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HIGH DENSITY CARRIER DYNAMICS
IN STRUCTURED III-V SEMICONDUCTORS

by
Georg Heinrich Mohs

A Dissertation Submitted to the Faculty of the
COMMITTEE ON OPTICAL SCIENCES (GRADUATE)
In Partial Fulfillment of the Requirements
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1996
As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Georg Heinrich Mohs entitled High Density Carrier Dynamics in Structured III-V Semiconductors and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

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This dissertation presents an investigation of the charge-carrier dynamics in highly excited III-V semiconductor compounds. More precisely, after femtosecond excitation the photoluminescence of the GaN and related materials based Nichia NLPB 500 blue-light emitting diode (LED) is temporally and spectrally resolved using streak-camera techniques. Emission spectra are gathered both at 20K and room temperature. In addition, the emission of a pure GaN film grown by metal organic chemical vapor deposition is studied and compared to the more complicated structure of the diode.

In either case, two spectrally distinct emission bands are found. Both samples show a large emission close to the band edge of the material. For the LED, amplified spontaneous emission is found in this band under very high excitation. The time resolved data shows simple, almost exponential, decays independent of pumping power or lattice temperature except for the amplified spontaneous emission in LED.

The second emission band is impurity related and very different for the two samples. In the LED, impurities are deliberately doped into the active region of the device to provide luminescence centers whereas the pure GaN film is not intentionally doped. The LED emission shows a two component decay that changes its time constant with pump power which is well explained with in a three-level rate-equation model with saturable intermediate state. In the case of the GaN film an exponential decay independent of excitation density is observed up to a certain pump power where a fast initial component appears.
Furthermore, spectral-hole burning experiments are performed on GaAs/AlGaAs multiple quantum wells. A new measurement technique for precise investigations of temporal gain evolution is given and subpicosecond gain in type II multiple quantum wells is demonstrated. Additionally, the experimental evidence for phonon sidebands of spectral holes in cool electron-hole plasmas is presented and theoretically investigated based on the Boltzmann equation coupled to the semiconductor Bloch equations. The carrier-dephasing time is studied as a function of plasma temperature, and indication for a strong dependence of carrier-carrier scattering rates on the temperature of the plasma is given. The findings are explained in a simple picture of blocked scattering channels for cold plasmas.
1. INTRODUCTION

The one invention with the probably biggest impact on our everyday lives in this century has been the discovery of the transistor in 1948. Researchers demonstrated that large currents could be controlled by small currents with this all solid state semiconductor device. Electrical amplifiers could readily be build as well as logic circuits. This was nothing new since these operations could already be accomplished by electronic tubes; however, tubes cannot be miniaturized and their power consumption is large compared to transistors. This miniaturization potential and power efficiency made it possible to shrink the first large scale general purpose electronic computer (ENIAC for "Electronic Numerical Integrator and Computer"), which occupied a room thirty by fifty feet and could perform only simple arithmetic operations, to the size of a pocket calculator with advanced graphical and mathematical capabilities.

Naturally, people wanted to know about the processes that make the transistor work in order to optimize its performance and possibly design new devices based on semiconductors, this fantastic class of materials from which the active part of the transistor is made. The investigations led to the invention of the light-emitting diode (LED), often encountered in displays, and the laser diode (LD), known to all of us from the compact-disk (CD) player. But the potential is much greater than only this. With the ever growing need of more and faster computational power in our world physicists are slowly reaching the limits imposed on electronics by nature.
To circumvent these limitations, scientists are now developing a new kind of technology that combines optics and electronics into optoelectronics. The emerging field of optoelectronics exploits the speed and negligible interaction of light with itself for data communication (e.g., optical fibers) and all the known advantages of electronics for data processing. These new devices are possible because of the interaction of the semiconductor with a light field which comes about from its unique electronic structure.

When the atoms of a semi-conducting material are brought close together to form the semiconductor, the discrete energetic levels of the electrons in the atom degenerate to form bands. In a semiconductor, the lowest lying completely empty band (first conduction band) is separated from the completely filled valence bands by an energy gap that cannot be easily overcome by the electrons. Since there are usually no free electrons available (no electron in the conduction bands and electrons packed so dense in the valence bands that they cannot move), a semiconductor is a good insulator at room temperature. However, free electrons can be created in the lowest lying conduction band or empty states (holes) in the highest valence band by doping, making the semiconductor a very good conductor. Alternatively, a photon with an energy larger than the energy gap can be absorbed in the semiconductor and promote an electron across the gap from one of the valence bands to the conduction band leaving behind a hole. It is the goal of this work to contribute to the fundamental understanding of the dynamics of those free electrons and holes in semiconductor materials.

Since photons can create free electrons and holes in the conduction and valence bands respectively, lasers are the ideal tool to investigate the interactions of these particles
among each other and with the lattice. In a sense, the created electrons and holes are not really free, but interact via their charges with the environment. Laser light has the unique property of being temporally and spatially coherent radiation, which means it is spectrally extremely pure and can be focused tightly to create enormous power densities. Additionally, because of this coherence, the electrons and holes created by it will initially have the same quantum mechanical phase in their wavefunction. The loss of this phase is one of the fastest processes known to occur in these materials and can be investigated using ultrafast lasers. Furthermore, with the large power densities achieved by laser light and its spectral purity, it is possible to inject large numbers of electrons and holes of a selected energy into the semiconductor. The presence of the charge carriers alters the absorption of the semiconductor at the corresponding wavelengths.

Monitoring this nonlinear absorption, it is possible to follow the spectral distribution of the injected electrons and holes as they relax. However, the scattering events leading to the loss of coherence and also to the redistribution of the carriers take place on an extremely fast (i.e. ultrafast) time scale. Typical dephasing times (characterizing the loss of coherence) in highly excited semiconductors are on the order of 100fs. To illustrate, in 100fs light travels approximately 30μm which is less than the thickness of a typical human hair. In comparison, in just one second light travels roughly seven and a half times around the earth. No detector in the world is fast enough to time-resolve such processes and therefore, laser pulses of less or at least comparable duration to these times are necessary to monitor the nonlinear absorption. The idea is to inject the carriers with a pump pulse and test the absorption with a weak probe pulse a certain time
delay after the pump pulse, so that the time resolution problem is reduced to a spatial resolution problem, which is well understood.

This pump-probe technique is not the only possibility to look at carrier dynamics in semiconductors. Just as well as a photon can be absorbed to promote an electron from a valence band to a conduction band, a photon can be emitted when the electron drops back into an empty state in the valence bands. The resulting light is called luminescence and its intensity is proportional to the product of the electron and hole occupation functions describing the charge carrier distributions in the sample. Therefore, monitoring the emitted light as a function of time or wavelength yields insight into carrier recombination processes, which are very important for the design of new devices.

Since different semiconductors have different band-gap energies structures with interesting optical properties can be grown. For example, if a very thin layer of a small band-gap material is sandwiched between two layers with large band-gap energy, charge carriers will be confined to the layer with the small band gap. Using molecular beam epitaxy it is possible to grow semiconductors one monolayer at a time with extremely high crystalline quality. These films can be made so thin that the electrons are confined to two-dimensional motion if their kinetic energy is not too large. This yields an important enhancement of nonlinear effects in these semiconductor structures.

All of the above techniques are used in this work to investigate the high density carrier dynamics in structured compounds from the third and fifths group of the periodic table of the elements. The experimental apparatus is introduced in chapter 2 of this dissertation. Time-resolved photoluminescence studies of III-Nitride compounds are
presented in chapter 3. Chapter 4 is concerned with ultrafast pump-probe spectroscopy of
highly excited semiconductors or, more precisely, with spectral-hole burning in inverted
GaAs/AlGaAs multiple quantum wells. A novel measurement technique with previously
unachieved accuracy for the investigation of gain is used to demonstrate subpicosecond
gain in a type II multiple quantum well system. Furthermore, the relative role of carrier-
carrier and carrier-LO-phonon scattering in cold plasmas is investigated and phonon
replicas of spectral holes are presented. The fifth and final chapter summarizes the results
and suggests further experiments.
2. EXPERIMENTAL APPARATUS AND PROCEDURES

The following chapter describes the experimental apparatus. Since the setup for the III-Nitride semiconductor measurements differs considerably from the spectral-hole burning setup, only a very general description of the experimental components is given. The details are described later on in the text. Also, an explanation of a very fundamental experimental procedure is presented. Section 2.2 on page 31 describes how the linear and parabolic chirp on the generated white-light continuum is measured and accounted for, whenever time and spectrally resolved measurements are performed.

2.1 Laser System

Carrier scattering processes and therefore carrier dynamics in semiconductors take place on ultra short time scales. To investigate these carrier dynamics, the temporal resolution of the measurement apparatus must be less than, or at least comparable to, the time constant of the processes under investigation. Pump-probe experiments with femtosecond pulses have proven to be a very powerful technique for the exploration of such ultrafast mechanisms since the time resolution is mostly governed by the temporal width of the laser pulses and therefore reaches the femtosecond regime. A schematic of the laser system used to perform the experiments is shown in Figure 1. It consists of a colliding pulse mode-locked (CPM) oscillator, a first amplification stage, a continuum generation and a second amplification stage. The laser yields one narrowband high power
Figure 1: Schematic of the laser system as used in the spectral hole burning experiments. CPM stands for colliding pulse mode-locked and indicates the oscillator, IF marks the interference filters and Amp. is short for amplifier. The double arrows denote delay stages.
output pulse from the second amplifier, tunable from 550nm to about 850nm with peak intensities of up to 220GW/cm$^2$ depending on the selected wavelength and bandwidth.

A second tunable and narrowband pulse can be obtained before the second amplifier by intercepting the beam reflected off the first interference filter. This pulse has considerably less power than the output of the second amplifier, but still enough to produce pronounced nonlinear effects in semiconductors.

The laser also provides a low power, very high bandwidth pulse obtained from the generated continuum. This makes the system ideal for pump-probe experiments since a wide wavelength range independent from the pump pulse can be tested simultaneously. The following describes the components in more detail.

2.1.1 Oscillator

To produce femtosecond laser pulses a CPM (Colliding Pulse Mode-locked) ring dye laser is used (see Figure 2) similar to earlier versions.$^{12,13}$ Three mirrors and two telescopes make up the ring cavity. Two dye jets are placed into the resonator separated by exactly 1/4 of the ring circumference. One of the two dye jets acts as the gain medium and uses a dye solution of R6G (Rhodamine 6G, also known as Rhodamine 590 Chloride [R590]) in ethylene glycol, pumped with an argon ion laser (Coherent Innova 90) at about 4W cw. The other jet uses 3,3'-Diethyloxadicarbocyanine Iodide (DODCI) in ethylene glycol as a saturable absorber. This jet is only 35μm thick so that the counter-propagating pulses can form a grating within the jet which scatters light from one pulse to the other keeping the two beams coupled and coherent.$^{14}$ The stable mode of operation of the CPM
Figure 2: Schematic of the CPM laser. \textit{DODCI} (3,3’-Diethyloxadicarbocyanine Iodide) and \textit{R6G} (Rhodamine 6G) label the dye jets which are indicated as small rectangles in the middle of the two mirror telescopes. \textit{Argon} marks the incoming pump beam, indicated in gray.

is two pulses counter-propagating in the ring cavity and colliding in the saturable absorber. This way the peak intensity in the DODCI jet is very high and the saturable absorber is bleached very efficiently. The result is small attenuation of the two pulses. Random noise in the cavity, however, will be absorbed by the DODCI. Due to the 1/4 cavity circumference separation of the two dye jets, both pulses have maximum temporal separation in the gain jet and experience maximum and equal amplification. The pulse shortening mechanism is a combination of the saturable absorption of the DODCI and the saturable gain of the R6G in conjunction with the linear losses in the cavity. The DODCI steepens the leading edge of the pulses whereas the R6G in connection with the linear losses of the cavity discriminates against the trailing edge. Pulse shortening continues until group-velocity dispersion (GVD) effects prevent the pulse from becoming narrower.

