Doctoral Thesis

GaInNAs SESAMs and VECSELs at 1.3 and 1.5 µm wavelength

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GaInNAs SESAMs and VECSELs at 1.3 and 1.5 μm wavelength

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DOCTOR OF SCIENCES

presented by

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2) A. Rutz, R. Grange, V. Liverini, M. Haiml, S. Schön, U. Keller: 1.5-µm GaInNAs SESAM passively mode-locking a solid-state laser, European Molecular Beam Epitaxy Workshop (Euro-MBE 2005), Grindelwald, Switzerland, 7.3 - 9.3. 2005


10) A. Rutz, V. Liverini, L. Li, P. Navaretti, D. J. H. C. Maas, A. Fiore, S. Schön, U. Keller: GaInNAs and InAs QD-SESAMs modelocking a 1.3 µm GaInNAs VECSEL, EMRS spring meeting 2007, Strasbourg, France, 28.5. – 1.6. 2007

11) A. Rutz, V. Liverini, L. Li, P. Navaretti, D. J. H. C. Maas, A. Fiore, S. Schön, U. Keller: GaInNAs and InAs QD-SESAMs modelocking a 1.3 µm GaInNAs VECSEL, MRC meeting ETHZ 2007, Zurich, Switzerland, 27.6. 2007

12) A. Rutz, V. Liverini, E. Müller, S. Schön, U. Keller, “GaInNAs und InAs-QD SESAMs für modengekoppelte 1.3 µm GaInNAs VECSELs”, Deutscher MBE-Workshop (DMBE 2007), Jülich, Germany, 1.10. – 2.10. 2007
Abstract

Modelocked solid-state lasers and vertical-external-cavity surface emitting lasers in the wavelength region of 1.3 to 1.5 μm are an interesting topic for several applications from telecommunication to frequency-doubled sources for video projection systems. Direct band gap semiconductor materials with specifically designed properties are the key to these applications. GaInNAs offers the possibility to choose the band gap energy and lattice constant independently and is thus a promising candidate as an active and passive semiconductor material in this wavelength range. An understanding of the material properties, as well as a stable growth process forms the foundation for a commercial application of such dilute nitride semiconductors in future.

This thesis discusses the properties and fabrication of GaInNAs material with different perspective. In a first step, GaInNAs-based semiconductor saturable absorber mirrors (SESAMs) for modelocking of solid-state lasers at 1.5 μm wavelength are developed. Prior to this project, 1.3 μm GaInNAs SESAMs were already fabricated in our group. On the basis of these devices, we developed SESAMs for an Er:Yb:glass laser (ERGO) operating at 1534 nm. The final structure showed a modulation depth of 0.39% and a saturation fluence of 20 μJ/cm² in an antiresonant structure, which is an exceptionally low value for quantum well devices. Due to the large number of growth-defects introduced during nitrogen incorporation, a bleaching recovery time of 18 ps was attained. Using this SESAM, pulses of 5 ps duration at a repetition rate of 61 MHz were obtained from the laser.

As a second step, a GaInNAs-based vertical external-cavity laser (VECSEL) was developed. For efficient laser operation, the active material needs to be as defect-free as possible. These requirements stand in contrast to the necessary properties for SESAMs. In order to find the right growth conditions, extensive experiments were performed. The growth temperature, V/III BEP ratio, plasma
cell operating conditions as well as the thermal annealing parameters were optimized. These studies indicated that the best quality active GaInNAs material for lasers is obtained at a growth temperature of 410°C at a V/III BEP ratio close to equilibrium, followed by an MBE in-situ annealing process at 700°C. Using such material, we fabricated a GaInNAs VECSEL, generating 600 mW continuous wave output. Modelocked operation was also demonstrated at a repetition rate of 6 GHz and a pulse duration of 18.7 ps using a GaInNAs SESAM specifically developed for this VECSEL.

As the processes limiting the radiative efficiency in GaInNAs are still largely unknown, an experiment to characterize deep level defects in GaInNAs was conducted. Photoinduced current transient spectroscopy (PICTS) was used for the characterization of deep-level defects in SESAMs and active structures. The goal was to find a correlation between the growth and annealing process and the resulting deep-level defect concentration. The results indicate that the method itself works well in the presented setup, allowing for measurements of single quantum wells with high resolution. However, we finally have to conclude that PICTS or other thermal spectroscopy techniques are unsuitable to understand the origin of fast carrier recombination in SESAMS or generally in dilute nitride semiconductors.
Modengekoppelte Festkörperlaser und oberflächenemittierende Halbleiterlaser mit vertikaler Kavität (VECSEL) im Wellenlängenbereich von 1.3 bis 1.5 μm sind für verschiedene Anwendungen von Telekommunikation bis hin zu frequenzverdoppelten Quellen für Videoprojektion interessant. Halbleitermaterialien mit direkter Bandlücke und speziell angepassten Eigenschaften sind der Schlüssel zu diesen Anwendungsgebieten. Mit GaInNAs ist es möglich, einerseits die Bandlücke als auch die Gitterkonstante des Materials unabhängig voneinander einzustellen. Daher ist GaInNAs ein vielversprechender Kandidat als aktives und passives Halbleitermaterial in diesem Wellenlängenbereich. Das Verständnis der Materialeigenschaften sowie ein stabiler Herstellprozess sind wichtige Grundlagen für eine zukünftige kommerzielle Verwendung von verdünnten Nitridhalbleitern.

Diese Arbeit behandelt die Eigenschaften und die Herstellung von GaInNAs in verschiedenen Aspekten. In einem ersten Schritt wird die Entwicklung von GaInNAs-basierenden sättigbaren Halbleiter-Absorberspiegeln (SESAMs) für modengekoppelte 1.5 μm-Festkörperlaser diskutiert. In einem dieser Arbeit vorhergehenden Projekt wurden in unserer Gruppe bereits GaInNAs SESAMs für 1.3μm Wellenlänge entwickelt. Auf der Basis dieser Bauelemente entwickelten wir SESAMs für einen Er:Yb:Glas Laser (ERGO) bei einer Wellenlänge von 1534 nm. Die verwendete Struktur zeigte eine Modulationstiefe von 0.39% und eine Sättigungsfluenz von 20 μJ/cm² in einer antiresonanten Struktur, was für Quantentopf-basierte Bauelemente ein außerordentlich niedriger Wert ist. Aufgrund der grossen Anzahl an Punktdefekten die durch den Stickstoffeinbau beim Wachstum entstanden sind, wurde eine Ausbleichungs-Erholzeit von 18 ps erreicht. Mit diesem SESAM konnte der Laser bei einer Pulswiederholfrequenz von 61 MHz und einer Pulsdauer von 5 ps betrieben werden.

Über die Prozesse welche den Strahlungswirkungsgrad von GaInNAs begrenzen ist immer noch wenig bekannt. Um mehr über die Rolle der tiefen Störstellen in aktiven und passiven Strukturen zu erfahren, wurden photoinduzierte Stromtransientenmessungen durchgeführt (PICTS). Das Ziel war es, eine Korrelation zwischen den Herstellbedingungen und der resultierenden Konzentration an tiefen Störstellen zu finden. Die Resultate zeigen dass die Methode mit den vorliegenden Strukturen gut funktioniert und auch die Messung von einzelnen Quantentöpfen mit hoher Auflösung erlaubt. Allerdings mussten wir feststellen dass PICTS als auch andere thermische Emissionsspektroskopie methoden nicht geeignet sind um die Ursache für die schnelle Ladungsträgerrekombination in verdünnten Nitriden zu untersuchen.
1. Introduction

Lasers have become indispensable in many parts of our life since their discovery in 1960 when Maiman demonstrated stimulated emission from synthetic ruby[1]. This was a pulsed red laser, at that time, no technical applications could be imagined. The Laser was a laboratory curiosity. Today, lasers have taken over many areas in our live, barely noticed by most people.

High-power infrared lasers are used for welding and cutting of metallic work pieces, from automotive parts to razor blades. Laser printers put our ideas, letters and drawings from the computer to paper. High-energy pulsed ultraviolet lasers are used for refractive surgery to correct eye vision. This list could be extended almost infinitely. In future, the use of lasers in our life will expand further without any doubt. Laser video projection for example promises a color-space never seen before with conventional projection technologies.

Each of these applications needs its laser system with suitable properties. Contrary to the situation when the first laser was developed, possible applications are already here, the only thing missing is the suitable laser source. Telecommunication systems are now continuously converted from copper cables to optical fiber, in order to increase the available bandwidth. Recent developments in network-based media have lead to a demand for affordable high-bandwidth connections. High-definition digital TV and video-on-demand applications will use a lot of bandwidth. Telecom industry experts estimate that the capacity of the actual internet architecture will be reached in 2010 unless large investments are taken and the existing infrastructure is massively expanded [2]. A possible solution is an expansion of fiber telecommunication also to short-range connections and an extended implementation of fiber to the home concepts. For these technologies to be successful, an improved cost-efficiency is necessary compared to today’s systems that are often based on discrete optical components. In order to use the existing technology as efficient as possible, a single fiber is used with many different channels at once. This
technology is called dense wavelength-division multiplexing (DWDM). For the generation of the necessary carrier, either an array of exactly specified DFB semiconductor lasers is used, or a mode-locked solid state laser, generating a frequency comb. Each of these channels is modulated individually by an electro-optic modulator (EOM). Although this approach allows for a very large bandwidth in a single fiber, it is also complicated and expensive.

In order to be suitable for widespread application, the transceiver devices need to be much smaller and at lower cost. A possible approach to this problem is to replace the solid-state lasers or sensitive InGaAsP DFB semiconductor lasers and EOMs by directly modulated vertical-cavity surface-emitting lasers (VCSEL) or to integrate a complete DWDM system into a photonic integrated circuit (PIC), fabricated on a single semiconductor chip. Such a InP-based DWDM PIC with 40x40Gbit/s was already demonstrated by Infinera corporation[3]. Common to all optical solutions is the need for a suitable laser gain material, that can be fabricated in the necessary wavelength range and offers good thermal properties, so cooling of the devices becomes obsolete. In the range of 1.3 to 1.5 μm, the market is almost entirely dominated by InGaAsP lasers, grown on InP substrates, despite their non-optimum properties, like a low $T_0$ that demands thermoelectric cooling. $T_0$ is the characteristic temperature of the laser. This is a measure of the temperature sensitivity of the device, where a high value denotes better thermal stability. GaInNAs is a material with more desirable thermal properties. Additionally, it is compatible with GaAs substrates, what also allows for the fabrication of VCSELS using GaAs/AlAs DBRs and also the direct integration of very high-speed electronics necessary for driving these transceivers.

Compact low-cost lasers in the wavelength range of 1300 to 1500 nm are also interesting for several non-telecom applications. As the advance of miniaturization and increase of the clock speed of microprocessors was not sufficient anymore in the past years, processor manufacturers have begun to parallelize multiple cores. Four cores is already state of the art for personal computers at this moment. This development will continue in future, leading to new challenges in communication between the individual CPU cores, as several centimeters are already a long distance at the operation frequencies of
actual microprocessors. This results in synchronization problems as well as to difficulties in transporting the large amounts of data between interacting CPU cores. Optical interconnects and optical clock signal distribution among the cores are possible solutions for these problems. Wavelengths of 1.3 \( \mu \text{m} \) could be interesting if transparency in silicon is desired. With the upcoming SiGe technology in high-frequency electronics, detectors for these wavelengths could easily be integrated in the chip fabrication process. GaInNAs lasers could therefore play an important role in future computer architectures.

With the advent of high-definition digital television, also the projection systems need advancements in technology to cope with the expectations of the consumers. As a first step, the resolution was increased, however, the colour reproduction is still limited. Current systems like LCD, DLP and others rely on conventional light sources like high-pressure arc lamps in combination with colour filters to achieve the three colours, red, green and blue, necessary for projection. This technology does not allow for reproduction of the whole colour-space of human perception. By using three high power laser sources in the corners of the colour triangle, almost the complete range of human colour perception will be covered, resulting in a much more vivid rendition compared to what we are used to today. For this technology to be successful, the laser sources need to be sufficiently high powered at a good beam quality. Semiconductor laser sources are the most promising technology for these requirements. Either by directly generating of the desired wavelengths or by using frequency doubled infrared laser sources [4]. So far, all three colours were successfully generated from electrically pumped vertical external cavity surface-emitting lasers (VECSEL) using intracavity frequency doubling. Such lasers are already commercially available from Novalux Inc. GaInNAs would be a very suitable material for red lasers around 650 nm, which need an efficient infrared emission of 1300 nm to be frequency doubled.

In applications like data transmission, optical processor clock generation or frequency doubling, ultrafast pulsed lasers have certain advantages. Such pulsed lasers can be built by introducing modelocking. For this technology to be efficient, a suitable saturable absorber material, matched to the laser medium is needed. GaInNAs also offers this counterpart to the gain structures. Low
saturation-fluence and low loss saturable absorbers with fast recovery rates are possible.

High-quality GaInNAs material for laser emission wavelengths of 1.3 μm with a robust fabrication process will probably find many future applications to make our life more easy and enjoyable. This thesis discusses the development of GaInNAs using molecular beam epitaxy (MBE). The devices developed range from 1.3 μm – 1-5μm saturable absorbers (SESAMs) for modelocked lasers to active structures in optically pumped 1.3μm VECSELs.
2. GaInNAs: Structure and properties

2.1 Introduction

Photonic devices largely rely on materials with a direct band gap, allowing for fast carrier recombination, as well as for radiative transitions with high efficiency. Many III-V semiconductors fulfil these requirements and allow for a free design of band gap and lattice constant by formation of mixed crystals. Classically, Ga, Al and In from group III and As, P and Sb from group V of the periodic table were the major workhorses in III-V photonic devices until the last decade, mainly operating in the near infrared to red wavelengths. During the last decade, Nitrogen attained more and more importance, first in wurtzite structure nitrides like GaN, AlN, InN and mixed crystals, giving access to the green to ultraviolet wavelengths. On the other hand, alloying nitrogen in small quantities to arsenide or phosphide zincblende structure semiconductors leads to the opposite effect of reducing the band gap energy. Already small amounts of a few percent lead to dramatic red shifts of the conduction band edge. This class of materials is called dilute nitrides. GaInNAs was first proposed by Kondow et al. in 1996 as a material for 1-3 to 1.5 μm laser applications [5].

In this work, GaInNAs was studied, either as an absorber material for SESAMs or as active material in VECSEL quantum wells. With GaInNAs, a material suitable for 1.3 -1.5 μm device fabrication on GaAs is available. This offers several advantages over the InP substrates used so far in this wavelength range. The particular properties and fabrication aspects of GaInNAs will be discussed in more detail in the following paragraphs.
2.2 Advantages of GaInNAs

![Figure 1: Band gap energy and lattice constant of different III-V compounds.](image)

Figure 1 illustrates the relationship between composition, lattice constant and band gap energy for different III-V semiconductor materials. Possible candidates for 1.3 μm respectively 1.5 μm wavelength are located on the horizontal lines crossing the graph. Using InGaAsP as active material, it is already possible to reach 1.3 as well as 1.5 μm on InP substrates. This system is mainly used commercially. However, the thermal properties of InGaAsP lasers are poor, the $T_0$ value lies around 60 K due to poor electron confinement [5]. This means in practice that the lasers need thermoelectric cooling. Additionally DBRs for vertical cavity lasers need also InGaAsP as a mirror constituent, which has a low thermal conductivity and a smaller index contrast to InP compared to the AlAs/GaAs system. GaInNAs lasers show a $T_0$ around 126K what allows for non-cooled operation [6]. Using GaInNAs as active material, it is theoretically
possible to fabricate lattice matched material with a band gap of 1.3 respectively 1.5 μm. However, this is not practical, as a large amount of nitrogen is necessary for lattice matching at these long wavelengths. Such a material was not demonstrated so far. Instead, an indium content of up to 40% is used, with the strain partially compensated by 1-3% of nitrogen. Additionally, the compressive strain of the quantum wells leads to an increased splitting of heavy hole and light hole bands, resulting in a lower threshold in lasers [7]. As GaInNAs can be grown on GaAs, distributed Bragg reflectors (DBRs) based on GaAs/Al(Ga)As can be used. DBRs are a stack of λ/4 layers with alternating refractive index, allowing for a reflectivity above 99.9%. Such AlAs/Al(Ga)As based mirrors are thinner than their InP counterparts due to the improved index contrast, which allows for a lower number of mirror pairs. Additionally, these materials offer a better thermal conductivity than the quaternary InGaAsP. The improved thermal properties of GaAs based mirrors are a large advantage in vertical-cavity lasers as the heat from the active zone has to be dissipated through the mirrors.

2.3 Electronic structure of GaInNAs

GaInNAs shows a smaller band gap than the corresponding binary or ternary compounds like zincblende GaN and InN as well as InGaAs. From Vegard’s law one would expect a wavelength shortening by alloying nitrogen to GaAs or InGaAs. In reality however, a huge band gap bowing is observed, the energy gap is shifted towards long wavelengths by alloying nitrogen. The most accepted model describing this unusual behavior is the band-anticrossing model, initially proposed for dilute nitrides by Shan et al. [8].

The introduction of nitrogen results in a highly localized band of acceptor-like states in GaInNAs. This band shows resonant interaction with the conduction band. It leads to a splitting of the conduction band into a coupled set of two bands, referred to as E+ and E-. what results to the observed band gap reduction in dilute nitrides. The dispersion relation for these conduction subbands is given in equation (2.1) [9].
\[ E_x(k) = \frac{1}{2} \left[ (E_M(k)) + E_N \pm \sqrt{(E_M(k) - E_N)^2 + 4xCMN^2} \right] \]  \hspace{1cm} (2.1)

\( E_M(k) \) is the energy of the conduction band of the semiconductor matrix as a function of the wave vector \( k \), \( E_N \) is the energy position of the nitrogen related level, \( x \) is the molar fraction of nitrogen and \( CMN \) is the hybridization matrix element.

Figure 2 shows the dispersion relations for \( \text{Ga}_{0.96}\text{In}_{0.04}\text{N}_{0.01}\text{As}_{0.99} \) with possible transitions 1-4 between the individual bands. The \( E_- \) band shows a flattening when approaching the nitrogen level, resulting in a nonparabolicity of the conduction band. This leads to an increase in electron effective mass compared to conventional semiconductors like GaAs. Experiments have also shown these
trends and confirmed that the BAC model is a good description for the phenomena observed\[9\].

