization threshold in addition to the prominent 1-2 transition peak, which correspond to the ground to above-barrier transitions. For the 80 Å sample, the oscillator strengths for the ground to above-barrier transitions are too small to be shown in Figure III.7(a). Since the above-barrier states have both even and odd wavefunctions as shown in Equation III.3, the ground state of even parity can make
transitions only to above-barrier states of odd parity although these transitions are negligibly small compared to the bound to bound transition. As the well width decreases so that the QW has only one bound state (40 Å and 35 Å QWs), the oscillator strengths between the ground and above-barrier states significantly increase. Unlike the bound to bound transition in wider QWs, the oscillator strength curves are continuous for bound to above-barrier transitions because the above-barrier states have continuous eigenenergies. The asymmetric shape of the oscillator strength is due both to the asymmetric density of states (Equation III.16) and to variation of dipole moments with the above-barrier state energies. Figure III.7(b) shows absorption spectra calculated from the oscillator strength assuming a Lorentzian lineshape according to\(^{15}\)

\[
\alpha(\omega) \propto \hbar \omega \int_{E_1}^{\infty} |\langle E|\mathbf{p}|1\rangle|^2 \frac{D(E)dE}{(E - E_1 - \hbar\omega)^2 + \Gamma^2}
\]  

(III.17)

where \(\Gamma\) is a Lorentzian linewidth of the transition. \(\Gamma = 5\, \text{meV}\) was used for all samples for the purpose of this calculation.
Figure III.8. FTIR spectra on four QW samples. (a) Brewster’s angle single pass measurements. (b) Normal incidence multi-bounce measurements. Ground to above-barrier state transitions for the 60 Å QW could be observed at low temperature. Offsets in the vertical scale are for clear view.

The FTIR absorption spectra were taken on each sample in both Brewster’s angle incidence (Figure III.8(a)) and multi-bounce geometries (Figure III.8(b)). As expected from the oscillator strengths, the 80 Å and 60 Å samples have prominent peaks at the intersubband energies, and the 40 Å and 35 Å samples have small and broad peaks for bound to above-barrier transitions. Multi-bounce measurements clearly show a broad and asymmetric lineshape for the 40 Å and 35 Å samples. It also shows a weak bound to above-barrier transition for the 60 Å sample in addition to the 1-2 transition. The multi-bounce measurement on the 60 Å sample was performed at 77 K to better resolve the small bound to above-barrier peak by narrowing the linewidth of the nearby bound to bound peak. One thing to note from the spectra is that the peak energy for 35 Å sample is smaller than that of the 40 Å sample. This is because the bound state energy increases with decreasing well width while the above-barrier state energies which contribute to the absorption peak are not much affected by well width change as depicted in Figure III.9. Thus in order to take advantage of above-barrier states for higher transition energies, it is necessary to keep the ground state at low energy and raise the above-barrier states which have a large oscillator strength with the ground state.
Figure III.9. Bound to above-barrier transitions for 40 Å and 35 Å QWs. The peak energy for the 40 Å QW is higher than the 35 Å QW because of the increase of the ground state energy for the narrower QW.

III.4. Intersubband transitions to quasi-bound states

As discussed in Section III.1 and III.2, wavefunctions of above-barrier states at certain energies are confined in the well region by the Bragg reflection from electron mirrors on both sides of the QW. In this section, we investigate the effect of electron mirrors on ISBTs. Samples with 40 Å GaAs/Al$_{0.3}$Ga$_{0.7}$As QWs were used for theoretical modeling and experimental measurements. We compare four samples: a bare QW sample and three mirror samples with one, two, and four periods of $\lambda/4$ mirror layers. All samples had 50 QWs which were uniformly n-type doped to $n = 1 \times 10^{18}$ cm$^{-3}$ in the well region. The QW has $E_i = 93$ meV and a transmission resonance at 307 meV in theory. At this transmission resonance, the QW becomes a $\lambda/2$ cavity and stacked $\lambda/4$-layers which consist of 20 Å GaAs and 35.7 Å Al$_{0.3}$Ga$_{0.7}$As confine the electron wavefunction to the well region due to Bragg reflection and make a quasi-bound state. (Figure III.10) The wavefunction (solid line) of the quasi-bound state becomes more strongly localized as more $\lambda/4$-layers are stacked while other above-barrier states (represented by the broken line) become forbidden since they don’t satisfy Equation III.14.
Figure III.10. Effects of electron mirrors on above-barrier states. (a) Bare QW with no mirror. (b) One period of mirror layers. (c) Two periods of mirror layers. (d) Four periods of mirror layers. Adding mirror layers enhances the amplitude of the quasi-bound state (solid line) and suppress the other above-barrier states such as the broken line. Electron mirrors also add several coupled states represented by dotted lines. Gray strips represent the minigaps created by superlattices of the electron mirrors.

The electron mirrors also create a number of bound states below the barrier energy because of tunnel coupling of bound states in each well of the mirror layers. Each discrete state in the QW in the mirror layers are strongly coupled to each other when they are separated by thin barrier layers (35 Å) as shown in Figure III.10(c). The number of the coupled states is the same as the number of mirror periods.
Figure III.11. (a) Calculated oscillator strengths. (b) Measured FTIR absorption spectra on the bare and 1, 2 and 4 λ/4 mirror pair QW samples at room temperature.

Figure III.11 illustrates the effect of electron mirrors on ISBTs between the ground and above-barrier states. Figure III.11 shows the calculated oscillator strengths and measured absorption spectra for a bare QW sample and three electron mirror samples with one, two, and four mirror periods. Also presented in Table III.1 are calculated oscillator strengths, measured transition linewidths and IAFs for the quasi-bound state of each mirror sample at room temperature and 77 K. All samples have fifty 40 Å GaAs / Al$_{0.3}$Ga$_{0.7}$As QWs which were doped in the well region with n = 1x10$^{18}$ cm$^{-3}$. Oscillator strength (Figure III.11a) for the bare QW sample has a broad, asymmetric peak above the ionization threshold (131 meV), which corresponds to the ground to above-barrier transitions. As more periods of electron mirrors are stacked, the oscillator strengths are more sharply peaked at the transmission resonance because the quasi-bound state is more tightly confined with more mirror layers as shown in Figure III.10. Samples with electron mirrors have δ-
function peaks of oscillator strengths below the ionization threshold corresponding to the transitions from the ground state to the coupled states of the mirror layers.

Table III.1. Calculated Oscillator strengths and Measured linewidths and IAFs for the quasi-bound state peak of samples with varying mirror periods.

<table>
<thead>
<tr>
<th>mirror periods</th>
<th>osc. strength</th>
<th>linewidth (meV)</th>
<th>IAF (meV-Abs)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>room temp.</td>
<td>77K</td>
</tr>
<tr>
<td>1</td>
<td>6.48</td>
<td>39</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>6.27</td>
<td>24</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>6.18</td>
<td>22</td>
<td>14</td>
</tr>
</tbody>
</table>

Measured absorption spectra (Figure III.11b) represent basically the same trend as the oscillator strengths. The bare QW sample has a broad and asymmetric peak above the ionization threshold for the transitions to the above-barrier states. When electron mirrors are added, the absorption peak becomes symmetric and occurs at the transmission resonance state. This effect of electron mirrors is remarkable, even with one period mirror layers on both sides of the QW. Additional peaks for the mirror samples below the ionization threshold correspond to the transitions between the ground and the coupled states. The linewidth of the quasi-bound peak becomes narrower with more mirror layers. At room temperature, the linewidth does not decrease much by going from a 2 period-mirror layers to a 4-period mirror. Intrinsic linewidth broadening of the QW and limited phase coherence length of the quasi-bound wavefunction at room temperature might nullify the tighter confining effect by more periods of mirror stacks. At a lower temperature (77 K), however, the linewidth decreases more steadily with increasing mirror layers up to 4 periods. The IAF of the quasi-bound peak decreases with increasing number of mirror periods. This is partly because a sample with more mirror layers takes a larger portion of the total oscillator strength for the ground state to coupled states transitions since it has
more coupled states. Thus the oscillator strength for the quasi-bound state peak becomes smaller as the number of the mirror layers increases. According to the sum rule, the total oscillator strength should be constant for all samples, thus the added transitions decrease the strength of the ground-quasi bound transition. Also a sample with more mirror layers may lose more electrons to the coupled states created by the mirrors due to thermal population of these states at room temperature.

III.5. Control of quasi-bound states by electron mirrors

In the previous section, the quasi-bound states were located at the transmission energy which was 307 meV for a 40 Å GaAs/Al$_{0.3}$Ga$_{0.7}$As QW. However, the transmission resonance is not the only energy where a quasi-bound state can be located. In fact, any periodic "potential-grating" layers combined with a square QW create quasi-bound states at energies where Equation III.14 is satisfied. Thus the energy of a quasi-bound state for the can be altered by changing electron mirror layers and keeping the same well width.$^{46}$ In this way, higher transition energies can be obtained without narrowing the QW thickness or increasing the barrier height.

We investigated five electron mirror samples stacked on 40 Å GaAs /Al$_{0.3}$Ga$_{0.7}$As QWs. All samples have two periods of λ/4 mirror layers on each side of the QW. The electron mirror layers for each sample have different duty cycles and become λ/4–layers at different energies, represented by E$_{\lambda/4}$, as shown in Table III.2. E$_{\lambda/4}$ for each set of mirror layers was calculated using Equation III.4. Each sample has 50 QWs and is n-type doped in the well region to a bulk concentration of 1x10$^{18}$ cm$^{-3}$. 

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Table III.2. Thickness and $E_{\nu/4}$ of electron mirror stacks in various mirror samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d_1$ (GaAs)</th>
<th>$d_2$ (Al$<em>{0.3}$Ga$</em>{0.7}$As)</th>
<th>$E_{\nu/4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>23.7 Å</td>
<td>134.5 Å</td>
<td>230 meV</td>
</tr>
<tr>
<td>#2</td>
<td>22.1 Å</td>
<td>54.9 Å</td>
<td>260 meV</td>
</tr>
<tr>
<td>#3</td>
<td>20.0 Å</td>
<td>35.7 Å</td>
<td>307 meV</td>
</tr>
<tr>
<td>#4</td>
<td>18.8 Å</td>
<td>29.9 Å</td>
<td>340 meV</td>
</tr>
<tr>
<td>#5</td>
<td>17.8 Å</td>
<td>26.5 Å</td>
<td>370 meV</td>
</tr>
</tbody>
</table>

Figure III.12. Conduction band diagrams, minigaps, and quasi-bound states for 40 Å GaAs / Al$_{0.3}$Ga$_{0.7}$As QWs with two electron mirror pairs with various electron energies, $E_{\nu/4}$. 
Although all samples have the same well width, so the ground state energy is the same, the quasi-bound state energy for each sample drastically changes by varying the $\lambda/4$ period of the electron mirror layers as shown in Figure III.12. Quasi-bound state energies and minigaps created by electron mirrors were calculated using Equations III.8 and III.14. Electron mirror layers with a shorter period create minigaps at higher energies, thus increasing the quasi-bound state energies confined by the minigaps in the mirror region. The quasi-bound state energy was increased more than 100 meV by reducing the period of the mirror stacks.

Intersubband absorption spectra were taken on all samples at room temperature using a Fourier transform infrared spectrometer (FTIR) and are presented in Figure III.13. The samples were polished at 45° on opposing edges to make a 15-pass waveguide to increase the absorption in the QWs. Light was incident normal to the polished face of the sample. In order to normalize the intersubband absorption, the transmission for TM-polarization (H-field parallel to the layer plane) was ratioed by the transmission for TE-polarization (E-field parallel to the layer plane). Theoretical absorption spectra were also calculated using Equation III.17 and shown with the measured spectra. The HWHM, $\Gamma$, of the Lorentzian function was used as a fitting parameter. Calculated absorption peaks are consistently lower than the measured values by 5 - 10 %, which may be accounted for by inaccurate material parameters used in the calculation, such as the effective mass and conduction band offset. Also the actual well width of the samples may be slightly off from the target value, 40 Å.
Figure III.13. Measured and calculated absorption spectra for the samples with varying mirror periods. Absorption peaks at lower energies for #3, #4 and #5 are due to the coupled states created by the mirror layers.