Positive GVD is introduced into the cavity by the dye jets and dielectric mirrors, which means blue frequencies need more time for one round trip than red. To compensate
for the positive GVD, four prisms are introduced into the resonator (see Figure 2). The first prism disperses the beam and forces higher frequencies in the pulse to travel on an outer path when measured from the mean beam path. Lower frequencies on the other hand travel on the inside of the mean beam path. The second prism collimates the different frequencies in the beam again and the third prism forces all frequencies to converge at the fourth prism which recombines the light spatially to a single pulse. This geometry results in additional positive GVD. However, if the laser beam is adjusted such that it traverses the apex of all the prisms, the blue components of the pulse travel through negligible amounts of glass whereas the red components have to pass through glass at the two middle prisms. Since the index of refraction of the glass is much higher than that of air the total optical path for red is greater than for blue, considering the whole setup. Therefore the complete setup introduces negative GVD that can compensate the positive GVD of the other elements in the laser cavity. Of course, the glass of the prisms itself causes positive GVD which adds to the GVD of the dye jets and mirrors. Thus, by choosing the right amount of glass in the beam it is possible to adjust the total GVD in the cavity to zero. For this purpose the prisms are mounted on translation stages that move the prisms into or out of the beam normal to their base. All prisms are used in the minimum deviation geometry and the apex angle is chosen such that the angle of incidence corresponds to the Brewster angle for the prism material. Depending on alignment, the CPM laser can achieve pulse widths between 60fs and 90fs at a repetition rate of about 82MHz and a time averaged output power of 10mW. However, this laser is not tunable and constantly running at
620nm since the mode locking depends sensitively on the gain and saturable absorber dye combination.

2.1.2 First Amplifier

One option to make the laser system tunable is the creation of a white-light continuum. For this purpose it is necessary to amplify the CPM laser pulses by a factor of 100,000. This is done in a first amplification stage. A schematic of the first amplifier is shown in Figure 3. It is a six-pass amplifier in a modified design of the bowtie configuration,\textsuperscript{16} pumped by a Q-switched Nd:YLF laser (TFR for Tightly Folded Resonator). This pump laser operates at 1kHz repetition rate, which limits the repetition rate of the total laser system. Its output power is 200\mu J in a 7ns pulse of green light (527nm, doubled Nd:YLF).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3}
\caption{Schematic of the first amplifier. \textit{Malachite Green} and \textit{R640} (Rhodamine 640 Perchlorate) mark the positions of the two dyes in this amplifier. \textit{TFR} labels the incoming pump beam from a TFR laser.}
\end{figure}
The gain medium in the amplifier is Rhodamine 640 Perchlorate (R640) dye in ethylene glycol flowing in a 2mm thick fused silica cell with an antireflection coating for 620nm. Between passes 4 and 5, a 300\(\mu\)m thick dye jet of Malachite Green in ethylene glycol works as a saturable absorber to reduce amplified spontaneous emission and unamplified pulses of the oscillator in the amplifier output. After the amplifier the pulses are recompressed by an SF10 prism pair with a spacing of approximately 260mm to about 90fs. At this point the pulse energy is approximately 4\(\mu\)J.

### 2.1.3 Continuum Generation and Reamplification

In order to create the white-light continuum the pulses are focused onto a 2mm thick ethylene glycol jet by a 30mm microscope objective after the GVD compensation of the first amplification stage. This creates a broad band continuum in the visible\(^\text{17}\) which extends from below 500nm to more than 850nm becoming increasingly noisy towards the infrared end of the spectrum. After the ethylene glycol jet, the pulses are collected by a 40mm microscope objective. Part of the continuum (4\%) is split off with a plano-concave lens and is used as a weak and extremely broad band probe pulse in the experiments. The remaining light of the continuum is sent through an interference filter and the resulting pulses are amplified in a second amplifier. For ease of operation this amplifier is set up in a telescope configuration\(^\text{18}\) (Figure 4) and uses different dyes, depending on the selected wavelength, in a 2mm thick flow cell. It consists of two confocal mirrors with different radii of curvature. M1 focuses the beam onto the gain medium while M2 recollimates the beam and sends it back to M1. Since the radius of curvature of M2 (260mm) is less than
that of M1 (280mm), the beam moves closer to the center of the mirrors with each successive pass. After the sixth pass, a small mirror sends the beam out of the amplifier. The pump source of this amplifier is another TFR laser which is coupled in through a central hole in mirror M1. After the second amplifier, the GVD is again compensated with a prism pair whose distance needs to be adjusted depending on selected wavelength and dye solution.

![Figure 4: Schematic of the second amplifier. M1 and M2 are two confocal spherical mirrors that make up the amplifier. Two prisms indicated by triangles stand for the GVD compensation setup at the bottom of the figure.](image)

### 2.2 Chirp: Measurement and Compensation

Almost all media encountered by the laser pulses are dispersive. Since a short pulse and especially the white light continuum consists of many different frequencies, different
spectral parts of the pulse travel with different velocities through these dispersive media. This can be described by a frequency dependent group velocity or group velocity dispersion (GVD). For positive GVD, which is encountered in normal dispersive media, red parts of the pulse travel faster than blue.

The resulting spatial distribution of wavelengths in the pulse is called chirp and causes a temporal stretch. The time-bandwidth product $\Delta t\cdot \Delta \lambda$ is no longer minimal which means that the temporal width $\Delta t$ of the pulse no longer corresponds to its spectral bandwidth $\Delta \lambda$ via Fourier transformation. However, the problem in pump-probe experiments is that different frequencies arrive at different times at the sample. This results in different time delays for blue and red wavelengths when the chirped continuum is used as a probe. As a result, in pump-probe data a dynamic of the nonlinear absorption is suggested that is not real. For example, if a bleaching signal is observed over a spectral region of considerable width the data will suggest that the sample bleaches first in the red part of the spectrum and later in the blue even though in reality all wavelengths bleach simultaneously.

Because of its nonlinear character, the chirp in the continuum cannot be compensated with a simple prism pair. It is therefore necessary to measure the chirp in the continuum and remove it from the data numerically. Two photon absorption in a ZnO single crystal was used for the chirp measurements as first suggested by Albrecht et al.\textsuperscript{19} Overlapping the probe-pulse with a narrow band, bandwidth limited pump pulse in a two
Figure 5: DeChirp at work. Part (a) of the figure shows the resulting signal from two photon absorption if the probe pulse is overlapped with a narrowband pump pulse in a ZnO crystal. From this data a wavelength versus delay curve can be extracted as shown in part (b). Part (c) shows the data of part (a) corrected for chirp. The structure of the probe spectrum in graph (c) is due to the spectral distribution of light in the pulse. It is also the envelope in graph (a). The equation in part (b) gives the calculated fit parameters for this data.
photon absorption active medium will result in induced absorption for those probe pulse wavelengths that overlap in time and space with the pump pulse in the sample. Monitoring the probe spectrum and changing the delay between the two pulses, the chirp in the probe beam can be measured. In this way, the parameters of the linear and parabolic chirp were extracted from experimental data and fed into a program that combines measured curves for different time delays to produce chirp-free data. Careful checks of the routine showed that the algorithm works extremely well and reliably.

Figure 5 shows the efficiency of the employed method. In part (a) of the figure the differential two-photon absorption in the ZnO crystal is shown for several time delays. As described above, the probe spectrum is monitored and induced absorption occurs for those wavelengths that overlap in time and space with the pump-pulse in the sample. Part (b) shows the extracted chirp from the measurement and a second-order polynomial fit to the data. These parameters are then used to dechirp the data set of part (a) by linear interpolation for time delay between the measured curves. For example, the data at 100fs time delay and 700nm is combined with the data at 684nm of the curve taken at 200fs time delay. This is done for all time delays and the result is a new set of curves which is plotted in part (c) of Figure 5. It can be seen, that virtually all the chirp present in the probe pulse has been eliminated from the data. The structure on the probe spectrum is not an artifact of the algorithm; rather it results from the spectral intensity inhomogeneity of the white light continuum which is amplified in the two photon absorption process. Since the original spectra consist of data skewed in time, the processed spectra have blank regions at their ends for the extreme time delays.
2.3 Detection Systems

There are three major detection systems that are available for the measurements. The first one is for spectrally resolving broad-band signals and consists of a spectrometer with optical multichannel analyzer. For spectrally integrated but temporally resolved data, a streak camera with picosecond resolution and remote control capability is available. Finally, for the investigation of time dependent narrowband signals, a monochromator with photomultiplier tube connected to a lock-in amplifier with analog-to-digital converter and GPIB interface is accessible. These systems are described in detail below.

2.3.1 Optical Multichannel Analyzer

For spectrally-resolved, broadband data an optical multichannel analyzer (OMA) is used. It consists of a 0.22m spectrometer (Jobin Yvon / Spex model 1681) with an EG&G intensified silicon photodiode array detector (detector model 1422 and controller model 1460). The detector contains a semitransparent photocathode coupled via fiber optics to a microchannel plate, which amplifies the electron stream and guides it to a phosphor screen. In turn, this phosphor screen is coupled via fiber optics to a linear silicon photodiode array with 1024 pixels.

The photosensitive material of the photocathode is S-20R and has sensitivity in the wavelength range of about 350nm to 900nm. The spectrometer can be equipped with one of three different gratings (300, 600 or 1200 line-pairs/mm). The whole system can work either stand-alone or can be computer controlled over a GPIB interface. Two shutters can
be driven by outputs of the OMA controller. The controller is programmable and complicated data acquisition schemes are possible.

2.3.2 Streak Camera

The streak camera is composed of a temporal disperser (Hamamatsu C1587), a video camera (Hamamatsu C1000 Type 18) and a temporal analyzer (Hamamatsu C2280) together with a floppy & hard-disk drive (Hamamatsu C2712). It can temporally resolve light at the input with a single sweep resolution of 2ps. The unit can work stand-alone with the temporal analyzer controlling the system. Or it can be run by an external computer over a GPIB interface and data transfer between the Computer and the temporal analyzer is possible.

The temporal disperser consists of a semitransparent photocathode, a high voltage streak unit and a microchannel plate in front of a phosphor screen. The microchannel plate voltage is adjustable so that a wide range of gains can be used. The photosensitive material is a multi-alkali compound similar to that in the OMA system with a spectral response of 200nm-850nm. However, the input optics are not made of UV grade glass cutting the spectral response of the system in the deep blue to about 350nm.

The phosphor screen is read out by a video camera with high spatial resolution. Two-dimensional images can be read from the video camera, divided into 512 horizontal and 480 vertical channels and digitized by the temporal analyzer with 16-bit resolution. Since the streak unit operates vertically it is be possible to insert a monochromator in front of the temporal disperser and obtain spectrally and temporally resolved data. However, no
Figure 6: Streak camera calibration using a Fabry-Perot resonator. The top graph shows the measured data with a mirror spacing of 0.274 inches on the 2ns/15mm streak-time setting. The lower plot shows a linear regression through the data points.
monochromator was available so that the data acquisition was confined to spectrally integrated vertical streaks with 480 pixel resolution.

<table>
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<th>Streak Time (ns/15mm)</th>
<th>Calibration (ps/channel)</th>
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<tr>
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Table 1: Calibration for the streak-time settings of the temporal disperser.

The streak unit has five settings ranging from 0.3ns/15mm to 10ns/15mm with 15mm being the effective length of the phosphor screen. Unfortunately, the calibration of the temporal disperser is not accurate and needs adjustment. For this purpose a Fabry-Perot resonator is set up and after passing a fs pulse through the Fabry-Perot the resulting pulse train was measured with the streak camera. A typical data set is shown in Figure 6. The mirror spacing is 0.274 inches and the streak time is set to 2ns/15mm. The first peak is located at channel 53 and the last at channel 460 with a total of 23 peaks. The time between two peaks is given by \( \tau = \frac{2L}{c} \) where \( L \) is the mirror spacing and \( c \) the velocity of
light. Therefore a calibration factor of 2.51\text{ps}/channel can be calculated. Table 1 summarizes the calibration results for all streak time settings.

![Streak camera time response to a femtosecond pulse with external triggering.](image)

**Figure 7:** Streak camera time response to a femtosecond pulse with external triggering.

To integrate weak signals the streak camera can be triggered externally. The time resolution in this case is governed by trigger jitter and measured to be 21\text{ps} (full width at half maximum) after femtosecond excitation with our laser system (Figure 7). It is found that the trigger jitter depends on the pulse to pulse intensity stability of the triggering pulse as well as on the overall trigger-signal strength itself, improving with higher input voltages. The maximum external trigger frequency is 1kHz and trigger delay is about 40ns depending on the streak time setting.
2.3.3 Narrowband Time-Scan Detection

To monitor narrowband and time-dependent signals a third major detection channel is available. It consists of a 0.25m monochromator (HR320 by ISA Instruments SA Inc.) with a fixed 1200 linepairs/mm grating and a photomultiplier tube (Hamamatsu 928) as a detector. The resulting signal can be fed directly into a lock-in amplifier (EG&G / Princeton Applied Research Model 5210) in current mode. The lock-in amplifier has a built-in analog to digital converter and can be read out by a computer over a GPIB interface.
3. TIME RESOLVED GROUP-III NITRIDE MEASUREMENTS

Group-III nitride wide-bandgap semiconductors and their alloys have received much attention for their potential in realizing compact light-emitting sources spanning the spectral region from the UV (200nm, AlN) to the red (620nm, InN). Their physical hardness, extremely large hetero-junction offsets, high thermal conductivity and high melting temperature make these materials superior to others in many respects. Already in the 1970s Pankove et al. and Dingle et al. had investigated the luminescence properties of single crystal GaN. However, device fabrication proved difficult and only very dim electroluminescent diodes could be fabricated since efficient p-type doping of the naturally n-type GaN crystals was not possible until 1991. Because of these problems a lot of work was and continues to be focused onto wide band-gap II-VI compounds such as ZnS and ZnSe. However, these materials are rather fragile and defect propagation limits device lifetimes to only a few hours.