2.4 Carrier recombination and defects in GaInNAs

Despite the large accessible band gap energy range and possible applications for near-infrared devices, dilute nitrides also have drawbacks. They suffer from low radiative efficiency compared to other III-V compounds and need special measures like unusually low growth temperatures and high-temperature annealing to be useful, for example as a laser gain material. The reason for this behavior lies in a large concentration of non-radiative recombination channels. A lot of work has already been done to shed some light on the mechanisms limiting the radiative efficiency in GaInNAs and related materials \[10-14\]. Possible routes of non-radiative recombination are carrier trapping and successive multiphonon recombination in deep levels or Auger recombination, which gains importance with shrinking band gap energy. The minority carrier lifetime in as-grown GaInNAs is only a few picoseconds, compared to several nanoseconds for “laser-grade” GaAs.

The defects responsible for this behavior are on one hand originating from the growth conditions necessary to fabricate GaInNAs, like the low temperature and also the crystal damage by high-energy species originating from the plasma source\[15\]. On the other hand, the properties of nitrogen facilitate the formation of a large number of different intrinsic defects like interstitials and clusters. Until today, the true path of recombination in GaInNAs could not be determined yet. An attempt to find additional hints towards the origin of nonradiative recombination in GaInNAs is discussed in 7. Photo induced current transient spectroscopy (PICTS) was used to probe the deep-level states present in GaInNAs and InGaAs quantum well structures, depending on different growth conditions. We tried to correlate PICTS to photoluminescence and pump-probe measurements.
3. MBE Growth and Characterization of III-V semiconductors

3.1 Molecular beam epitaxy

Molecular beam epitaxy (MBE) is a crystal growth technique, suitable for high-precision semiconductor heterostructure fabrication, as it is necessary for photonic devices like Lasers, DBRs and SESAMs.

MBE belongs to the family of physical vapour deposition (PVD) processes. Individual elemental components are evaporated from heated crucibles (effusion cells) and form a molecular beam of particles reaching the substrate at thermal energy. At the heated substrate, they adsorb and react to the desired material like for example GaAs. By using shutters in front of each cell, the molecular beams can be switched on and off, to achieve abrupt composition changes and exact thickness control of the deposited layers. Typical growth rates are between 0.5 and 2 μm per hour. Figure 3 illustrates the general layout of the MBE system used in this project.

![Figure 3: Schematic MBE system setup as it was used in this project](image-url)
The MBE process takes place in ultrahigh vacuum (UHV), with a base pressure below $1 \times 10^{-9}$ mbar. The vacuum environment is very important to several aspects of the MBE process. The long mean free path of several kilometers ensures that the particles emitted from the effusion cells do not interfere with atmospheric molecules, so a beam like propagation of evaporated material is possible. Furthermore, the vacuum protects the evaporation materials from oxidation. Most important, it minimizes contamination of the deposited structure and the source material by foreign material. The contamination rate can be estimated by assuming a surface coverage rate of approximately 1 monolayer (ML) per second at $1 \times 10^{-6}$ torr. So at $1 \times 10^{-9}$ torr, it takes approximately 15 minutes to cover the surface with 1 ML of residual gas atoms. The lowest pressure vacuum, as well as a controlled residual gas composition is therefore highly desirable. The residual gas is mainly composed of hydrogen, arsenic and phosphorus, which do not lead to doping effects. Figure 4 shows a typical residual gas composition of our MBE system in standby conditions.

![Quadrupole mass spectrometer analysis](image)

**Figure 4:** Quadrupole mass spectrometer analysis of the residual gas composition in the MBE system at standby conditions. The most important constituent is hydrogen, which is two orders of magnitude higher than any other substances. The rest is mainly nitrogen (m/Z=28) left over from the last nitride growth run, phosphorus (m/Z=31, 62, 93) and arsenic (m/Z=75)
3.1.1 UHV system

Such an ultra-high vacuum needs special precautions to be maintained, especially in an environment like an MBE where high temperature heaters and high-vapour-pressure materials like arsenic and phosphorus are present. The Veeco Gen III MBE used in the present work, is pumped with a 1200 l/s turbomolecular pump as well as a large ion getter pump with included titanium sublimator. Additionally, liquid nitrogen cooled shrouds are installed on the inner chamber walls, that act as a cryopump, condensing most contaminants. Until a base pressure below $10^{-9}$ torr can be attained, the chamber has to be baked for 1-2 weeks at 200°C to desorb all water inside of the chamber. Utmost cleanliness has to be used during handling of all UHV parts, as even tiny traces of organic material like a fingerprint result in unacceptable contamination. The construction materials of the MBE chamber are specially chosen to prevent outgassing and vacuum contamination. Such suitable materials are electropolished stainless steel, ceramics like alumina or pyrolytic boron nitride (PBN), and refractory metals like molybdenum, tantalum or tungsten. Seals on flanges leading to environment are generally metallic, mainly copper sealed CF flanges, electrical feedthroughs are brazed metal-ceramic joints. Mechanical motion is coupled to internal mechanics either magnetically or by flexible metal bellows. Lubrication of internal mechanics can only be done using dry lubricants, either directly deposited on the parts or in solid form. However lubricants like PTFE, MoS$_2$ or graphite pose additional contamination risks, so often no lubrication is used.

3.1.2 Materials

Materials suitable for usage inside of a MBE system need to fulfil several properties. A suitable material has a very low vapour pressure, even at high temperatures of 200°C and above for the necessary bake out procedure. Components like the cryoshrouds have to operate at -196°C without turning brittle, while in inside of the effusion cells temperatures far above 1000°C are encountered, nevertheless, the materials have to maintain negligible vapour pressure and reactivity. Due to these stringent requirements, only a few materials are acceptable. Table 1 summarizes the construction materials and typical applications in the MBE system.
### Table 1: Typical construction materials used in the components of the MBE system

<table>
<thead>
<tr>
<th>Material</th>
<th>Application examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>stainless steel (1.4301)</td>
<td>recipient, external hardware, flanges,</td>
</tr>
<tr>
<td></td>
<td>cryoshrouds, structural components</td>
</tr>
<tr>
<td>pyrolytic boron nitride (PBN)</td>
<td>effusion cell crucibles, substrate heater</td>
</tr>
<tr>
<td>tungsten</td>
<td>heated filaments</td>
</tr>
<tr>
<td>tantalum</td>
<td>heat shields on effusion cells</td>
</tr>
<tr>
<td>molybdenum</td>
<td>Substrate holders, high temperature</td>
</tr>
<tr>
<td></td>
<td>mechanical parts</td>
</tr>
<tr>
<td>alumina ceramics</td>
<td>electrical insulation</td>
</tr>
<tr>
<td>copper</td>
<td>CF flange gaskets</td>
</tr>
<tr>
<td>Viton and related fluoropolymers</td>
<td>gate valve gaskets</td>
</tr>
<tr>
<td>glass, fused silica</td>
<td>view ports</td>
</tr>
</tbody>
</table>

As MBE is done in this work from elemental sources, it is very important to use extremely pure precursor materials. Any contamination of these materials results directly in unintentional doping of the grown structures. During this project, aluminium (6N5), Ga(7N), In (7N) was used. 7N for example means 99.99999% purity.

The structures fabricated during this project were mainly grown on 3” GaAs (100) wafers, supplied by Freiberger Compound materials, Germany. The substrates were semi-insulating, non-intentionally doped material grown by the vertical-gradient freeze (VGF) method.

#### 3.1.3 MBE sources

##### 3.1.3.1 Thermal sources

In elemental source MBE, the precursor materials are evaporated from pure elemental sources. The group III elements Ga, In and Al are evaporated from Knudsen cells. These sources consist of a PBN crucible, inserted into a heater filament, with an exactly controlled temperature. The flux is controlled exclusively via cell temperature, which is held constant to +/- 0.1 K.
Figure 5: Group III materials effusion cell and a valved cracker for arsenic. (Images by VEECO [16, 17])

Arsenic and phosphorus are needed at high fluxes and in large quantities. At the same time, these materials exhibit a high vapour pressure, already at low to moderate temperatures. For these materials, valved crackers are used. A large reservoir of material is held at constant temperature, while the flux is controlled by a needle valve after the reservoir. Inside the cracker cell, the material evaporates in form of quadromers, As₄ and P₄ respectively. These molecules are then thermally cracked into dimers As₂ and P₂ by a baffle, heated to 900°C. After cracking, these molecules are also formed into a molecular beam, like it is emitted by group III Knudsen cells.

3.1.3.2 Nitrogen plasma cell

Before incorporation into the host crystal, group V molecules need to be cracked into reactive species. While with As₂ and P₂, this is not very critical and thermal energy is sufficient for surface dissociation after adsorption. Nitrogen molecules, however, are extremely stable triple bound dimers. Thermal dissociation does not occur at practical temperatures. To circumvent this, less stable nitrogen compounds as ammonia, tertiary butyl hydrazine or dimethyl hydrazine are sometimes used as nitrogen precursors in gas source MBE or MOVPE. Unfortunately, high substrate temperatures are necessary to dissociate these molecules, preventing the use in dilute nitride MBE growth that needs temperatures below 450°C. Otherwise the materials contain large organic groups, not suitable for MBE usage. The most successful approach so far is the usage of a plasma cracking cell, in our case a “Veeco Uni bulb”[18, 19]. A
nitrogen plasma is ignited inside of a small PBN chamber (a few cm³), held under an elevated pressure compared to the growth chamber. The elevated pressure is maintained by a perforated plate in front of the cell. The plasma cell pressure is defined by the gas flow, controlled by a 1 sccm range mass flow controller (MKS instruments). The plasma is powered by 50-600 W of RF power (13.56 MHz, Advanced Energy RFX600). This high-power-density plasma dissociates the nitrogen entering the cell. Most of it recombines, but a few percent of the molecules remain dissociated or excited when they are exiting from the cell.

![Diagram of plasma cell](image)

**Figure 6:** Cracking of molecular nitrogen by inductively coupled RF plasma

Unfortunately, the external efficiency of such a cell is low, leading to a high gas load during nitride growth and therefore requiring a large pumping capacity. Additionally, it is expected that excited molecular nitrogen is incorporated into dilute nitrides, forming a so called split interstitial defect. This is a N₂ molecule sitting on a single lattice space which acts as a deep level defect [20]. Moreover, plasma cells produce medium energy ions, with energies up to 35 eV as measured by Wistey et al. [15]. They report that these ions disturb the growth process by impact onto the crystal surface, resulting in crystalline defects. This is easily understood when comparing the ion energy to the lattice energy of GaAs, which is in the order of magnitude of 1 eV. Several groups used magnetic or electrostatic fields to deflect these ions from the growth surface what has lead to an improvement of the optical material quality of GaInNAs[15, 21]. The number of ions impacting the surface also largely
depends on the cell type used. The VEECO cell used in this work is designed for a low flux of high energy ions [19].

There are different possible operating conditions of the plasma cell resulting in the same incorporation of nitrogen, determined by flow and RF power. This changes the conditions under which the active nitrogen is generated. An experimental series of plasma operation conditions is discussed later in 5.3.

3.1.4 Beam flux measurement

For an exact control and reproducibility of layer thickness and material composition in MBE, the beam flux of each effusion cell has to be known exactly. As the filling level of the cells is depleted continuously during growth, the fluxes have to be calibrated before each growth run. The flux is then adjusted by changing the cell temperature, which is controlled by a precise digital PID controller. The individual beam fluxes are measured by a Bayard-Alpert ionization gauge, which is mounted at the back of the substrate manipulator. This device is commonly named beam flux monitor (BFM). By rotation, either the substrate or the BFM can be placed in the center of the chamber where all molecular beams intersect.

The BFM reads a value that is proportional to the flux of material emitted from the cell. Ionization gauges are usually calibrated for nitrogen molecules, while as a BFM it is used for the much heavier MBE precursors. As these molecules have a different ionization cross-section, a calculation of beam flux ratios directly from the BFM readings is not possible. The specific gauge used for the measurements influences the indicated beam flux by its mechanical construction. Also a large influence of the angle under which the beam flux is entering the BFM is observed. Despite all these drawbacks, if the BFM is operated under known conditions, it is a very reliable indicator for a calibrated beam flux to reproduce the growth conditions from day to day, which is the most important application. By applying if a correction factor for the ionization cross-section of the different MBE precursor materials, the measured value from the BFM can be converted into a value more close to the real molecular flux observed by the BFM. Such a corrected value is then used to calculate the beam
equivalent pressure (BEP) ratio, which is the ratio between group V elements like As and group III elements like Ga.

3.2 MBE Growth process for III-V semiconductor materials

3.2.1 GaAs and Al(Ga)As

The basic operation of arsenide epitaxy is the homoepitaxial growth of GaAs. This is the first step successive to the thermal oxide desorption after loading of the substrate wafer into the growth chamber. GaAs Wafers are delivered with a defined, chemically prepared oxide layer to protect the wafer surface from environmental contamination. This protective layer is desorbed from the wafer surface inside of the MBE machine under a constant flux of elemental arsenic. The oxide layer desorbs then at a temperature above 580°C. Together with desorption of this oxide, eventual contaminants are removed at the same time. To ensure complete desorption, we used a temperature of 600°C, held for at least 30 minutes. The deoxidation process is constantly monitored by reflection high-energy electron diffraction (RHEED), as it is described in 3.4.3. Before deoxidation, the RHEED pattern is purely diffuse due to the amorphous nature of the oxide. During desorption, streaks start to appear, getting sharp and distinct at full deoxidation. Some surface roughness remains, which is evident by a slightly spotty RHEED pattern, also a certain amount of oxygen remains embedded into the substrate as SIMS measurements have shown. After this thermal cleaning step, a buffer layer of homoepitaxial GaAs is deposited. Using a growth rate of around 0.8 μm/h, a buffer layer of 400 nm thickness is deposited at a As/Ga BEP ratio of about 40. The purpose of this buffer layer is planarization of the substrate, as well as being highly pure and defect-free. Under the applied growth conditions using a V/III BEP ratio of 40 and a temperature near the deoxidation temperature, GaAs with optimum planarity and excellent electronic properties can be grown. These growth conditions are characterized by a (2x4) reconstruction during growth [22-24].
In MBE growth of GaAs, arsenic is always offered in excess. Arsenic has a high vapour pressure. Its evaporation from the crystal surface has to be prevented by constantly offering an overpressure that exceeds the vapor pressure of arsenic at the surface of the wafer. This leads to a chemisorbed surface layer of arsenic atoms. At the growth temperature, a condensation of arsenic is not possible, even at a very high overpressure. Figure 7 illustrates the conditions present on a GaAs surface under an incident As$_2$ flux. The molecules undergo dissociative chemisorption upon arrival on the surface. Then they either find a Ga atom as a binding partner, or they reassociate and desorb again. Depending on the amount of arsenic offered, the surface is either Ga or As stabilized. At high surface coverage, the sticking coefficient of incident As$_2$ reduces to zero, as there is no available site for chemisorption[25]. For the growth of smooth GaAs layers on a (100) surface, arsenic stabilization is preferred. The state of the surface is determined by RHEED as arsenic or gallium stabilized surfaces show different reconstructions.

Figure 7: Growth of GaAs using As$_2$. The possible behavior of arsenic on the surface is surface migration in molecular form, desorption or dissociative chemisorption and incorporation into the crystal [26].

This behavior allows for the growth of a stoichiometric compound crystal without having to keep the arrival rate of the constituents exactly at the correct ratio.
Aluminium arsenide is grown under similar conditions, the growth temperature is ideally kept even higher, around 620°C. As the lattice mismatch of AlAs is very small to GaAs, the growth is almost homoepitaxial, even in thick layers up to 100 nm as they are necessary in the fabrication of DBRs for SESAMs and VECSELs. Binary compounds like GaAs and AlAs are also a starting point to develop the growth process for ternary and quaternary alloys, as they are described in the following paragraphs.

3.2.2 InGaAs

Indium gallium arsenide is a ternary alloy, formed from the binary constituents GaAs and InAs. When InAs, having a band gap of 0.354 eV is alloyed to GaAs, the wavelength range from 870 nm to 3.5 µm is theoretically accessible. On GaAs substrates however, the lattice mismatch limits the maximum indium content to approximately 40% without experiencing relaxation at layer thicknesses exceeding 10 nm. In this project, the maximum indium content was limited to 35%, which resulted in a PL emission wavelength of around 1180 nm. InGaAs has to be grown at a surface temperature below 520°C, as indium has a very low sticking probability at higher temperatures and does not incorporate. In this project, all InGaAs samples were grown at 450°C to be comparable with the GaInNAs structures based on this composition. The arsenic overpressure was kept at the same value as for GaAs growth.

3.2.3 GaInNAs

By introducing small amounts in the order of a few percent of nitrogen into InGaAs, GaInNAs is obtained. Nitrogen is ideally introduced into the InGaAs host crystal substituting arsenic. Compared to arsenic, which shows a very low sticking coefficient at high fluxes, active nitrogen is incorporated with almost 100% yield. The reason for this behaviour is the different properties of nitrogen radicals and As$_2$. Arsenic undergoes a dissociative chemisorption at the surface. There it does not immediately form stable bonds, it is still able to diffuse or desorb again. Nitrogen in contrary arrives as a highly reactive radical, forming very stable bonds to any indium or gallium atom encountered, desorption or competition to As is not observed. This is of great advantage for the process
stability, as the N/As ratio or the growth temperature shows none or very little influence on the final nitrogen concentration. In contrast to this favourable behaviour, the composition of other mixed group V alloys like GaAsP is very sensitive to these parameters.

However, due to the small size of the nitrogen atom, different kinds of point defects are incorporated into the growing layer [10]. Due to the high reactivity and small size of the nitrogen radicals, they tend to incorporate also in unwanted configurations like N-N or As-N split interstitials. Also ordinary interstitials and clustering of several nitrogen atoms are known. At growth temperatures of more than 450°C, GaInNAs also tends to phase separate and to grow in a three-dimensional mode, which is undesirable. If the growth temperatures are too low, an increased concentration of intrinsic crystal defects are formed, like excess arsenic incorporation. Growth experiments have shown that substrate temperatures between 360°C and 450°C result in a material with measurable PL emission. Lower growth temperatures result in GaInNAs without PL emission, even after annealing. These experiments are described in more detail in 5. As many of the growth-related defects in GaInNAs can be removed by post-growth thermal annealing, the optimum optical quality material is not necessarily the material with the best as-grown luminescence. To find the optimum growth process and annealing procedure for a specific application, extensive studies were performed and discussed in detail in Chapter 4 and 5.