As expected from the calculation shown in Figure III.12, the quasi-bound peak energy shown in Figure III.13 changes by varying the resonant energy of the mirror layers: a shorter mirror period yields a higher quasi-bound peak energy. The absorption peak energy increases by over 110 meV and the peak energy (intersubband energy) for sample #5, 278 meV, is larger than the well depth by 54 meV. The quasi-bound state energy, $E_{qb}$, of each sample was obtained from the measured spectra by adding $E_1$ to the peak energy. $E_1$ varies from 88 meV to 93 meV depending on the thickness of the mirror layers. The results are compared in Table III.3 with the theoretical values from Equation III.14. Table III.3 also
shows dipole moments which were calculated from the integrated absorption fraction (IAF)\(^1\) of both measured and calculated absorption spectra. The electron density for the calculation was obtained from a Hall measurement and the spectra were fitted to a Lorentzian shape to calculate the IAF. As the period of the mirror layers decreases, the quasi-bound state energy increases and so does the absorption peak energy. However, the dipole moments or absorption peak strengths for the ground-quasi bound transitions decrease as the transition or absorption peak energy increases: the additional transitions between the ground and the coupled miniband states created by the mirror layers become stronger for thinner mirror barriers thus reducing the strength of the ground-quasi bound transition. In addition, the quasi-bound states at a higher energy should be less confined to the well region as electrons with higher kinetic energies will be less reflected by the electron mirror layers. Figure III.13 also shows second and third (very small) absorption peaks in addition to the first large one for sample #1 which has the largest mirror period. These additional peaks are from the second and third quasi-bound levels as shown in Figure III.12. These higher quasi-bound states are located relatively close to the barrier \((E_{\text{qb2}} = 299 \ (280) \ \text{meV}, \ E_{\text{qb3}} = 377 \ (351) \ \text{meV}, \ \text{values in parentheses are from Equation III.14})\) and they have reasonably large dipole moments.

Even though the quasi-bound states increase the ISBT energies beyond the barrier energy, the well depth still needs to increase in order to achieve higher energies up to 800 meV. In the next chapter, we will discuss higher energy transitions to bound and quasi-bound states in deep InGaAs / AlGaAs QWs.
Table III.3. Comparison of experimental and theoretical data.

<table>
<thead>
<tr>
<th>sample</th>
<th>$E_{\varphi}$ (meV)</th>
<th>dipole moment (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>experiment</td>
<td>Eq. III.14</td>
</tr>
<tr>
<td>#1</td>
<td>257</td>
<td>238</td>
</tr>
<tr>
<td>#2</td>
<td>288</td>
<td>271</td>
</tr>
<tr>
<td>#3</td>
<td>317</td>
<td>307</td>
</tr>
<tr>
<td>#4</td>
<td>341</td>
<td>329</td>
</tr>
<tr>
<td>#5</td>
<td>366</td>
<td>349</td>
</tr>
</tbody>
</table>
Chapter IV.

Short Wavelength Intersubband Transitions in InGaAs / AlGaAs QWs

In this chapter, we describe investigation of intersubband transitions (ISBTs) which are resonant at short wavelengths in high indium content InGaAs / AlGaAs quantum wells (QWs). Growth techniques for strained InGaAs / AlGaAs QWs will be discussed first, followed by observation of ISBTs of large energies from bound and quasi-bound states. Very short wavelength ISBTs up to 1.59 μm will be reported from a coupled InGaAs/AlAs QW sample which also has very large nonlinearity for difference frequency generation (DFG) of mid-infrared light.

IV.1. Quantum well materials consideration

Among many III-V semiconductors, most commonly used materials for intersubband applications are GaAs / AlGaAs with low aluminum content (< 45 %) on a GaAs substrate and InGaAs / InAlAs lattice-matched to InP. The advantage of using these materials is that they are lattice-matched to commercially available substrates (GaAs and InP) and yield high quality crystals from mature growth techniques. However, ISBTs in these QWs are restricted to wavelengths longer than 4 μm because of the small conduction band offsets. In Chapter III, we investigated QW above-barrier and quasi-bound states in GaAs / Al$_{0.3}$Ga$_{0.7}$As QWs and increased ISBT energies using the quasi-bound states located above the barrier potential. Yet, the maximum ISBT energies are comparable to the conduction band offset because the quasi-bound state cannot be lifted indefinitely high above the barrier potential. Thus it is necessary to use materials with larger conduction band offsets in order to obtain larger ISBT energies.
With higher aluminum content, GaAs / AlGaAs yields a large conduction band offset: 900 meV for GaAs / AlAs (Γ-valley). However, AlGaAs becomes an indirect bandgap material with aluminum content more than 45 % and the QW loses the carriers to the AlGaAs X-valley unless special care is taken. Schneider, et. al.\textsuperscript{47} used thin AlAs barriers in GaAs / AlAs QWs to avoid this carrier loss problem but the demonstrated ISBT was only at 350 meV (3.5 μm). Pan, et. al.\textsuperscript{48} used wide GaAs / AlAs QWs so that the ground state is located well below the AlAs X-valley, and observed a 1-6 transition at 434 meV (2.9 μm). With InGaAs / InAlAs QWs on InP, 1-2 ISBT energy of 295 meV (4.2 μm) was reported in lattice matched QWs and 400 meV (3.1 μm) in strained QWs.\textsuperscript{49} Using more exotic materials (InGaAs / AlAsSb) on the same substrate, 515 meV (2.4 μm) was achieved\textsuperscript{50}.

Our approach to achieve larger ISBT energies is to use InGaAs for the well material instead of GaAs in GaAs / AlGaAs QWs. InGaAs has a narrower bandgap and causes a larger conduction band offset from the AlGaAs barrier than GaAs as illustrated in Figure II.2. For instance, the conduction band offset between In\textsubscript{0.5}Ga\textsubscript{0.5}As and AlAs is about 1.4 eV. Higher aluminum content can be used in the barrier without the carrier loss because the conduction band edge of the InGaAs well is much lower in energy than the X-valley of AlGaAs. Another advantage of using InGaAs for the well layer is that InGaAs has a lighter electron effective mass than GaAs, which results in larger ISBT energy for the same well width. However, one serious problem with these materials is that InGaAs and AlGaAs layers are not lattice matched to each other and are highly strained with any useful indium composition. For instance, there is a 2.2 % lattice mismatch between In\textsubscript{0.3}Ga\textsubscript{0.7}As and AlGaAs. Material quality is very subject to deterioration with high strain, although strained
layers have been utilized to tailor electronic and optical properties through proper choice of materials and thickness.

J. H. Smet, et. al.\textsuperscript{51} reported an ISBT at 800 meV (1.55 μm) in a single QW of In\textsubscript{0.53}Ga\textsubscript{0.47}As / AlAs on an InP substrate, where the well is lattice-matched to the substrate but the barrier is highly strained. Due to the strain, they could not grow multiple QW layers and also the barrier layers for the single QW were limited to very small thickness (10 mono-layers), which results in very weak ISBTs. In order to grow multiple InGaAs / AlGaAs QWs with high indium composition, we need to solve the strain problem. In the next section, we will discuss a growth technique which alleviates the strain between lattice-mismatched layers and allows reliable epitaxial growth of thick strained layers.

IV.2. Growth of strained InGaAs / AlGaAs quantum wells

IV.2.1. Critical layer thickness

GaAs and InAs have quite different lattice constants; 5.65 Å for GaAs, 6.06 Å for InAs. Linear extrapolation for the lattice constant of the ternary compound, In\textsubscript{y}Ga\textsubscript{1-y}As, is given by

\[
a(\text{In}_y\text{Ga}_{1-y}\text{As}) = ya(\text{InAs}) + (1-y)a(\text{GaAs}) = 5.6536 + 0.4054y \quad \text{(IV.1)}
\]

Thus In\textsubscript{y}Ga\textsubscript{1-y}As has a larger lattice constant than GaAs by 0 - 7 % depending on y. Since it has a larger lattice constant than GaAs, the In\textsubscript{y}Ga\textsubscript{1-y}As film is compressively strained when it is grown on a GaAs substrate. On the other hand, if the lattice constant of the film is smaller than that of the substrate, the film is under tensile strain and the film tries to conform to the substrate by expanding its lateral constant. In either case, if the film is
sufficiently thin, the mismatch can be accommodated by lattice deformation and the strain caused by shrinking or expanding its lateral lattice constant can be sustained in the film. In such cases, the resulting strain is not necessarily harmful to the material quality of the film and could result in high quality material with few defects. Above a certain thickness, however, the strain accumulated in the film becomes too large to be accommodated by lattice deformation and the film relaxes to its equilibrium lattice constant via creating defects, especially misfit dislocations. Figure IV.1 shows the cases of strained and relaxed heterostructures. The thickness where a strained layer forms dislocations to relax is known as the critical layer thickness (CLT).

Figure IV.1. Compressive strain due to lattice mismatch and critical layer thickness ($h_c$).
Above the CLT, creating defects to relieve the strain is more energetically favorable than strain accommodation by lattice deformation. These defects spoil the subsequent overlayers which end up with a poor crystal quality. Thus growth of strained layers is normally restricted to thicknesses below the CLT in order to get high quality materials. It is not an easy task to accurately determine the CLT in real situations and there is still disagreement among experiments.\textsuperscript{52,53} In the ideal case, the CLT $h_c$ is given by \textsuperscript{54}

\[
\epsilon = \frac{a_s(1 - \nu/4)}{2\sqrt{2\pi h_c(1 + \nu)}} \left( \ln\frac{\sqrt{2}h_c}{a_s} + 1 \right)
\]  

(IV.2)

where $\nu$ is the Poisson's ratio for the film and $\epsilon$ is the strain given by

![Graph](image)

Figure IV.2. Critical layer thickness for In$_x$Ga$_{1-x}$As on GaAs.
with the substrate ($a_s$) and film ($a_f$) lattice constants. Using these equations, Figure IV.2 shows the calculated CLT for $\text{In}_{y}\text{Ga}_{1-y}\text{As}$ grown on GaAs with varying $y$. The CLT is only 40 Å for $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$, which is the material we desire to use for large ISBT energies. Thus in order to grow multiple $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ QWs with AlGaAs barriers on GaAs substrates and still maintain high material quality, we need to take an approach which decreases the strain and increases the CLT.

### IV.2.2. Linearly graded InGaAs buffer technique

As discussed in the previous section, the fundamental difficulty of growing InGaAs / AlGaAs MQWs comes from the lattice mismatch between the two materials. No single substrate can match two dissimilar lattice constants: $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ has a mismatch of 3.5 % to a GaAs substrate and AlGaAs has a similar mismatch to an InP substrate. Such mismatch results in small CLT, around 40 Å for a single layer, which is too small to be practical for most device applications. Many growth techniques have been investigated for high quality growth of high indium content InGaAs on GaAs substrates, including reduced area growth, short period superlattices, and various buffer layers. Among them, we adopted the buffer layer growth technique which is basically to grow graded buffer layers that have a final intermediate lattice constant midway between the well and barrier materials so they are alternatively compressively and tensilely strained. MQW layers are then grown on the top of these buffer layers which acts as a new substrate. This growth scheme has two advantages in increasing the CLT. First, by providing an "effective" substrate with an intermediate lattice constant, each well and barrier layer has less mismatch to the substrate and has a larger critical thickness. Figure IV.3 shows the CLTs for InGaAs layers grown on a $\text{In}_{0.25}\text{Ga}_{0.75}\text{As}$ buffer. The CLT for $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ increases to 100 Å from 40 Å on a
GaAs substrate in Figure IV.2. The other advantage is strain compensation between the well and barrier layers. Because the buffer lattice constant is an intermediate value between the well and barrier lattice constants, the well layer is under compressive strain and the barrier layer is under tensile strain. These strains in opposite directions partially cancel each other reducing net strain, which brings additional increase of the CLT. In our case of InGaAs / AlGaAs MQWs, a natural way to obtain the buffer layer is to grow an InGaAs layer with an indium composition lower than that of the well layer before growing the MQW layers. The indium composition for the buffer layer is usually chosen to be the average indium composition of one QW period in order to give balanced strain compensation.

![Graph](image)

Figure IV.3. Critical layer thickness of $\text{In}_y\text{Ga}_{1-y}\text{As}$ on $\text{In}_{0.25}\text{Ga}_{0.75}\text{As}$. 