Recently, high-brightness blue and green light-emitting diodes (LEDs) based on III-Nitride materials have been demonstrated and have become commercially available. The potential commercial market for these devices is incredibly large and includes daylight full-color displays, traffic lights, optical data storage and medicine.

The common goal for most of the future efforts in this area is the development of the first commercial blue laser diode. Reducing the wavelength of optical data storage devices by half will result in four times higher storage capacity than with the old near infrared laser sources. On December 11, 1995 Nakamura announced their first electrically...
pumped laser diode based on the III-nitride material system. Under pulsed conditions, the device produced 215mW at a forward current of 2.3 A (34 V) and a wavelength of 417 nm at room-temperature. Since then several improvements have been made but so far no blue laser diode is commercially available.

To optimize the structure designs it is important to understand the phenomena and timescales involved in the radiative recombination process in this material system. In this chapter, time-resolved investigations of photoluminescence in pure GaN as well as in an InGaN/AlGaN/GaN double-heterostructure blue LED are presented. Using the doubled output of the first amplifier of the laser system, the samples are excited high in the band, and the photoluminescence is measured spectrally and temporally. By varying the intensity and wavelength of the excitation, the details of the photoluminescence can be understood.

### 3.1 Experimental Setup

Figure 8 shows a schematic of the laser and data acquisition setup used in the GaN experiments. The light of the CPM laser is amplified in the first amplifier and then focused onto a 300μm thick KDP crystal to generate the second harmonic. These pulses are then used to excite the GaN samples. The fundamental of the laser light is suppressed by an interference filter with a center wavelength of 310nm and an additional color glass filter (Schott UG-5). The spot size on the semiconductor of about 50μm diameter yields a maximum incident intensity of about 50MW/cm². The sample is set up in a typical backscatter geometry. The pump beam is inclined at about 15 degrees with respect to the surface normal of the sample and the photoluminescence is collected along the normal.
Scattered pump light is suppressed with a Schott WG-9 absorptive colored glass filter. The sample is mounted onto the coldfinger of a closed cycle helium refrigeration system so that measurements at low (20K) as well as room temperature can be performed.

Figure 8: Schematic of the setup used during the photoluminescence experiments on the Nichia GaN LED and the pure GaN layer. The emitted light can be directed to either a streak camera or a .22m spectrometer with OMA.
Two different detection channels are available. A streak camera can temporally resolve the spectrally integrated light with a single sweep resolution of 2ps. However, for improved signal-to-noise ratio, long integrations of the collected photoluminescence are necessary, limiting the time resolution to about 21ps due to trigger jitter (see section 2.3.2).

Since the maximum external trigger rate of the temporal disperser is 1kHz and less trigger jitter is observed at lower triggering frequencies the repetition rate of the laser system was lowered to 750Hz (see Appendix A).

Part of the laser beam is split off from the fundamental beam and brought as close as possible to the temporal disperser unit, where it is incident onto an Avalanche Photodiode (Texas Optoelectronics Inc. TIED59). The signal of the photodiode is then used to externally trigger the temporal disperser. Since the trigger circuit of the streak camera has a delay of approximately 40ns from the reception of the electrical trigger signal to the actual firing of the temporal disperser, it is necessary to optically delay the pump pulse that excites the sample on a 12m long "race track". Despite the long optical path the spatial quality of the pump beam is reasonably good upon entering the second harmonic generation stage.

An optical as well as electrical delay is introduced into the trigger channel since the trigger delay of the temporal disperser circuitry changes with streak-time setting. A rail and retro-reflector is used for the optical delay and two delay units (Hamamatsu C1097) are used for the electrical. Each electrical delay unit introduces up to 32ns delay
switchable in .25ns increments and both units are introduced in series between the photodiode and temporal disperser.

The other detection channel is used to spectrally resolve the collected photoluminescence. It consists of a 0.22m spectrometer with an EG&G intensified silicon photodiode array operating as an optical multichannel analyzer (OMA; see section 2.3.1). The spectrometer is equipped with a 300 lines/mm grating resulting in a resolution of about 2nm with the selected slit width of 100µm. The blaze wavelength of this grating lies in the visible part of the spectrum resulting in a nonuniform detector response over the wavelength region under investigation. The spectra shown have not been corrected for this decreasing detector response with shorter wavelengths, although the effect may be large.

Furthermore, a camera system was set up in these experiments to monitor the pump spot on the structure as well as to choose appropriate parts of the sample for linear absorption measurements. As described below, the sample was imaged onto an iris which in turn could be imaged onto a CCD camera using a cemented achromat.

### 3.2 Pure GaN

Time-resolved photoluminescence measurements are performed on a nominally undoped 4µm thick layer of GaN. The sample is provided by the group of Prof. Dr. Ravi Jain (University of New Mexico) and was grown by metal organic chemical vapor deposition on a sapphire substrate. Linear absorption measurement reveal little structure at the band edge even at low temperatures (20K). After femtosecond excitation the epitaxial
layer emits light in two distinct spectral regions, typical for nominally undoped GaN. Figure 9 shows spectra at 20K for four different pump intensities in a semi-logarithmic plot. One emission band is very close to the band edge whereas the other one is peaked in the yellow portion of the spectrum and very broad. The former is attributed to radiative recombination at the band edge, and the latter to impurity related transitions.\textsuperscript{36,37}

![Figure 9: Spectrally resolved, time-integrated photoluminescence of the epitaxial GaN layer at 20K for four different pump powers.](image)

The modulation of the recorded spectra can be accounted for by Fabry-Perot fringes. A slight peak shift of the band-edge luminescence towards lower energy is
observed with increasing carrier density. The two different portions of the photoluminescence are separated with absorptive colored glass filters, and each is time-resolved for itself.

Figure 10: Time-resolved band-edge photoluminescence of the epitaxial GaN layer at 20K for four different pump powers corresponding to Figure 9.

Figure 10 shows the results for the band-edge emission with incident intensities corresponding to Figure 9. An almost single exponential decay whose time constant slightly increases with decreasing pump power is found. For the highest intensity, which is just below the damage threshold of our sample, the decay time is about 40ps increasing to about 55ps at the lowest pump level. Decreasing the pump power even further, surprisingly an accelerated decay with a time constant of only 23ps is found (not shown).
A completely different scenario is observed for the impurity related photoluminescence in Figure 11. Here the decay shows two separate components for high pump powers. A very fast part that is close to the time resolution limit of our detection system and a slow part that, if fitted with a single exponential, shows a time constant of about 570ps, independent of excitation level.

![Figure 11: Time-resolved yellow photoluminescence of the epitaxial GaN layer at 20K for four different pump powers corresponding to Figure 9.](image)

The overall behavior does not change when the lattice temperature is raised to 300K. With increasing temperature the luminescence efficiency decreases and all spectral characteristics broaden. We observe a shift of the band edge towards longer wavelengths
of 8nm as the temperature increases from 20K to 300K. At room-temperature the time-resolved photoluminescence of the band edge has a time constant of 60ps, no longer dependent on carrier density. For the yellow photoluminescence a similar behavior as for low temperature is observed, with no qualitative changes in the spectral and temporal emission pattern.

In summary, a simple exponential decay is found only at the band edge of GaN. Here a rather fast time constant of about 50ps is measured. On the other hand, the inherent defect-related yellow photoluminescence of pure GaN shows a highly nonexponential decay with time at high pump powers whose origin has yet to be determined.

3.3 Nichia LED NLPB500

Time-resolved photoluminescence measurements are also performed on a blue light-emitting diode (LED) based on the III-Nitride material system. Figure 12 shows a schematic of the NLPB500 blue LED of Nichia Chemical Industries, Ltd., measuring about 200μm by 200μm. It is removed from its original case to allow optical access. The LED is a double heterostructure design in which two AlGaN layers, with an Al concentration of about 15% and therefore a bandgap around 320nm, enclose the active region consisting of InGaN, with 6% In concentration. Luminescence centers are provided in the active layer by codoping it with Si and Zn. Si is a shallow donor in GaN, whereas Zn acts as a deep acceptor. The electrode layers consist of GaN doped with Si for n-type conduction or Mg for p-type conduction. The whole structure is grown by metal organic chemical vapor
deposition) onto a sapphire substrate. At low temperatures a 30nm thick GaN buffer layer is grown directly onto the substrate first, which reduces lattice defects in the LED.$^{41}$

Figure 12: Architecture of the Nichia NLPB500 blue LED. Materials and layer thicknesses are indicated.$^{28}$ The active region consists of $\text{In}_{0.06}\text{Ga}_{0.94}\text{N}$ codoped with silicon and zinc.$^{52}$ Lateral dimensions are 200$\mu$m x 200$\mu$m.

To improve ohmic contact at the p-electrode a Au/Ni spreading layer is evaporated onto the top surface of the LED before contacting it with an Au electrode. After growth the whole structure is etched to allow access to the n-type GaN layer which is then contacted from above with another Au electrode. Light emission occurs through the top layers which are all transparent to the emitted wavelengths except for the Au/Ni top contact layer; here a large portion of the emitted light is reabsorbed.
Figure 13 shows the room-temperature emitted photoluminescence collected with the setup described in Section 3.1 on page 42. The pump beam is incident through the top of the LED structure and the photoluminescence is collected in a backscatter geometry. The sample emits in two distinct spectral regions; a broad band, labeled A, between 400nm and 550nm, and a narrow band, labeled B, at 373nm (300K). The broad region (A-band) is spectrally very similar to the measured electroluminescence of the device at low drive currents (not exceeding 30mA), and is therefore attributed to impurity-related emission in the active Si, Zn: In_{0.06}Ga_{0.94}N layer. The B-band originates from band-edge emission in the thick GaN layers (see Figure 12).

The linear absorption of the sample, plotted in the inset of Figure 13, has to be measured very carefully due to the small sample dimensions (200μm x 200μm). A Deuterium high pressure lamp is used to illuminate the sample with a concave mirror that images the emissive region of the lamp onto the LED with a magnification of 1. Since the image of the lamp overfills the LED, light goes around the sample making accurate linear absorption measurements impossible. Furthermore, Figure 12 shows that the LED is a complicated structure and only certain areas of the device are appropriate for linear absorption measurements.
Figure 13: Photoluminescence of the Nichia LED at room temperature with pulsed excitation at 310nm. $I_0$ corresponds to 50MW/cm² excitation intensity. Impurity related emission is labeled A and band-edge emission is labeled B. The inset shows the measured absorption of the device in the wavelength range covered by the inset.

The problem is solved by imaging the sample onto a pinhole with suitable magnification before detection. To increase the image quality which in turn determines the accuracy of the measurement, a thin doublet is used for this purpose instead of a quartz singlet more appropriate for the wavelength range. By moving the image of the LED on the pinhole it is possible to select regions of the sample with a spatial resolution of about 30μm diameter.
The measurements are limited to $\alpha L < 5$ due to scattered light in the spectrometer. The A-band and linear absorption spectrum of the sample are periodically modulated by Fabry-Perot modes of the LED structure. The observed increase in energetic peak-to-peak separation of the modulation with increasing wavelength for both photoluminescence and linear absorption can be accounted for by a change in the refractive indices of the LED materials with wavelength. The large offset of about 1 in the linear absorption curve is due to absorption in the top-contact layer.

To further verify the origin of the two emission bands of the LED the following experiment is performed. Using the doubled output of the second amplifier, which is tuned to 742 nm resulting in 371 nm light, the sample is excited through the sapphire, first under the n-type electrode and then under the full structure.

The results are plotted in Figure 14 and compared to excitation from above. The new pump wavelength excludes both AlGaN layers of the structure from excitation since the band gap for the given Al concentration is close to 320 nm. When exciting through the sapphire under the n-electrode only, a faint yellow photoluminescence is detected, which is typical for GaN$^{43}$ (compare section 3.1 on page 42). However, moving the pump spot onto the structure while exciting through the sapphire results in strong photoluminescence as seen in Figure 14. This emission can now be clearly identified as emanating from the active region. For comparison a typical spectrum for top excitation with 371 nm pump light is also included in Figure 14.
Figure 14: Verification of the origin of the A-band. The two different excitation geometries and the changed pump wavelength prove that the emission must come from the active layer.