3.2.4 InGaP

For the substrate-removal process used in the fabrication of VECSEL gain structures, an etch stop material is needed as discussed in more detail in 6.3.2. Al$_{85}$Ga$_{15}$As was used mainly in this project, but this structure requires time-consuming manual processing for each chip to be successful. With the goal of developing a more robust substrate-removal process that uses non-critical chemical process steps, a new etch stop was necessary. The ideal etch-stop layer can be grown lattice matched to GaAs in MBE, and offers very selective etching behavior to GaAs. It should resist against an etching solution etching GaAs,
while being dissolved by an etchant not attacking GaAs. InGaP is such a material. Being a phosphide, it offers very different properties compared to arsenides. It is etched by dilute HCl, to which GaAs is completely resistant. On the other side, GaAs is etched well by citric-acid/hydrogen peroxide etchants or sulfuric acid/hydrogen peroxide solutions. InGaP is very resistant against these substances.

**In_{48}Ga_{52}P** is perfectly lattice matched to GaAs and can be grown in thick layers. InGaP does not grow as a homogenous layer, it spontaneously decomposes into a short-period superlattice of InP and GaP. This is however not seen in RHEED and does not prevent the growth of a smooth surface for following growth steps. Test structures were grown on top of such InGaP layers, to demonstrate the suitability as an etch stop and as a substrate for high-quality epitaxial growth. An InGaAs quantum well, embedded in GaAs was grown on such a InGaP etch stop layer substrate and then processed into a substrate-free layer on glass. The photoluminescence of this structure was identical to a standard test structure. From these tests, InGaP was a promising candidate for facilitating the processing of upside-down VECSELs. This topic will be discussed in more detail in 6.3.5.

### 3.3 Annealing process

Annealing is not a growth process in its strict sense. However, it is discussed in this context, as it is an essential process step in the fabrication of GaInNAs for laser application. As already discussed in 3.2.3, GaInNAs needs to be grown at low temperatures to prevent phase separation. At these low temperatures of 410-450°C, the crystalline perfection of the material grown is inferior to high-temperature grown GaAs. Intrinsic point defects are formed. Additionally, the nitrogen incorporation process itself results in a quite imperfect crystal, what ultimately leads to a poor radiative efficiency of the material. Many of these flaws can be fixed after growth by high temperature annealing, which dramatically increases the radiative efficiency of the material, making it useful as an active medium for lasers.
Annealing can be done in- or ex-situ of the MBE growth system. During this project, both approaches were followed. For ex-situ experiments, a commercial rapid thermal annealing (RTA) furnace (Jipelec JetFirst) was used. RTA offers good flexibility in designing the annealing process, as the cycle times are short and samples of arbitrary size are usable. A drawback is the furnace atmosphere, which is low-pressure inert gas that prevents sample oxidation, but it cannot supply a continuous arsenic overpressure to prevent arsenic loss during long time annealing. A local arsenic-rich atmosphere however can be created by placing a piece of wafer upside-down onto the chip to be annealed. This technique is named proximity capping and was used all the time in the RTA experiments conducted during this project.

Complementary to the RTA process, MBE in-situ annealing was also applied. This process is done inside of the MBE system after growth of the structure. An ultrahigh vacuum environment as well as the possibility to offer a constant arsenic overpressure at the sample surface makes the conditions ideal for optimization of the device efficiency. A drawback, however, is the limited flexibility for process development, as full quarter-wafers have to be used, and the cycle times are longer than in RTA. These process properties suggest using RTA for development and optimization of the annealing process, and performing the thermal treatment of final laser structures in the MBE system.

GaInNAs not only improves in radiative efficiency during annealing, it also shows a strong emission wavelength blueshift. Different explanations are discussed in literature. Out-diffusion of indium and nitrogen from the quantum well would explain such a blueshift, as this would reduce the band gap of GaInNAs. Another possibility discussed is a change of Ga-N bond lengths during annealing [27]. This change in bond length is the observed in a band gap energy shift. The most accepted theory, however, suggests a change in the local chemical conditions around the nitrogen atoms by short-range diffusion processes [28]. During growth, nitrogen preferentially binds to Ga atoms, as the bond strength is larger than for In-N bonds. Inside of the lattice, however, this situation is reversed. Local strain is contributing a significant portion of the lattice energy. As indium atoms are larger than gallium, local strain imbalances are compensated better when nitrogen atoms are coordinated by indium than
by gallium. During annealing, a diffusive reordering process takes place, changing the initial GaN-like coordination towards a InN coordination [28]. These rearrangements have also been shown by EXAFS measurements [29] on as-grown and annealed GaInNAs samples.

Our own experiments do not support the out-diffusion theory either [30]. We used 10 nm wide GaInNAs single quantum wells, capped by 60 nm GaAs for the experiments. XRD simulations based on a linearly graded indium profile show that out-diffusion would already be detectable at a very small magnitude. Figure 8 shows simulated XRD rocking curves, based on the indium profiles shown in the insert. The total indium content is identical in all cases, while a linear grading of different extension is introduced. The nitrogen concentration is kept in a perfectly rectangular profile, as nitrogen out-diffusion from GaInNAs has not been observed so far to our knowledge.

**Figure 8:** Simulated HRXRD rocking curves, resulting from different indium concentration profiles as they are shown in the insert. The total amount of indium is constant in all cases.
A justification of the observed annealing blueshift in InGaAs is not possible based on indium out-diffusion. Annealing experiments, using temperatures up to 800°C, on GaInNAs samples did not show any diffusion-effects that could be detected by XRD at all, while the photoluminescence (PL) wavelength shifted by more than 50 nm at the same time.

Klar et al. state that the reordering process takes place via group V lattice sites [28]. However, this seems unlikely by our interpretation. MBE grown material is mostly group V-rich, so vacancies are expected to be mainly V_{Ga}. Experiments with variable V/III ratio also indicated larger blueshifts with increased group V abundance, what facilitates the formation of Ga vacancies. We postulate a diffusion process via the group III sublattice, being a short range exchange process, accelerated by strain and mediated by group III vacancies. The blueshift reaction shows a thermal activation energy of around 1.3 eV for the nitrogen content observed [30]. This is a much lower value than what is usually observed for interdiffusion activation energies in III-V semiconductors. For indium/gallium interdiffusion in In_{0.2}Ga_{0.8}As quantum wells, an activation energy of 2.33 eV was observed [31]. For As interdiffusion in In_{0.66}Ga_{0.33}As/In_{0.66}Ga_{0.33}As_{0.7}P_{0.3} heterostructures an activation energy of 3.7 eV was measured [31]. These numbers clarify, why no long-range diffusion is observed at typical annealing temperatures of up to 700°C.

3.4 Material and structure characterization

The characterization of epitaxial nanostructures like they are used in semiconductor photonics needs a set of tools to analyze layer thickness to a precision of less than a nanometer, measure the exact composition of tiny amounts of material in the order of a few micrograms, as well as finding information about the crystal perfection and the presence of point defects that lead to nonradiative recombination. Also during growth, instrumentation is needed to analyze the morphology, temperature and chemical properties of the growth surface. In the next paragraphs, the most important methods are briefly discussed.
3.4.1 High resolution X-Ray diffraction (HRXRD)

HRXRD is used for the measurement of layer thickness and composition of layers with a very good precision. Also qualitative information on the interface homogeneity is extracted. The method relies on the measurement of the lattice constant and distortion of the single crystalline structures grown by MBE. We used a three-crystal X-ray diffractometer 3003PTS by GE inspection technologies. The measurement system uses a Cu Kα radiation source, consisting of a copper anode X-ray tube in the focus of a parabolic graded multilayer mirror, collimating the output of the X-ray tube. The collimated radiation is then filtered by a four-bounce Ge(220) monochromator for pure Cu Kα radiation with a very small angle of divergence and a line width of less than 50 fm [32].

Figure 9: Schematic setup of a double axis high-resolution X-ray diffractometer [32]. The angle between beam and sample surface is generally named omega, the angle between sample surface and detector is theta. The tilt and rotate angles are named chi, respectively phi. These naming conventions are used in this work.

This conditioned X-ray beam is then diffracted on the single crystalline sample, which is rotated with respect to the incident beam. The diffracted
radiation is then detected by a scintillation counter without additional slit or analyzer crystal. Such a double-axis diffractometer setup is shown in Figure 9. This arrangement offers relatively high signal intensity while allowing for a sufficient resolution for routine analysis of the MBE grown structures. The usual approach in this project is to scan the angle of incidence around a Bragg reflex, acquiring a so-called rocking curve. Most of the measurements in this project used the GaAs(400) reflex, which offers a high diffraction intensity and is exactly parallel to the specimen surface. These properties allow for rapid alignment of the sample for measurement. Additionally, the Bragg angle of this reflex is very sensitive to perpendicular lattice distortions generated by pseudomorphic epitaxial growth.

A typical XRD rocking curve measurement is shown in Figure 10. The structure contained 12 GaInNAs quantum wells with an individual thickness of 10.1 nm and a barrier thickness of 64.3 nm as determined by simulation of the rocking curve using the Takagi-Taupin dynamical theory of diffraction [33] that is implemented into the analysis software from the instrument manufacturer. Three different features of the rocking curve provide the needed information. First, the angular position of the (400) Bragg reflex, being at an angle of 33.024° to the surface for GaAs and offset to 31.4° for the GaInNAs quantum well due to lattice distortion. This angle is determined by the lattice parameter in
perpendicular direction and gives information on composition of the strained layer, assuming perfectly pseudomorphic growth. The line width of the reflex contains information on the thickness of the diffracting layer, in the case of the GaInNAs QW, the thinner the corresponding layer the wider is the measured peak. Finally, periodic multilayer structures show additional interference effects, the so-called pendellösung fringes. In the rocking curve presented in Figure 10, these fringes are very pronounced due to the large number of periodic layers, resulting in sharp peaks modulating the diffraction curve. All these effects, together with a diffuse scattered background signal contribute to the measured rocking curve. Numerical simulation and curve fitting is used to reconstruct the measured signal as perfectly as possible. The simulation parameters give an accurate analysis of the grown structure. Fitting of these X-ray rocking curves has to be done very carefully, as the simulation uses many free parameters, partially counter-effecting each other. For a precise and trustworthy analysis, the sample needs to be designed suitably and the simulation fit needs to be nearly perfect. HRXRD analysis of simple test structures resulting in non-ambiguous analysis results is the most important thickness and composition control we used for MBE growth process calibration. We used a 10 nm single quantum well, overgrown by 60 nm GaAs as a standard test structure. This structure can be grown without relaxation and gives thickness, as well as the perpendicular mismatch of the analyzed layer to a good precision.

3.4.2 Room temperature photoluminescence

The band gap energy of quantum well structures is strongly influenced by their composition and thickness. Photoluminescence (PL) measurements are a suitable method to measure the band gap energy in any semiconductor that emits light from band-to-band recombination. The intensity of this emission reflects the concentration of nonradiative recombination centers present in the structure. The band gap energy shift has a higher sensitivity to minor composition changes than XRD, so PL was always used as the instrument of choice for final wavelength adjustment for devices like SESAMs and VECSELs. A map of the PL spectrum over a complete wafer gives information about growth homogeneity and process stability, as well as an indication on the expected properties of a device at this point.
The measurements were taken using an Accent RPM2000 photoluminescence mapper. A 785 nm laser with a power of up to 45 mW or a 532 nm solid state laser with a power of up to 10 mW was used as an excitation source. The PL signal was then analyzed by a grating monochromator equipped with an InGaAs photodiode array or silicon CCD line detector, simultaneously acquiring 128 wavelengths. The sample is mounted on a rotating platter for full wafer scanning.

![Photoluminescence maps](image)

Figure 11: Photoluminescence maps of an in-situ annealed GaInNAs MQW test structure. The left image shows the wavelength distribution, while the right map shows the respective peak intensity.

The map of the annealed test structure in Figure 11 shows first a gradient in the PL peak wavelength, originating from a radial composition gradient during growth on a full 3” wafer. The intensity map shows a different distribution, as this piece was in-situ annealed in the MBE using a ¼ 3” substrate holder. Along the circumference of the wafer, the annealing temperature was apparently lower, while the lower intensity towards the center originates from the higher nitrogen content in this region. As seen in this example, PL maps give valuable information about the growth process and parameter stability.

3.4.3 Reflection high-energy electron diffraction (RHEED)

When developing an MBE growth process, it is important to know the conditions on the growth surface. Properties like substrate cleanliness, growth stoichiometry, growth mode, surface reconstructions and surface morphology
are of interest. RHEED is an in-situ method to give insight into these questions. This method is based on the scattering of fast electrons in a grazing angle on the crystalline surface of the growing structure. A high-brightness electron beam is generated by an electron gun using a LaB₆ cathode, supplied by Staib instruments. We used an acceleration voltage of 14 kV in our MBE system. The beam strikes the sample surface under a grazing angle of a few degrees, penetrating only the topmost monolayers of the crystal. The forward-scattered electrons are then visualized on a phosphor screen opposite to the electron gun.

![Figure 12: Schematic principle of RHEED [34]](image)

The basic RHEED diffraction pattern can be understood by looking at the situation in reciprocal space as illustrated in Figure 12. As RHEED is extremely surface-sensitive, the relevant reciprocal space is a set of rods instead of a lattice of points as it is the case in volume scattering experiments. A reflection in the diffraction pattern is formed when a reciprocal lattice rod intersects with the Ewald sphere. Due to thermal diffuse scattering and the limited scattering area, these rods have a non-negligible reciprocal radius. At a electron energy of 14 keV, the Ewald sphere is very large compared to the reciprocal lattice
parameter of GaAs. This grazing intersection of the lattice rods with the Ewald sphere results in a set of streaks on the phosphor screen, instead of sharp points. The large Ewald sphere also results in a low angular distortion of the image when the diffraction pattern is used for in-situ measurement of the lattice constant of the growing layer. Such a technique allows for the determination of relaxation effects during growth. However, during this project, this and other advanced capabilities of RHEED were not used, it was mainly applied as a quantitative instrument for visual observation of the growth process.

By observing the RHEED diffraction pattern on the screen, it is possible to determine the surface reconstruction, which gives an indication the growth conditions as GaAs and derivatives show different known surface reconstructions at different temperatures, depending on the surface stoichiometry. This allows for example an estimation of the necessary group V element flux, which is always offered in excess.

![RHEED Images](image1.png)

**Figure 13:**

(a) RHEED diffraction pattern of a growing GaAs(100) surface with the typical (2x4) reconstruction along the [110] azimuth with proper 2-dimensional growth. 
(b) Spotty diffraction pattern of a three-dimensionally growing surface with sharp reflections due to volume scattering.

The morphology of the growing surface is also easily observed in RHEED. An atomically flat surface only shows surface scattering with the distinctive reciprocal lattice rods resulting in a streaky image. When three-dimensional islands start to grow, the electron beam experiences volume scattering that
changes the reciprocal rods into a set of points, which result in a spotty diffraction pattern compared to the streaky appearance of the surface diffraction. Figure 13 illustrates the difference between a properly growing MBE layer and a 3D- surface morphology, like it is observed in phase-separated GaInNAs or quantum-dot growth.

3.4.4 Band gap thermometry

The temperature of the growth surface is a very important parameter in MBE. Depending on the growth process, an accuracy of better than +/- 10 K is absolutely necessary for reproducible results. In the vacuum environment of the MBE, direct temperature measurements are not possible. The wafer is heated by radiation from a PBN heater inside of the substrate holder. Thermocouples in front of the heater are used for temperature control of the wafer. However, the temperatures measured in between of the heater and the substrate easily differ by 100 K. The classical approach is to use certain temperature-dependent properties of GaAs for calibration and calculation of a correction factor. One possibility is to heat slowly to the point of deoxidation, on (100) surfaces this takes place at 580°C. This approach is however not very reliable as it excludes any effects like radiative heating from the effusion cells. Pyrometry is also used often, but its use is usually limited to high temperature and the measurement is susceptible to surface emissivity modulations, induced by growing layers of different refractive index. For reliable measurements of the substrate temperature under these conditions, band gap thermometry (also named diffuse reflection spectroscopy (DRS) by the manufacturer -Thermionics corporation) is very suitable.

The band gap energy and thus the absorption edge of semiconductor materials is temperature dependent. With increasing temperature, the absorption edge is shifted towards longer wavelengths. The absorption edge can be easily detected by remote optical spectroscopy and gives an accurate measurement of the substrate temperature itself. The measurement system uses a tungsten-halogen lamp as a white light source, which is then modulated by a tuning fork chopper. This light is imaged onto the substrate wafer by a lens system, mounted externally on the growth chamber. The light is transmitted through the substrate wafer, diffusely scattered at the wafer backside and on
the ceramic plate of the heater. This diffusely scattered light is again transmitted through the wafer and imaged onto an optical fiber bundle by another lens system. The arrangement is such that no specular light is collected directly from the source. Additionally a lock-in amplifier is filtering out the effects of any external light present in the growth chamber. The collected light is then analyzed by a spectrometer, connected to software, which determines the position of the absorption edge. From this position, the exact substrate temperature is then determined using a calibration table specific to the substrate used.
4. SESAMs for modelocked 1.5 and 1.3 µm lasers

4.1 Introduction

Pulsed lasers are interesting in many fields of technology. From high-speed data transmission over precision metrology to materials processing, ultrafast pulsed lasers find widespread applications. Such lasers will gain more importance in the future as the industry is just starting to adapt to this still new technology.

The technique to generate such ultrashort pulses from lasers at a stable repetition rate is called modelocking. Typical pulse durations range from a few femtoseconds to some tens of picoseconds. This pulsed operation originates from the constructive interference of all longitudinal modes coexisting at the same time in the laser cavity. Such a pulse-generating interference occurs only if a proper phase relation exists between the oscillating modes and is kept stable. To ensure stable pulse generation, this phase-locking has to be enforced. A laser operating under these conditions is called mode locked. Figure 14 illustrates the output pulsetrain from a modelocked laser, compared to a single mode continuous wave laser.

Figure 14: Typical output of a single longitudinal-mode continuous-wave (cw) wave laser and the pulsed power of a high-repetition rate modelocked laser.
In modelocked operation, the peak power of the laser is maximized during nicely shaped pulses. By introduction of a nonlinear element into the cavity that generates lower losses for high intensity pulses, the modelocked operation can be self-stabilized. Different approaches are suitable to mode-lock a laser like kerr-lensing in the amplifier crystal of solid-state lasers or even active modulation using AOMs is used to stabilize the pulsing. A very elegant and easy solution is to use a saturable absorber [35, 36]. DeMaria et al. demonstrated the first modelocked laser already in 1966 by using a saturable dye solution to modelock a Nd:glass laser [37]. Instead of an organic dye, a semiconductor absorber also exhibits the required saturable absorption properties. Additionally, it can be tailored exactly to the needed parameters and is easier to handle than a liquid absorber. Various modelocked lasers using semiconductor saturable absorbers were demonstrated in the following time [38]. As the absorption cross-section of direct band gap semiconductors is very large with values of $10^4 \text{ cm}^{-1}$, semiconductor absorbers can be made very thin. A single 10 nm quantum well is sufficient in most cases. An epitaxially grown quantum well was then integrated into a laser cavity mirror, which greatly simplified the insertion of the absorber into the cavity and allowed for new degrees of freedom in absorber design by using different structures. This device was first demonstrated in 1992 [39] and modified several times in the following years until it was finally named “semiconductor saturable absorber mirror” SESAM [40].