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However, great precaution should be given to the growth of the InGaAs buffer. Simply growing the InGaAs buffer layer directly on a GaAs substrate is also problematic because the dislocations created in the buffer layer propagate into the MQW region on the top of it, which is called a threading dislocation. Researchers at the University of Florida have observed that there is a critical indium composition, 18% for their growth conditions, above which the dislocations penetrates in the active overlayers. They observed dislocation propagation only downward below this critical composition. Thus more elaborate growth efforts are required in order to prevent the dislocations from propagating into the overlayer on InGaAs buffer layers with indium content higher than 18%. Susan M. Lord was the first to demonstrate the growth of high quality high indium content InGaAs / AlGaAs MQWs on GaAs substrates using graded InGaAs buffer layers. She compared two buffer layer configurations: step graded and linearly graded buffers, and found that the linearly graded buffer yielded superior material quality to the step graded buffer. This was verified by X-ray diffraction, transmission electron microscopy (TEM) and excitonic absorption in quantum well structures grown on the buffer layers.

The difference between the two buffer configurations lies in how to increase indium composition in the buffer layers as shown in Figure IV.4. The step graded buffer takes multiple steps where the indium composition jumps to a higher value until it reaches the final desired indium composition. The increase of indium composition at each step is usually kept under 18% to avoid propagation of threading dislocations into the overlayers as described above. In this multiple-step strain relief structure, underlying layers are sacrificial layers which accommodate most of the strain and misfit dislocations that are confined to the interfaces between the steps. Thus the top buffer layer can be relaxed with low dislocation density. It has been observed that fine-step grading creates more complete relaxation of the buffer layers than coarse-step grading, which leads to higher material quality of overlayers. The ultimate case of the fine-step grading is a linearly grading scheme.
where the indium composition continuously increases up to the final composition as shown in Figure IV.4. Detailed comparison between the step and linearly graded buffers is found in S. M. Lord’s dissertation.\textsuperscript{56} We adopted the linearly grading method for our growth of InGaAs / AlGaAs MQWs, where the buffer grading actually consists of many fine steps (≈ 0.05 % In) with increasing indium composition at every 50 Å.

Figure IV.4. Indium composition vs. growth depth for step and linearly graded InGaAs buffers.
IV.2.3. Growth conditions

Figure IV.5 represents a typical growth structure of InGaAs / AlGaAs MQWs for QW ISBT applications grown atop a linearly graded InGaAs buffer on a GaAs substrate. The growth procedure is as follows. First, a GaAs buffer layer on the order of 500 Å is deposited on the substrate. Then graded InGaAs buffer starts with very low indium composition (typically of In₀.₀₁₅Ga₀.₉₈₅As) of ~ 1000 Å. The indium composition increases every 50 Å by ramping the temperature of the indium diffusion cell. The rate of increase is determined by the final indium composition and the thickness of the buffer. Typical indium grading rate for In₀.₅Ga₀.₅As QWs is 16 % indium / µm. The final indium composition is usually chosen around the average indium composition of the MQW layers to give optimum strain compensation. When the indium composition reaches the final value, 1000 - 2000 Å constant composition InGaAs layer is deposited as the final buffer prior to the growth of QWs

<table>
<thead>
<tr>
<th>Layer Description</th>
<th>Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In₀.₅Ga₀.₅As</td>
<td>40 ~ 80</td>
</tr>
<tr>
<td>AlGaAs</td>
<td>~ 100</td>
</tr>
<tr>
<td>InᵧᵦGa₁₋ᵧᵦAs Linearly Graded InGaAs Buffer (GR 7 - 25 % In / µm)</td>
<td>1~ 3 µm</td>
</tr>
<tr>
<td>GaAs</td>
<td>~ 500</td>
</tr>
</tbody>
</table>

Figure IV.5. Typical growth structure of InGaAs / AlGaAs MQWs on a linearly graded InGaAs buffer.
In this rather complicated growth structure, there are many parameters to be optimized for best results in the growth of the buffer and QW layers, such as growth temperature of the buffer and QWs, final buffer indium composition, and indium grading rate, etc. S. M. Lord investigated the effect of growth temperature and indium grading rate of the buffer on the material quality and she found that low growth temperature and slow gradient yield the best material quality in terms of strong and sharp photoluminescence, exciton peaks and large transmission contrast in her modulator structure. Herman C. Chui who first demonstrated that high indium content InGaAs / AlGaAs QWs on linearly graded buffers could be used for short wavelengths ISBT applications\textsuperscript{57}, continued the growth optimization, especially for ISBT applications. He did a great deal of systematic growth and characterization work which lead to the following optimized conditions.\textsuperscript{58}

IV.2.4. Growth optimization

Growth parameters are divided into two groups: buffer parameters and QW parameters. Important parameters for InGaAs buffer growth are substrate temperature ($T_{\text{buf}}$), indium grading rate, and final buffer indium composition ($y_b$). Substrate temperature is a very important factor to epitaxial film growth because it significantly affects the dynamics and nucleation of atoms and molecules on the substrate. At low temperature, the mobility of the atoms or molecules decrease during deposition, which results in rough surface morphology. GaAs and AlGaAs layers are usually grown at substrate temperatures over 600 °C. However, InGaAs can hardly grow at that high temperature because indium starts to desorb above 400 °C. Thus the substrate temperature was kept around 400 °C during the InGaAs buffer growth. Intersubband absorption spectra were almost identical for samples grown in the temperature range $T_{\text{buf}} = 380 - 430$ °C. All substrate temperatures referred to here are measured by a thermocouple and the thermocouple temperature ($T_{\text{tc}}$) has the following relation with the real temperature ($T_{\text{real}}$).
\[ T_{\text{real}}(^\circ\text{C}) = a_0 + a_1 T_{\text{tc}} + a_2 T_{\text{tc}}^2 \quad \text{for } T_{\text{tc}} \geq T_b \]

\[ T_{\text{real}}(^\circ\text{C}) = b_0 + b_1 T_{\text{tc}} + b_2 T_{\text{tc}}^2 \quad \text{for } T_{\text{tc}} \leq T_b \]

where \( T_b = 380 \, ^\circ\text{C} \), \( a_0 = -167.93 \, ^\circ\text{C} \), \( a_1 = 1.61522 \), \( a_2 = -0.0007220365 / ^\circ\text{C} \), \( b_0 = 0.27 \, ^\circ\text{C} \), \( b_1 = 0.971556 \), and \( b_2 = -0.0002007307 / ^\circ\text{C} \). Thus for thermocouple readings of 380 °C and 430 °C, the real substrate temperatures are approximately 340 °C and 380 °C, respectively.

As for the indium grading rate, higher quality MQW samples were obtained with lower grading rate, in the 8 - 24 %In/μm range. The sample quality was determined by the following ISBT characteristics; absorption linewidth and integrated absorption fraction (IAF). The IAF is the area under an absorption peak in the spectra and is equivalent to the absorption strength. Narrow linewidth and large IAF indicate high material quality. Although lower grading rate yields higher material quality, the trade-off is a very long growth time and an unnecessarily thick buffer layer which takes a lot of material just for a buffer. Thus we usually used a grading rate which makes the buffer layer thickness less than 2 μm. For the final indium composition of 20 - 30 %, the typical grading rate we used was 16 % In / μm.

Interestingly, the optimal value of the final buffer indium composition \( (y_b) \) was found to be higher than the average indium composition \( (y_{\text{avg}}) \) of the QW. It was expected that the buffer with an indium composition of \( y_{\text{avg}} \) would produce the most balanced strain both to the well and barrier layers and yield the best material quality. However, for MQW samples consisting of 40 Å-In\(_{0.5}\)Ga\(_{0.5}\)As / 80 Å-AlGaAs \( (y_{\text{avg}} = 17 \%) \), the linewidth keeps
decreasing and IAF keeps increasing with increasing $y_b$ up to $y_b = 30 \%$ above which the QW layers relaxed and generate a lot of dislocations because the AlGaAs barrier thickness exceeds the CLT as the buffer indium composition increases. It seems that the QW quality improves when the $\text{In}_y\text{Ga}_{1-y}\text{As}$ well layer has less strain from the $\text{In}_y\text{Ga}_{1-y}\text{As}$ buffer as long as the AlGaAs barrier does not exceed the CLT on the buffer. Thus we usually used $y_b$ of 25 - 30 % for $y_{\text{avg}}$ of 15 - 20 %.

The substrate temperature during the QW layer growth is also an important parameter. As discussed above, appropriate substrate temperature for InGaAs is around 400 °C. However, this is not the best temperature for the QW layers, especially for the AlGaAs barrier and such a low temperature could roughen the interface due to the low aluminum mobility at low temperature. By using different substrate temperatures, 400 °C for the InGaAs well and 600 °C for the AlGaAs barrier, the linewidth and IAF were improved by 10 - 15 %, which is an indication of better interface quality. This requires ramping the substrate heater temperature up and down at every interface and waiting for more than 5 minutes until the heater temperature is stabilized, thus prolonging the growth time a lot, especially for MQW samples with many QWs.

The interface quality was further improved by inserting a single monolayer of GaAs at the interface between the well and barrier layers. Growth is interrupted for 30-60 seconds after the GaAs monolayer deposition. The deposition of a GaAs single monolayer (ML) and growth interruption smooth the interface by compensating the surface roughness of the InGaAs and AlGaAs layers. Figure IV.6 shows the ISBT absorption spectra for 40 Å $\text{In}_{0.3}\text{Ga}_{0.5}\text{As} / \text{Al}_{0.45}\text{Ga}_{0.55}\text{As}$ QWs with and without the 1 ML GaAs smoothing layer. Substrate temperature during the growth of AlGaAs barriers was increased to 600° C for the
sample with the GaAs smoothing layer and was kept at 400°C for the sample without the smoothing layer. This combination of an interface smoothing layer and increased $T_{\text{barrier}}$ brings about 30% improvement of the linewidth and IAF, which shows the significance of smooth interfaces on material quality of ISBT QWs. The peak energy for the sample with the smoothing layers is smaller because the effective well width is larger because of the smoothing layers at the well-barrier interfaces.

![Absorption spectra](image)

Figure IV.6. Absorption spectra on 40 Å In$_{0.5}$Ga$_{0.5}$As / Al$_{0.45}$Ga$_{0.55}$As QWs with and without interface smoothing layer (SL). $T_{\text{barrier}}$ was also varied, 600°C for the sample with SL and 400°C for the sample without SL.
IV.3. Short wavelength intersubband transitions

IV.3.1. Intersubband transitions in In_{0.5}Ga_{0.5}As / Al_{0.45}Ga_{0.55}As QWs

1-2 (bound-bound) ISBTs in In_{0.5}Ga_{0.5}As / Al_{0.45}Ga_{0.55}As QWs have been studied by H. C. Chui. Figure IV.7 shows the well width dependence of ISBTs. These samples consisted of 50 QWs grown on linearly graded InGaAs buffers which were graded at a rate of 16% In/μm from GaAs to the final indium composition near the average indium concentration of the QWs. The samples were uniformly doped in the well region to a sheet charge density per QW of 2.8 \times 10^{12} \text{ cm}^{-2} and were grown at a substrate temperature of 400 °C. The intersubband energy monotonically increases with decreasing well width up to 30 Å.

![Graph showing intersubband absorption spectra](image)

Figure IV.7. Intersubband absorption spectra on In_{0.5}Ga_{0.5}As / Al_{0.45}Ga_{0.55}As QW with varying well widths from H. C. Chui.¹³
Å but decreases beyond that so the peak energy for 23 Å is smaller than that for 30 Å. This is because the second energy level is close to the top of the well at 30 Å and further narrowing the well width causes the ground state energy to increase faster than the second state energy. Thus the ISBTs in this In$_{0.5}$Ga$_{0.5}$As / Al$_{0.45}$Ga$_{0.55}$As QW system is limited to wavelengths longer than 3 μm. Transition linewidths are broadened monotonically with decreasing well width. Well width fluctuation and surface roughness which have more significant effects on narrow QWs are believed to be the reason.

![Graph showing absorption spectra](image)

**Figure IV.8.** Absorption spectra from above-barrier and quasi-bound states in 20 Å In$_{0.5}$Ga$_{0.5}$As / Al$_{0.45}$Ga$_{0.55}$As with various mirror structures.