The slight red shift of the photoluminescence with respect to excitation from the top can be explained by reabsorption of the emitted light in the thick n-type GaN layer when collecting from the bottom. Also, it can be seen from Figure 14 that the emission of the A-band through the substrate is actually greater than the emission collected from the top. This can be understood by noting that for excitation from the top, a significant loss for both pump and emission is caused by the Au/Ni top contact layer. At shorter excitation wavelengths we observe the relative efficiencies of top and substrate excitation reverse due
to increased absorption of the pump in the thick n-GaN layer, reducing the pumping efficiency of the active region.

3.3.1 Time Traces

In the following the time resolved photoluminescence data of the Nichia NLPB500 LED are presented. The figures always show time traces for different excitation intensities in the lower part (normalized to one), while in the top part they show corresponding spectrally resolved data. The two photoluminescence bands (A-band and B-band) are separated before temporal dispersion by means of absorptive colored glass filters (Schott GG400 for the A-band and UG5 for the B-band). Figure 15 shows the results for the long-wavelength emission (A-band) at room temperature. Two distinct time constants for the PL decay are seen in part (b) of the figure: a short component, too short to be resolved by our system (FWHM 21ps time resolution) and a long component, changing from 700ps to 200ps with increasing pump intensity.

A much simpler behavior is observed in the decay of the photoluminescence at the band edge (B-band), depicted in Figure 16 (b). The time traces here show a very similar, almost exponential decay for low and intermediate pump power, with a time constant of about 60ps at room temperature, and an extremely fast decay for high carrier densities. This suggests amplified spontaneous emission as the dominant recombination mechanism at high excitation levels. Interpretation of this as amplified spontaneous emission is also supported by the acquired spectra in Figure 16 (a) that show line narrowing for the
Figure 15: Spectrally (a) and temporally (b) resolved A-band photoluminescence of the Nichia NLPB500 LED at room-temperature.
Figure 16: Spectrally (a) and temporally (b) resolved B-band photoluminescence of the Nichia NLPBS00 LED at room temperature.
Figure 17: Spectrally (a) and temporally resolved (b) A-band photoluminescence of the Nichia NLPB500 LED at 20K.
Figure 18: Spectrally (a) and temporally resolved (b) B-band photoluminescence of the Nichia NLPB500 LED at 20K.
highest excitation intensity with a peak wavelength of 375nm agreeing very well with other reports of room-temperature photopumped amplified spontaneous emission in GaN.\textsuperscript{45,46}

A very similar behavior is found if the sample is cooled down to approximately 20K. The results are shown in Figure 17 and Figure 18. It is apparent, that the same qualitative behavior as at room temperature is found. The B-band spectrally narrows as is expected for low temperatures and the overall quantum efficiency increases as the temperature decreases. Additionally, the band gap shifts about 80meV towards higher photon energies when cooling the sample from room temperature to 20K.

3.3.2 Three-Level Model

It is possible to reproduce the qualitative behavior of the experimental data with a simple three-level model. A schematic of the model is shown in Figure 19.

In this model, the photoluminescence from the A-band originates from electrons in the conduction band or electrons bound to Si donors (level 1) recombining radiatively with holes bound to the Zn acceptor sites in the active layer (level 2). The Si levels are not considered separately, since the known ionization energy of the Zn acceptors and the In content of the active layer account for the relative spectral positions of the A-band compared to the B-band. In addition, Si doping of InGaN results in no spectral shift of the photoluminescence,\textsuperscript{39} suggesting that Si is a shallow donor in InGaN. The third level of the model represents the valence band, to which all carriers eventually relax.
If the recombination from the upper level to the Zn sites has a decay rate $\gamma_2$ that depends on the carrier density $N_2$ occupying the Zn acceptor level, the model can account
for the initial fast decay as well as the roll-off in the photoluminescence data at later times.

The two rate equations describing this process are

$$\dot{N}_1 = -\gamma_1 N_1 - \gamma_2 (N_2) N_1$$  \hspace{1cm} \text{Equation 1}$$

$$\dot{N}_2 = \gamma_2 (N_2) N_1 - \gamma_3 N_2$$  \hspace{1cm} \text{Equation 2}$$

where \(\gamma_2(N_2)\) is given by:

$$\gamma_2(N_2) = \gamma_2^{(0)} \left(1 - \frac{N_2}{N_2^{\max}}\right).$$  \hspace{1cm} \text{Equation 3}$$

\(N_i\) is the carrier density in level \(i\) \((i=1,2)\). Associated with each transition is also a decay rate \(\gamma_j\) \((j=1,2,3)\) which is constant except for level 2. The decay rate for level 2 is dependent on the carrier density in level 2 as seen from Equation 3. At higher excitation, once all the Zn acceptor sites in the active layer have been occupied with electrons, the radiative decay from the upper level to the Zn sites is governed by the time it takes to free Zn acceptors (constant decay rate \(\gamma_3\)) and hence the much longer time constant of the photoluminescence, after the initial fast decay.

Figure 20 shows calculated curves using Equation 1 - Equation 3. Plotted are the number of photons emitted per time interval at the respective transition \((N_i \gamma_i)\). The same qualitative behavior as in the experiment is found. A simple, almost exponential decay can
be seen at the band edge, and a two component slope is shown for the impurity related decay. The fast initial decay is followed by a roll-off into a much slower temporal decline.

![Graph](image)

**Figure 20:** Calculated LED photoluminescence using the parameters given in the picture. The solid line indicates the intensity at the band edge and the dashed line shows the intensity in the impurity related decay channel. The dotted trace represents the carrier density in level 2.

The intensity dependence of the emission can be explained when accounting for the recombination at the band edge (level 1 to level 3) which is a competitive process for the impurity-related recombination (level 1 to level 2 to level 3). The former changes its decay constant rather drastically once amplified spontaneous emission sets in, and therefore its relative importance in the total recombination process increases; this results in an effectively shortened time constant for the photoluminescence at long wavelengths. Figure
21 shows the results for the calculations when the decay constant at the band edge ($\gamma_1$) is changed by a factor of 3.

![Graph showing LED photoluminescence](image)

**Figure 21:** Calculated LED photoluminescence with the same parameters as used in Figure 20 except for a much faster decay rate at the band edge. The graph demonstrates the influence of amplified spontaneous emission at the band edge on the impurity related decay.

Although evidence for amplified spontaneous emission is seen only in the B-band (Figure 16), which must be largely from the thick n-type GaN electrode layer, the carrier density in the thin active region will be approximately the same. If one assumes the same threshold for amplified spontaneous emission in both materials, stimulated recombination in the active layer also becomes plausible. It should be pointed out that the two-component decay of the A-band can be achieved by simply introducing the saturable, intermediate state...
(the Zn-levels). No further assumptions about the relative sizes of the decay rates are necessary. However, since the impurity-related recombination efficiency is high, the assumption of a fast initial decay is reasonable.

In summary, time-resolved PL measurements in a Nichia InGaN/AlGaN/GaN double-heterostructure blue LED are presented. A complicated, two component behavior of the impurity related PL is found and explained by a simple saturable three-level model. Measurements at the band edge indicate amplified spontaneous emission as the dominant recombination process for high carrier densities.
4. SPECTRAL-HOLE BURNING IN INVERTED SEMICONDUCTORS

The investigation of charge-carrier dynamics in semiconductor optical amplifiers is not only of importance for the understanding of the fundamental physical limits of semiconductor lasers and related devices, but is also a sensitive tool allowing a detailed study of basic many-body effects related to charge-carrier scattering and carrier-phonon interaction. The question of how certain scattering processes affect nonequilibrium charge-carrier distributions can best be investigated by ultrafast nonlinear optical techniques, such as pump-probe spectroscopy. The relative importance of different scattering events (such as carrier-carrier, carrier-LO-phonon or carrier-phonon-plasmon, carrier-acoustic phonon, carrier-impurity) depends strongly on the details of the experimental configuration, such as sample temperature, pump intensity, the center frequency of the pump pulse, and the time scale under consideration as well as material parameters such as the band structure.

This chapter presents spectral-hole burning experiments performed on type I and type II multiple quantum well samples under various excitation conditions. The carrier relaxation towards thermal equilibrium and carrier dephasing is investigated as a function of plasma temperature. Furthermore, a novel technique for dynamic gain measurements is introduced and ultrafast gain in type II multiple quantum wells is demonstrated.
4.1 Experimental Technique

Spectral-hole burning is a very powerful experimental technique to measure the incoherent scattering dynamics of charge carriers in semiconductors on an ultrafast timescale. A strong pump pulse, tuned close to the band edge but into the highly absorptive continuum-states of the semiconductor, is incident onto a sample. In the simplest case, it is absorbed and creates carriers in the conduction band and valence band. If probed on a short enough time scale, the carrier distribution in both bands will be highly nonthermal and will follow the spectral shape of the pump pulse. This is depicted schematically in Figure 22 (a).

![Figure 22: Spectral-hole burning in the absorptive region of a semiconductor.](image-url)
Part (b) of Figure 22 shows the effect of the presence of these carrier distributions in the bands on the absorption of the semiconductor. Since electrons and holes are Fermions, each state in the bands of the sample can be occupied by, at most, one charge carrier. This means that if a carrier is present at a certain position in the band no other fermion can be promoted into this state (Pauli principle). Optical absorption is no longer possible at the corresponding wavelength and the absorption of the semiconductor is locally bleached at this spectral position. A spectral hole develops [Figure 22 (b)].

![Figure 23: Destruction of the nonequilibrium distribution caused by the pump pulse due to carrier-carrier scattering (a) which transforms the distribution into a Fermi distribution that changes as it cools (b).]
However, carrier-carrier scattering, one of the fastest and most efficient scattering mechanisms in semiconductors at high densities, drives these nonthermal distributions very quickly towards thermal equilibrium and destroys the burned spectral hole. This is schematically depicted in Figure 23. Graph (a) shows a highly nonthermal carrier distribution function that follows the spectral shape of the pump pulse. The arrows indicate the redistribution of carriers due to carrier-carrier scattering processes. Graph (b) shows the result: a hot Fermi distribution (solid line) that slowly cools by phonon emission (dashed and dotted lines). If a short, weak pulse now probes the absorption of the sample at a certain time delay after the pump pulse has passed the semiconductor, the distribution functions of the carriers can be measured as a function of time and scattering processes can be investigated. This technique is well known and has been used to study carrier-scattering dynamics extensively.\footnote{48,49}

Spectral-hole burning can be employed not only to investigate charge-carrier dynamics in the absorptive region of semiconductors, but it can also be used to look at inverted systems, as was first demonstrated by Ken Meissner et al.\footnote{50} Figure 24 shows a schematic for spectral-hole burning in this case. If the pump pulse is tuned into the gain region of the inverted sample it will no longer be absorbed but it will be amplified due to stimulated recombination. This process removes carriers from the system and causes "inverted" distributions in the bands where charge carriers are missing from an otherwise thermal distribution of Fermions. Again, if probed on a short enough time scale these inverted distributions follow the spectral shape of the pump pulse. At the pump wavelength free states become available and optical absorption becomes possible, reducing
the gain at the corresponding spectral position. The resulting induced absorption in turn causes a spectral hole to develop in the gain region of the sample (Figure 24).

![Spectral-hole burning in the gain region of an inverted semiconductor.](image)

**Figure 24:** Spectral-hole burning in the gain region of an inverted semiconductor.

### 4.1.1 Spectral-Hole Burning Setup

For the spectral-hole burning experiments in inverted semiconductors, three pulses are necessary. A schematic is shown in Figure 25. The first pulse (gain pulse) has to optically invert the sample and is obtained from the output of the second amplifier. The pump pulse, which burns the spectral hole, is created from the continuum reflected off the first interference filter. A second interference filter is used to select its spectral position and bandwidth. To interrogate the sample, 4% of the created continuum are split off before encountering any interference filters and are used as a weak broadband probe beam.
Two delay stages make it possible to retard the gain and the pump pulse independently with respect to the probe pulse. The delay between gain and probe pulse is labeled $\tau_{\text{Gain}}$, whereas the pump-probe delay is denoted by $\tau_{\text{Pump}}$ (see Figure 25). Autocorrelations of the pump and gain pulses indicate that both are nearly transform-limited with full widths at half maximum of about 90fs for the gain and 210fs for the pump pulses.