4.1.1 SESAM device structure

As already described in the introduction, the SESAM is a laser mirror with integrated absorber layer. As an absorber layer, we used quantum wells consisting of GaInNAs, typically with a thickness of 10 nm. For material characterization and laser experiments, mainly two different structures were used. First the antiresonant structure, with lowest possible field strength inside of the device, and in contrary, a resonant design with a roughly 8 times larger field strength. The difference is achieved only by changing the thickness of the GaAs capping layer on top of the structure. The antiresonant structure results in a linear absorption of approximately 0.5%, which is suitable for actual mode-locking of solid-state lasers. The resonant structure is suitable for nonlinear optical characterization with a linear absorption of approximately 4%, resulting
in a good signal-to-noise ratio. Figure 15 shows the field intensity distribution inside of the different SESAM designs.

![Figure 15](image)

**Figure 15**: Resonant and antiresonant SESAM designs. The difference between the structures is the thickness of the topmost layer, indicated in dashed lines for the antiresonant case. The field inside of the quantum well absorber depends on the electric field intensity on the surface of the device.

### 4.1.2 Material requirements

In order to be useful as a SESAM absorber, the material of the quantum wells need to fulfill several requirements. First and most important is the lifetime of the excited carriers. In order to work with short pulses at high repetition rates, equilibrium conditions have to be restored quickly after bleaching by a laser pulse. This bleaching is achieved by filling of the available states in the conduction band by photogenerated carriers, which leads to a saturation of the absorption until these carriers recombine. High quality III-V semiconductor quantum wells show lifetimes in excess of 1 ns which is far too long for this application. Carrier recombination occurs mainly by radiative transitions in such materials. For SESAMs, recovery times of 250 ps and below are desired to achieve pulse durations in the range of a few picoseconds [36]. This can be achieved by using fast nonradiative recombination through deep-level defects deliberately introduced into the material. Low-temperature growth below 300°C is a classical technique to achieve desired properties in
InGaAs or GaAs quantum well structures [41]. During the growth of GaInNAs, such defects are also introduced by nitrogen incorporation. This is easily observed in the very low PL efficiency of the material, so it is very suitable for SESAMs at wavelengths of 1.3 μm [42] up to 1.55 μm [43].

Figure 16: Schematic recovery dynamics in a SESAM after saturation. The inserts show the two cases of recombination, direct band-to-band recombination and defect-assisted nonradiative recombination [44].

SESAMs are intracavity elements, so even small nonsaturable losses are undesirable, as they are enhanced strongly. These nonsaturable losses have diverse origins. Most obvious is surface scattering due to non-perfect device growth. When using heavily strained quantum wells, like they are necessary to use InGaAs at long wavelengths beyond 1200 nm, strain relaxation with a resulting non-even surface is often observed. GaInNAs has proven to be a very suitable material to produce low-loss absorber structures. Due to the lower strain in the quantum wells, the growth morphology is very good. Additionally, the growth temperature of 450°C higher than classical InGaAs or GaAs absorber layers needed to achieve fast recombination, so the formation of nonsaturable absorbing centres is suppressed.
4.2 SESAMs for modelocking of 1.5 μm Er:Yb:glass lasers

Passive semiconductor devices such as saturable absorbers are still a great challenge for the wavelength-range around 1.5 μm due to a lack of a proper absorber material lattice-matched to a high-contrast mirror. InGaAs can provide a band gap in the requested wavelength range and can be grown lattice-matched to InP. However, InP-based distributed Bragg reflectors (DBRs) suffer from a small refractive index contrast and poor thermal properties. 1.5-μm InGaAs grown on high-contrast AlAs/GaAs DBRs, on the other side, is so strongly lattice-mismatched that mostly 3D growth occurs. In general, this can cause surface roughness and increases the number of defects. By using GaInNAs, absorber layers with an absorption edge up to 1700 nm can be grown on AlAs/GaAs DBRs. Here, only a small amount of nitrogen is alloyed to InGaAs addressing two problems: (i) the nitrogen drastically decreases the band gap of InGaAs to meet 1.5 μm with much less indium and (ii) the incorporation of nitrogen additionally shifts the lattice constant towards the one of GaAs and, thereby, strongly decreases the lattice mismatch. GaInNAs is known to contain a high number of non-radiative defects, which make this material attractive for the application as saturable absorbers [45].

So far, GaInNAs SESAMs were only demonstrated to mode-lock solid-state lasers at 1.3 μm [42, 46]. Low saturation fluences and low nonsaturable losses proved well their suitability for passive mode locking in this wavelength range. At 1.5 μm, however, two problems were encountered: (i) fast temporal response and (ii) increased nonsaturable losses. The temporal response was accelerated by ion implantation but at the expense of very high nonsaturable losses preventing the SESAM from mode locking [47]. Up to now, only a fiber laser at 1.5 μm could successfully be mode-locked using a GaInNAs saturable absorber since fiber laser are much more tolerant against losses [48]. Fiber lasers require SESAMs with a high modulation depth, which was obtained with multiple quantum wells (MQWs) for the absorber region. A complicated absorber structure with barrier layers and even strain relaxation layers was reported. No information about nonsaturable losses was provided. However, solid-state lasers at 1.5 μm have a need for very small modulation depths and low
nonsaturable losses[49, 50]. In the following paragraphs, such a SESAM, using a GaInNAs absorber layer is discussed.

4.2.1 Material development for 1.5 μm absorbers

The main objectives for development of a suitable 1.5 μm GaInNAs absorber are: (i) a sufficiently low lattice mismatch to GaAs for relaxation-free growth, (ii) low nonsaturable losses due to surface scattering or defect absorption, and (iii) fast recovery of the saturated absorber layer within a few ten picoseconds.

As a starting base, we used an InGaAs quantum well with an indium content of 35% and a thickness of 10 nm. This structure had a photoluminescence peak emission wavelength of around 1180 nm as shown in Figure 17. The PL peak wavelength could be successfully shifted to 1550 nm by adding 2.6% of nitrogen to the otherwise similar InGaAs structure. While the wavelength red-shifted by 370 nm, the PL intensity was decreased by a factor of 200 under the same excitation properties. This suggests fast carrier recombination, suitable for SESAMs.

![PL spectra](image)

Figure 17: PL spectra measured from SQW test structures of InGaAs with 35% In (dashed) compared to the as-grown PL of 1.5 μm GaInNAs (solid, intensity multiplied by 100)

To grow GaInNAs with the proper wavelength, the plasma source operating conditions were varied in flow as well as in power. The nitrogen incorporation can be influenced either by varying the flow as well as by
changing the RF power. With our VEECO plasma cell, no differences were found between material grown at high flow with low power compared to high power/low flow conditions. This will be discussed in more detail in 5.3. As the material quality does not depend on the nitrogen cell operating conditions, the parameters can be chosen in a way that ensures maximum process stability and flexibility. The nitrogen flow is regulated by a thermal mass flow controller, rated at a maximum flow rate of 1 sccm. The rated precision is 1% of full range. RF power is controlled to a precision of 1W. Thus robust process conditions are achieved at larger flow rates and at low to intermediate power level. The influence of the individual parameters was evaluated in a series of experiments.

For the growth of 1.3 μm material in our earlier work on 1.3 μm SESAMs [42], a RF power of 200 W was used. In order to extend the wavelength to 1550 nm, we tried first to increase the nitrogen gas flow at constant power. As Figure 18 illustrates, the wavelength of the test structures does not increase linearly with the nitrogen flow in the plasma cell. At lower flow rate, a linear behavior can be assumed for smaller wavelength adjustments. At flow rates higher than 0.08 sccm, the nitrogen incorporation saturates. The higher chamber pressure in the nitrogen source leads to a reduction of the external cracking efficiency, probably by an increased recombination rate of the nitrogen radicals.

Figure 18: PL peak wavelength of test structures grown at 1.3 μm/h with a RF power of 200 W, as a function of the nitrogen flow into the plasma source.
In order to achieve wavelengths of 1550 nm and above for annealed SESAMs, the RF power was increased to 250 W. As annealing leads to an absorption-edge blueshift, the absorption edge needs to be at a wavelength of approximately 1600 nm. This requires a nitrogen incorporation that cannot be reached at 200W plasma power. At 250 W, however, no nitrogen flux saturation was observed for N\textsubscript{2} flow rates up to 0.14 sccm.

The final growth conditions for the 1.5 \textmu m SESAM was fixed at 250W RF power and at a nitrogen flux of 0.12 sccm. The growth rate was kept at 1.25 \textmu m per hour with an indium content of 35%. These conditions resulted then in an incorporation of 2.6% of nitrogen and in a PL emission wavelength of 1590 nm in the centre of the wafer. Due to nitrogen composition gradients obtained with the plasma source used in our MBE system, the absorption edge of the Ga\textsubscript{In}N\textsubscript{As} quantum well varied from 1584 in the centre, to 1500 nm in the outer part.

### 4.2.2 SESAM design and fabrication

An absorber grown under these conditions was then incorporated into a SESAM. A 40-pair Al\textsubscript{In}As/Ga\textsubscript{As} DBR with a stop band centre wavelength of 1590 nm was used as substrate. This mirror was grown by MOVPE, cleaved into quarters and overgrown by the absorber structure using MBE. Figure 19 shows the reflectivity spectrum of the final device, together with the PL spectrum of the included absorber layer. As the absorption is less than 1%, it is only barely visible in the scaling of the figure. For SESAM and absorber layer structures, we always used the PL peak wavelength as an indication for the absorption edge position. We observed that the onset of the absorption is at the PL peak maximum. PL is much more convenient to measure compared to the absorption, as it can be done in the PL mapper.
The SESAM was an antiresonant design, this means that the field intensity at the surface of the device is zero and very small inside of the mirror as it is shown in Figure 20. This results in a absorption of less than 1%, using a single GaInNAs quantum well.

**Figure 19:** Reflectivity spectrum of the antiresonant GaInNAs SESAM. The photoluminescence spectrum of a similar quantum well as it is included as an absorber is overlaid. SESAMs are not suitable for PL spectrum measurements as the mirror induces spectral modulations.

**Figure 20:** Design of the 1.5 μm GaInNAs SESAM. The refractive indices as well as the electric field intensity inside of the device are plotted.

### 4.2.3 Nonlinear optical characterization

The nonlinear properties of a SESAM are characterized by the saturation fluence ($F_{\text{sat}}$), modulation depth ($\Delta R$) as well as the nonsaturable losses ($\Delta R_{\text{ns}}$).
These numbers describe the temporal behavior of the device. The saturation fluence is the pulse fluence where saturation of the absorber starts. In most cases, it is desirable to keep this value low, to avoid the need for tight focusing on the device in the laser cavity. The modulation depth indicates the difference in reflectivity between a fully saturated SESAM and the device in equilibrium state. It defines the magnitude of the losses for longer pulses and can be modified either by the field intensity in the absorber layer, as well as by changing the number of absorbing quantum wells. The part that cannot be saturated is named nonsaturable loss; these losses serve no purpose, but reduce the efficiency of the laser and should be minimized. Figure 21 gives a schematic illustration of a nonlinear reflectivity curve as it is encountered in SESAMs.

![Nonlinear reflectivity curve](image)

**Figure 21:** Schematic representation of the SESAM parameters obtained by nonlinear optical characterization.

Nonlinear optical characterization [51] of the as-grown SESAM was carried out and revealed a saturation fluence, $F_{\text{sat}}$, of 20 $\mu$J/cm$^2$ and nonsaturable losses, $\Delta R_{\text{ns}}$, of 0.17% at a linear reflectivity, $R_{\text{lin}}$, of 99.4%. These losses are higher than those found for the 1.3-$\mu$m GaInNAs SESAM reported earlier [42], but still low considering the increase in defect concentration by the rise in nitrogen content. A modulation depth, $\Delta R$, of 0.39% was determined to be in good agreement with the design as it is shown in Figure 20. Pump-probe experiments were performed using 61 MHz, 5 ps pulses from an Er:Yb:glass laser (ERGO) at 1534...
nm to evaluate the temporal recovery from absorption bleaching. We obtained a fast temporal response of 18 ps. It is interesting to note, that the temporal response of the as-grown GaInNAs absorber layer at 1.5 μm (18 ps) is very similar to the one found for our 1.3-μm GaInNAs absorber (30 ps). This is surprising since the nitrogen content increased from 1.6% to 2.6% while all other growth parameters were kept constant. Usually, the increase in nitrogen content of GaInNAs is accompanied by a strong decrease in the PL intensity suggesting a higher incorporation of non-radiative defects. We observed this too. In addition, we expected a clear decrease in the temporal response. However, there was only a negligible decrease in the temporal decay for the 1.5-μm GaInNAs SESAM, which suggests that the defect concentration relevant for recovery from absorption bleaching stayed nearly constant. Applying annealing at 650°C for 1 min leads to the expected increase in PL intensity but, again, the temporal response did not change accordingly as generally observed for other material systems upon annealing (e.g. low-temperature GaAs [41]).

The only change we observed after annealing is a reduction in the nonsaturable losses from 0.17% to about 0.08 % for the benefit of a higher linear reflectivity. Hence we conclude that defects generated by an increase in the nitrogen content are not relevant for the recovery from absorption bleaching but contribute to nonsaturable losses, e.g. by additional absorption.

4.2.4 Laser performance

Laser testing was carried out using a 61 MHz Er:Yb:glass laser at 1534 nm [52]. For the first time, a GaInNAs SESAM successfully demonstrated self-starting and stable mode locking of a 1.5-μm solid-state laser as shown in Figure 22 [43]. The microwave spectra show clean cw mode locking without any Q-switching instabilities. Pulses as short as 5 ps were measured and fitted with a sech² function. An average output power of 70 mW with 690 mW incident pump power was obtained using a 3% output coupler. We observed no degradation of the SESAM over several hours.
4.2.5 Conclusions and discussion

A GaInNAs SESAM was used for the first time to modelock a 1.5-μm solid state laser [43]. The short pulses of 5 ps and proper self-starting behavior without Q-switching instabilities, combined with a good lifetime of the SESAM has proven that GaInNAs is a suitable material for the fabrication of 1.5 μm SESAMs on GaAs substrates. Due to the inherent defects from the growth process, no special measures like low-temperature growth or ion implantation were necessary to achieve a fast recovery time. This resulted in a fast recovering device with a good morphology and low nonsaturable losses.

4.3 Parameter tuneable SESAMs for 1.3 μm solid-state lasers

The nonlinear optical parameters of SESAMs strongly depend on the position of the absorption edge with respect to the laser wavelength [53]. Therefore, post-growth wavelength tuning is very useful for final tuning of the absorber to the laser characteristics. However, rapid thermal annealing (RTA) applied for wavelength fine-tuning removes defects from the material and
increases the recovery time. This is especially true for 1.3 μm SESAMs. Nitrogen pretreatment of the growth surface is a way towards more flexible SESAMs even better matched to the specific application. Previously, it has been demonstrated for InGaAs quantum wells that the carrier recombination time can be drastically reduced by incorporating a thin GaNAs layer into the adjacent GaAs barrier [54]. Here we have explored the option of growing a GaInNAs quantum well directly on such a nitrogen-enriched layer.

4.3.1 Device fabrication

Test structures and SESAMs with GaInNAs single quantum wells (SQWs) were grown on semi-insulating GaAs (100). The test structure consisted of a 11-nm GaInNAs SQW grown on a GaAs buffer layer at a temperature of 450°C monitored by diffuse reflectance spectroscopy (DRS) and capped with a 60-nm GaAs layer. The SESAMs incorporated the same SQW absorber. The quantum well growth rate was 1.7 μm/h at an As/III beam equivalent pressure (BEP) ratio of 15. For the nitrogen enriched layer at the barrier/quantum-well interface, the normal growth was interrupted and the surface was exposed to a nitrogen and As₂ flux for different time intervals before the growth was continued with the GaInNAs SQW using the same nitrogen flux. This results in a thin GaNAs layer between the barrier and quantum well. The N exposure time was varied between 5 s and 145 s. A sample without such a nitrogen-enriched interface was grown as a reference. The growth interface was monitored in situ by RHEED to determine the degree of deterioration of the interface by the nitrogen species from the plasma source. Parts of the test structures and SESAMs were treated with RTA at 600°C for 1 min. With the test structures we determined the as-grown and annealed photoluminescence (PL) wavelength of the GaInNAs SQWs because the underlying DBR of a SESAM can alter the PL emission spectrum of the SQW and gives a false position of the absorption edge.

The antiresonant GaInNAs SESAMs were based on a 30-pair AlAs/GaAs DBR with 93-nm GaAs spacer layer, a 11-nm GaInNAs SQW absorber and 93-nm GaAs cap layer. Such SESAMs have been described in more details in [42] but without the additional nitrogen treatment before the GaInNAs SQW. The composition of the GaInNAs SQWs was obtained by X-ray rocking curve
measurements after a 35.2% In concentration was determined using an additional InGaAs SQW test structure grown under the same conditions. This resulted in a nitrogen concentration in the GaInNAs SQWs between 1.05% and 1.10% depending on the nitrogen exposure time before the overgrowth by a GaInNAs SQW. This slight increase in nitrogen content explains the PL wavelength red shift with increasing pre-growth nitrogen exposure as shown in Figure 23.

![Figure 23](image)

**Figure 23:** Photoluminescence (PL) spectra of GaInNAs SQW test structures for different N exposure time, as-grown (a) and annealed at 600°C for 1 minute (b). The annealing significantly increases the PL intensity while the intensity ratios between the different samples remain mostly unchanged.

### 4.3.2 Time-resolved optical characterization

To characterize the recovery time of the nitrogen treated GaInNAs SESAMs, degenerate pump-probe measurements were carried out [51]. The pump- and probe pulse wavelengths were chosen 10 nm above the PL emission peak using 200-fs pulses from a commercial optical parametric oscillator (OPO). The energy for the pump pulses was two times the saturation fluence. A double exponential fit of the pump-probe measurements was used. The slow decay time is the relevant component to quantify the defect related recovery dynamics in such SESAM devices [40].