Having seen the upper limit of the ISBT energy from bound states, we constructed QWs with above-barrier states as an upper state to get higher energies. These samples were composed of fifty periods of 20 Å In$_{0.5}$Ga$_{0.5}$As / Al$_{0.45}$Ga$_{0.55}$As QWs grown atop InGaAs buffers which were linearly graded at a rate of 12 % In/μm. Three samples were grown at
Figure IV.9. Maximum 1-2 intersubband energies (solid line) from bound states and corresponding well widths vs. aluminum composition $x$ in $\text{In}_{0.5}\text{Ga}_{0.5}\text{As} / \text{Al}_{x}\text{Ga}_{1-x}\text{As}$ QWs. The square dots are largest 1-2 energies measured in $\text{In}_{0.5}\text{Ga}_{0.5}\text{As} / \text{Al}_{0.45}\text{Ga}_{0.55}\text{As}$ and $\text{In}_{0.5}\text{Ga}_{0.5}\text{As} / \text{AlAs}$ QWs. The round dot represents an increased transition energy from a quasi-bound state confined by narrow mirror layers.

substrate temperature of 400 °C and they were uniformly doped to the sheet carrier density of $6.6 \times 10^{11}$ cm$^{-2}$ per QW in the well region. One of the three samples has plain AlGaAs barriers and the other two samples have mirror structures on each side of the QW. The electron mirror structures are composed of two periods of $\text{In}_{0.5}\text{Ga}_{0.5}\text{As} / \text{Al}_{0.45}\text{Ga}_{0.55}\text{As}$ layers with a duty cycle of 4 ML / 9 ML for one sample and 5 ML / 13 ML for the other, where ML stands for mono-layer. Figure IV.8 shows intersubband absorption spectra from these samples which were taken using the multi-bounce method. Using the quasi-bound states, the transition energy was extended to 460 meV (2.7 µm). A higher transition energy might be available from a narrower QW and mirror structure. But it is difficult to reliably grow well and mirror layers thinner than 7 and 4 monolayers. Figure IV.9 presents
calculated curves for maximum $E_{12}$'s from bound states and corresponding well widths vs. aluminum composition $x$ in Al$_x$Ga$_{1-x}$As barriers. It shows that for bound-bound ISBT wavelengths shorter than 2 $\mu$m (620 meV), aluminum composition more than 80% is required in AlGaAs barriers.

![Graphs showing absorption spectra](image)

Figure IV.10. Absorption spectra taken from In$_{0.5}$Ga$_{0.5}$As / AlAs QWs with various well widths. (a) is from H.C. Chui$^{13}$ and is taken in the Brewster's angle geometry. (b) is taken in the multi-bounce waveguide geometry for narrower QWs.
IV.3.2. Intersubband transitions in InGaAs / AlAs QWs

In this section, AlAs barriers are utilized to obtained higher transition energies. The $\text{In}_{0.5}\text{Ga}_{0.5}\text{As} / \text{AlAs QW}$ has a conduction band offset as large as 1.3 eV. Figure IV.10 shows absorption spectra for 1-2 transitions in $\text{In}_{0.5}\text{Ga}_{0.5}\text{As} / \text{AlAs QW}$ samples with varying well widths. These samples were grown on InGaAs buffers linearly graded up to a final buffer indium composition of 20 % at a rate of 16 % In/μm and were n-type doped in the well region to the sheet charge density per QW of $4.0 \times 10^{12}$ cm$^{-2}$. The substrate temperature was 400°C. Figure IV.10(a) shows FTIR spectra taken in the Brewster’s angle sample geometry. The transition energy increases as the well width decreases from 80 Å to 30 Å. The transition wavelength for the 30 Å QW is 2.4 μm as compared to 3.1 μm for $\text{In}_{0.5}\text{Ga}_{0.5}\text{As} / \text{Al}_{0.45}\text{Ga}_{0.55}\text{As QW}$ of the same width. For narrower QW samples (23 Å and 18 Å), intersubband absorption was not detectable with the Brewster’s angle single pass geometry, so we used the multi-bounce measurement technique and observed a 1.77 μm transition from the 18 Å QW sample. In the multi-bounce sample geometry, light was incident normal to a 45° polished side facet of an 8 mm long sample. In this case, the multi-bounce measurement yields about 105 times stronger absorption peak than the Brewster’s angle measurement.

Even shorter wavelength transitions were obtained from deeper $\text{In}_{0.5}\text{Ga}_{0.4}\text{As} / \text{AlAs QWs}$ which have a conduction band offset of 1.37 eV (Figure IV.11). These samples were grown in similar conditions to the earlier $\text{In}_{0.5}\text{Ga}_{0.5}\text{As} / \text{AlAs QW}$ samples. The nominal doping concentration in the well region was $n = 3 \times 10^{18}$ cm$^{-3}$ and the number of QWs of each sample was adjusted to make the total sheet charge density $1.4 \times 10^{14}$ cm$^{-2}$. The transition energy of 720 meV (1.72 μm) obtained from 17.0 Å QW sample is the largest $E_{12}$ ever reported on GaAs substrates.$^{59}$
Figure IV.11. Short wavelengths ISBTs from narrow In$_{0.6}$Ga$_{0.4}$As / AlAs QWs.

The well width dependence of the ISBT energy discussed so far is presented in Figure IV.12 for In$_{0.5}$Ga$_{0.5}$As / Al$_{0.45}$Ga$_{0.55}$As and In$_{0.5}$Ga$_{0.5}$As / AlAs QWs. The solid lines are calculated energies at each well thickness using the energy dependent effective mass model which was discussed in Section II.3. Although the quasi-bound states increase the transition energies above the maximum bound to bound transition energy in In$_{0.5}$Ga$_{0.5}$As / Al$_{0.45}$Ga$_{0.55}$As (hollow dots), it is difficult to obtain the same improvement in In$_{0.5}$Ga$_{0.5}$As / AlAs QWs because of the deep potential well. In order to obtain above-barrier states for 1-2 transitions in In$_{0.5}$Ga$_{0.5}$As / AlAs QWs, the well thickness needs to be smaller than 13 Å which less than 5 monolayers thickness. In such narrow QWs, intersubband absorption was too weak to detect, even with the highly sensitive multi-bounce technique.
Figure IV.12. Well width dependence of $E_{12}$ of $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ QWs. The Solid line is calculated values for $\text{Al}_{0.45}\text{Ga}_{0.55}\text{As}$ barriers and the broken line for AlAs. Dots are measured values. Hollow dots are from above-barrier states.

IV.3.3. Asymmetrically coupled quantum wells

So far we have investigated 1-2 transitions in square QWs. By narrowing the well width in InGaAs / AlAs QWs, we achieved ISBT wavelengths as short as 1.78 μm. Further increase of the transition energy has been limited by the growth of very thin QWs of a few monolayers. In order to obtain a higher intersubband energy without further reduction of QW width, we investigated ISBTs involving higher states in asymmetric QWs, especially asymmetrically coupled QWs. Asymmetric QWs could yield 1-3 and 1-4 transition strengths comparable to an 1-2 transition, which is not possible in a symmetric QW where the 1-3 transition is forbidden and 1-4 transition is weaker than 1-2 transition by about two orders of magnitude. There are several ways of constructing asymmetric QWs.
including external bias field, nonuniform doping, step QWs and coupled QWs. As discussed in section II.6.3, coupled QWs have the advantage of readily making a double resonance for difference frequency generation (DFG) of mid-infrared (MIR) light using two near-infrared (NIR) inputs.

Figure IV.13. 1-2, 1-3, and 1-4 transitions in an asymmetrically coupled In_{0.5}Ga_{0.5}As / AlAs QW.
The sample contains 100 coupled QWs, each coupled QW consisting of 10 and 7 monolayers (MLs) of In$_{0.5}$Ga$_{0.5}$As separated by a 3 MLs thick AlAs layer as shown in the inset of Figure IV.13. GaAs single monolayers were deposited at each boundary between the wells and barriers to smooth the interface. These MQW layers are atop an InGaAs buffer layer with $y_b = 0.25$. The QWs are highly n-type doped to $n = 1 \times 10^{19}$ cm$^{-3}$ which gives a sheet charge density of $\sigma = 4.81 \times 10^{12}$ cm$^{-2}$ per QW. The $E_{12}$, $E_{13}$, and $E_{14}$ are predicted to be 126 meV, 507 meV, and 758 meV. Calculated dipole moments are $z_{12} = 10.58 \, \text{Å}$, $z_{13} = -7.03 \, \text{Å}$, and $z_{14} = 2.57 \, \text{Å}$. Strong absorption peaks were observed from the 1-3 and 1-4 transitions as well as the 1-2 transition (Figure IV.13). The 1-2 absorption peak is at 141 meV and the 1-3 and 1-4 transition energies are 530 meV (2.34 μm) and 780 meV (1.59 μm), respectively. This $E_{14}$ is the largest ISBT energy ever reported on GaAs substrates. The half width at half maximum (HWHM) linewidths from the absorption spectra are $\Gamma_{12} = 10.8$ meV, $\Gamma_{13} = 58.7$ meV, and $\Gamma_{14} = 89.3$ meV. The 1-3 and 1-4 transition peaks are not completely separated because of their large linewidths. The measured IAFs are 0.721 meV-Abs, 1.765 meV-Abs, and 0.605 meV-Abs for 1-2, 1-3, and 1-4 transitions, respectively. Assuming $z_{12} = 10.58 \, \text{Å}$ from theory, the measured IAFs yield an effective sheet charge density of $\sigma_{\text{eff}} = 1.35 \times 10^{12}$ cm$^{-2}$ / QW and $|z_{13}| = 8.59 \, \text{Å}$, $|z_{14}| = 4.15 \, \text{Å}$ using Equation II.22. This asymmetric QW has a large $\chi^{(2)}$ for DFG of mid-infrared (MIR) light by mixing two near-infrared (NIR) pumps, which originate from the resonant transitions at MIR ($E_{12}$) and NIR ($E_{13}$ or $E_{14}$). Using Equation II.28, Figure IV.14 is the calculated DFG $\chi^{(2)}$ for the output wavelengths of 7 - 13 μm. One of the two input wavelengths was fixed at 1.55 μm and the other was tuned between 1.99 μm and 1.76 μm. The peak $\chi^{(2)}$ occurs around an output wavelength of 8.80 μm which corresponds to $E_{12}$. 
when two input beams are resonant to $E_{14}$ and $E_{24}$. The peak DFG $\chi^{(2)}$ of 3.7 nm/V is more than 20 times that of bulk GaAs (180 pm/V for these wavelengths as calculated with Miller's rule$^{60}$). More elaborate optimization of the sample such as narrowing linewidth, larger dipole product and more QWs should increase further DFG $\chi^{(2)}$ using two NIR inputs whose wavelengths are shorter than 2 μm.

Figure IV.14. Theoretical DFG $\chi^{(2)}$ vs. output wavelengths for mixing 1.55 μm and a tunable wavelength around 1.8 μm.
Chapter V.

Intersubband lifetime and saturation

In this chapter, we will discuss intersubband lifetime and saturation effects. ISBT saturation intensity limits the maximum pump power a nonlinear optical process can utilize and the upper state carrier lifetime is a key factor in determining the saturation intensity of an ISBT. A finite ISBT lifetime is limited by the various scattering mechanisms causing energy relaxation of a carrier from an upper subband to a lower subband. There has been a large amount of work, both theoretical and experimental, to figure out how fast these scattering processes occur. Among many possible mechanisms, LO phonon scattering is believed to be the most dominant process for intersubband relaxation.\textsuperscript{61} We numerically calculate the LO phonon scattering time for both bound to bound and bound to quasi-bound samples and compare it with time-resolved pump-probe intersubband lifetime measurements. In later sections, we will discuss absorption saturation measurements from which we can independently deduce the relaxation time and compare with results from the pump-probe measurements. This work was done in close collaboration with Dr. G. L. Woods\textsuperscript{62} and Dr. K. L. Vodopyanov.\textsuperscript{63,64} I designed and fabricated the samples and they did most of the optical measurements.

V.1. Intersubband relaxation due to LO phonon scattering

Electrons in a QW subband undergo various scattering processes with various time scales, such as interface roughness and ionized dopant scattering, electron-electron scattering and electron-phonon scattering. Among them, phonon scattering, especially longitudinal optical (LO) phonon scattering is believed to be the dominant mechanism for intersubband relaxation.\textsuperscript{61} Figure V.1 schematically shows an intersubband relaxation
process of excited electrons where LO-phonon scattering is involved. We will derive equations for LO phonon scattering rate following Ferreira and Bastard’s approach\textsuperscript{65} and Woods’ refinement\textsuperscript{62} to calculate upper subband lifetimes.

Figure V.1. Intersubband and intrasubband relaxation due to LO-phonon absorption or emission.