Figure 25: Schematic of the experimental setup. The 90fs long gain pulse is centered at 660nm. The pump pulse is narrowband ($\Delta\lambda=3.7\text{nm}$) with a duration of 210fs.
For alignment support, a CCD-camera system is set up after the sample. The transmitted probe light as well as the transmitted pump and gain pulses are collected and collimated by a fast lens (F/2). Before an iris, used to eliminate pump and gain light in the detection channel, a kinematic mirror mount is positioned to direct all three beams towards a Sony XC-73 CCD camera. After the kinematic mirror a second lens images the sample and all three laser spots onto the CCD with a magnification of approximately 10. Both lenses (collecting and imaging lens) are cemented doublets to achieve high image quality.

The sample illumination is coupled into the probe path via a pellicle (to minimize group-velocity dispersion in the probe beam path) which is used as a beam splitter in front of the sample. In this way, good spatial resolution and contrast is obtained although aberrations are clearly present in the images introduces by inherent lens imperfections. If all three laser foci are brought onto a pinhole so that each beam had maximum transmission, three slightly separated images are obtained on the CCD. This indicates that the camera is not a reliable tool to maximize beam overlap. However, it proves to be very valuable for initial alignment and for choosing the best position on the sample as well as in the determination of laser induced damage.

Since most of the aberrations are introduced by the fast collecting lens, an improved design could make use of a microscope objective with a large field of view and small magnification as suggested by B. Fluegel. Utilizing the microscope objective at the conjugates it is designed for will probably result in much improved imagery. However, such a system will form a real image behind the sample, making it necessary to introduce an additional lens into the detection channel.
4.1.2 Data Acquisition

The spectrally resolved data acquisition is done with the optical multichannel analyzer and is completely automated. Two shutters, one in the pump beam and one in the probe beam, make it possible to account for scattered light and detector noise during the measurements.

A typical scan is taken in four steps. First one exposure with both shutters closed is taken (Exp. 1) for the background, which consists of dark current, remaining room light and scattered light from the gain beam. Next, one exposure is taken (Exp. 2) with only the pump shutter open, measuring the background plus scattered light from the pump and gain beam. Then both shutters are opened and the spectral hole burning data is taken (Exp. 3). In the last step only the probe shutter is opened to acquire the linear transmission of the sample (Exp. 4). All four exposures are then combined by a computer to yield the differential absorption of the sample according to the formula:

$$-\Delta \alpha L = -(\alpha - \alpha_0)L = -[\ln\left(\frac{I_p}{I_0}\right) - \ln\left(\frac{I}{I_0}\right)] = \ln\frac{I}{I_p} = \ln\left(\frac{Exp. 3 - Exp. 2}{Exp. 4 - Exp. 1}\right)$$

Equation 4

Here $\alpha$ stands for the absorption of the sample with both the gain beam and the pump beam present whereas $\alpha_0$ describes the absorption of the sample with only the gain beam on. $I_p$ and $I$ indicate the associated transmitted probe intensities and $I_0$ is the incident probe intensity. To further suppress scattered light in the detection channel both gain and pump beam were linearly polarized perpendicular to the probe beam.
Figure 26: Schematic of the data acquisition and resulting signal. $E_G$ labels the renormalized band gap and $T$ the transparency point.

A schematic of the data acquisition algorithm and of the resulting data are shown in Figure 26. Effectively, first the absorption of the sample with the pump beam off is taken, as shown in the first graph of Figure 26. Since all the spectral-hole burning experiments are performed on inverted semiconductors the gain pulse is always present and the "unexcited" sample exhibits gain. Second, the absorption of the semiconductor is measured again, this time with the pump pulse present (second graph of Figure 26). Depending on the pump wavelength a spectral hole is either burned into the absorptive region of the sample (bleaching) or into its gain region (induced absorption). The absorption spectrum with the pump beam on is then subtracted from the absorption

$$\alpha L - \alpha L(\text{pump}) = -\Delta \alpha L$$
spectrum without the pump pulse present. The resulting curve is shown in the third graph of Figure 26. Only the burned spectral hole can be seen in the differential absorption data with a positive sign for bleaching (spectral hole in the absorptive region) and a negative sign for induced absorption (spectral hole in the gain).

Figure 27: Experimental spectral-hole burning data. Gain delay is approximately 400fs and pump-probe delay is incremented in 80fs steps. The pump spectrum is plotted on top of the wavelength scale.

Figure 27 shows actual experimental spectral-hole burning curves in inverted semiconductors. The plots are shown here for illustration purpose only and will be
discussed in detail later in this chapter. The negative differential absorption is plotted as a function of wavelength for five different pump-probe delays. Since the pump-probe delay increment for these curves is 80fs and the temporal width of the pump pulse is on the order of 200fs it is possible to literally see the pump pulse passing through the sample.

At early time delays (solid curve) a sharp negative dip develops slightly blue-shifted from the pump-pulse spectrum shown atop the wavelength scale. The front end of the pump pulse starts to penetrate the sample and the stimulated recombination process begins. The next two curves (dashed and dotted) show the spectral hole deepen as more and more carriers are taken out of the system with the pump pulse moving through the sample. The effects of carrier-carrier scattering become apparent in the last two curves (dash dot and dash double dot) as the pump pulse leaves the sample. Stimulated recombination slows down but carrier-carrier scattering is still an ongoing process. The spectral hole widens as carriers from surrounding states scatter into the vacancies of the spectral hole. The resulting broad and featureless signal at long pump-probe delays is due to the fact that the pump pulse reduces the carrier density in the sample and changes the distribution temperature (see below). This carrier depletion signal remains and changes only on the timescale on which the carriers recombine. The total spectral width of this remaining differential absorption is here defined as the signal bandwidth.

The origin of the slight blue-shift of the spectral hole with respect to the pump pulse is not understood satisfactorily so far. It has been suggested that a shifting band gap due to the change in carrier density might be the cause for the observed blue shift. However, it is obvious from Figure 27 that the hole does not shift dynamically with the
pump pulse. The time-delay separation between curves in Figure 27 is far less than the pump pulse width itself. This means that carriers are constantly taken out of the system and therefore the carrier density changes continuously between curves. The bandgap shift should follow this density change dynamically so that a different blue shift between curves would be expected. This is not the case. In fact the blue shift of the spectral hole is constant with time delay suggesting that it is independent of carrier density as well as instant pump intensity.

Figure 28 explains the origin of the carrier-depletion signal. In the spectral-hole burning process carriers are taken out of the system reducing the carrier density and changing the plasma temperature. This means that even after thermal equilibrium among the carriers is reached again, the Fermi functions before and after the pump pulse differ. The difference is measured in the differential absorption data as the carrier-depletion signal. Figure 28 displays a schematic of this process. The left figure shows the Fermi distribution of carriers at 100K with a burned spectral hole (solid line). Due to carrier-carrier scattering (indicated by the arrows) the spectral hole is filled up and thermal equilibrium among the carriers is again established but at a lower carrier density (dotted line). For simplicity the same temperature before and after the pump pulse has been assumed in the figure. The right-hand figure illustrates the resulting differential absorption: the carrier-depletion signal is the difference between the Fermi function before (dotted line) and after (solid line) the spectral-hole burning.
Two time delays can be varied in the spectral-hole burning experiments. The pump-probe delay governs the development of the spectral hole itself as one is able to see the pump pulse passing through the sample (described above). The second delay time is the gain delay which determines the plasma temperature at which the pump-probe experiment is performed. In the experiments described in this work, the samples have always been inverted optically to circumvent the problems associated with electrically pumped waveguide structures such as propagation effects and difficult beam coupling. The inverting pulse was tuned into the continuum states of the semiconductor, 90meV above
the heavy-hole exciton resonance. The initially nonthermal carrier-distribution function, which follows the gain pulse spectrum, is driven towards thermal equilibrium in less than 1ps by carrier-carrier scattering (compare Figure 23), which conserves the initial excess energy. The resulting carrier temperature may be very high depending on the wavelength of the gain pulse. On a considerably slower timescale (order of 50ps) this hot carrier distribution cools down by phonon emission, equalizing with the lattice. In the experiments described here the sample was always held at about 20K. Therefore, by varying the gain-delay time different plasma temperatures can be chosen at which the spectral-hole burning experiment is performed.

4.1.3 The Spectral-Hole Burning Samples

Two different samples were used in the spectral-hole burning experiments. Both are epitaxially grown GaAs/Al_xGa_{1-x}As multiple quantum wells (MQWs) of similar well width. However, they differ in their barrier widths and Al content, thus resulting in one type I and one type II MQW. In contrast to the type I MQW the type II heterostructure is characterized by an indirect-gap barrier material and appropriate well and barrier widths, such that the barrier's first quantized electron state is the lowest electron state of the system (see Figure 29). Absorption occurs at the quantized Г-states of the direct-gap well. Within about 1 psec, electrons scatter down to the X-point of the barriers, achieving a spatial as well as momentum-space separation from the holes. The type II sample is made up of 150 28Å GaAs wells separated by 56Å AlAs barriers.
Figure 29: Bandstructure of the type II and type I sample. The arrows in the type II sample indicate the scattering process of electrons from the well into the barrier.

The lowest confined state at the X-point of the Brillouin zone in the barrier is about 65meV lower than the lowest confined state at the Γ-point of the well, as was confirmed by photoluminescence spectra (Figure 30).

The type I sample on the other hand consists of 150 periods of 26Å GaAs wells and 80Å Al$_x$Ga$_{1-x}$As barriers ($x=0.41$). Both samples have their substrate removed to enable transmission experiments and are anti-reflection coated on both sides to virtually eliminate Fabry-Perot structures in the linear absorption. They are mounted free standing on a copper plate and held on the cold finger of a closed-cycle helium refrigeration system at about 20K.
Figure 30: Linear absorption (solid lines) and photoluminescence after cw excitation with a HeNe-laser (dashed lines) of the two samples at 20K. The Γ-X splitting of the type II multiple quantum well can be seen very well. Whereas the type I sample shows only one strong luminescence peak slightly Stokes shifted with respect to the heavy-hole exciton, the type II multiple quantum well exhibits two. One peak close to the heavy-hole exciton similar to the type I sample but 400 times weaker resulting from the direct Γ-Γ transition and one strong peak from the indirect Γ-X transition. The peak separation of about 100meV corresponds to the Γ-X splitting (65meV) and one LO-phonon energy (35meV).
4.2 Phonon-Induced Spectral Holes

Concerning the relaxation of hot electrons in non-inverted intrinsic and n-doped semiconductors, it is well known that energetically equidistant replicas of the initial carrier distribution occur as a consequence of carrier-LO-phonon scattering or scattering with phonon-plasmon coupled modes.\textsuperscript{52,53} In analogy to this effect, it is reasonable to expect the occurrence of phonon-induced replicas of a spectral hole in the gain region of an inverted semiconductor. One condition for the existence of these replicas is that the build-up time of such replicas needs to be faster than the relaxation time associated with carrier-carrier scattering. This section describes the experimental observation of LO-phonon emission by charge carriers in systems with gain.\textsuperscript{54} The measurement technique is spectral-hole burning in the type I multiple quantum well with very high carrier density. A simple model based on the semiconductor Bloch equations for noninteracting particles in conjunction with the Boltzmann equation for carrier-LO-phonon scattering supports the interpretation of the experimental data.

4.2.1 Experimental Data

Figure 31 shows spectral-hole burning data for four subsequent pump-probe delays at three different gain delays. The gain pulse is tuned to 660nm to inject the carriers with some excess energy so that the effects of a cooling plasma may also be observed. At all three gain delays (indicated in the lower left-hand corner of each graph) a spectral hole slightly blue-shifted from the pump-pulse spectrum is clearly developing for
Figure 31: Spectral-hole burning data in the type I multiple quantum well sample at very high carrier densities (~5x10^{13}/cm^2) and low temperature (20K).
increasing pump-probe delays. In this data the depth of the spectral hole increases dramatically in going from 1ps gain delay to 20ps gain delay. Also, the width of each of the three spectral holes decreases as well as the total signal bandwidth with increasing gain delay. It is extremely interesting to note that on the background of the carrier depletion signal an additional peak, approximately 40meV higher in energy than the original spectral hole, can be observed for gain delays of 10ps and 20ps.

Induced light-hole absorption, where the carrier depletion in the conduction band induces absorption at the light-hole band to conduction band transition, can not explain this phenomenon. Although the spectral separation between heavy and light hole excitons of about 39meV corresponds well to the peak separation in the spectral-hole burning data, this explanation can be ruled out for the following reasons. A careful analysis of the valence-band structure in the multiple quantum well sample reveals that the expected peak separation for induced light-hole absorption is not 40meV.