### 4.3.3 Formation of nonradiative defects

Nitrogen treatment affects a growth interface by surface damage and nitrogen accumulation. Surface damage is generated by unintentional N ion
bombardment from the plasma cell. The damage increases with increasing exposure time until the growth interface becomes noticeable rough. This can be observed by a change of the RHEED image which turns from a streaky pattern for the 2-D growth to blurred lines with weaker intensities to finally a spotty pattern representing 3-D growth. The surface morphology of the subsequent GaInNAs SQW depends strongly on the underlying growth interface and will turn to 3-D growth for longer exposure times. For a low exposure dose of 5 and 10 s, there was a slight 3D growth immediately from the beginning of the GaInNAs SQW which recovered already during the SQW growth and completely restored to 2D growth during the subsequent capping layer. For an exposure time of 20 s, the 3D growth was already stronger from the beginning and only recovered quickly during the GaAs capping layer growth. For even longer exposure times of 65 and 145s, the stronger 3D growth needed almost the complete cap layer growth time to recover to 2D.

Figure 24: X-ray rocking curve measurements of test structures with different N exposure times (each shifted up in intensity for clarity). Good single quantum well (SQW) growth is observed up to a 20-s N exposure time. For longer treatments we observe a deterioration of the growth from a shallow SQW signal and a broadened GaAs signal from the cap layer.

High-resolution XRD showed later that no recognizable quantum well was obtained for the longest exposure times. Figure 24 clearly shows the transition
from acceptable SQW growth at 20 s exposure to complete deterioration of the growth process at 65 s exposure time.

Nitrogen accumulation occurs at the growth interface and contributes to a higher nitrogen concentration in the SQW with increasing N exposure time. The red shift in the PL measurements and reduced PL intensity (Figure 23 – black curves) indicate a higher average nitrogen concentration for longer N exposure times. Figure 23 also shows the PL of a different GaInNAs SQW sample without any interface treatment but with a higher N concentration (gray curve). This PL peak intensity is higher than the analogous curve with the same red shift from the N-treated sample (i.e. an N exposure time of 10 s). Thus, the decay of the PL intensity with increased N exposure time is much stronger than by just alloying more nitrogen.

RTA of the samples was performed for 1 minute at 600°C under reduced nitrogen pressure of about 10 mbar using a GaAs proximity capping to prevent As evaporation. All samples improved in PL intensity by roughly the same factor as shown in Fig. 1a and b. Only samples that start without any PL emission do not recover during the annealing. The blueshift induced by annealing is 23 meV for the samples with 0 s and 5 s nitrogen treatment. The sample with 10 s N exposure time blue shifted only by 14 meV which indicates a change in the material properties compared to quantum wells grown under usual conditions. For the other samples no PL emission was observed.

4.3.4 Fast carrier recombination

Nitrogen exposure of the growth surface strongly decreased the carrier recombination time Figure 25. RTA has been performed on the test structures as well as on the SESAMs used for nonlinear characterization. Note that for a N exposure time of 20 s and longer, no PL signal was measured, as it is also seen in Figure 23. The absorber however is still working but with lower performance (as will be discussed in the next section). In this regime we see no change in the recovery time after annealing. Therefore, these defects do not heal out during annealing in contrast to the native defects generated by nitrogen incorporation in GaInNAs.
Below a 20-s nitrogen exposure time, the as-grown absorbers show relatively low PL intensity and fast carrier recombination, below 66 ps as seen in Figure 25. The recovery time of the untreated absorber is 65.4 ps and increases after RTA to more than 250 ps. For the nitrogen treated absorber structures this effect is strongly reduced and the absorbers remain much faster even after the annealing procedure. The sample with an exposure time of 20 s changed only from 21.6 ps as-grown to 22.3 ps after annealing.

![Figure 25: The slow component of the recovery time from a double exponential fit of pump-probe measurements clearly indicates the strong effect of the nitrogen exposure. At exposure times longer than 20 s, no PL was measurable, even after annealing.](image)

4.3.5 Saturation fluence and nonsaturable losses

We fully characterized the SESAM parameters according to the method described in [51]. The data of these measurements is given in Table 2. The saturation fluence and nonsaturable losses of SESAMs are important parameters that have to be tightly controlled. The product $F_{\text{sat}} \Delta R$ must be low to suppress Q-switched modelocking [53]. Nonsaturable losses absorb intracavity power, reduce the efficiency of the laser and can lead to thermal damage of the SESAM. Samples with exposure times up to 10 seconds do not show remarkable differences in the saturation fluence for both as-grown and annealed samples. However, for longer nitrogen exposure times (>10 s), we notice a strong increase in $F_{\text{sat}} \Delta R$. The reason for this increase is the strongly growing saturation fluence with exposure time, which is caused by the
deteriorated SQW structure and is further recognized by RHEED and XRC measurements. A more bulk-like material typically has a higher saturation fluence because of a higher density of states. All these observations indicate a strong change of the electronic band properties of the absorber.

<table>
<thead>
<tr>
<th>exposure time, s</th>
<th>$F_{\text{sat}}, \mu J/cm^2$</th>
<th>$\Delta R$, %</th>
<th>$\Delta R_{\text{ns}}$, %</th>
<th>$F_{\text{sat}} \times \Delta R$</th>
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<td>0.21</td>
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</table>

Table 2: Measured SESAM parameters: Saturation fluence $F_{\text{sat}}$, modulation depth $\Delta R$ and nonsaturable losses $\Delta R_{\text{ns}}$ for different nitrogen exposure times together with the product $F_{\text{sat}} \times \Delta R$. These values are measured at 1360 nm using 200-fs pulses.

The nonsaturable losses for the as-grown samples are significantly lower than the modulation depth. The 0.2% are even further reduced with increased N exposure time. RTA reduces these nonsaturable losses in samples exposed to N for up to 10 s without degrading the modulation depth. Generally better performance is obtained up to about 20 s N exposure time. The much higher nonsaturable losses at 10 s are most likely an artifact and due to increased surface scattering of the sample induced by the RTA process and not something inherent to the structure. However, the increased losses after RTA in the samples exposed to N for 65 and 145 s suggest that such long exposure times are not recommended for high-performance SESAMs.
4.3.6 Conclusions

Nitrogen exposure of the growth surface is a suitable method to grow fast absorbers based on GaInNAs using RTA as a fine-tuning tool for the absorber wavelength. At the same time, it is possible to keep the recovery time low despite of the defect-removal effect of thermal annealing. These results allow for more flexible SESAM designs with the possibility of post-growth wavelength tuning by RTA without changing the recovery time, saturation fluence, modulation depth and nonsaturable absorption of the absorber in an unacceptable way. Nitrogen exposure times from 0 to 20 s result in SESAMs with suitable parameters for modelocking of solid-state lasers. For the annealed SESAMs an exposure time of 20 s resulted in a fast absorber with a recovery time of 22 ps and a saturation fluence of 81 μJ/cm² and an exposure time of 10 s resulted in 79 ps and 25.5 μJ/cm². This is a higher value than th values measured in conventional quantum-well SESAMs, however, it is still low enough for usage in solid-state lasers. Depending on the requirements of the laser, a suitable nitrogen exposure time of the barrier/quantum-well growth interface can be chosen for optimum nonlinear optical parameters.

4.4 GaInNAs SESAMS for modelocked GaInNAs VECSELs

For the modelocking of GaInNAs VECSELs as it will be discussed in 6.4.3, a suitable SESAM was necessary. GaInNAs has already demonstrated its excellent properties as an absorber material in solid-state lasers. Offering low saturation fluence and low nonsaturable losses it is also suitable to modelock a GaInNAs VECSEL. The SESAMs for 1.3 μm we had fabricated earlier did not have a suitable absorption edge position for low saturation fluence operation. A new SESAM with optimized absorption edge position was grown. The topmost layers of the device structure, as well as the field enhancement inside of the SESAM is shown in Figure 26. The field enhancement describes the electric field intensity inside of the devices, in units of the external field intensity.
The GaInNAs SESAM was fully grown by MBE starting with a 35-pairs AlAs/GaAs DBR, centered at 1310 nm, on top of which were grown a 90 nm GaAs spacer layer, a 10 nm Ga$_{0.65}$In$_{0.35}$N$_{0.016}$As$_{0.984}$ absorber, and a 90 nm GaAs cap layer, to make the device antiresonant to obtain negligible group delay dispersion at the central wavelength of 1310 nm [55]. We designed the absorber to be in the antinode of the electric field. The PL emission peak of the GaInNAs absorber corresponds to the onset of the absorption edge and was at 1311 nm. A fast carrier recombination of the absorber was achieved with an absorber growth temperature of 450°C without any post-growth annealing. The absorption edge was designed very close to the laser emission to achieve minimum saturation fluence [53]. This SESAM was characterized by degenerate pump-probe experiments and nonlinear reflectivity measurements [51]. We measured a low saturation fluence of 6.8 (+/- 0.2) μJ/cm$^2$, a low modulation depth of 0.76%, nonsaturable losses of 0.12% and a recovery time of about 47 ps which is suitable for modelocking in picosecond pulse width [36, 56]. The performance of this SESAM is a VECSEL cavity is reported in 6.4.3.
5. Growth and annealing optimization of 1.3 µm laser gain material

5.1 Introduction

After successful demonstration of GaInNAs based saturable absorbers, the material was then further optimized for usage in laser gain structures. To be useful as a laser gain material, semiconductors with a high radiative efficiency are necessary in order to achieve a population inversion with practical pump power densities. High radiative efficiency also determines the slope efficiency of the laser. Additionally, this efficiency needs to be maintained at the elevated operating temperatures as they occur in a laser. Radiative efficiency is greatly influenced by the existence of defects acting as nonradiative recombination channels as already discussed in 2.4. By carefully optimizing the MBE growth parameters towards the optimum material after annealing we achieved a laser material exceeding the state of the art in terms of slope efficiency. The slope efficiency describes the slope of the input-to-output power-transfer function of the laser.

5.2 Growth temperature and V/III ratio

To successfully grow GaInNAs, it is necessary to use low growth temperatures as already discussed earlier. The growth temperature greatly influences the homogeneity of the material and the resulting carrier localization. Although lower growth temperatures lead to a lower radiative efficiency directly after growth, this does not directly translate to the annealed material. In this project, we investigated the growth temperature range between 300°C and 450°C. Equally important is the proper V/III ratio for the chosen growth temperature. The amount of arsenic offered during GaInNAs growth has several influences on the material growth. First, it has to be sufficient for a
Optimization of 1.3 μm laser material

stoichiometric growth of GaInNAs, i.e. no excessive gallium or indium is present. As arsenic is quite volatile at the growth temperature, a constant counter-pressure has to be maintained at the surface to prevent arsenic loss from the crystal. With increased substrate temperature, the necessary counter-pressure rises exponentially, so the minimum V/III ratio is expected to be higher at 450°C than at 410°C. Additionally, a large concentration of arsenic at the growth surface is known to decrease the surface mobility of adsorbed group III atoms before incorporation into the crystal. A high abundance of arsenic is thus expected to reduce effects like phase separation and compositional inhomogeneities. At the same time, the risk of incorporation of arsenic-excess dependent defects like V_{Ga} and A_{Ga} is increased at higher V/III ratios.

In order to find the optimum conditions and relations between the different parameters, a series of experiments was performed with the parameters varied individually and in combination. As a first step, the growth temperature was varied from 300°C to 450°C, while keeping the V/III BEP ratio at a constant value of 24.

![Integrated PL signal vs. growth temperature](image)

Figure 27: As-grown integrated PL intensity signal of GaInNAs test structures grown at different substrate temperatures. Integrated PL intensity describes the total power emitted from the sample in form of PL, irrespective of the wavelength.
Looking at the integrated photoluminescence intensity from the individual samples in Figure 27, it is evident that lower growth temperatures result in an increased concentration of non-radiative recombination centers as it was already expected. The samples grown at temperatures between 410°C and 450°C show no drastic deterioration, while the PL emission drops rapidly at lower temperature, being completely dark at substrate temperatures below 360°C. Even high-temperature annealing did not result in any PL emission from these structures. Normalization and overlaying of the photoluminescence spectra in Figure 28 shows a constantly narrow line shape for structures grown in the interval of 410°C to 450°C. At lower temperatures, broadening of the PL signal occurs at the high-energy side, indicating a deterioration of the quantum well. In comparison, an InGaAs sample grown at 360°C also shows this kind of line broadening. This indicates that this effect is caused by the low growth temperature itself and is not a nitrogen related effect.

An adverse effect is seen in the photoluminescence line-shape, as well as a significantly decreased PL signal intensity occurs in all samples grown below 410 °C. The following experiments were conducted in the temperature interval of 410°C to 450°C where no such line broadening was observed.
GaInNAs for laser gain medium applications has to be strongly annealed to reach the necessary radiative efficiency. To find the proper conditions in growth temperature and V/III ratio, a series of 10 nm GaInNAs SQW test structures was grown and then annealed by RTA at 700°C for 2 minutes. The plasma source was operated at 200W with a flux of 0.04 sccm N₂, the quantum well growth rate was 1.25 μm/h with a nominal indium concentration of 35%. The PL peak wavelength was at 1340 nm on average. The variable growth conditions, substrate temperature and arsenic flux with the resulting V/III ratio are listed in Table 3.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>T₆, °C</th>
<th>p₆, torr</th>
<th>V/III BEP ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP416</td>
<td>410</td>
<td>1.5x10⁻⁵</td>
<td>72</td>
</tr>
<tr>
<td>EP395</td>
<td>410</td>
<td>1.0x10⁻⁵</td>
<td>48</td>
</tr>
<tr>
<td>EP424</td>
<td>410</td>
<td>5.0x10⁻⁶</td>
<td>24</td>
</tr>
<tr>
<td>EP409</td>
<td>410</td>
<td>2.5x10⁻⁶</td>
<td>12</td>
</tr>
<tr>
<td>EP400</td>
<td>450</td>
<td>1.5x10⁻⁵</td>
<td>72</td>
</tr>
<tr>
<td>EP389</td>
<td>450</td>
<td>1.0x10⁻⁵</td>
<td>48</td>
</tr>
<tr>
<td>EP370</td>
<td>450</td>
<td>5.0x10⁻⁶</td>
<td>24</td>
</tr>
<tr>
<td>EP406</td>
<td>450</td>
<td>2.5x10⁻⁶</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 3: Growth temperature (T₆), arsenic flux and resulting V/III BEP ratio for the different SQW samples used for the evaluation of the optimum VECSEL growth conditions

From each structure a 3x3 mm² sample was cleaved from central position. These samples were then annealed and measured in the PL mapper. As high-temperature RTA leads to an inhomogeneous intensity distribution due to minor arsenic loss and sample oxidation, the maps were statistically evaluated for reliable results. The average integrated PL intensity after annealing is shown in Figure 29.
It is clearly recognizable that a substrate temperature of 410°C and low V/III ratio is optimum. No recognizable difference is seen in the final PL intensity between a V/III ratio of 12 and 24.

Figure 29: Average value of the integrated PL intensity on GaInNAs test structures after annealing at 700°C for 2 minutes.

Figure 30: Wavelength blueshift of the GaInNAs test structures after annealing at 700°C for 2 minutes, depending on growth temperature and arsenic flux.
When evaluating the blueshift of the GaInNAs samples, it can be seen from Figure 30 that the wavelength blueshift upon annealing is independent of the arsenic flux for a growth temperature of 450°C. At 410°C however, the blueshift increases with larger V/III BEP ratio from a value almost similar to the 450°C Tc samples at a ratio of 12 to more than 70 meV at a ratio of 72. This is a sign that at 410°, the V/III ratio has an influence on the concentration of certain defects in the material that facilitate diffusion, leading to an increased blueshift. These defects are probably gallium vacancies due to an excess of As atoms. This suggests a blue shifting mechanism on the group III sublattice, mediated by gallium vacancies. This observation is however in contradiction to the mechanism postulated by Klar et al. [28], where a blueshift is postulated via the group-V sublattice.

As a conclusion, 410°C is a suitable growth temperature for GaInNAs used as a laser gain material. However, the arsenic flux is a critical parameter as the concentration of certain blueshift-mediating defects is influenced by the V/III BEP ratio. From these results, the optimum growth conditions would be 410°C at a V/III ratio of 12 or even closer to stoichiometry. The PL intensity after annealing is maximum, while exhibiting the minimum blueshift of all Tc 410°C samples. This allows for the usage of the lowest amount of nitrogen to achieve the final wavelength. However, this arsenic flux is quite close to the limit for an arsenic-stabilized surface, which is absolutely necessary for smooth growth of the structure. This transition occurs at an arsenic BEP of around 1.0x10^-6 torr under these growth conditions. In order to achieve a robust growth process, an increased V/III ratio of 24 was chosen. The PL intensity of the structures is still very good, but a comfortable safety margin is included if the arsenic flux should decrease during the growth of the device. The slightly decreased blueshift is not sufficiently significant to justify the increased process risk by using a very low V/III ratio.

5.3 Plasma cell operating conditions

In order to create active species from the inert N2 molecules, they have to be cracked into radicals by using a high-power-density inductively coupled plasma. This produces not exclusively radicals but also ions with energies up to 35 eV [15]. Compared to the average bond-strength of a semiconductor crystal, which is approximately 1 eV, it is clear that these ions result in material
Optimization of 1.3 µm laser material degradation. The flux of active species of the nitrogen plasma cell can be varied either by changing the RF power supplied to the cell, as well as by changing the flow rate of nitrogen. Both methods show a linear relationship between the variable parameter and the resulting nitrogen incorporation. In order to find the effect of the cell operating conditions that result in the lowest ion damage, a series of growth experiments was conducted.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>RF power (W)</th>
<th>N2 flow rate (sccm)</th>
<th>PL peak (nm)</th>
<th>[N] (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP233</td>
<td>200</td>
<td>0.035</td>
<td>1370</td>
<td>1.30</td>
</tr>
<tr>
<td>EP253</td>
<td>250</td>
<td>0.035</td>
<td>1408</td>
<td>1.32</td>
</tr>
<tr>
<td>EP254</td>
<td>300</td>
<td>0.035</td>
<td>1438</td>
<td>1.96</td>
</tr>
<tr>
<td>EP255</td>
<td>350</td>
<td>0.035</td>
<td>1484</td>
<td>1.98</td>
</tr>
<tr>
<td>EP305</td>
<td>500</td>
<td>0.020</td>
<td>1402</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Table 4: Plasma cell operation conditions and resulting parameters

The operation conditions used in these experiments are summarized in Table 4. HRXRD was used to measure the resulting nitrogen concentrations from the fitted perpendicular mismatch, assuming identical indium concentration. Due to difficult fitting, the concentration values should be interpreted only as an indication for the nitrogen concentration range obtained, from 1.3 to 2% N.

Figure 31: PL spectra obtained from samples with different plasma source operation conditions
Figure 31 shows the increased nitrogen incorporation with increased RF power applied to the cell. Surprisingly, there is no significant difference between a low-power/high-flow condition (250 W / 0.035 sccm) and a high-power / low flow condition (500W / 0.020 sccm). From these results, we decided to use generally lower plasma power and higher flows, as the mass flow controller precision is better under these conditions, resulting in better wavelength reproducibility of the samples.