Considering the phase and polarization of a phonon in a two-atom basis crystal such as GaAs, there are four types of phonons: longitudinal optical (LO), longitudinal acoustic (LA), transverse optical (TO), and transverse acoustic (TA). Among them, the LO-phonon has the strongest interaction with an electron through a long-range dipole force in the $\Gamma$ valley of a polar semiconductor with cubic symmetry, such as GaAs.\textsuperscript{61} Thus when subbands are separated by more than the optical phonon energy $\hbar \omega_{LO} = 36$ meV, intersubband lifetime is determined by the electron-LO phonon scattering rate. For subband separation less than $\hbar \omega_{LO}$, other types of phonon scattering, such as acoustic phonon, become significant contributors.
The scattering by a phonon is represented by the electron-phonon Hamiltonian

\[ H_{e-\text{ph}} = \sum_{\bar{q}} \left[ \alpha(\bar{q}) e^{-i\bar{q} \cdot \vec{r}} \vec{b}^\dagger_{\bar{q}} + \text{c.c.} \right] \quad (V.1) \]

where \( \vec{b}^\dagger_{\bar{q}} \) is the creation operator for a phonon in the mode \( \bar{q} \) and

\[ |\alpha(\bar{q})|^2 = \hbar \omega_{LO} \frac{e^2}{2\varepsilon_0 \varepsilon_p \Omega q^2}; \quad \varepsilon_p^{-1} = \varepsilon_\infty^{-1} - \varepsilon_{dc}^{-1} \quad (V.2) \]

represents the strength of electron-LO phonon interaction. The MKS unit is being used. This interaction Hamiltonian is used in Fermi’s golden rule to give a scattering rate from the \( i \)-th to \( f \)-th subbands, written as

\[ \frac{1}{\tau_{if}} = \frac{2\pi}{\hbar} \sum_f |\langle f | H_{e-\text{ph}} | i \rangle|^2 \delta(E_i - E_f) \quad (V.3) \]

where the summation is over all final states. \( |i\rangle \) and \( |f\rangle \) refer to the initial and final states combining the electron and phonon states. The delta function enforces energy conservation.

For a phonon emission process, we can write the initial and final states as

\[ |i\rangle = |\psi_i\rangle |0\rangle, \quad |f\rangle = |\psi_f\rangle |\vec{p}\rangle \quad (V.4) \]

where \( \vec{p} \) represents the final phonon momentum emitted in the scattering process. The initial and final electron states, \( |\psi_j\rangle \) (\( j = i, f \)), are represented by envelope functions

\[ |\psi_j\rangle = \frac{1}{\sqrt{A}} e^{i \vec{k}_j \cdot \vec{r}} \chi_j(z) \quad (V.5) \]

for a subband energy.
\[ E_f(\vec{k}_\perp) = E_f(0) + \frac{\hbar^2 \vec{k}_\perp^2}{2m^* (E)} \]  

(V.6)

where \( E_f(0) \) is the bottom of the j-th subband at \( k_\perp = 0 \) and the band nonparabolicity is taken care of by an energy dependent effective mass, \( m^*(E) \). Then the energy conservation becomes

\[ E_i(0) + \frac{\hbar^2 \vec{k}_\perp^2}{2m^* (E_i)} = E_f(0) + \frac{\hbar^2 \vec{k}_\perp^2}{2m^* (E_f)} \pm \hbar \omega_{LO} \]  

(V.7)

where the \( \pm \) represents phonon emission (+) or absorption (-) processes. From this equation, final electron momentum, \( k_{f\perp} \), is obtained for a given initial momentum, \( k_{i\perp} \). For now, we will calculate the phonon emission rate which is the only possible process at \( T = 0 \). Phonon absorption and finite temperature effects will be incorporated later in this section. The scattering matrix element in Equation V.3 is calculated using Equations V.4 and V.5 to yield

\[ \langle f | H_{e-ph} | i \rangle = \frac{(2\pi)^2}{A} \delta^{(2)}(\vec{k}_{i\perp} - \vec{k}_{f\perp} - \vec{p}_\perp) \alpha(\vec{p}) \int dz \cdot \chi^*_f(z) \chi_i(z) e^{-ip_z z} \]  

(V.8)

Calculation of the scattering rate by using Equation V.8 in Equation V.3 requires careful algebra. The sum over all final states converts to integration over all \( \vec{k}_{f\perp} \) and \( \vec{p} \), and the in-plane momentum conservation

\[ \vec{k}_{i\perp} - \vec{k}_{f\perp} - \vec{p}_\perp = 0 \]

makes \( |\alpha(\vec{p})|^2 \) proportional to

\[ \left[ (k_{i\perp} - k_{f\perp})^2 + p_z^2 \right]^{-1}. \]

Then the integration over \( p_z \) is the Fourier transform of this Lorentzian which can be done by a contour integral to yield the scattering rate as
\[
\frac{1}{\tau_{fi}} = \frac{\omega_{LO} e^2}{8 \pi \epsilon_0 \epsilon_p} \int d\theta dk_{f\perp} k_{f\perp} \delta(\Xi - \Xi_i) \frac{I(Q)}{Q} \tag{V.9}
\]

where the phonon overlap integral I(Q) is

\[
I(Q) = \int dz dz' \chi_i^*(z) \chi_f(z) \chi_f^*(z') \chi_i(z') e^{-Q|z-z'|}. \tag{V.10}
\]

Q is the momentum transfer to the emitted phonon defined by

\[
Q = |\vec{k}_{i\perp} - \vec{k}_{f\perp}| = \sqrt{k_{i\perp}^2 + k_{f\perp}^2 - 2 k_{i\perp} k_{f\perp} \cos \theta}. \tag{V.11}
\]

Using \( \Xi_f = E_f(0) + \frac{\hbar^2 k_{f\perp}^2}{2m'(E_f)} + \hbar \omega_{LO} \), integral over \( k_{f\perp} \) in Equation V.9 is performed and gives

\[
\frac{1}{\tau_{fi}} = \frac{\omega_{LO} e^2}{8 \pi \epsilon_0 \epsilon_p} \frac{m'}{\hbar^2} \int_0^{2\pi} d\theta \frac{I(Q)}{Q} \tag{V.12}
\]

where \( m' \) is defined as

\[
m' = \frac{m'(E_f(k_{f\perp}))}{1 - \frac{1}{2} \left[ \frac{dm'(E_f(k_{f\perp}))}{dk_{f\perp}} \right]} \left[ \frac{m'(E_f(k_{f\perp}))}{k_{f\perp}} \right] \tag{V.13}
\]

If the band is perfectly parabolic or \( \frac{dm'(E_f(k_{f\perp}))}{dk_{f\perp}} = 0 \), then \( m' \) in Equation V.12 becomes the constant effective mass, \( m^* \).
From Equation V.12, we can see that the maximum transition rate (infinite in this approximation) occurs when \( Q = 0 \), i.e. when there is no momentum transfer to a phonon during the scattering process, which is called resonant phonon scattering. This requires the initial and final in-plane electron momenta be the same and the intersubband energy separation be the same as the LO phonon energy \( \hbar \omega_{\text{LO}} \) as can be seen in Equations V.7 and V.11. The quantum cascade lasers utilizes this fast (\( \sim 0.1 \) ps) resonant phonon scattering to quickly drain electrons from the lower subband, which improves the population inversion and thus the laser gain.\(^{66}\)

So far, we have considered only the zero temperature case where only spontaneous phonon emission is possible. At a finite temperature, the stimulated phonon emission process by ambient phonons should exist as well as the phonon absorption process. The stimulated phonon emission process is accounted for by the thermal phonon occupancy at a temperature, \( T \), given by the Bose factor

\[
\frac{1}{e^{\hbar \omega_{\text{LO}} / k_B T} - 1}
\]  

(V.14)

Thus the total phonon emission rate is given by the spontaneous rate in Equation V.12 times \(( n_{\text{ph}} + 1 )\). For the phonon absorption process, we should use the (-) sign in the energy conservation relation of Equation V.7, which gives a different \( k_{f\perp} \) from the phonon emission process for the same \( k_{i\perp} \). However, if the phonon energy (\( \sim 36 \) meV) is much smaller than the intersubband spacing, the phonon scattering can be approximated as an elastic process neglecting the phonon energy transfer to simplify the calculation. The phonon absorption process then adds another factor of \( n_{\text{ph}} \) to the total scattering rate which is written as
\[
\frac{1}{\tau_f(T)} = \frac{1}{\tau_f(T = 0)} \cdot (2n_{ph} + 1). \tag{V.15}
\]

\(\hbar \omega_{LO}\) (36 meV in GaAs) corresponds to 415 K and \(n_{ph}\) is equal to 0.335 at room temperature (300 K). Thus the lifetime at room temperature will be shorter than at zero temperature by a factor of 1.67.

We developed a computer program to calculate the LO phonon scattering time in QWs according to the formulation described above. The initial and final electron wavefunctions are obtained by the method described in Chapter II and the band nonparabolicity is taken care of by the energy dependent effective mass model. Figure V.2 represents intersubband energy (\(E_{12}\)) and scattering time (\(\tau_{12}\)) for GaAs / Al\(_{0.3}\)Ga\(_{0.7}\)As QWs with varying well width (\(L_w\)) which agrees well with Ferreira and Bastard's calculation. The LO-phonon scattering time at zero temperature was calculated by Equation V.12, from which the scattering time at 300 K is calculated by Equation V.15. Short lifetimes below one pico-second are exhibited for wide QWs and this increases up to a few pico-seconds for narrower QWs. The increase of \(\tau_{12}\) with decreasing well width is because a large intersubband energy requires a large phonon momentum scattering process and phonon emission with a large momentum change is slow according to the Equation V.12. At \(L_w = 180\ \text{Å}\), the intersubband energy is very close to the LO-phonon energy (36 meV) where the momentum transfer during the scattering event and the scattering time is very small (\(\sim 0.15\ \text{ps at zero temperature}\)). As the well width approaches 50 Å, the second subband energy increases close to the barrier energy and the wavefunction is loosely confined in the well and the overlap with the ground state wavefunction becomes small, which causes a rapid increase of \(\tau_{12}\).
Figure V.2. Calculated intersubband lifetime (solid line) and transition energy (dotted line) vs. well width in a GaAs/Al$_{0.3}$Ga$_{0.7}$As QW.

V.2. Intersubband pump-probe experiments

There has been a large amount of work, both theoretical and experimental, to investigate intersubband electron relaxation. Various experimental techniques have been used to determine electron lifetimes in upper subbands which are distributed from a few hundred femto-second to tens of pico-second. Most of them identify the LO-phonon scattering as the dominant relaxation mechanism. Recent experiments appear to consistently yield lifetimes on the order of hundreds of femtoseconds or a picosecond depending on the sample structure and temperature, which agree well with the theory. Among various experimental techniques, such as time-resolved Raman scattering\textsuperscript{67}, intersubband\textsuperscript{68} and interband\textsuperscript{69} pump-probe, CW saturation\textsuperscript{70}, and excited state spectroscopy\textsuperscript{71}, we use the
intersubband pump-probe technique to resolve excited carrier relaxation in an upper subband. This technique uses two temporally separated pulses with picosecond or sub-picoseconds temporal width; one (pump pulse) for exciting carriers to upper states and the other (probe pulse) for probing carrier dynamics which gives a direct measure of the carrier decay from the upper state.

We used the Stanford FEL for the single color intersubband pump-probe experiment to measure QW intersubband lifetime. The pump-probe setup was built by C. Rella in Prof. A. Schwettman’s group. Before describing the experiment we have done with samples with bound and quasi-bound states, we will briefly describe the theory of pump-probe measurements followed by a description of the pulse structure and the optical setup for the pump-probe measurements.