To determine the actual heavy hole light hole valence band splitting, the binding energies of the excitons need to be subtracted from their peak positions. This valence-band splitting should govern the peak separation in the differential absorption data since excitonic effects are significantly reduced in inverted semiconductors due to screening and phase space blocking. The three-dimensional 1s-exciton binding energy can be calculated according to the formula:

\[ E_o = -\frac{e^4 m_e}{2\varepsilon_0^2 \hbar^2} \]

Equation 5
where e stands for the electron charge ($e = 4.8 \times 10^{-10}$ esu), $m_r$ is the reduced mass of the electron and hole, defined as $1/m_r = 1/m_e + 1/m_h$ ($m_e = 0.067m_0$ in GaAs), $\varepsilon_0$ describes the background dielectric constant ($\varepsilon_0 = 10.9$ in GaAs) and $\hbar$ is Dirac's constant. In a quantum well the heavy hole ($m_{hh}$) and light hole ($m_{lh}$) in plane band masses are given by:

$$m_{hh} = \frac{m_0}{\gamma_1 + \gamma_2}, \quad m_{lh} = \frac{m_0}{\gamma_1 - \gamma_2}$$

Equation 6

with $\gamma_1 = 6.85$ and $\gamma_2 = 2.1$ for GaAs. $m_0$ is the free electron mass ($m_0 = 9.1 \times 10^{-28}$ g). Therefore, the three-dimensional 1s-exciton binding energy for heavy and light hole equate to 4.8meV and 5.8meV respectively. To account for the quasi-two-dimensional quantum confinement it is reasonable to multiply these values by a factor of 2, yielding a binding energy difference for the two excitons of about 2meV. This results in a 41meV heavy hole light hole valence band splitting at the $\Gamma$-point of the Brillouin zone. However, the spectral-hole burning experiments are not performed at the $\Gamma$-point but approximately 47meV above the renormalized band gap as can be seen from Figure 31. The beginning of the carrier depletion signal at long wavelengths marks the position of the renormalized band edge and its energetic distance to the burned spectral hole translates into k-space via the dispersion diagram (Figure 32).

In Figure 32 the thick solid arrow indicates the spectral-hole burning position in the experiment. At this position the k-state in the conduction band lies 47meV above its corresponding state in the heavy hole valence band. Due to the dispersion in the two valence bands, the band splitting at this particular k value has decreased to 32meV. This
rules out induced light-hole absorption as an explanation for the second peak in the experimental data of Figure 31.

Figure 32: Band structure close to the band edge of the quantum well. The band gap energy is set to zero.
Additional proof can be obtained when examining the spectral-hole burning data in Figure 33. Here the carrier density induced by the gain pulse has been reduced by one order of magnitude as compared to Figure 31. Although a very sharp and well resolved spectral hole is measured, no additional structure appears on the high energy side of the original spectral hole. The appearance of induced light-hole absorption, however, should be independent of carrier density as long as a pronounced spectral hole can be found. This is further evidence that the observed second peak cannot be accounted for by induced light-hole absorption.

![Figure 33: Spectral-hole burning data at low carrier densities.](image-url)
Closer inspection of the data in Figure 31 reveals even more interesting details. At 20ps gain delay a third peak, about 35meV higher in energy than the second, is visible for certain pump-probe delays. Even in the 10ps data, a shoulder in the differential absorption curves is observed in this wavelength region. Of course, induced light-hole absorption is not able to account for this peak at all.

The explanation for this very interesting experimental data is shown in Figure 34. Electrons higher in the band than the original spectral hole can emit one LO phonon and relax down into the vacancies of the non-equilibrium carrier distribution left behind by the pump pulse. Disregarding carrier-carrier scattering, the same non-equilibrium distribution develops one LO-phonon energy higher in the band as the spectral hole fills up with relaxing electrons, indicated in Figure 34 by a dashed line. This phonon replica of the original non-equilibrium carrier distribution causes a replica of the original spectral hole in the pump-probe spectra (dashed and solid arrows in Figure 34, respectively). Its energy, however, will be greater than the spectral-hole energy by not only one LO-phonon energy ($\hbar \Omega_{LO} = 35.1 \text{meV in GaAs}$), but by $\hbar \Omega_{LO} + \Delta$, taking the hole dispersion into account (see Figure 34).

For simplicity only single LO-phonon emission by the electrons is depicted in Figure 34 but multiple phonon emission as well as phonon emission of the holes is also possible, accounting for multiple spectral-hole sidebands. The inset in Figure 34 reminds the reader of the complicated valence-band structure.
4.2.2 Theory

In order to interpret the most basic and dominant features of the experimentally observed gain nonlinearities, a simple theoretical model is employed. This model is based
on the Boltzmann equation for carrier-LO-phonon scattering

\[ \frac{d}{dt} f^a_k |_{\omega = \phi} = \Gamma_{\text{in}}^a(\vec{k}) [1 - f^a_k] - \Gamma_{\text{out}}^a(\vec{k}) f^a_k \]

Equation 7

where \( f^a_k \) is the distribution function for electrons or holes (\( a = \) electron, hole). \( \Gamma_{\text{in}} \) and \( \Gamma_{\text{out}} \) describe the scattering rates into and out of the state with wavevector \( \vec{k} \), respectively, and are given by:

\[ \Gamma_{\text{in}}^a(\vec{k}) = \frac{2\pi}{\hbar} \sum_{\bar{q}} M^2_{\bar{q}} \left\{ \delta(\varepsilon^a_k - \varepsilon^a_{\vec{k}+\bar{q}} + \hbar\Omega_{LO}) [g_\theta(\Omega_{LO}) + 1] \\
+ \delta(\varepsilon^a_k - \varepsilon^a_{\vec{k}+\bar{q}} - \hbar\Omega_{LO}) g_\theta(\Omega_{LO}) \right\} f^a_{\vec{k}+\bar{q}} \]

Equation 8

\[ \Gamma_{\text{out}}^a(\vec{k}) = \frac{2\pi}{\hbar} \sum_{\bar{q}} M^2_{\bar{q}} \left\{ \delta(\varepsilon^a_k - \varepsilon^a_{\vec{k}+\bar{q}} - \hbar\Omega_{LO}) [g_\theta(\Omega_{LO}) + 1] \\
+ \delta(\varepsilon^a_k - \varepsilon^a_{\vec{k}+\bar{q}} + \hbar\Omega_{LO}) g_\theta(\Omega_{LO}) \right\} [1 - f^a_{\vec{k}+\bar{q}}] \]

Equation 9

Here \( M_{\bar{q}} \) is the carrier-LO-phonon coupling matrix element (Fröhlich coupling)

\[ M^2_{\bar{q}} = \frac{\hbar\Omega_{LO}}{2} \left( \frac{1}{\varepsilon_\omega} - \frac{1}{\varepsilon_0} \right) \frac{2\pi e^2}{|\bar{q}|} \]

Equation 10

\( g_\theta \) is the phonon-population Bose function and \( \hbar\Omega_{LO} \) is the LO-phonon energy. \( \varepsilon^a_k \) describes the carrier energy at wavevector \( \vec{k} \) according to \( \varepsilon^a_k = \hbar^2 |\vec{k}|^2 / 2m_a \), where \( m_a \) is the effective band mass. For a quantitative analysis, screening of the carrier-phonon
interaction, the finite well width form factor, as well as the effects of phonon-plasmon coupled modes, should also be included.\textsuperscript{52-53} To extract the relevant information from the carrier-phonon Boltzmann equation regarding optical nonlinearities in inverted semiconductors, Equation 7 has to be solved together with the simplest model for semiconductor optical nonlinearities, which is the non-interacting particle version of the semiconductor Bloch equations:\textsuperscript{11}

\[ i\hbar \frac{\partial}{\partial t} \left( \mathcal{E}_k^e + \mathcal{E}_k^h \right) P_k = (f_k^e + f_k^h - 1) d_{cv,k} E + \hbar \frac{\partial}{\partial t} P_k|_{\text{scatt}}, \]

Equation 11

\[ \frac{\partial}{\partial t} f_k^a = -\frac{2}{\hbar} \text{Im}(d_{cv,k} E) P_k^* + \frac{\partial}{\partial t} f_k^a|_{\text{scatt}}. \]

Equation 12

The semiconductor Bloch equations are the equations of motion of the carrier-momentum dependent optical polarization function $P_k$ and the corresponding occupation functions. They also contain excitonic effects due to the Coulomb potential. However, in inverted semiconductors, excitonic effects are significantly reduced due to screening and phase-space blocking. In the following analysis those contributions will be neglected because they modify the results only slightly. For clarity, carrier-carrier scattering will also be neglected, which only leads to additional spectrally broad changes as was carefully checked in numerical test calculations. If included, carrier-carrier scattering could be modeled by another Boltzmann equation that would add to the carrier-LO-phonon
Boltzmann equation (Equation 7) to form the occupation scattering term \( \frac{\partial}{\partial t} f_k^\xi \rvert_{\text{scat.}} \) in the semiconductor Bloch equations (Equation 12). However, carrier-carrier scattering cannot introduce distinctive and sharp spectral features as those observed in the experiment. In Equation 11, \( d_{\alpha k} E \) stands for the product of the dipole-matrix element and the electric field, representing the on resonance Rabi frequency of the system if divided by \( \hbar \).

The theoretical model is a simple parabolic two-band description of the semiconductor that does not include light-vector polarization effects. The experimental results were obtained using orthogonal linearly polarized pump-probe beams and for this reason the density grating, which yields the scattering of pump light into the probe direction if the pulses are co-linearly polarized, is set to zero. Hence, the results describe solely the phase-space-blocking effects as seen by the probe pulse due to the time-dependent carrier distribution function, determined by the pump-pulse and carrier-LO-phonon scattering.

Typical calculated curves are shown in Figure 35 (a) for four different pump-probe delays. The following parameters are used in the calculations: \( m_e = 0.067m_0 \) (\( m_0 = \) vacuum electron mass), \( m_h = 0.22m_0 \), \( T_{\text{phonon}} = 60 \) K, \( \hbar \Omega_{\text{LO}} = 35.1 \) meV, \( \varepsilon_0 = 12.7 \), \( \varepsilon_\infty = 10.9 \). The initial carrier density is chosen to be \( 2.1 \times 10^{12} \) cm\(^{-2} \) at a temperature of 60 K. The pump pulse is centered 20 meV above the bandgap \( E_{\text{Gap}} \), and has a duration (full width at half maximum of intensity) of 240 fs. In the equation for the optical polarization, a phenomenological dephasing time of 100 fs is used so that \( \hbar \frac{\partial}{\partial t} P_\xi \rvert_{\text{scat.}} = -\frac{\hbar}{100\text{fs}} P_\xi \) in Equation 11.
Figure 35: Comparison between theory (a) and experiment (b). The parameters for the calculation are given in the text. The experimental data corresponds to a gain delay of 10ps.
The qualitative agreement between theory in Figure 35 (a) and experiment in Figure 35 (b) is striking for this simple model. All major experimental features are reproduced. Similar replicas of the spectral hole to those found in the experiment are seen in the calculations. It can therefore be concluded that these additional structures to the spectral hole are created by the scattering of higher energy carriers into the vacancies of the spectral hole via LO-phonon emission.

The most serious limitation of the calculations is the restriction to a parabolic two-band model. Since, in the experimental conditions, the gain bandwidth exceeds the heavy hole light hole splitting, it is not immediately clear which value for the hole mass is most appropriate in a two-band simulation of the quantum wells. This becomes apparent from the circled inset of Figure 34, which schematically shows the effects of the heavy hole light hole anticrossing resulting in strong nonparabolicities of the hole dispersion. In the calculations, which are restricted to the parabolic two-band approximation, a valence-band in-plane mass of $m_h = 0.22m_0$ was chosen. This value corresponds to the light hole in plane mass derived from the Luttinger theory for quantum wells and is used because the quasi-chemical potential of the heavy-hole is of the same order of magnitude as the heavy hole light hole splitting. Consequently, for a description of processes occurring close to the quasi-chemical potential, it is unreasonable to simply use the heavy-hole mass at the top of the heavy-hole valence band. The hole mass, however, critically determines the spectral separation of the LO-phonon sidebands among each other and with respect to the original spectral hole. If, for example, the hole had an infinite mass (no curvature), the optically
detected sidebands corresponding to electron-phonon scattering would occur with one LO-phonon energy separation. This would be analogous to the method used in reference 52, where the observed transition involved acceptor levels instead of valence-band holes. If, on the other hand, the hole had a mass equal to the electron mass, the optically observed sidebands would occur at twice the LO-phonon energy. One therefore expects to observe sidebands with an energy separation larger than one LO-phonon energy.