![Graph showing linear relationship between PL wavelength and plasma power](image)

Figure 32: PL wavelength of test structures grown at 0.035 sccm flow with varied plasma power

Figure 32 illustrates the linear relationship between applied plasma power and resulting PL wavelength. This linear behaviour is useful when designing growth parameters for a specific band gap energy, as linear interpolation gives a good indication of the necessary source settings. The resulting material quality does not depend on the operating conditions of the plasma source. Nitrogen flow and plasma power can be varied freely to achieve the desired nitrogen incorporation. Both parameters behave linear to the resulting nitrogen incorporation.

5.4 Migration enhanced epitaxy

During GaInNAs growth, we always observed a slight 3D growth at the end of the QWs in RHEED. One reason for such 3D growth to occur is insufficient surface migration of the group III elements after adsorption due to the low growth temperature. It was already demonstrated by Hong et al. [57]
that migration enhanced epitaxy (MEE) is capable of producing high optical quality material GaNAs. MEE is a technique to improve the surface diffusion of adsorbed group atoms III before being incorporated into the crystal. This is accomplished by separation of the group III and group V element fluxes during growth. The background arsenic pressure in the growth chamber is sufficient to prevent surface damage while the arsenic shutter is closed. The group III atoms are deposited onto a surface without excess arsenic. Due to this absence of a binding partner, the atoms have the opportunity to diffuse to preferential adsorption sites like steps and kinks. The growth conditions were kept constant during these experiments, only the shutter times were varied. The respective beam fluxes were: Ga: 1.52x10⁻⁷ torr, In: 1.62x10⁻⁷ torr, As: 5.0x10⁻⁶ torr and 0.035 sccm N₂ at 200 W. The substrate temperature was kept at 450°C for the MEE process, while a GaAs buffer layer was grown before at 600°C. In a first attempt, a shutter sequence with all fluxes completely separated was used. The amount of material deposited was approximately one monolayer of Gallium and 0.5 ML for Indium. The shutter sequence for this process is shown in Figure 33. Ga was deposited first and then saturated with As after a migration time of 2 s. After a waiting period of 2 s to evaporate all excess As on the surface, In was deposited. Another 2 s waiting period was inserted for indium migration. Then the surface was again saturated with As and exposed to nitrogen immediately afterwards. Finally, another waiting period completes the cycle. This was then repeated 23 times to achieve the final QW thickness of 10 nm. At the end, a 60 nm GaAs cap was deposited using conventional MBE technique.

![Figure 33: Shutter sequence for MEE growth with completely separated elemental fluxes](image)

During the MEE growth process, a pronounced 3D surface morphology developed. This is undesirable as it is a sign for phase separation in the
GaInNAs layer. The structure did not show any photoluminescence while XRD indicates a partially relaxed structure with insufficient interface quality to show any pendellösung fringes. In a second experiment, Ga and In respectively As and N were combined. Additionally, the pause after group V deposition was reduced to 0.1 s to avoid possible As loss as it eventually occurred during the first experiment. Figure 34 shows the exact shutter sequence applied in this experiment.

![Figure 34: Shutter sequence in combined flux MEE](image)

The changes did not show any positive effect. The growth surface turned also 3D with a very rough interface at the end of the QW growth. Again, no PL emission was observed and a similar XRD as in the first MEE experiment. The expected quantum well signal was not observed, also no pendellösung fringes were visible at all, which results from very rough interfaces. The GaAs peak also shows broadening at the base, which indicates a low crystalline quality of the capping layer grown on top of the quantum well.

5.4.1 Conclusions and Discussion

Migration enhanced epitaxy did not lead to acceptable results in the few experiments conducted during this study. The fact that GaNAs can be grown successfully using this technique does not imply that this has to be the case with GaInNAs. MEE under the conditions used did not improve the growth morphology as expected in the beginning, but resulted in an opposite effect. The enhanced group III migration led probably to a structure closer to equilibrium with a phase separation into In-rich and Ga-rich regions. These results suggest that GaInNAs requires growth conditions that suppress long range diffusion. Such a method is the growth under normal MBE conditions at
low temperatures, high growth rates and a large As overpressure. From this perspective, the MEE growth experiments confirm that the standard growth conditions are the right choice.

5.5 Digital alloying

Digital alloying was also applied successfully on GaInNAs solar cell material [58]. We expected to be able to modify the annealing behaviour, by trying to enforce indium-nitrogen bonds by growing InNAs/GaAs structures in the form of short-period superlattices. Such a material is expected to exhibit similar electronic properties like homogenous material with the same constituents.

For the digital-alloying technique, two short period superlattice samples were grown with an individual layer thickness of nominally one unit cell of InNAs respectively GaAs. The samples were grown on a (100) undoped GaAs substrate on top of a standard GaAs buffer grown at 600°C. The fluxes were kept the same as used in usual growth of GaInNAs quaternary material, a combined growth rate of 1.25 μm/h at a V/III ratio of 25 and a substrate temperature of 450°C. During growth, the structures started out nicely 2D in RHEED, however, the growth mode turned into pronounced 3D towards the end. After growth of the cap layer, a smooth surface was again attained. XRD measurements showed a structure similar to a homogenously grown GaInNAs quantum well, and a photoluminescence wavelength similar to homogenous quaternary material was observed. After growth, the samples were annealed under similar conditions as used for homogenous GaInNAs at 700°C for 2 minutes. A blueshift of 48 meV was observed, which is a typical value for 1.3 μm GaInNAs grown at 450°C.

5.5.1 Discussion and conclusions

Digital alloying did not result in the intended reduction of the blueshift by enforcing In-N bonds. This can be explained by indium segregation. Indium tends to segregate on the growth surface, instead of incorporating directly. During the InNAs shutter sequence, the indium was probably accumulated on the growth surface while the nitrogen was incorporated into the underlying crystal transforming the previously deposited layer of InGaAs into GaInNAs. During the GaAs shutter sequence, InGaAs was grown, using the indium
accumulated on the surface. This resulted in a growth of GaInNAs layers instead of individual GaAs and InAs layers, rendering the digital alloying technique ineffective in this material system. Due to the lower overall growth rate, the atoms had a longer time for diffusion, resulting in more pronounced phase separation and 3D growth, what could be an explanation for the observations in RHEED.

5.6 Annealing process

The last process step in the preparation of laser-gain–quality GaInNAs is thermal annealing at high temperature. During this process, most of the nonradiative recombination centers in the material are removed, resulting in a material with a high optical emission efficiency. To find optimum conditions for the annealing process, a series of experiments was conducted, which will be discussed in the next paragraphs.

5.6.1 Rapid thermal annealing

In order to optimize the radiative efficiency of the material, different annealing processes were examined. At the beginning, rapid thermal annealing was used exclusively. The annealing treatment was done using a Jipelec JetFirst 1000 rapid thermal annealing furnace. The furnace atmosphere was low-pressure flowing nitrogen, at a pressure of 10 mbar. The samples were placed inside of a thin-walled SiC coated graphite susceptor, covered also by a graphite plate. The susceptor was then uniformly heated by radiation from an array of tungsten-halogen lamps. The temperature was controlled by a thermocouple in contact with the susceptor. This method ensures uniform heating of the samples, as well as a confined space for the substrate with little gas exchange.

In order to minimize arsenic loss from the surface, resulting in damage and formation of point defects, the samples were always covered with a piece of fresh GaAs wafer. Prior to covering, the samples and cover pieces were ultrasonically-cleaned in an 1:1 acetone-water mixture for a few minutes to remove any loose surface particles. Then the samples were dipped in 30% ammonia solution for oxide removal, rinsed in ultra pure water and spin-dried. This technique reduces the arsenic depletion of the surface. However, it cannot
supply an overpressure completely preventing damage. Both, the substrate wafer used for capping, as well as the structure to be annealed, have a stoichiometric surface composition. When heated, both surfaces lose arsenic until they are in equilibrium with the atmosphere in between of the two wafers. This results in the formation of arsenic vacancies that diffuse into the sample. Additionally, oxygen that is always present on GaAs surfaces exposed to air diffuses into the structure. These effects are of course more pronounced for long-time annealing and at higher temperature. Despite of these drawbacks, RTA was a useful technique to evaluate the annealing behaviour of GaInNAs.

Figure 35 summarizes the experiments undertaken to evaluate the best annealing conditions [59]. GaInNAs test structures were annealed for 1 minute at different temperatures up to 800°C. Annealing temperatures of 700 to 750°C resulted in the best PL intensity for all different nitrogen content samples that were analyzed.

At 700°C, and even more pronounced at 750 and 800°C, surface damage was observed that could be seen by bare eye. Due to this arsenic loss during longer high temperature annealing steps, optically scattering surfaces as well as inhomogeneous PL intensities occurred. For device fabrication, a more robust
and controlled annealing process is necessary as it is discussed in the following paragraph.

5.6.2 MBE in situ annealing

In order to grow best possible quality laser material, MBE in situ annealing was used. In situ annealing offers the advantage of improved control over the annealing conditions and atmosphere. In our RTA process, arsenic loss and sample oxidation by residual oxygen represents a significant problem. The PL intensity map in Figure 36 shows such inhomogeneities of the final PL intensity.

![Figure 36: PL intensity map of a GaInNAs test structure annealed using RTA and GaAs proximity capping, for 2 minutes at 700°C. Arsenic loss and oxidation leads to diffusion of surface defects into the quantum wells and the adjacent barriers, resulting in an inhomogeneous PL intensity distribution.](image)

MBE in situ annealing, in contrast, allows for a constant arsenic overpressure during annealing, to completely suppress the loss of arsenic. Also oxidation is not an issue due to the UHV atmosphere. This annealing treatment was optimized to achieve optimum conditions for device fabrication. However, this process also has its limitations in the maximum allowable annealing temperature. We found the most significant limitation in re-evaporation of the topmost layer during annealing at temperatures of 700°C and above. One test structure was also annealed at 750°C for 5 minutes, which resulted in uncontrollable evaporation of more than 100 nm of material. At the same time, a deteriorated PL intensity was observed, compared to a 700°C annealing,
probably due to insufficient arsenic overpressure at this high temperature. As VECSELS are very sensitive on layer thickness precision, an annealing step at 700°C for 5 minutes was considered the optimum. During this annealing time, a re-evaporation of approximately 5 nm GaAs takes place, which can be compensated for in the growth recipe. As the following structures on top of the quantum well are grown at 600°C, this results in additional annealing. During the development of the structures, this effect was simulated by adding an annealing step at 400°C for 4 hours.

5.6.3 MOVPE in situ annealing

In the fabrication process of two VECSEL structures used for the laser experiments, only the AR structure and the active zone were grown by MBE, while the DBRs were grown by MOVPE. In a first annealing step, 700°C for 5 min, MBE annealing was performed and the structure was then capped by arsenic. The structure was then transferred into the MOVPE system for DBR overgrowth. The conditions used in the mirror growth process were 720°C for a duration of 2 hours, what resulted in additional extensive annealing, while at the same time preventing material loss from the active zone or formation of intrinsic defects like As vacancies due to arsenic loss. In conclusion, MOVPE growth of DBRs in GaInNAs SESAMs is a very successful approach, as it leads to a high-temperature annealing, not available using MBE in situ annealing or RTA. Additionally, the mirror growth process is much faster than in MBE, saving time, what would be an important aspect for commercial production of such devices.

5.7 Strain compensation and critical thickness

Pseudomorphic growth of highly strained quantum wells leads to large internal stresses in the semiconductor structures. This stress can lead to relaxation by gliding and multiplication of dislocations. As dislocations are efficient nonradiative recombination centers, they lead to formation of dark-lines inside of the structure, ultimately resulting in device failure.

In InGaAs VECSELS, dark lines were observed along <110> directions, multiplying during laser operation[60]. These dark lines originate from the
Optimization of 1.3 µm laser material

Gliding of threading dislocations in \{111\} planes. As the dislocation only experiences a force inside of the strained layer, the dislocation is pinned in the surrounding barrier layers. Due to this pinning, the dislocation is elongated along the interface, forming a segment of misfit dislocations, which then acts as a dark line defect as misfit dislocations are efficient recombination centers. Threading dislocations are always present in epitaxial structures, as they are already present in the substrate and are continued by MBE growth. The wafer quality used in this project was specified for up to 500 threading dislocations per cm². According to the Matthews-Blakeslee-model(M-B) [61], misfit dislocations are formed by elongation of threading dislocations when the force on the dislocation segment, exerted by the layer strain $F_\varepsilon$, exceeds the force of the dislocation line tension $F_l$. These relations are illustrated in Figure 37, the critical case represents the equilibrium between the forces generated by dislocation line tension and strain.

Figure 37: Threading dislocations under the influence of misfit strain in a) coherent, b) critical, c) incoherent multilayers [61].

In this case of strain relaxation, the dislocation segment glides in the epitaxial layer, leaving a misfit dislocation segment along the interface. Equation (4.1) describes the force exerted on a threading dislocation segment by epitaxial misfit strain. This force is linearly increasing with growing layer thickness and with strain. Equation (4.2) gives the force exerted on the dislocation segment by line tension of the misfit dislocation segment. With the shear modulus $G$ of the two materials, under assumption of identical elastic constants, Poisson’s ratio $\nu$, the Burger’s vector $b$, strained layer thickness $h$, misfit strain $\varepsilon$, the angle between Burger’s vector and dislocation line $\alpha$, and finally the angle between the dislocation slip direction and the direction in the
layer plane, perpendicular to the intersection line of slip plane and layer plane [62].

\[ F_ε = \frac{2G(1 + ν)}{(1 - ν)} bhεcosλ \]  \hspace{2cm} (4.1)

\[ F_i = \frac{Gb^2}{4π(1 - ν)}(1 - νcos^2α)\left[ln\left(\frac{h}{b} + 1\right)\right] \]  \hspace{2cm} (4.2)

The equilibrium of these two forces leads the critical thickness for the formation of misfit dislocations [61] as it is given in equation (4.3). The line tension is counted double, as it occurs in both interfaces of the epilayer. \( f \) is the difference in lattice constant between unstrained substrate and layer material.

\[ h_c = \frac{b \left(1 - νcos^2α\right)}{2πf(1 + ν)cosλ}\left[ln\left(\frac{h}{b} + 1\right)\right] \]  \hspace{2cm} (4.3)

According to this theory, already the growth of a single 10-nm wide In\textsubscript{0.2}Ga\textsubscript{0.8}As quantum well leads to misfit dislocations in the lower growth interface. In the overgrown state such a structure is then barely stable. A GaInNAs quantum well containing 35% In could not be grown dislocation-free at 10 nm width due to excessive strain. In reality, a dislocation-free growth is observed, what will be discussed further on in this paragraph.
When stacking several strained layers, the force exerted on the dislocations in the layers has to be supported by the unstrained barriers in between. If the dislocation pinning in the barriers is overcome, threading dislocations start to travel through the complete MQW structure, even when the critical thickness of the individual quantum wells is not exceeded, resulting in relaxation. The situation may be metastable at room temperature, however, laser operation results in a temperature rise, energy transfer to the lattice by nonradiative multiphonon recombination as well as electronic effects on dislocations by the intense excitation [63]. The supplied energy is sufficient to promote gliding of dislocations pinned in metastable state inside of an InGaAs/GaAs heterostructure. By inserting strain compensation layers inside of the barriers, this can be prevented. Strain compensation layers are oppositely strained to the quantum well, that results in a force on the dislocation into the opposite direction. Averaged over the structure, the net force on threading dislocations is zero in the strain compensated case. As long as individual layers do not exceed the critical thickness, no dislocation movement occurs in the strain compensated case as the situation is not metastable anymore. Using this method, a large improvement could be made in the lifetime of InGaAs MQW VECSELs [64]. So we also expected a necessity for strain compensation, as Ga$_{0.65}$In$_{0.35}$N$_{0.015}$As$_{0.985}$ quantum wells for 1.3 μm contain much higher strain than In$_{0.13}$Ga$_{0.87}$As used in 960 nm VECSELs, resulting in a larger force on
dislocations. However, we did not observe any dark lines in our VECSEL structures after processing and also after laser operation of non-strain-compensated structures.

We attribute this resistance against dislocation gliding to a hardening effect by nitrogen. First, nitrogen is assumed to decorate the dislocation core, resulting in a strong pinning effect. Additionally, the small nitrogen atoms lead to an alloy hardening effect by increasing the Peierls-Nabarro (P-N) stress of the material. The P-N stress describes the minimum shear stress necessary to move a dislocation through the crystal lattice. The M-B model for critical thickness does not include the effect of the P-N stress, what is only valid for a material with negligible alloy hardening effects at high temperatures. In GaInNAs, the critical thickness is expected to be much higher than predicted from M-B theory. Momose et al. [65] demonstrated that 2% of nitrogen in GaNAs increased the critical thickness for misfit dislocation formation from calculated 30 nm to 300-400 nm experimentally measured. This increased resistance against relaxation made strain compensation obsolete in GaInNAs VECSELs, resulting in an easier structure to grow with more favorable electronic properties.

5.8 Conclusions and outlook

By careful optimization of growth and annealing parameters, as well as taking advance of inherent hardening effect in GaInNAs, we designed a robust fabrication process for a laser gain structure, useful for a 1.3 μm VECSEL. Such material was grown at a temperature of 410°C and a growth rate of 1.25 μm/h. The plasma source was operated at a RF power of 200W resulting in an incorporation of approximately 1.8 % of nitrogen. The V/III BEP ratio was kept at a value close to stoichiometry, with an added safety margin for source instabilities during growth. The quantum well thickness was 8 nm. After growth, a MBE in-situ annealing process at 700°C for 5 minutes was performed. Additional annealing by DBR overgrowth was simulated using annealing at 600°C for 4 hours after the high-temperature step.

In the next chapter, the implementation of this GaInNAs gain material into a VECSEL will be discussed.
GaInNAs VECSEL at 1.3 µm

GaInNAs has been successfully applied as an active material in edge-emitting lasers, VCSELs [66] and VECSELs in the past [67-69], and we already demonstrated the usability of GaInNAs for SESAMs modelocking of solid state lasers [42, 43]. In this chapter, the fabrication of a 1.3 µm GaInNAs VECSEL and its modelocked operation using a GaInNAs SESAM is described. GaInNAs VECSELs at 1.3 µm emission wavelength have already been demonstrated earlier by Hopkins et al. [70], however, modelocking could not be demonstrated prior to our project.