V.2.1. Pump-probe theory

The principle of the pump-probe experiment is straightforward: A fast optical pulse excites carriers to the upper state bleaching the absorption line. A delayed probe pulse then monitors the recovery of the bleaching. Actually, the data we record are normalized differential transmission at each relative delay \( t \), \( \frac{T(t) - T_0}{T_0} \), where \( T_0 \) is the reference transmission before the bleaching. If we assume no thermally populated excited carriers and a \( \delta \)-function like pump pulse hitting the sample at \( t = 0 \), the number of carriers in the excited state with a lifetime \( T_1 \) is given by

\[
n_{ex}(t) = \begin{cases} 
0 & \text{if } t < 0 \\
n_0 \exp \left( -\frac{t}{T_1} \right) & \text{if } t > 0 
\end{cases} \quad (V.16)
\]
where \( n_0 \) the number of the instantaneous excited carriers proportional to the pump intensity. If the excited carriers are not a significant fraction of the total carriers, the absorption due to the ground carriers is proportional to their number, i.e.

\[
A(t) \propto n_g(t) = n_{g0} - n_{ex}(t). \tag{V.17}
\]

Then the differential transmission is given by

\[
\frac{T(t) - T_0}{T_0} \propto A_0 - A(t) \propto n_0 \exp\left(-\frac{t}{T_1}\right). \tag{V.18}
\]

Thus the differential transmission exhibits an exponential decay with a time constant \( T_1 \). In reality, however, the pump and probe pulses have finite temporal pulse widths, which can be typically described by a Gaussian pulse given by

\[
I(t) = I_0 \exp\left(-\frac{t^2}{\tau^2}\right). \tag{V.19}
\]

In this case, it is after a few pulse widths of delay that the signal starts to show the exponential decay of Equation V.18. Thus it is important to have a short pulse width at least comparable to \( T_1 \). Otherwise, the signal becomes very weak and the signal to noise ratio very poor by the time it exhibits the exponential decay.

V.2.2. Experimental setup

As mentioned above, intersubband pump-probe lifetime measurement requires a short pulse mid-IR laser with a pulse duration on the order of 1 ps. However, obtaining and maintaining such short optical pulses in mid-IR wavelengths is not a trivial task. Fortunately, we have been privileged to use the pump-probe setup in the Stanford Free
Electron Laser (FEL) facility built by Prof. A. Schwettman’s group. The Stanford FEL is driven by a superconducting linear accelerator and generates widely tunable (3 - 10 μm) mid-IR optical pulses. The temporal width of each pulse is in the 0.8 - 1.2 ps range and they come in bunches called “macropulses” which last about 2 ms and repeat at 10 Hz. The repetition rate of pulses in a macropulse is 11.8 MHz or the interval between pulses is 84.7 ns which is long enough for an acousto-optic modulator (AOM) to pick appropriate pulses to be used as pump and probe pulses. The maximum energy per pulse is about 1 μJ, which gives about 1MW peak power. This high peak power allows significant bleaching of the population and a good signal to noise ratio.

The experimental setup is shown in Figure V.3. Two adjacent pulses are selected among a FEL pulse train by a germanium AOM. A low-reflection beamsplitter divides these pulses into two parts; the reflected pulses for probe beams and the transmitted ones for the pump beam. The transmitted pulse is about 20 times stronger than the reflected pulse. The second AOM selects a single pulse out of the transmitted pulses, which becomes the pump pulse. The pump pulse comes to the sample between the two probe pulses with a variable delay caused by a moving mirror. The leading pulse of the two probe pulses is called a pre-probe which hits the sample before the pump pulse and provides a reference transmission to the subsequent probe pulse. Transmitted pre-probe and probe pulses from the sample are detected by a fast detector and the signals are integrated separately by two boxcar averagers whose outputs are fed into a differential amplifier to record the differential transmission as a function of delay between the probe and pump pulses.
Next two sections describe pump-probe experiments we have done on two kinds of samples. The first sample is a square MQW structure which has both the ground and excited states confined in the QW region (bound/bound sample). The second sample has Bragg mirror layers on both sides of a QW and the ground state is a bound state and the excited state is located above the barrier potential and confined by the electron Bragg mirrors (bound/quasi-bound sample). Both sample structures were designed to be resonant at around 5 µm. All pump-probe experiments were performed in collaboration with G. L. Woods who was then a student in Prof. Fejer's group.

V.3. Intersubband lifetime measurements

V.3.1. Bound/bound sample

We have tested 3 bound/bound samples which have the same structure but different doping levels as summarized in Table V.1. The basic structure of each sample is multiple
symmetric quantum wells with a 58.5 Å In$_{0.5}$Ga$_{0.5}$As layer for the well and an 100 Å Al$_{0.45}$Ga$_{0.55}$As layer for the barrier. The large strain due to lattice mismatch between the well and barrier layers are relieved by a linearly graded buffer under the MQW layer, which was described in detail in the previous chapter. The conduction band edge diagram and the bound states of the QW are illustrated in Figure V.4. The sample was designed to have a 1-2 transition at about 5 μm. Absorption spectra taken from sample #4009 at room temperature and 77 K are shown in Figure V.5. We can see a blue shift of the peak energy and reduced linewidth at low temperature which can be explained by various many-body effects, including depolarization shift, exciton-like shift, and exchange effect in addition to sharpening of the Fermi distribution at a low temperature. The calculated lifetime for this sample structure is 0.8 ps at room temperature and 1.3 ps at 0 K.

Table V.1. Bound/bound samples for intersubband lifetime measurements. The carrier density was measured by Hall measurement. Other data were extracted from absorption spectra. The absorption cross-section, σ, and saturation fluence, $U_{sat}$, are for Brewster's angle incidence and TM-polarized light.

<table>
<thead>
<tr>
<th>sample</th>
<th># of wells</th>
<th>doping per well (cm$^{-2}$)</th>
<th>$z_{12}$ (Å)</th>
<th>peak energy (meV)</th>
<th>$\lambda_{peak}$ (μm)</th>
<th>HWHM (meV)</th>
<th>$\sigma_{peak}$ (Å$^2$)</th>
<th>$U_{sat}$ (μJ/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4009</td>
<td>75</td>
<td>5.8e11</td>
<td>11.9</td>
<td>250</td>
<td>4.96</td>
<td>11.0</td>
<td>10.5</td>
<td>38</td>
</tr>
<tr>
<td>4103</td>
<td>100</td>
<td>3.4e11</td>
<td>12.0</td>
<td>260</td>
<td>4.77</td>
<td>9.2</td>
<td>12.8</td>
<td>33</td>
</tr>
<tr>
<td>4130</td>
<td>100</td>
<td>1.9e12</td>
<td>11.1</td>
<td>245</td>
<td>5.06</td>
<td>12.5</td>
<td>7.6</td>
<td>52</td>
</tr>
</tbody>
</table>
Figure V.4. Conduction band diagram and calculated ground and the first excited states of the bound/bound sample. The 1-2 transition is resonant at around 5 μm.

Figure V.5. Absorption spectra of sample #4009 at room temperature and liquid nitrogen temperature.
Figure V.6. Pump-probe data taken on sample #4013 at its absorption peak wavelength 4.99 µm. The pump fluence was 1.9 µJ/cm². Also shown is a single exponential fit with a time constant τ = 1.45 ps.

Typical pump-probe data are plotted in Figure V.6 which represents the recovery of the intersubband absorption bleaching by a pump pulse as a function of probe delay. A lifetime of 1.45 ps was obtained for a pump intensity of about 2.3 MW/cm² at the peak absorption wavelength (4.99 µm) in sample #4009. This lifetime turned out to depend on the pump intensity as shown Figure V.7. We used the term "fluence" instead of intensity because we are dealing with pulses shorter than the intersubband lifetime.62 Fluence is defined by the energy in a pulse per unit area. For such a short pulse, the fluence is a more relevant factor than the intensity because a sample should respond to the total energy contained in the pulse rather than to the intensity. The pump fluence in Figure V.7 was calculated by dividing the pulse energy with the "effective area" which was measured by a
pin hole in the sample plane: for a pin hole of diameter $D$ which transmits a fraction $r$ of the beam, the Gaussian beam waist parameter is $w_0^2 = -D^2 / 2\ln r$ and the effective area is defined as $A_{\text{eff}} = \pi w_0^2 / 2$.

![Graph](image)

Figure V.7. Intersubband lifetime ($\tau$) vs. pump fluence in sample #4009, measured at room temperature with pump and probe wavelengths at the absorption peak (4.99 μm). Data represented by solid circles and open circles were taken from different shifts.

From Figure V.7, we find that the intersubband lifetime stays around 1.5 ps at low fluence and increases up to 3.5 ps at higher fluence. The boundary turned out to be the saturation fluence, defined by $U_{\text{sat}} = \hbar \omega / \sigma$, which is about 40 μJ/cm² for Brewster's angle incidence at the peak absorption wavelength 4.99 μm for sample #4009. Since this effect occurs near the saturation fluence, we suppose the cause to be a carrier heating effect: if a significant fraction of lower subband carriers are pumped into the upper subband and they relax back to the lower subband, a hot carrier gas is created in the lower subband which is subject to the Pauli blocking and phonon re-absorption against the intersubband

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and subsequent intrasubband relaxation increasing the effective lifetime.\textsuperscript{73} Other groups have also observed increased lifetime at high pump fluence\textsuperscript{74} but the mechanism is not yet fully understood. In order to avoid these unwanted carrier heating effects, we used pump fluences as small as possible for most of measurements reported below.

Even at very low pump fluences, the measured lifetime \( \approx 1.5 \) ps is much longer than the theoretical prediction of 0.8 ps based on intersubband LO phonon scattering theory. A clear explanation of this discrepancy requires more detailed experimental and theoretical work. It is possible that the bleaching recovery involves not only the intersubband scattering but also intrasubband scattering. If the phonon emission is also the main mechanism for the intrasubband relaxation, it requires about six intrasubband phonon emission steps for the electrons to return to the thermal equilibrium Fermi sea. Intrasubband phonon emission takes about 100 fs at room temperature, thus the total recovery time is given as roughly \( 0.8 \) ps + \( 6 \times 0.1 \) ps = 1.4 ps.

Lattice temperature also affects the scattering rate and lifetime as well as the carrier temperature because phonon occupancy depends strongly on the lattice temperature. As shown in Equations V.14 and V.15, the phonon scattering rate at room temperature is greater by about 70 \% than that at zero temperature due to the higher phonon occupancy at higher temperature. The temperature dependence of the lifetime was investigated on several samples in a liquid nitrogen cryostat. This is summarized in Table V.2, where the lifetime at low temperatures only increases by about 20 \% compared to that at room temperature. This means that the intersubband absorption recovery in this experiment cannot be explained by intersubband LO-phonon scattering theory alone.\textsuperscript{75} If we assume that subsequent intrasubband scattering plays a role, which may be a fairly temperature-insensitive process, such as carrier-carrier scattering, then the intersubband lifetime should not be strongly temperature dependent as expected from the intersubband LO-phonon
theory. Further experiments which separate intersubband and intrasubband relaxation should help explain the temperature dependence of intersubband relaxation more clearly.

Table V.2. Temperature dependence of intersubband lifetime of three samples with different doping densities.

<table>
<thead>
<tr>
<th>sample</th>
<th>temperature (K)</th>
<th>peak wavelength (µm)</th>
<th>pump-probe wavelength (µm)</th>
<th>decay time $T_1$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4009</td>
<td>300</td>
<td>4.99</td>
<td>4.99</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>4.85</td>
<td>4.85</td>
<td>1.7</td>
</tr>
<tr>
<td>4103</td>
<td>300</td>
<td>4.95</td>
<td>4.99</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>4.75 (est.)</td>
<td>4.99</td>
<td>1.7</td>
</tr>
<tr>
<td>4130</td>
<td>300</td>
<td>5.06</td>
<td>4.99</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>5.0 (est.)</td>
<td>4.99</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The doping dependence of the intersubband lifetime was investigated on three samples with $n_s = 3.4 \times 10^{11}$ cm$^2$, $5.8 \times 10^{11}$ cm$^2$ and $1.9 \times 10^{12}$ cm$^2$, respectively. The absorption peak energy of these samples red-shifted for higher doping. Pump-probe experiments were performed at a pump and probe wavelength of 4.99 µm which is the peak absorption energy of sample #4009. The pump fluence was kept well under the saturation limit and the results are summarized in Table V.3. The lowest doped sample shows the shortest lifetime, but all values are within one error bar of each other. Thus we see no significant doping dependence of the intersubband lifetime from these well-doped samples. Pump-probe experiments on well-doped vs. modulation doped samples would be rather interesting and might reveal the role of ionized impurity scattering if the dominant
phonon scattering is suppressed, for instance, at a low temperature and for intersubband energies less than the LO-phonon energy.

Table V.3. Doping dependence of intersubband lifetime.