The intuitive understanding of the dynamics of the spectral hole and its replica is very well supported by the model. At negative time delays (i.e., the probe pulse precedes the pump) the spectral hole is more pronounced than its replica, showing that vacancies have to be established first before the scattering process can take place. As the pump pulse passes through the sample (0 fs), both spectral hole and replica rise quickly, indicating that carriers are constantly taken out of the system by the pump pulse at the spectral-hole position and, at the same time, higher energy carriers scatter down, filling up the spectral hole. At later time delays (+80 fs), stimulated recombination is slowed down as the pump pulse leaves the sample. The scattering, on the other hand, is still an ongoing process, causing the phonon-induced spectral hole to further deepen and the relative weights between spectral hole and its replica to change.

In conclusion, phonon-induced spectral holes in the gain region of an inverted semiconductor are observed experimentally. Numerical solutions of a simplified version of the semiconductor Bloch equations based on the carrier-phonon Boltzmann equation support the interpretation of scattering of higher energy carriers into the spectral hole via
4.3 Carrier Dephasing in Cooling Plasmas

The observation of phonon-induced spectral holes comes unexpected for many people involved in inverted semiconductor research. This is due to the fact that in hot plasmas carrier-carrier scattering is a very efficient scattering mechanism which drives charge-carrier distributions towards thermal equilibrium on an extremely fast timescale. Spectral holes, however, are caused by highly nonthermal carrier distributions, and the observation of phonon replicas requires these nonthermal distributions to persist long enough for sidebands to develop. Therefore, the LO-phonon emission of high energy carriers has to occur faster than the destruction of the nonthermal carrier distribution by carrier-carrier scattering. This seems unreasonable, since scattering times for carrier-carrier scattering in hot plasmas are often less than 100fs and LO-phonon emission times are on the order of several hundred femtoseconds. However, this is only true for hot plasmas. It has been shown that the carrier dephasing rate in a cold plasma strongly depends on the carrier's momentum and can reach values up to 750fs. Close to the combined chemical potential of electrons and holes (also called the transparency point since at this wavelength gain turns into absorption and the semiconductor is transparent), the dephasing time exhibits a maximum due to blocked carrier-carrier scattering channels. This effect makes it possible to observe phonon-induced spectral holes in cold plasmas.
Figure 36: Typical spectral holes and carrier dephasing times as a function of gain delay. Also shown in the graph for 20ps gain delay is the pump-pulse spectrum with its Gaussian fit.
Figure 36 shows typical spectral holes for gain-delay times of 1ps, 10ps and 20ps, each with a best Gaussian fit. From the width of the spectral hole it is possible to determine the homogeneous linewidth of the transition and therefore the carrier-dephasing time. The homogeneous linewidth is connected to the lifetime of the corresponding state via Heisenberg's uncertainty principle $\Delta \omega \cdot T_1 \geq 1$, where $\Delta \omega$ is the full width at half maximum of the homogeneous linewidth and $T_1$ the lifetime.$^{58}$ In the relaxation time approximation for a semiconductor, $T_1$ translates to the effective occupation relaxation time for a two component plasma $T_1^{\text{eff}}$ which relates to the dephasing time $T_2$ according to $T_2 = 2 \cdot T_1^{\text{eff}}$. Therefore homogeneous linewidth and dephasing time follow the equation $\Delta \omega \cdot T_2 = 2$.

To obtain the homogeneous linewidth of the transition it is necessary to deconvolve the pump-pulse spectrum from the burned or real spectral hole. However, the burned spectral hole is not what appears in the data. To detect the burned spectral hole it is probed with a white light continuum which results in an additional convolution with the homogeneous lineshape. This last convolution can be understood intuitively when considering the smallest spectral window possible to sample. Even if the probe pulse were monochromatic the best resolution that can be obtained is governed by the homogeneous linewidth of the transition. This makes it clear that the detected spectral hole is a convolution of the burned spectral hole with the homogeneous linewidth. Equation 13 summarizes (the * symbolizes a convolution in $\omega$):
\[(\text{detected spectral hole}) = (\text{burned spectral hole}) \cdot (\text{homogeneous line})\]
\[= [(pump\ pulse) \cdot (\text{homogeneous line})] \cdot (\text{homogeneous line})\]
\[= (pump\ pulse) \cdot [(\text{homogeneous line}) \cdot (\text{homogeneous line})]\]

Equation 13

In general this equation has to be solved numerically but if the pump pulse can be assumed to be Gaussian and its width is comparable to the homogeneous linewidth, Equation 13 can be replaced by the approximation

\[(\text{detected spectral hole}) = [(pump\ pulse)^2 + (2 \cdot \text{homogeneous line})^2]^{1/2}.

Equation 14

The approximation is based on the fact that if the detected spectral hole can be assumed Gaussian then the pump pulse can be deconvolved analytically since the square of the width of two Gaussians convolved with one another is the sum of the squares of the single Gaussian widths. The resulting Gaussian has to be interpreted as the convolution of a Lorentz function with itself so that the width of the underlying homogeneous lineshape (assumed Lorentzian) can be easily found since the width of two Lorentzians convolved with one another is simply the sum of their individual widths. Combining all of the above, it follows that the dephasing time \(T_2\) can be found from the observed spectral-hole width \(\Delta \lambda\) (FWHM) and pump pulse width \(\Delta \lambda_p\) (FWHM) according to:
Here $\bar{\lambda}$ denotes the central wavelength of the observed spectral hole and $c$ the speed of light in vacuum.

The carrier-dephasing times listed in Figure 36 are calculated using Equation 15. It is interesting to note that the approximation works very well for broad spectral holes as the one for 1ps gain delay. Taking the determined dephasing time and translating it into a theoretical spectral hole width, the calculation can be reversed to check the accuracy of the retrieved dephasing time.

Figure 37 shows the convolution of the determined Lorentzian line with itself and a Gaussian line with the width of the pump pulse for all three considered gain delays along with the constituent curves. The results are fitted with Gauss functions to determine their widths. The discrepancy of the calculated, expected spectral hole width from the measured spectral hole width is only 5% at 1ps gain delay, but increases to about 18% for 20ps gain delay. The uncertainties given in Figure 36 try to accommodate this error as well as uncertainties arising from the fitting procedure. The extraction method for $T_2$ from the experimental data tends to underestimate the numerical value of the dephasing time. Therefore, it is still safe to state, that for gain delay increasing from 1ps to 20ps the dephasing times increase by at least 300% from 130fs to 390fs.

$$T_2 = \frac{\bar{\lambda}^2}{\pi c} \frac{1}{\frac{1}{2} \sqrt{(\Delta \lambda)^2 - (\Delta \lambda_p)^2}}.$$  

Equation 15
Figure 37: Calculated real spectral holes for the three gain delays. The procedure is described in the text.
This dramatic increase of the carrier dephasing time with decreasing plasma temperature and the large numerical values of $T_2$ that can be encountered in cold plasmas comes unexpected for many scientists although it has been known in plasma physics for a long time.\textsuperscript{59} However, the reason for this behavior can be easily understood intuitively and is schematically depicted in Figure 38. With decreasing plasma temperature, scattering channels that were open at higher temperature become blocked due to phase space filling.

Only those carriers between the spectral hole and the transparency point are allowed to take part in carrier-carrier scattering processes efficiently. Carrier-carrier scattering conserves the total energy as well as the total momentum of the scattering partners so that if one carrier is to lose energy, it has to be gained by another. Carriers other than those between the spectral hole and the transparency point cannot find a scattering partner, since either the final state is already occupied or no scattering partner with a matching energy and momentum is present. An example for a blocked scattering channel is indicated in Figure 38 by dotted arrows. At high temperature all states are only partially filled with the result that all scattering events are possible. It is clear, that this mechanism can have a large impact onto the carrier dephasing close to the transparency point.

From these considerations also follows that in a cooling plasma, close to the combined chemical potential of electrons and holes, the relative significance of carrier-carrier and carrier-LO-phonon scattering can change dramatically with temperature. This is also apparent from the spectral-hole burning data in Figure 31. No phonon sidebands
are detected for 1 ps gain delay when the spectral hole is still broad and shallow. At this gain delay the plasma temperature is simply still too high and carrier-carrier scattering too efficient for phonon-induced spectral holes to develop. With increasing gain delay, and therefore decreasing plasma temperature, the spectral-hole replicas become more and more pronounced.

Figure 38: Schematic for the mechanism causing the carrier dephasing time to be a function of plasma temperature.
In summary it can be said that unambiguous experimental evidence is presented showing that plasma temperature and carrier-carrier scattering are inherently connected. The higher the plasma temperature, the more scattering channels are open for the charge carriers and the lower the dephasing time. It would certainly be fruitful to quantify this relationship in further investigations.

4.4 Ultrafast Gain

This section is concerned with spectral-hole burning in inverted type I and type II multiple quantum wells and a comparison between the charge-carrier dynamics in the two systems is made. The samples are introduced in Chapter 4.1.3 on page 70. A new technique to accurately measure dynamic transitions from gain to absorption and vice versa will be presented, and it will be demonstrated that subpicosecond gain in type II multiple quantum wells is possible.60

The work was stimulated by the research of Ken Meissner et al. who compared the ultrafast nonlinear optical response of type I and type II quantum wells.61 In the type II samples a scattering time of less than 1ps was found for the photoexcited electrons to move from the well into the barriers.62 It should be possible to exploit this mechanism to make an ultrafast optical amplifier. However, Winston Fu et al.63 showed that for very high carrier densities, gain persists in type II samples even longer than in type I. Here the electrons in the barriers can act as a reservoir, replenishing the electrons at the direct transition so that the inversion can sustain even longer.
4.4.1 Measurement Technique

Gain measurements are commonly made using a simple two beam pump-probe experiment. A strong pump pulse hits the sample and a weak probe interrogates the absorption after a certain time delay. Data taken with the pump beam active is subtracted from the transmission without the pump pulse present to yield the two-beam differential absorption signal. This signal, taken as a function of time delay between the two pulses, is then compared to the linear absorption of the sample. Wherever the two-beam differential absorption exceeds the linear absorption, gain is said to be present.

Figure 39 gives an example of this technique in the type II and type I samples. The pump pulse is tuned resonantly to the heavy hole exciton transition to inject the carriers as cold as possible. This is done to avoid any carrier loss in the type II sample during the cooling process. In each case the thick solid line represents the linear absorption of the sample.

It is apparent from this figure that no accurate gain measurements are possible with this technique since the crossover points are difficult to determine. Furthermore, the linear absorption shown in the figure represents only one certain measurement. If compared to other linear absorption curves taken under the same conditions, it becomes evident that the offset of the linear absorption exhibits an uncertainty of approximately 0.1. This is due to scattering and reflection losses at the surfaces despite the fact that great care was taken to antireflection coat both surfaces of each sample. This is not tolerable in delicate measurements as these.
Figure 39: Two-beam differential absorption spectra for the type II and type I sample as a function of time delay. On top of the wavelength scale each pump pulse spectrum is depicted.
To overcome the disadvantages of the two-beam differential absorption method a new technique based on spectral-hole burning was developed. Figure 40 shows typical spectral-hole burning data for the two samples at the carrier density under investigation. Great care was taken to inject equal carrier densities into the two samples (see Appendix B). The data are very similar in both cases, aside from the apparent difference in signal strength. A spectral hole slightly blue-shifted from the pump spectrum clearly develops at early time delays and changes into a broad and featureless carrier-depletion signal at longer pump-probe delays. The gain delay for this data is 500fs.

The depth of the spectral hole at any certain time delay, before carrier-carrier scattering noticeably sets in, must be proportional to the amount of gain present at this wavelength. On the basis of this understanding the new experimental technique is developed. Monitoring the dashed curve in Figure 40 for each of the two samples and varying the gain delay allows to accurately trace the gain evolution at this particular wavelength. This method has several advantages. First, it is independent from any linear absorption measurements. No longer have two sets of data to be compared. Second, this technique is not sensitive to any surface effects since only the “internal” gain is measured. Finally, the signal changes sign as gain becomes absorption and vice versa, allowing for extremely accurate dynamic measurements. This can be seen in Figure 26. In the gain region of a semiconductor, spectral-hole burning yields a negative signal, whereas in the absorptive region a positive signal is found.
Figure 40: Spectral-hole burning data in the type II (top) and type I (bottom) sample at 500fs gain delay. The pump pulse is depicted on top of the wavelength scale. For the gain pulse spectrum see Figure 39.
Figure 41 shows a schematic of the utilized setup. The probe light transmitted by the sample can be either sent to an optical multichannel analyzer to take spectral-hole burning data or to a 0.25m monochromator with photomultiplier (PMT) to monitor a bandwidth of 5nm as a function of gain delay. The signal of the PMT is read with a lock-in amplifier that is referenced to a mechanical chopper modulating the pump at a frequency of about 100Hz. The pump-probe delay is kept fixed at about 0fs for all the measurements.