6.1 VECSEL introduction

A VECSEL is a semiconductor laser that emits its output perpendicular to the laser chip surface [71], compared to the more well-known edge emitting lasers. This design offers numerous advantages, as well as new challenges compared to edge emitters. Optically pumped VECSELs can be designed to emit a diffraction limited output beam at even very high output powers, 20 W in fundamental transverse mode have been demonstrated recently at 960 nm [72]. More than 30 W with an M² of 3 was also demonstrated [73]. By designing the layer structure accordingly, also properties like group delay dispersion (GDD) or electric field intensity inside of the gain structure can be modified. VECSELs gained more and more interest in the past time, successful commercial products already use the technology for example in forensic light sources [74] and as a replacement for argon ion lasers in laboratory or OEM applications [75].

The general layout of a VECSEL is given in Figure 39. It consists of a laser cavity, formed by external optics, in this case a single concave mirror. The pump energy is supplied optically, by a diode laser. The beam quality of the pump laser needs to be good enough to allow for a nearly Gaussian pump intensity distribution, but a multimode source is sufficient. The pump laser
wavelength is 808 nm what is readily absorbed by GaAs, avoiding the need for an in-well pumping scheme [76]. Additionally, 808 nm diodes are available at very high power for pumping of neodymium lasers.

The VECSEL then contains the semiconductor gain structure, consisting of a highly reflective mirror, an active region where the laser radiation is generated and an antireflective coating, necessary for efficient pumping and adjustment of the electric field intensity inside of the active structure. In this work, the acronym VECSEL often denotes the gain structure itself, even if a VECSEL is strictly spoken the gain structure and all its peripheral components. In Figure 39 is also shown, that no substrate is present in between of the heat sink and the VECSEL structure. This substrate was removed for better cooling of the structure. The process we refer to as “upside-down processing” [77]. The individual constituents of the VECSEL structure are described in the following paragraphs.

### 6.2 VECSEL device structure

The GaInNAs VECSEL consisted of four parts: an etch-stop structure, the antireflection layers, the active region, and two stacked distributed Bragg reflectors (DBRs) for the laser wavelength and the pump light. The whole structure was grown upside-down on a GaAs (100) undoped substrate to allow for removal of the GaAs substrate after growth. The etch-stop consisted of three layers of the following materials Al_{0.85}Ga_{0.15}As, GaAs and AlAs. The
antireflection structure consisted of 10 alternating layers of AlAs and Al$_{0.20}$Ga$_{0.80}$As with numerically optimized thicknesses for low reflectivity of both the pump wavelength at $45^\circ$ of incidence and the laser wavelength of normal incidence. Al$_{0.20}$Ga$_{0.80}$As was used in the mirrors instead of pure GaAs, to avoid absorption of the pump wavelength outside of the active region. The active region consisted of five 8-nm thick Ga$_{0.65}$In$_{0.35}$N$_{0.018}$As$_{0.982}$ quantum wells (QWs) separated by 178 nm GaAs barriers to place each QW into the antinodes of the standing wave pattern of the laser electric field. Up to this point the structure was grown by molecular beam epitaxy (MBE). The DBRs were grown by metal-organic vapour phase epitaxy (MOVPE). The first mirror consisted of a 32-pair AlAs/Al$_{0.20}$Ga$_{0.80}$As DBR centred at the laser wavelength of 1300 nm for normal incidence. The second one was a 10-pair DBR of the same materials composition, designed for high reflectivity of the 808 nm pump wavelength at $45^\circ$ of incidence. The overall design of the VECSEL structure can be seen in Figure 40. The topmost layers of the laser mirror are seen on the left side with its $\lambda/4$ layers of alternating refractive index. Then the active structure, containing the quantum wells in the antinodes of the electric field, followed by the antireflection structure.

![Design of the topmost VECSEL layers. The refractive indices of the materials as well as the field enhancement factor are plotted.](image)

Figure 40:  Design of the topmost VECSEL layers. The refractive indices of the materials as well as the field enhancement factor are plotted.

### 6.3 Device fabrication

The GaInNAs VECSELs were grown in several steps, each on the machine most suitable for the task. As already mentioned before, the device was grown in upside-down order, the etch-stop structures were grown first, followed by
the antireflection structure. The active structure, containing the GaInNAs quantum wells embedded in GaAs pump absorption barriers is grown in the phosphorus-MBE. Finally, the DBRs for laser and pump are grown by MOVPE for a faster regrowth process than it had been possible by MBE at that time.

6.3.1 Material growth

The first layers form an etch stop structure for the wet-chemical substrate removal process. This structure starts with a 200-nm thick layer of Al$_{85}$Ga$_{15}$As. This material serves as a stop layer for the ammonia-hydrogen peroxide etch. A GaAs layer of 20 nm thickness is then grown stopping the HF etch step applied for removal of the previous Al$_{85}$Ga$_{15}$As layer. This GaAs is then followed by 75 nm AlAs, resistant against diluted ammonia-peroxide etch. The wet-chemical process is then described in more detail in 6.3.2.

The antireflection layers are subsequently grown using AlAs /Al$_{0.20}$Ga$_{0.80}$As pairs, numerically optimized for low reflectivity at the pump wavelength as well as for the laser wavelength. This structure is then capped with a layer of elemental arsenic for contamination-free transfer into the nitride growth chamber. For deposition of the arsenic cap, the substrate temperature is lowered to 0°C. Due to the liquid-nitrogen cooled chamber walls, the substrate is cooled by radiation. Arsenic is then deposited in an amorphous layer until a uniform coverage is observed by RHEED. After transfer into the nitride growth chamber, the nitrogen plasma source was ignited and stabilized to growth conditions. After stable chamber conditions were established, the arsenic capping layer was evaporated at 300°C during heating of the sample to growth temperature under constant arsenic flux.

The active structure was then grown at 410°C under the optimum growth conditions found during the optimization experiments outlined in 5 and subjected to MBE in-situ annealing. At the end of the structure, another arsenic cap was applied for transfer of the wafer into the MOVPE system for overgrowth. The mirrors for the laser wavelength, as well as for the pump wavelength were then deposited by MOVPE at temperature of 720°C in a growth time of approximately 2 hours.
6.3.2 Post-growth processing

In order to remove the heat efficiently from the VECSEL, the structure was processed upside-down for efficient heat removal. The chip is mounted epilayer-down onto a heat sink and the substrate is then removed. An indium-based reflow soldering process was used to mount the chips to copper submounts. First, the wafer was diced into 4x4 mm² chips and cleaned from dust by acetone/water solution in ultrasonic. The oxide is then removed by a short dip in 30% NH₄OH. Finally, the chips are rinsed using DI water and spin-dried.

For soldering, a layer structure as outlined in Table 5 was deposited onto the VECSEL chips using vacuum-evaporation. The metallization structure starts with 30 nm of titanium as an interface layer. Titanium is highly reactive and reacts with residual oxide and water present on the surface of the semiconductor chip. Following the titanium, 200 nm of platinum is deposited, acting as a diffusion barrier to prevent indium diffusion into the semiconductor chip. The solder itself is 5μm of pure indium evaporated on top of the diffusion barrier layer. To prevent oxidation of the In solder layer, 100 nm of gold is coated on top forming the intermetallic compound In₂Au. This layer is oxidation resistant and dissolves partially during reflow soldering. The metallurgical details of this process are described in the paper of So et al. [78].

![Table 5: VECSEL metallization structure](image)

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>30</td>
</tr>
<tr>
<td>Pt</td>
<td>200</td>
</tr>
<tr>
<td>In</td>
<td>5000</td>
</tr>
<tr>
<td>Au</td>
<td>100</td>
</tr>
</tbody>
</table>

For efficient heat removal, the VECSEL chips have to be attached to submounts with high thermal conductivity. These submounts were first cut from rectangular electrical grade copper bar stock by wire erosion. They were then lapped for good planarity and low surface roughness. The lapped submounts were then coated similarly to the semiconductor chips, without indium as summarized in Table 6.
1.3 μm GaInNAs VECSEL

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>30</td>
</tr>
<tr>
<td>Pt</td>
<td>200</td>
</tr>
<tr>
<td>Au</td>
<td>100</td>
</tr>
</tbody>
</table>

Table 6: VECSEL submount metallization structure

Soldering of the semiconductor chips to the copper submounts was done in vacuum to prevent oxidation and voids in the solder layer. The soldering setup consisted of a fused silica tube, pumped by a turbomolecular pump. The operating vacuum was around 5x10^{-5} mbar. The device to be soldered was placed on an electrically heated copper block which was installed inside of the vacuum chamber. A 50 W/12 V tungsten halogen lamp was used as a heater while the temperature was monitored with an embedded thermocouple. At 50 W, a heating rate of 100 K/min was achieved. This electrically heated and controlled hotplate allowed accurate control of the temperature profile during soldering. A pressure of 300 kPa was applied during the soldering process to achieve a thin solder layer. This pressure was applied using glass weights. Reflow soldering was then performed according to the temperature profile outlined in Figure 41.

![Figure 41: VECSEL soldering temperature profile](image-url)
In a first step, the parts were degassed at 80°C while the vacuum was established. The temperature was then raised to 130°C what is 26 K below the melting point of indium. This temperature was held for 10 minutes to ensure complete degassing and a homogenous temperature distribution. The temperature was then raised to 200°C for 5 minutes for bonding and cooled down to room temperature afterwards. After reflow soldering, the devices were inspected under a binocular for proper soldering along the edges, as otherwise mechanical failure would occur during the following lapping process. This would not only result in the loss of the corresponding device, but the debris would as well damage the other chips lapped at the same time.

In the following step, the substrate was removed to a residual thickness of 50 μm by lapping. This processing was done on a Logitech PM5 wafer lapper using 3 μm size alumina abrasive slurry. Following the lapping step, the devices were polished using Chemlox solution available from Logitech, a slurry of nanometer-sized alumina in sodium hypochlorite solution. This chemo-mechanical polish removed the structurally damaged layer present after lapping and leaved a mirror-like finish for the following jet-etching process.

The remaining 50 μm of GaAs were then etched in a jet-etcher by a solution of H₂O₂(35%):NH₄OH(30%) = 25:1. The etch rate for GaAs is approximately 5 μm/min, while a good selectivity is obtained for Al₈₅Ga₁₅As. A 200-nm thick etch-stop layer resists for approximately 5 minutes. This also allows for processing of devices that show a certain wedge from the lapping process. After jet-etching, the remaining AlGaAs layer is removed using a solution of 0.7% HF with an etching time of approximately 30 s. During this etching step, the device was agitated vigorously in the etching solution, to remove the insoluble oxide layer present on top of AlGaAs. The now-exposed GaAs layer was then removed using diluted ammonia-peroxide etch of the composition H₂O:H₂O₂(35%):NH₄OH(30%) = 25:25:1. An etching time of approximately 5 s was used, while the process was complete after 2 s. This ammonia-peroxide etch resulted in a better resulting surface than the previously used citric acid etch. Most evident was the complete absence of square etch pits in the exposed AlAs last etch stop layer. As a final step, the device was again etched in 0.7% HF under vigorous agitation, as an insoluble oxide layer is also present during this process step. Finally, the device was rinsed thoroughly in ultra pure water and blown dry using nitrogen.
6.3.3 Optical post-processing characterization

After removal of the etch-stop layers, the device was characterized for its reflectivity spectrum as well as the PL emission spectrum to check for compliance with the initial design. Figure 42 shows the result of these measurements on central, intermediate and positions towards the edge of the wafer. It can be seen that the stop band position is suitable, compared to to the Fabry-Perot resonance wavelength of the structure. Also, the reflectivity at the pump wavelength is low what will allow for efficient pumping. PL measurements indicate that the emission of the quantum wells is properly matched to the resonance wavelength on the complete wafer. Both, the mirror stop-band center, as well as the band gap of GaInNAs, show a gradient in direction of shorter wavelengths towards the wafer edge. These effects partially counter-effect each other, resulting in functional structures of different wavelength.

![Figure 42](image_url)

Figure 42: Measured optical reflectivity spectrum a) as well as the PL emission spectra b) for processed GaInNAs VECSEL structures, at different positions on the wafer.

As the optical characterization resulted in a suitable compliance to the initial specifications, the VECSEL structures were mounted on a heat sink and tested in a laser cavity. The results of these experiments are described in 6.4.
6.3.4 Problems with the classical process route

This process with soldering onto a heat sink and following substrate removal involves some technological problems. Dicing and soldering the chips individually followed by lapping and chip-by-chip etching is a very time consuming process. The heat sinks were usually made from pure copper with a coefficient of thermal expansion (CTE) of 16.7 ppm/K while GaAs has a value of 5.73 ppm/K at room temperature [79]. After soldering and substrate removal, the thin semiconductor structure is under large compressive strain. In the GaInAs VECSEL samples prepared for this work, this strain has lead to complete structural failure of the GaAs chip after approximately 6 months on the shelf. Table 7 summarizes the relevant material constants.

<table>
<thead>
<tr>
<th>Material</th>
<th>E (GPa)</th>
<th>ν</th>
<th>α (ppm/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>128</td>
<td>0.36</td>
<td>16.7</td>
</tr>
<tr>
<td>GaAs</td>
<td>85.9</td>
<td>0.31</td>
<td>6.03</td>
</tr>
</tbody>
</table>

Table 7: Young’s modulus, Poisson’s ratio, coefficient of linear thermal expansion for GaAs and Cu. The values for GaAs are given in (100) direction, copper is treated as an isotropic polycrystalline solid.

This compressive strain is a result of the soldering process. To calculate the magnitude of the resulting strain, the copper submount is assumed to be thick and stiff compared to the VECSEL structure. This results only in elastic deformation in the VECSEL but not in the submount. Additionally it is assumed that the solder joint is non-plastic below the solidus temperature of the Au-In system at high indium concentrations which is 156°C. Due to the thin layer and In2Au precipitation hardening, plasticity below liquidus is assumed not to be relevant. This results in a temperature difference of 136 K between room temperature and the solidification temperature of the soldering joint. The resulting biaxial strain is calculated from the difference in CTE between GaAs and Cu as outlined in equation (5.1). This strain then results in a biaxial stress with main stress axes along [110] as given in equation (5.2).

\[
\varepsilon_{\text{chip}} = \varepsilon_{\text{Cu}} - \varepsilon_{\text{GaAs}} = \Delta T \cdot (\alpha_{\text{Cu}} - \alpha_{\text{GaAs}})
\]  

(5.1)
\[ \sigma_{\text{chip}} = \frac{E}{(1 - \nu^2)} \left[ \varepsilon_{\text{chip}} + \nu \varepsilon_{\text{chip}} \right] \]  

(5.2)

Using the values from Table 7 and a \( \Delta T \) of 136 K, an equibiaxial compressive strain of 0.149% is induced in the semiconductor chip. This leads to an equibiaxial stress of 185 MPa. As long no defects are present, this stress level is no problem, a yield strength of 1800 MPa has been measured for GaAs on micro scale [80]. However, as soon mechanical defects or instabilities are introduced into the material, fracture occurs. In our VECSELs, the soldering joint between submount and VECSEL failed, leading to complete destruction of the devices as shown in Figure 43.

Figure 43: Surface of VECSEL after one year of shelf storage. The structure is crushed by internal stresses after the soldering joint failed below.

Figure 44 shows a SEM micrograph of the failed interface layer. The cubic precipitates consist of In\(_2\)Au intermetallic compound, crystallizing in CaF\(_2\) structure.
Figure 44: Fracture surface between copper submount and semiconductor chip in a failed structure.

Very little metallic In matrix is visible between the precipitates, additionally the failure surface shows only small areas with ductile fracture which indicates improper bonding. During the soldering process, the surfacial In\textsubscript{2}Au layer on the solder structure has to be penetrated by indium. As seen in the In-Au binary phase diagram in Figure 45, In\textsubscript{2}Au is almost insoluble in indium at the soldering temperature of 200°C.

This means that only a limited thickness of In\textsubscript{2}Au can be penetrated. Eventually, the gold layer on top of the indium was deposited too thick, leading to an In\textsubscript{2}Au layer that is only partially penetrated by metallic In, resulting in incomplete bonding and in a porous interface layer. Such an incomplete bonding with the inclusion of intermetallic precipitates could also be the explanation for the observed inhomogeneous distribution of the laser performance, which were not correlated with the PL efficiency observed on the structure. A porous or incompletely soldered area shows much higher thermal impedance than expected and impairs the performance of the VECSEL.
For reliable devices, a more robust bonding process between chip and heat sink is necessary. Additionally, the stress by CTE mismatched submounts should be reduced. Different approaches are possible to avoid this stress. One possibility is to use a heat sink made from CTE matched material like copper-tungsten or diamond-cobalt composite. However, the thermal conductivity of these materials is inferior to copper and the mechanical preparation of sufficiently planar heat sinks is very difficult. A stress-free device can also be fabricated if the bonding is done at room temperature. A possible process route of fabricating a high-conductivity heat sink directly at room temperature using electrochemical deposition is discussed in the following chapter.

Figure 45: Au-In binary phase diagram [81].
6.3.5 Electroplated VECSEL process

As the induced stress resulted in degradation and finally destruction of the processed VECSELs, an alternative route of stress free processing was developed. As lapping is not a suitable substrate-removal technique in this process route, we used a wet-chemical method to remove the substrate wafer. In order to have an improved etch-stop selectivity, InGaP was used as a single-layer etch stop instead of the AlGaAs-based multilayer etch stop.

The first step of processing also starts with a metallization. The purpose is to create an electrically conductive interface layer with a high adherence to the semiconductor chip as well as to the following electrodeposited copper. A titanium-platinum-gold sequence was considered suitable. To increase the bond strength, an annealing step at 250°C for 1 minute was performed. The chip was then inserted into an adjustable transparent plastic (PMMA) jig, to prevent excessive copper build-up on the sidewalls of the chip. In between of the individual VECSEL chips, glass slides of 5x5 mm size were used as separators. Electrical contact was then made individually to each of the VECSEL chips using 0.3 mm diameter enamelled copper wire. The jig with contacted devices was then lowered carefully into the plating solution without tipping over the separators. An acid copper electrolyte without organic additives was chosen for optimum electrical and thermal conductivity. Organic additives are unwanted, as they are partially incorporated into the deposited metal. Such impurities result in lowered thermal conductivity of the heat sink material. The exact bath composition is given in Table 8. For planar uniform deposition without additives, a periodic reversal deposition process was used [82]. The bath temperature was kept at 35°C using a thermostatized water bath. This electroforming process is also used to fabricate high-conductivity particle accelerator parts.