<table>
<thead>
<tr>
<th>sample</th>
<th>doping (cm$^{-2}$)</th>
<th>peak wavelength (µm)</th>
<th>decay time $T_1$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#4103</td>
<td>3.4e11</td>
<td>4.85</td>
<td>1.4 ± .2</td>
</tr>
<tr>
<td>#4009</td>
<td>5.8e11</td>
<td>4.99</td>
<td>1.5 ± .1</td>
</tr>
<tr>
<td>#4130</td>
<td>1.9e12</td>
<td>5.06</td>
<td>1.45 ± .1</td>
</tr>
</tbody>
</table>

V.3.2. Bound/quasi-bound sample

After we had done detailed studies on intersubband relaxation between bound states, our interest moved to quasi-bound states which are created over the barrier potential energy by electron mirror layers. As we discussed in Chapter 3, these states are spatially localized in the QW region by the $\lambda/4$ electron mirrors which act as a Fabry-Perot resonator for particular energy states reflected by the superlattice mirrors on either side of the QW. However, the envelope function of a quasi-bound state spreads more broadly than a bound state, which should differentiate the intersubband relaxation process of the quasi-bound state from those of the bound state. Below, we describe the intersubband lifetime measurements performed on a quasi-bound state sample. This is the first reported time domain lifetime measurement on a quasi-bound upper state.
The quasi-bound sample (#3917) is composed of GaAs/Al_{0.45}Ga_{0.55}As QWs and two periods of electron mirror layers on both sides of each QW. The sample was n-type doped in the well to a nominal (measured) carrier density of $7.0 \times 10^{11}$ cm$^{-2}$ ($6.7 \times 10^{11}$ cm$^{-2}$). A conduction band diagram and wavefunctions for the sample are shown in Figure V.7. The 35 Å GaAs QW layer has only one bound state at $E_1 = 125$ meV above the well conduction band edge. The electron mirror layers composed of GaAs (17.5 Å) / Al_{0.45}Ga_{0.55}As (46.9 Å) create a first quasi-bound state 45 meV above the barrier conduction band edge, where the mirror layer thickness is $\lambda/4$ of the electron wavelength of the quasi-bound state. The observed transition energy and dipole moment were $E_{12} = 253$ meV and $z_{12} = 11.0$ Å, and thus $U_{sat} = 14 \mu$J/cm$^2$. Since the electron wavefunction of the quasi-bound state extends further into the barrier region than that of a bound upper state, the overlap with the ground state decreases and hence the lifetime for the quasi-bound state is expected to be longer than that of a bound upper state because the phonon emission rate is proportional to the overlap integral between the upper and lower states. The predicted lifetime of the quasi-bound state by direct decay to the ground state in this sample was 3.3 ps at 0 K (2.1 ps at 300 K) which is about 3 times longer than the previous bound state sample with almost the same transition energy. In addition to the ground state, four other bound states are created by coupling between side wells in the mirror layers, which are concentrated in each side well as shown in Figure V.8. These states have small, but finite overlap with the ground and quasi-bound states (dipole moments are about 3 - 5 Å.) and thus they should play a role in the carrier relaxation from the quasi-bound state to the ground state. The electron relaxation time for the indirect decay through these miniband states was calculated to be about 18 ps at 0 K (11 ps at 300 K). This indirect decay is much slower than the direct decay due to the small overlap of the coupled miniband states to the quasi-bound and ground states.
Figure V.8. Conduction band diagram of sample #3917 whose bound to quasi-bound transition is resonant at around 5 μm. Electrons in the upper quasi-bound state relax to the ground state through two paths: direct decay from the quasi-bound state to the ground state and indirect decay via coupled states from the λ/4 electron mirrors.

Figure V.9 illustrates the pump-probe data taken from the quasi-bound sample #3917 at room temperature with the pump and probe wavelength of 5 μm. The data shows a bi-exponential decay with two time constants; an initial time constant of 3.6 ps and a second time constant of 20 ps. These time constants are in the same order as the predicted time constants of direct relaxation from the quasi-bound state and the two-step process through the miniband states, respectively. Thus we can infer that the short time constant is due to the direct decay and the long time constant due to the miniband-mediated process. However, the observed time constants are much longer than the predicted values for room temperature based on LO-phonon scattering theory, even considering the carrier cooling
time in the ground state. However, we should point out several problems with this measurement which may explain the discrepancy between the theory and experiment.

![Graph showing bi-exponential decay](image)

Figure V.9. Pump-probe data on sample #3917 showing a bi-exponential decay.

First of all, an extremely high pump fluence (200 μJ/cm²) was used to get a sufficient signal to noise ratio. This was about 14 times higher than the calculated $U_{sat}$. As discussed in the previous section, a high pump fluence causes excessive carrier heating, which results in longer bleaching recovery. The other point to note is that the upper quasi-bound state is above the $X$ valley edge of the barrier ($Al_{0.45}Ga_{0.55}As$) in which $\Gamma$ and $X$ valley edges have about the same energy. We might expect very fast intervalley scattering in this case. Actually, we did a single beam saturation measurement on this sample using a z-scan technique in which the sample transmission was recorded with respect to the
position through the beam waist. The saturation intensity at Brewster’s angle incidence was about 100 MW/cm², which gave an upper state lifetime of 150 fs in terms of short pulse saturation. This fast lifetime should correspond to the fast intervalley scattering which is too fast to measure with the FEL pulses. Then the initial and second time constants measured by the probe pulse should correspond to the direct decay to the ground state and indirect decay via the miniband states from the upper quasi-bound state after scattering back from the X valley.⁷⁴ Carrier cooling in the ground state also takes a long time due to the excessive heating by the high intensity pump which is probably the main cause of the discrepancy between the prediction and measurement. Possible improvements for a future experiment are to use a lower aluminum fraction in the barrier and lower pump intensity to avoid unnecessary intervalley scattering and carrier heating. In order to get decent signal to noise ratio with a low pump intensity, a prism coupling or 45°-polished side facet incidence may be needed to increase the electric field coupling of light to the ISBT since the Brewster’s angle incidence yields a very small Eₚ, thus the intersubband absorption to a quasi-bound state is small.

V.4. Intersubband absorption saturation experiments

So far, we have discussed time domain pump-probe experiments to resolve intersubband lifetime in bound and quasi-bound states, which requires short laser pulses comparable to the intersubband lifetime. On the other hand, it is also possible to infer an upper state lifetime by measuring the saturation intensity of the sample using long pulses or CW lasers. In this section, we discuss saturation intensity measurements performed on the bound and quasi-bound samples, #4009 and #3917. This work was done in collaboration with Dr. K. Vodopyanov of Imperial College in London.⁶³,⁶⁴
In a two-level system with homogeneous line broadening, the local absorption $\alpha$ depends on incident intensity, $I$ as$^{26}$

$$\alpha(I) = \frac{\alpha_0}{1 + I/I_{\text{sat}}} \quad \text{(V.20)}$$

where $\alpha_0$ is the unsaturated absorption. The absorption significantly decreases beyond the saturation intensity given by

$$I_{\text{sat}} = \frac{h\omega}{2\sigma T_1} \quad \text{(V.21)}$$

where $\sigma$ is the optical cross section and $T_1$ is the upper state lifetime. Thus the upper state lifetime can be obtained by measuring the saturation intensity. The actual saturation behavior of ISBTs should be more complicated than this simple model because QW subbands are not just simple discrete two-level systems but continuous energy bands with respect to a proper $k$-vector. However, all the authors performing the QW intersubband saturation experiments, to our knowledge, have used this simplistic model and we also employ this simplistic model to estimate the intersubband lifetime from saturation behavior.

Since the lifetime, $T_1$, depends strongly on the optical cross section and the saturating laser intensity, it is very important to accurately measure these values. The optical cross section, $\sigma$, is obtained from the absorption measurement according to the following relation.

$$\sigma(\theta_i) = \frac{\text{Absorbance} \cdot \cos(\theta_i) \cdot \ln 10}{n_s N} \quad \text{(V.22)}$$
where $\theta_i$ is the angle of incidence internal to the wafer, $n_s$ is the sheet electron density per QW, and $N$ is the number of QWs. $\theta_i = 17^\circ$ and $45^\circ$ in the Brewster’s angle incidence and normal incidence waveguide geometries, respectively.

One thing to note about the saturation intensity is that the actual intensity which saturates the absorption in the sample is different from the measured external intensity. The relation between the external laser intensity, $I_{\text{ext}}$, and the “acting” intensity, $I_z$, in the sample depends on the experimental geometry. In the Brewster’s angle geometry, where the Fresnel reflection for TM-polarization is zero and $\theta_c = 73^\circ$ and $\theta_i = 17^\circ$ in Figure II.5, we have

$$\frac{I_z}{I_{\text{ext}}} = \sin^2 \theta_i \cos \theta_c = \sin^3 \theta_i = \frac{1}{(n_s^2 + 1)^{3/2}} = 0.025$$  \hspace{1cm} (V.23)

whereas in the $45^\circ$-incident waveguide geometry, we have

$$\frac{I_z}{I_{\text{ext}}} = \sin 45^\circ \cos 45^\circ (1 - R) = 0.25$$ \hspace{1cm} (V.24)

where $R$ is the Fresnel reflection loss of 29%. In the above two equations, sine terms account for the z-component of the E-field inside the sample and cosine terms for the area increase in the beam cross section for the QW layers due to oblique incidence. Thus the acting intensity in the $45^\circ$ waveguide geometry is about a quarter of the measured external intensity, which is higher than in the Brewster’s angle geometry by a factor of 10.
The light source to saturate the QW samples was a widely tunable (λ = 3 - 10 μm) optical parametric generator (OPG) based on a ZnGeP₂ crystal \(^{76}\) which was pumped by 100 ps pulses (λ = 2.8 μm) from a Q-switched Er:Cr:YSGG laser-amplifier system with a repetition rate 3 Hz. The OPG pulses with energies of 10 μJ and 90 ± 15 ps pulse duration were tuned to the intersubband absorption peak of each sample and focused onto the sample achieving a peak intensity up to \(10^9 - 10^{10}\) W/cm\(^2\). The sample transmission was then measured as a function of the incident light intensity over three decades of dynamic range using both z-scan and attenuating filter methods. The 45° wedge waveguide geometry described in Section II.5 was used with 4 bounces inside the sample. The sample transmission was normalized by ratioing the TM-polarized (polarization in the plane of incidence) to the TE-polarized (polarization in the plane of the QW layer) spectra and all the measurements were performed at 300 K.

Figure V.10 shows integral intersubband absorption as a function of peak incident light intensity. Also shown are theoretical curves, where the local absorption given by

\[
\alpha(I) = \frac{\alpha_0}{1 + I(x,y,z,t)/I_{\text{sat}}} \tag{V.25}
\]

was integrated over time and three space coordinates with the single fitting parameter, \(I_{\text{sat}}\), the external saturation intensity. We assumed a Gaussian intensity distribution in time and spatial cross section. The best fits in Figure V.10 were obtained with \(I_{\text{sat}} = 9.7\) MW/cm\(^2\) and 6.8 MW/cm\(^2\) for #4009 and #3917, respectively, which yielded an upper state lifetime of 0.6 ps and 1.4 ps, respectively, from Equation V.21. Theoretical intersubband lifetimes at room temperature were 0.8 ps and 1.8 ps for samples #4009 and #3917, respectively. The lifetime for #3917 (1.8 ps) is the combination of direct decay from the quasi-bound
state (2.1 ps) and indirect decay through the coupled states (11 ps). One important thing to note for calculating the lifetime for the multi-bounce waveguide geometry is the standing wave effect of the incident beam, which was discussed in Section II.5. This may not significantly change the linear absorption if the MQW layer is thick compared to the wavelength of the incident light inside the sample. The MQW layer thickness is more than two times of the wavelength inside the sample for both samples, thus the effective saturation intensity needs to be corrected when there are crests and nodes of intensity in the sample due to interference because the QWs near crests see a much higher intensity than the external intensity. We modeled this effect numerically and found that the effective $I_{\text{sat}}$ were about 2.8 times that of $I_{\text{ext}}$.