Figure 41: Schematic of the setup for the ultrafast gain measurements. The mirror behind the sample is kinematic so that the transmitted probe light can either be directed to an optical multichannel analyzer or into a monochromator with photomultiplier.

4.4.2 Experimental Data

The experimental method described in the previous section is used to analyze the dynamic gain behavior of the type II and type I samples. Typical resulting curves are
Figure 42: Gain dynamics in the type II (top) and type I (bottom) sample. Note the different time scales for the two graphs.

shown in Figure 42. Negative signal corresponds to gain and positive to absorption. In the type II sample gain exists from 250fs gain delay to about 1ps. In contrast, the type I
sample shows gain for more than 45ps. The carrier density in both cases was adjusted to about 9*10^{12}/cm^2. The reason for this striking difference is the scattering of electrons from the direct well into the barrier. The carriers are optically excited by the gain pulse, tuned resonant to the first quantum confined state at the Γ-point of the well. However, in the type II sample the electrons do not stay at this location, since an energetically more favorable state lies within the barrier. Therefore, the electrons scatter from the Γ-point of the well to the X-point of the barrier, resulting in a momentum as well as real space separation from the holes which stay at the Γ-point. This process terminates all stimulated recombination, and any gain decays very quickly.

Figure 42 also demonstrates the accuracy of the dynamic measurement. The slope at time delay 0 is not due to lack of response but shows the actual gain build up in the sample. The full width at half maximum of 90fs for the gain pulse accounts for the measured slope.

In summary, the gain dynamics in type II and type I multiple quantum wells are investigated and compared. In the type II sample, ultrafast gain persisting for less than one picosecond is observed in contrast to the type I sample, where gain can be monitored for more than 45 ps under the same conditions. A new experimental technique is presented which allows to unambiguously measure very small amounts of gain, and to accurately determine dynamic transitions from gain to absorption and vice versa that can also be used in other experiments.
5. CONCLUSIONS AND OUTLOOK

This dissertation described a comprehensive study of high density carrier dynamics in structured III-V semiconductors. The research was concentrated onto the carrier-recombination dynamics in the exciting III-Nitride material system as well as the gain dynamics and carrier scattering processes in GaAs/AlGaAs multiple quantum wells. The results can be summarized as follows:

The photoluminescence of the Nichia NLPB 500 super bright blue light-emitting diode (LED) as well as of a pure GaN layer was measured temporally and spectrally as a function of incident intensity and lattice temperature using streak-camera techniques. Spectrally two dominant emission bands are found for both types of samples. One is identified as band-edge luminescence whereas the second one is associated with impurity related recombination. The band-edge luminescence shows simple almost exponential decays qualitatively independent of pump power or lattice temperature. Typical time constants were found to be on the order of 50ps. For highest pump powers amplified spontaneous emission was found at the band edge of the electrode layers in the LED. The impurity related emission was very different for the two samples. In the pure GaN layer the yellow luminescence decayed with a time constant of approximately 570ps for low pump powers which was preceded by a very fast component at higher pump intensities. In contrast, the LED showed a two-component decay for all pump powers. The first part was too fast to be measured with our system and the second part showed a decay time ranging
from 200ps to 700ps, highly dependent on pump intensity. This behavior was well explained in a three-level rate equation model with saturable intermediate state.

A new experimental technique was introduced for accurate measurements of gain dynamics based on spectral-hole burning. Using this technique subpicosecond gain in type-II multiple quantum wells was demonstrated and explained by the fast \( \Gamma-X \) scattering process of the electrons.

Phonon-induced sidebands to spectral holes in inverted semiconductors were measured and identified using a numerical model based on the Boltzmann equation in connection with the optical Bloch equations. This was the first demonstration of phonon replicas at carrier densities much higher than \( 10^{10}/\text{cm}^2 \).

A study of the dephasing time as a function of electron-hole plasma temperature was presented. It was shown that in cool plasmas carrier-carrier scattering channels become blocked increasing the dephasing time by a factor of three as compared to hot plasmas.

Future work in these projects should include time-resolved photoluminescence measurements in the recently demonstrated blue laser diode based on the III-Nitride material system to identify and solve problems with respect to roomtemperature cw lasing. In the GaAs/AlGaAs material system a quantitative study of the dephasing time as a function of plasma temperature should be conducted since a strong dependence like the one demonstrated comes to a surprise to many scientists and could very well be used as input for theoretical calculations.
APPENDIX A: LASER SYSTEM ALIGNMENT AND TRIGGERING

The following gives a brief introduction to the most crucial alignment procedures and maintenance responsibilities of the femtosecond laser system in the Royal Science Force Lab. A brief description of the triggering setup is also given.

The concentrations of dye in the CPM laser jets need to be matched to each other for stable operation. If too much R6G is present in the gain jet the laser will tend to oscillate with more than two pulses propagating in the cavity; if too little dye is supplied, the laser will tend to go off. Nothing will replace experience in this matter, but here is a rough recipe on how to choose initial concentrations: add R6G to fresh ethylene glycol in the gain circulator until the argon light transmission decreases to a value 95% of the initial transmission with only ethylene glycol in the circulator. Then add DODCI to fresh ethylene glycol in the saturable absorber circulator until the laser mode locks satisfactorily. Add dye carefully since it takes a while for it to disperse homogeneously. The argon power for this process should be around 3.5 W. As the dyes grow old, fresh dye solution can be added to the circulators to improve performance and argon power can be adjusted.

Most of the dyes dissolve very well in methanol and not so well in ethylene glycol. Therefore, it is often necessary to dissolve the dye in methanol first and then add the solution to ethylene glycol. However, the viscosity of methanol is much lower than that of ethylene glycol and too much methanol in the circulator will upset the jet. Therefore, when preparing new dye solutions especially for circulators with a jet, as little methanol as possible should be used. The suggested procedure for a dye change is as follows: drain as
much old dye solution as possible from the circulator. Rinse the circulator several times with methanol until the circulating methanol remains reasonably clear. Don't forget to clear out the filter housing after each rinse. To remove any excess methanol from the system it is necessary to rinse the circulator at least once with ethylene glycol or whatever solvent is to be used before filling it up with the liquid to which the fresh dye will be added.

Should it ever be necessary to align the CPM cavity from scratch, proceed as follows: remove the prisms from the cavity. Align the prism setup outside the cavity using a HeNe laser. The total prism setup must not deviate the beam and all prisms should be in the minimum deviation configuration. Using only the gain jet trace the ASE (amplified spontaneous emission) through the ring cavity and try to get it lasing cw. Once it lases well cw introduce the prisms into the cavity and realign. After bringing it back to lasing switch on the saturable absorber jet and try to get it mode locking. Good luck.

For the day to day adjustments of the CPM it is usually sufficient to realign the spot of the argon pump beam on the R6G dye jet. Also the pump power and GVD compensation should be adjusted for best stability and pulse spectrum. Average output power should be around 10mW and pulse duration down to 60fs can be achieved. During operation the covers of the CPM laser should be kept closed since it is very sensitive to thermal fluctuations (AC outlet is just above it). Only very seldom it is necessary to tweak up the cavity or the dye jet positions.

The high output power of the TFRs (the pump lasers of the first and second amplifier) makes them sensitive to pulse amplitude fluctuations which can damage the Q-switch. It is therefore necessary for them to be “soft started”. When switching on the
emission, the laser should first be run on internal triggering and afterwards be switched to external triggering. Starting the TFR directly with external triggering will result in an extremely high power first pulse that may damage the Q-switch. Therefore, adjusting the CPM with the TFRs on external triggering should be avoided since the trigger signal might get lost.

The first amplifier should be completely realigned on a regular basis (e.g. when changing the setup or changing the R640 dye). The amplifier should be realigned such that the power is maximized after each pass. Output pulse energy should be around 4\(\mu\)J per pulse in a 90fs pulse after the GVD compensation stage. The prisms here have a separation of about 260mm.

The alignment of the second amplifier is limited to adjusting the input as well as the position and focus of the pump beam on the dye cell. When changing the selected wavelength from the continuum, the dye in the second amplifier has to be matched to that wavelength. Four different circulators are available that all fit the second amplifier so that not always a complete dye change is necessary but only a circulator change, if a circulator is equipped with the correct dye solution. To change circulators unscrew the connectors of the two dye hoses and remove the circulator from the system. Link the dye outlet of the amplifier to a beaker with a short hose and rinse the dye cell with methanol. Connect the new circulator.

The whole laser system is triggered by a photodiode in the CPM oscillator. The leakage from one of the resonator mirrors is imaged on an avalanche photodiode. To shape the output electrical pulses, the signal is routed to an amplifier with an integrated
discriminator. The outlet of the discriminator is connected to a prescaler that cuts the pulse repetition frequency by a factor of 16 and further conditions the signal. A fancy AND gate then combines the pulses with a reference oscillator which is usually set to run at 1kHz. This is the maximum trigger frequency for the TFR lasers without significant loss in pulse energy.

This reference oscillator controls the repetition rate of the whole system. It is a self-made design with external power supply. To change its frequency the housing has to be opened and one of the trim pots inside adjusted. For the experiments with the streak camera, the repetition rate of the laser was reduced to 750Hz since trigger jitter limited the time-resolution in these measurements and the maximum external trigger frequency of the streak camera was specified to be 1kHz. Lowering the repetition rate resulted in improved trigger jitter of the streak camera.

The signal from the AND gate now has a frequency specified by the reference oscillator and is synchronized to the CPM output. It is used to trigger a Stanford Research Systems four channel digital delay/pulse generator which in turn triggers the TFR lasers and the oscilloscope used for pulse diagnostics after each amplifier. By adjusting the delay of the trigger signal for the TFRs, the temporal pump pulse overlap in the amplifiers can be optimized. The timing of the trigger setup shows a slow drift with time so that readjustment of the TFR triggering is necessary several times during a day.
APPENDIX B: CARRIER DENSITY MEASUREMENTS

A calibrated avalanche photodiode is available to measure pulse energies. To determine how many carriers have been excited by a single pulse, the pulse energy before and after the sample must be measured. The number of photons absorbed in the sample gives an estimate of the excited carrier density. This method, of course, does not account for any other loss mechanisms (like surface losses) other than absorption in the sample and can therefore only be regarded as giving rough estimates.

The detector used in these measurements is an avalanche photodiode (Texas Optoelectronics Inc. TIED59). Three such photodiodes are available in The Royal Science Force Lab. The calibrated one has a cardboard back and is usually used to monitor the output of the second amplifier. It was calibrated using the output of the CPM laser and a reliable cw power meter. The calibration factor was found to be $1.2 \times 10^{-10} \text{J/V}$ at 620nm. For the measurement the detector has to be connected to an oscilloscope, and the range has to be kept between 10mV and 100mV using calibrated ND-filters. If a different wavelength than 620nm is used, the result has to be corrected for the spectral response of the detector. Even very little discrepancy from 620nm can make an appreciable difference.
REFERENCES


3 "...With the advent of everyday use of elaborate calculations, speed has become paramount to such a high degree that there is no machine on the market today capable of satisfying the full demand of modern computational methods. The most advanced machines have greatly reduced the time required for arriving at solutions to problems which might have required months or days by older procedures. This advance, however, is not adequate for many problems encountered in modern scientific work and the present invention is intended to reduce to seconds such lengthy computations..."

From the ENIAC patent (No. 3,120,606), filed 26 June 1947.

4 See your local computer dealer.

5 The first observation of radiation emission in GaAs was made by Braunstein in 1955 [R. Braunstein, Phys. Rev. 99, 1892 (1955)]. However, it was not until 1962 before it was realized that a p-n junction could prove an efficient light source [J. I. Pankove, Phys. Rev. Lett. 9, 283 (1962)].

6 The first laser diodes were reported almost simultaneously by groups at General Electric Corporation, IBM Corporation, and the Lincoln Laboratory associated with the Massachusetts Institute of Technology:
REFERENCES - Continued


REFERENCES - Continued


30 Nichia Chemical Industries, Ltd., Anan, Tokushima-ken 774, Japan.
REFERENCES - Continued

31 Nakamura announced their invention to his colleagues around the world on Dec. 11, 1995 by sending an email. There were also articles in Japan’s daily press but the first scientific paper is: S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Yamada, T. Matsushita, H. Kiyoku, and Y. Sugimoto, Jpn. J. Appl. Phys. 35, L74 (1996).


REFERENCES - Continued


REFERENCES - Continued

(1993).


REFERENCES - Continued


57 G. Mohs, R. Binder, B. Fluegel, H. Giessen, N. Peyghambarian, “Phonon emission by non-equilibrium carriers in the gain region of an inverted semiconductor”, Quantum
REFERENCES - Continued

Electronics and Laser Science Conference (QELS), June 2-7, 1996, Anaheim, California.