Figure V.10. Intersubband absorption saturation data on bound/bound and bound/quasi-bound samples. Solid curves are theoretical best fit.
V.5. Pump-probe vs. saturation experiments

Intersubband lifetimes deduced from the saturation intensity, 0.6 ps and 1.4 ps, are close to the theoretical values, 0.8 ps and 1.8 ps for samples #4009 and #3917 respectively, whereas the pump-probe experiments yielded much longer decay times. We attributed the long decay time from the pump-probe experiments to the subsequent intrasubband scattering which brings the hot electrons back to the equilibrium Fermi distribution after the initial intersubband scattering. We reached this conclusion because the exponential decay of #4009 was much slower than predicted and the temperature dependence did not conform to the single LO-phonon emission model. Then the question is, why does the saturation intensity yield a shorter time constant, which agrees better with the theory than the pump-probe measurement? The key difference between the pump-probe and saturation experiments is the pulse length of the excitation light source. In the pump-probe experiment, the time domain data were taken with short pulses compared to the lifetime for LO phonons to decay into acoustic phonons which is about 5 ps and were referenced to the transmission prior to the pump pulse excitation. Thus they should be able to show the time constant slowed by the carrier cooling process. However, in the saturation experiment with much longer laser pulses of about 100 ps, the phonon gas should essentially be at the lattice temperature, making the phonon re-absorption insignificant and then the intersubband scattering should be the most significant absorption limiting factor at high laser intensity. In order to verify this hypothesis, a few improvements need to be made in future experiments such as careful measurements of lattice temperature vs. saturation intensity and using a two-color pump-probe system, one color for the intersubband excitation and the other for the interband probe to resolve intrasubband relaxation.75
Chapter VI. Conclusion

In this chapter, the work of this thesis is first summarized, followed by suggestions possible future directions.

VI.1. Summary

In Chapter III, we discussed above-barrier and quasi-bound states which are extended and localized states at energies higher than the barrier potential. Not being confined by potential barriers, above-barrier states are allowed at continuous energies and yield oscillator strengths distributed over a wide range of energies which lead to a broad and asymmetric absorption peak. Extended above-barrier states are confined and localized in the well region by “electron mirrors” which are periodic potential $\lambda/4$ grating layers on both sides of the quantum well and cause the Bragg reflection of electron waves at each interface. These confined above-barrier states called, “quasi-bound” states, were solved in the Kronig-Penney model in which the quasi-bound states are given as minigap states satisfying the boundary conditions across the quantum well region. The energy of a quasi-bound state for the same quantum well varies significantly with the design of the electron mirror layers because the quasi-bound states are strongly dependent on the potential grating period of the electron mirrors: a shorter mirror period creates a higher quasi-bound state. This property was used to produce large intersubband energies by lifting the quasi-bound state up and keeping the ground state at the same low energy as the mirror layers narrow. For 40 Å GaAs / Al$_{0.3}$Ga$_{0.7}$As quantum wells, an intersubband energy greater than the well depth was achieved by stacking narrow mirror layers. However, quasi-bound states yield smaller dipole moments and absorption strengths as the energy becomes higher because they are spatially less localized and also create additional mini-band states below the barrier.
In Chapter IV, we discussed short wavelength intersubband transitions in InGaAs / AlGaAs quantum wells on GaAs substrates. Indium was introduced into the well layer to deepen the potential well and increase the intersubband energies. Unfortunately, this also causes a lattice mismatch and hence strain between the well and barrier layers. In order to overcome the strain problem, we used a special growth technique of growing a thick linearly graded InGaAs buffer layer up to approximately the average indium composition of the quantum well period. Defects (mostly misfit dislocations) created by lattice relaxation are buried in the thick graded buffer layer and a final constant composition buffer layer acts as a defect free substrate with an intermediate lattice constant, which relieves the strain and also gives strain compensation between the well and barrier layers. High quality InGaAs / AlGaAs quantum wells yielding narrow transition linewidths were grown with optimized growth conditions for substrate temperature, indium grading rate, and interface smoothing layers. Above-barrier and quasi-bound states were utilized in narrow In_{0.5}Ga_{0.5}As / Al_{0.45}Ga_{0.55}As quantum wells to get a high intersubband energy transition of 460 meV (2.7 μm). A higher 1-2 transition energy could be achieved using quasi-bound states in deeper quantum wells. The main limitation is precisely controlled growth of very thin layers of a few monolayers. Deeper quantum wells consisting of In_{0.5}Ga_{0.5}As / AlAs or In_{0.6}Ga_{0.4}As / AlAs yielded 1-2 transition energies as large as 720 meV (1.72 μm). A higher transition energy (780 meV, 1.59 μm) was obtained from a 1-4 transition in an asymmetrically coupled quantum well sample which is doubly resonant for DFG at 8.83 μm from 1.55 μm and 1.88 μm pumps and should have large $\chi^{(2)}$ for output wavelengths of 7 - 13 μm (more than 10 times the $\chi^{(2)}$ calculated for bulk GaAs).
In Chapter V, we performed a theoretical derivation of an intersubband LO phonon scattering time followed by intersubband carrier lifetime and absorption saturation intensity measurements. A pump-probe technique which detects the recovery of absorption bleaching was used to measure intersubband lifetimes from bound or quasi-bound upper states. The bound sample consists of 58.5 Å In_{0.5}Ga_{0.5}As / Al_{0.45}Ga_{0.55}As quantum wells and the quasi-bound sample consists of 35 Å GaAs / Al_{0.45}Ga_{0.55}As quantum wells with electron mirror layers on both sides to confine the above-barrier states. 1-2 transitions for both samples are resonant at around 5 μm. We observed a single exponential decay from the bound sample at room temperature with a time constant \( \tau = 1.45 \) ps which increased with the pump intensity above the saturation intensity, probably due to carrier heating effects. The quasi-bound sample at room temperature exhibited a bi-exponential decay with \( \tau_1 = 3.6 \) ps and \( \tau_2 = 20 \) ps where the fast and slow decays were attributed to direct relaxation from the quasi-bound to the ground states and to indirect relaxation through coupled states of the side wells in electron mirror layers, respectively. However, these measured values are much larger than theoretical values based on the LO-phonon scattering theory which predicts \( \tau = 0.8 \) ps for the bound sample and \( \tau_1 = 2.1 \) ps, \( \tau_2 = 11 \) ps for the quasi-bound sample at room temperature. This discrepancy indicates that the measured lifetimes are not fully accounted for by the intersubband LO-phonon scattering alone, which also could be inferred from the temperature dependence of the measured lifetime of the bound sample, as it was much weaker than expected from the LO-phonon scattering theory. This might be explained by significant contribution of carrier cooling processes in the lower subband due to various intrasubband scattering mechanisms which are not very sensitive to temperature.\(^{73,75}\) In addition to the carrier cooling contribution, intervalley scattering into the Al_{0.45}Ga_{0.55}As barrier in the quasi-bound sample may also affect the carrier relaxation from the upper quasi-bound state. Intersubband lifetimes for these samples were also obtained from absorption saturation experiments where lifetime can be
inferred from the saturation intensity. A high intensity pulsed laser with a temporal pulse width of about 100 ps was used to saturate the intersubband absorption and the upper state lifetimes were extracted from the saturation intensities. The lifetimes were 0.6 ps and 1.4 ps for the bound and quasi-bound samples, respectively. These values are close to the theoretical values for intersubband LO-phonon scattering time whereas the pump-probe experiments yield much longer lifetimes. The differences were explained by the excitation laser pulse widths used in the two experiments. In the pump-probe experiment using pulses comparable to the LO-phonon emission time, the probe pulse should see the absorption recovery due to both the initial intersubband LO-phonon scattering and subsequent intrasubband scattering in the lower subband. The observed time constant was explained by the combination of the intersubband LO-phonon scattering and intrasubband scattering which bring the excited carriers back to the thermal equilibrium prior to the pump beam excitation. On the other hand, in the saturation experiment using much longer pulses, the carriers in the lower subband are basically at thermal equilibrium of the hot carriers during the saturating laser pulse duration and hence intersubband relaxation due to LO-phonon emission will be the dominant factor in determining the saturation intensity.

VI.2. Future work

VI.2.1. Intersubband nonlinear optical device

Even though quantum well intersubband transitions yield very large $\chi^{(2)}$ for SHG and DFG, this alone is not sufficient to achieve efficient frequency conversion in a compact device. As discussed in Chapter 2, quasi-phaseshifting and waveguide structures are necessary to maintain high optical field intensities over long interaction lengths. Quantum well design and processing technology offers degrees of freedom to optimize a waveguide structure for desired wavelengths. Quasi-phaseshifting to periodically modulate $\chi^{(2)}$ in non-birefringent QW structures can be obtained by several technique, such as periodic sign
reversal by electric field bias or periodic turn-off by proton bombardment. For QW ISBTs, however, resonant enhancement of $\chi^{(2)}$ causes high absorption losses. Thus an ordinary collinear waveguiding scheme where both pump and output beams are confined collinearly along the waveguide would result in significant losses of pump and/or output beams, which is detrimental to conversion efficiency. In order to overcome this loss problem, a non-collinear scheme, called the Cerenkov geometry, where either the pump or output beams radiate at an angle from the waveguide is a better approach. In this case, the radiating beam suffers less loss because of a shorter interaction length and the QW should be designed to cause small loss to the other guided beams. A detailed study on the Cerenkov waveguide device can be found in G. L. Woods’ dissertation.\textsuperscript{62} Figure VI.1 shows a Cerenkov geometry device for DFG where the output beam at $\omega_3$ is radiating. This device has a significant advantage in not requiring a waveguide for the long wavelength output which is far more difficult to grow by MBE due to the thick layers needed. The peak efficiency for this Cerenkov geometry for DFG generation of 9 $\mu$m output by mixing two pumps around 2 $\mu$m was estimated to be about 30 % / W.\textsuperscript{77} This is a very high conversion efficiency comparable to the peak conversion efficiency for SHG at a much shorter wavelength in a periodically poled lithium niobate (PPLN) quasi-phasematching waveguide.\textsuperscript{80} Unfortunately, the PPLN waveguide is not transparent for wavelengths longer than 5 $\mu$m and thus is not useful for the wavelengths of our interest.
VI.2.2. Linewidth study

To maximize the QW nonlinearities or frequency conversion efficiencies, transition linewidths should be minimized as clearly illustrated in Equation II.29. Thus understanding linewidth broadening mechanisms for ISBTs is very important. ISBT linewidth broadening is believed to result from several interactions, such as various free carrier scattering processes, band structure and many-body effects.\textsuperscript{25,78,79} The overall picture is thus relatively complicated as it is difficult to isolate each contributing mechanism from the others. There has been a good amount of systematic research on ISBT linewidth broadening, but there is still no comprehensive theory to incorporate all mechanisms and give quantitative explanation of each contributing mechanism. For large energy ISBTs in heavily doped narrow InGaAs / AlGaAs QWs, band nonparabolicity, interface roughness scattering, and well width fluctuation are believed to be the most significant effects among many possible linewidth broadening mechanisms. Since the band nonparabolicity effect depends upon carrier distribution, which in turn depends on the carrier density and temperature, the nonparabolicity effect could be investigated by just varying the temperature and doping density for the same QW structure. This should enable isolation of the nonparabolicity contribution from other contributing effects. For example, Figure VI.2 shows the absorption spectra taken on QW samples of the same structure (In\textsubscript{0.5}Ga\textsubscript{0.5}As (40Å) / Al\textsubscript{0.45}Ga\textsubscript{0.55}As (80 Å)) with different doping densities at different temperatures. With increasing doping density and temperature, the linewidth broadens and become
asymmetric, which results largely from increasing nonparabolicity. Also shown in the figure are theoretical curve fits to the lineshapes using the nonparabolicity factor, $\alpha$, as a fitting parameter which increases with doping density and temperature. However, these values are much smaller than $\alpha = -0.86$, which has been used for subband energy and wavefunction calculations. This means that although the nonparabolicity effect plays some significant role in linewidth broadening, other mechanisms which effectively suppress the nonparabolicity effect to some extent must also be considered. Thus in order to solve this discrepancy, it will be necessary to build a more complete picture, including other many-body effects, such as the depolarization effect which is known to have a canceling effect to nonparabolicity broadening.\textsuperscript{25} Other broadening mechanisms, such as interface roughness scattering and well width fluctuation should also be investigated through systematic growth and measurement studies. Such investigations should lead to significantly narrower linewidths and enable higher conversion efficiencies with optimized ISBT structures.

Figure VI.2. Absorption spectra on 40Å In$_{0.5}$Ga$_{0.5}$As / Al$_{0.45}$Ga$_{0.55}$As QWs with different doping densities at room and high temperatures. Sheet charge density/QW: (a) 2.1x10$^{11}$ cm$^{-2}$, (b) 3.7x10$^{11}$ cm$^{-2}$, (c) 9.1x10$^{11}$ cm$^{-2}$, (d) 2.7x10$^{12}$ cm$^{-2}$.
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