<table>
<thead>
<tr>
<th>component</th>
<th>concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₄•5H₂O</td>
<td>220 g/l</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>60 g/l</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>30 mg/l</td>
</tr>
</tbody>
</table>

Table 8: Electrolyte composition for heat sink deposition
For good mechanical strength of the heat sink, a small grain size is beneficial. This growth behavior is achieved by a pulsed current reversal process as described in [82]. This pulsed deposition uses large current densities but a low duty cycle of 10%. This operating mode reduces the influence of diffusion in the plating solution and leads to a more uniform deposition with lower tendency to dendrite growth. The following current reversal phase uses a duty cycle of 30% and leads to an electropolishing effect of the surface, etching preferentially on growing dendrites. Passivation layers eventually forming on the growth surface are also removed. The combination of pulsed deposition and repeated electrochemical back-etching allows for deposition of thick metal layers with low surface roughness and good uniformity. Figure 46 illustrates the electrical pulse pattern used in the process. During forward- and reverse current phases, the average current is 1 A/dm². This results in a peak current density of 10 A/dm² forward and 3.3 A/dm² in reverse, according to the respective duty cycles of 0.1 and 0.33. The anode area is kept at the same size as the plated surface to achieve comparable current densities. Electrical installation wire was used as anode as this is pure, high conductivity copper and was readily available. Due to the short pulse times, no gas is formed at the electrodes at any times. Anode sludge is also not produced, as it is the case in DC plating, eliminating the need for electrolyte filtering or anode bags.

![Pulse current pattern](image)

**Figure 46:** Pulse current pattern used for electroforming of copper heat sinks on VECSELs. This figure shows the transition between forward- and reverse-current. The pattern is repeated infinitely with a period time of 24 s until the desired metal thickness is attained.

This pulsed current is generated by a custom made pulsed current source with individually adjustable currents and pulsetrains for forward and backward operation. The theoretical deposition rate is 212 μm per day assuming a current efficiency of 100%.
After deposition of 500 μm of copper, the electroforming process was stopped and the contact wire removed. Then the backside of the newly formed heat sink as well as the surface of the GaAs chip was covered using AZ1518 photo resist, leaving the edges open. Then the device was etched in a mixture of H₂O:H₂O₂(35%):HCl(36%) = 4:1:2. This step removed excess copper, grown on the sidewalls of the chip. Figure 47 shows a photograph of a structure after these process steps.

Figure 47: GaAs chip after electrodeposition and sidewall-backetching. A solid layer of 500 μm Cu is deposited on the structure.

After applying photoresist to the complete heat sink and the now etched sidewalls of the chip, the substrate was etched in a solution of citric acid(50%):H₂O₂(35%) = 4:1. An etching time of 24h was sufficient to remove the substrate to a remaining thickness of 50μm with excellent planarity. The remaining GaAs was then etched using H₂SO₄(96%):H₂O₂(35%) = 1:1 by weight at room temperature. The etch rate of this solution is around 3 μm/min, with a rough surface morphology. During etching, the samples were agitated vigorously until the InGaP etch stop layer was reached. InGaP has an observed selectivity of 200 to GaAs and Al(Ga)As in H₂SO₄:H₂O. Upon reaching the etch stop layer, the surface changed from a rough grey appearance to shiny and smooth. The growth process of the InGaP etch stop structure is described in more detail in 3.2.4. This layer was then removed using concentrated HCl. Unfortunately, the InGaP did not dissolve completely. At the interface to GaAs, a thin layer of InGaAsP was formed during growth that cannot be etched selectively to GaAs. Due to this residual layer at the surface, the processed
structures were not suitable for laser operation. These structures were then coated with 20 nm PECVD SiN to check if this process step is suitable with the electroformed copper heat sink. No damage or cracking was observed by visual inspection and optical microscopy. Compatibility to surface passivation after processing is an important aspect for the fabrication of reliable laser devices with useful lifetimes.

6.3.5.1 Discussion and outlook

Direct electroplating of heat sinks is an interesting alternative to soldering. It allows for a very thin interface layer with good thermal conductivity and adhesion. The process is stress free and does not need mechanical processing like lapping for substrate removal. Using InGaP as a single layer etch stop is however not advisable as it forms InGaAsP at the interface which cannot be etched selectively to GaAs with any known wet etchant. An AlAs/InGaP double layer etch stop would be a possible alternative, where the InGaP is etched by non-selective ICP etching, and continuing halfway into the sacrificial AlAs layer. This layer could then be removed by HF etching. This process could probably be used to process full wafers for an economic production of VECSEL chips.

Additionally electroplating offers the possibility of depositing a composite material with even better properties than copper. Copper-diamond composite could be deposited for example, which has a higher thermal conductivity than copper and a CTE matched to GaAs. Such a material is expected to allow for the simple production of high performance VECSELs, with better properties than the soldered copper heat sink version. At the same time, it would be at much lower cost than the diamond intracavity heat spreaders used for high power VECSELs by many researchers, also for the most powerful 1.3μm VECSEL demonstrated so far by Hopkins et al. [70].
6.4 Laser operation

6.4.1 Experimental setup

The processed VECSEL chips were installed in a simple V-shaped laser cavity for experimental testing, which is described in more detail in [83]. The general cavity setup is shown in Figure 48.

![Figure 48: V-cavity setup, used for cw-operation of GaInNAs VECSEL structures. The overall cavity length was 45 mm with a pump spot size of 75 µm on the VECSEL.](image)

An 808 nm free-space pump laser was used, with a maximum output power of 5 W, focused onto a pump spot radius of 75 µm. In a first experiment, the VECSEL structures were operated in cw mode. After stable single-transverse-mode operation had been established, the DBR was replaced by a SESAM for mode-locked operation.

6.4.2 CW operation

The VECSEL gain chip was mounted on a copper heat-sink and temperature stabilized by a Peltier element. An 808-nm free-space pump laser diode was positioned at a 45° angle with respect to the VECSEL. Using a 1.5% output coupler with a radius of curvature (ROC) of 50 mm, we achieved a cw output power of 200 mW TEM$_{00}$ and 500 mW multimode at 1286 nm with an optical-to-optical slope efficiency of 15.8%. The emission spectrum at an output power of 480 mW is shown in Figure 49, with a centre wavelength of 1286 nm and a spectral width of 2 nm. The slope of the optical-to-optical conversion
efficiency is plotted in Figure 50. This structure showed the highest slope efficiency demonstrated by an optically pumped 1.3-μm GaInNAs VECSEL so far. A higher output power of 600 mW was demonstrated by Hopkins et al. [70], however, by using a pump power of 7W.

Figure 49: Optical spectrum of the most efficient GaInNAs laser, GINAV008 operating in cw mode at an output power of 480 mW

Figure 50: Cw slope of GINAV008, the output was TEM₀₀ up to 200 mW, with multimode output power up to 500 mW.

In order to achieve a higher output power while maintaining a diffraction-limited beam profile, experiments with optimized cavities were undertaken. High fundamental mode efficiency requires a good matching between the laser mode size and the pumped area, as well as low scattering losses in the cavity. Additionally, the spot size on the gain structure should be large enough to
remain in the linear regime of the input-to-output power transfer function. A straight cavity, as shown in Figure 39, was then set up using a 100 mm ROC mirror with a transmission of 0.8% and a cavity length of 40 mm. Due to the better matching between pumped area and laser mode, an output power of 600 mW was obtained at a pump power of 6.5 W. Beam profile measurements indicated near-diffraction limited output with an M² value better than 1.14. A higher output power could not be obtained from this GaInNAs VECSEL due to thermal limitations. We believe that an output power exceeding 1W could be obtained, by using different cooling concepts like an intracavity diamond heat spreader. Such a device, however, has undesirable properties, like high cost and it acts like an etalon in the laser cavity, which is problem in modelocked lasers.

6.4.3 SESAM modelocking

Modelocked VECSELs have already been demonstrated in a wide wavelength range from 960 to 1555 nm [84]. A modelocked VECSEL around 1.3 μm was however not demonstrated so far. Using the GaInNAs VECSEL that already demonstrated excellent properties in cw operation, we attempted to fill this gap. For this purpose, a V-cavity, suitable for SESAM modelocking was built. The SESAM was mounted approximately 8 mm away from the VECSEL. A 0.7% transmission output coupler with a radius of curvature of 25 mm was positioned at a distance of about 16 mm from the VECSEL for a total cavity length of 24.7 mm. A 25 μm uncoated fused silica etalon was also placed in the cavity to allow for wavelength stabilization and dispersion management.

Using this setup, we obtained stable self-starting cw modelocking at 6.1 GHz repetition rate as it can be seen in Figure 51(a) from the RF spectrum at a full frequency span from DC to 25 GHz. In Figure 51(b) a 50-MHz-span RF spectrum centered around the pulse repetition rate with 100 kHz resolution bandwidth (RBW) provides a more detailed view of the modelocking stability. The small peaks at around 20-MHz offset from the main peak at the pulse repetition rate are suppressed by more than 30 dB. We believe that higher-order mode beating is the most likely reason for this instability because they move further away or closer to the main peak depending on slight cavity length changes.
1.3 μm GaInNAs VECSEL

Figure 51: RF spectrum measured from a GaInNAs VECSEL, modelocked at 6 GHz repetition rate.

The pulse duration of 18.7 ps was measured with a noncollinear intensity autocorrelation and fitted with a sech² pulse shape as seen in Figure 52 (b). Figure 52 (a) shows the measured optical spectrum with a FWHM of 0.29 nm obtained with a 0.1 nm resolution optical spectrum analyzer. The average output power was 57 mW, operating the laser with 3 W of pump power and cooling the VECSEL to a temperature of 5°C. The use of the etalon was necessary to stabilize the laser emission wavelength. Beam profile measurements were done on an identical setup at a later time, giving M² values of 1.03 in the horizontal and 1.13 in the vertical direction, being slightly higher than for a fundamental Gaussian beam (i.e. M²=1). This confirms the possibility of higher spatial mode beating being the reason for the observed side-peaks.

Figure 52: Optical spectrum and autocorrelation traces from the modelocked GaInNAs VECSEL
6.5 Discussion and outlook

With these experiments, passive modelocking of a GaInNAs VECSEL at 6 GHz was demonstrated for the first time, using a low-saturation fluence GaInNAs quantum well SESAM. This is a first proof of principle that GaInNAs is suitable to fabricate the gain material, as well as the saturable absorber necessary for passively modelocked VECSELs. By further optimizing the radiative properties of GaInNAs, as well as using an improved thermal concept in the fabrication of the gain structures, much higher output powers and efficiencies are expected, for cw as well as for modelocked operation.
7. Defect characterization in InGaAs and GaInNAs quantum wells

7.1 Introduction

Semiconductors always contain a certain number of crystal imperfections, impurities as well as native defects. These defects largely influence the electronic properties of the material. For optical applications like VECSELS and SESAMs, nonradiative recombination via deep level defects is a very important defect-dependent process. In SESAMs, such defects are responsible for the fast recombination behaviour, while in VECSELS, defect recombination leads to low efficiency and accelerates the degradation of the devices. A direct observation of the defects would be desirable for materials development, instead of having to rely on indirect methods like PL or pump-probe. Thermal spectroscopy techniques like deep-level transient spectroscopy (DLTS), thermally stimulated current (TSC) or photo induced transient spectroscopy (PICTS) are used for the characterization of deep level defects in semiconductor materials. A more direct observation of nonradiative recombination channels is possible using optically detected magnetic resonance (ODMR). PICTS was chosen for this project. PICTS allows for the usage of semi-insulating samples. The specific excitation of the material of interest is possible, by choosing the proper excitation wavelength. This chapter gives an introduction into the theory of PICTS and describes the custom-built spectrometer and analysis methods. Then the results obtained from InGaAs and GaInNAs quantum wells are discussed.

7.2 Theory

Mid gap traps are characterized by their energetic position in the band gap and their carrier capture cross section. Carriers in the conduction and valence band respectively are in thermal equilibrium with the trap states. The cumulated free
carrier concentration in the valence and conduction band can be measured by electrical conductivity.

![Diagram](https://via.placeholder.com/150)

**Figure 53:** Schematic of the possible transitions between deep-levels and the valence- or conduction-band. PICTS is capable of detecting band-defect interactions as shown in (B) and (C). Generation (A) and recombination (D) are not directly observed [85].

Optical excitation now generates a large concentration of free carriers, which are then trapped in the deep level defects. Almost complete trap saturation can be obtained in most defects by using a sufficiently high intensity. When the excitation is switched off, the free carriers recombine within their lifetime. At the same time, carriers are now thermally emitted from the defect states that were saturated during the excitation and contribute to the electrical conductivity of the sample that is insulating when not excited. The transient behaviour of the conductivity can be used to measure the thermal emission behaviour of the trapped carriers. This technique is called photo induced current transient spectroscopy (PICTS). As given in equation (6.1), each defect shows a distinctive emission rate $e_n$ for carrier emission, depending on the temperature $T$, the activation energy $E_a$, the capture cross-section $\sigma_n$, and a material-dependent parameter $\gamma_n$. The parameter $\gamma_n$ depends on the effective mass of the carriers involved as given in equation (6.2) with Boltzmann’s constant $k_B$, Planck’s constant $\hbar$ and the effective electron mass $m^*$. Similar relations are valid for the holes involved [86].

$$e_n(T) = \tau^{-1} \approx \gamma_n \sigma_n T^2 \exp\left(\frac{-E_a}{k_B T}\right)$$  \hspace{1cm} (6.1)
\[ \gamma_n = \frac{16\pi n^* k_B^2}{h^3} \]  

(6.2)

This carrier emission and following recombination leads then to a time dependent conductivity of the sample. Using a DC bias, an exponential decay of the measured current signal is observed. Equation (6.3) describes the current transient \( i(t) \) generated by a single defect state, with a sample dependent parameter \( C \) and the density of states in the observed trap \( N_t \), which is proportional to the number of defects of the observed kind. A sufficiently large saturation of the involved defect levels is assumed due to high excitation intensity.

\[ i(t) = C N_t \epsilon e^{(\epsilon e,t)} \]  

(6.3)

\( C \) and \( N_t \) cannot be separated experimentally, so they are combined into the signal \( S(\epsilon) \). In reality, not only one defect is involved but an unknown number of different defects over a wide range of emission rates. The total measured current transient is expressed in the more general form of equation (6.4). \( I(t) \) is the Laplace transform of \( S(\epsilon) \).

\[ I(t) = \int_0^\infty S(\epsilon) e^{-\epsilon e,t} d\epsilon \]  

(6.4)

In order to find the defect concentration spectrum \( S(\epsilon) \), the inverse Laplace transform of \( I(t) \) has to be calculated. This is an ill-posed problem without a mathematically closed solution. Only real data of a limited interval is available from the measurement. Literature proposes several methods to solve this problem, many of them are either unstable algorithms, very computationally intensive or low resolution. A method without these problems is the Gaver-Stehfest algorithm [87, 88]. It delivers a good approximation of the inverse Laplace transform, with adjustable precision and noise tolerance. Equations (6.5) and (6.6) describe the transformation operation. It uses only one free parameter (\( N=4,6,8,\ldots \)) which defines the resolution. Higher \( N \) results in better resolution, however at the expense of noise. Practical values for \( N \) are 4 and 6, where 6 already needs a very good signal-to-noise ratio (SNR) of more than 2000 while 4 works already with a SNR of 200.
The extremal points of the spectra obtained by the Gaver-Stehfest algorithm are then plotted two-dimensionally into an Arrhenius plot for determination of the defect activation energy and capture cross section. Equation (6.7) is a converted form of (6.1), showing the linear relationship. $E_a$ is then found from the slope and the capture cross-section $\sigma_n$ from the axis intercept.

$$\ln\left(\frac{e_n(T)}{T^2}\right) = -\frac{E_a}{k_B} \frac{1}{T} + \ln(\gamma_n \sigma_n)$$  \hspace{1cm} (6.7)
Defect Characterization

7.3 Measurement setup

The sample is located inside of a cryostat for accurate temperature control. An electrically pulsed semiconductor laser source, either fibre coupled or a direct diode laser is focused on the sample for carrier generation. The sample conductivity is measured using a 9V bias voltage and a transimpedance amplifier via alloyed indium contacts. Data acquisition and system control is handled by a PC using Matlab.

7.3.1 Cryo system

Temperature control and stabilization is done in a liquid nitrogen cryostat supplied by Oxford research instruments. The liquid nitrogen reserve is held inside a vacuum insulated container, from where it is dispensed via a manually operated needle valve into a capillary tube. The liquid is then evaporated inside of an electrically heated and temperature controlled heat exchanger. The temperature stabilized nitrogen gas is fed into the sample room from where it is extracted again by a membrane vacuum pump after flowing around the sample and sample holder. This setup ensures a highly stable temperature control from
80 K up to 320 K, which was the upper limit due to cryostat construction materials.

![Cryostat Schematic](image)

Figure 55: Schematics of the cryo system used in PICTS experiments.

The cooling power of the liquid nitrogen supply was adjusted using the needle valve in a way that 50% of the electrical heating power of 40 W was necessary to keep the temperature stable, this ensured an optimum regulation behaviour.

### 7.3.2 Sample excitation

For sample excitation, lasers of two different laser wavelengths were used. 980 nm was chosen to pump the quantum wells exclusively while 808 nm was used for bulk excitation of the entire sample. For 980 nm, a fibre coupled laser diode with 650 mW rated cw output power was used (Bookham LC96). As the 808 nm source, a 1 W multimode pump diode was used in free-space
configuration (Thorlabs L808P1WJ). The lasers were first collimated, then imaged onto the sample using a 150 mm focal length lens through windows on the cryostat. For safety reasons, all the optical parts were enclosed inside a heavy black PVC foil enclosure that was sealed lightproof. For sample alignment and observation, an USB video camera was also inserted into the enclosure. Using these measures, the requirements for a class 1 laser system according to EN 60825 could be fulfilled. As such the system was suitable for unattended operation in a non-controlled laboratory environment.

The laser diodes were driven using a commercial laser diode driver (Newport 560) and an external switching circuit for shaping the trailing edge of the excitation pulse. Using a MOSFET bridge circuit, a trailing edge fall time of 500 ns could be attained.

During laser operation, the constant current source is connected to the laser diode. To switch the laser off, the current source is disconnected from the laser diode and redirected into a dummy resistor in order not to trip the safety circuits of the diode driver. At the same time, the laser diode is short-circuited what results in a very fast switch-off. Tests using silicon rectifier diodes as dummy loads indicated severe problems with wire inductances, leading to a reverse-biasing of the diode by 7V. Laser diodes will be destroyed by these high voltages. Due to this inductive spiking when the diode current is switched off, a fast Schottky rectifier diode was connected directly to the diode leads as a freewheeling path. This has been proven successful to limit the transient reverse bias voltage to less than 1V, acceptable for laser diodes.

7.3.3 Measurement system

To probe the cumulative carrier concentration, a bias voltage of 9V was applied to alloyed indium contacts. The sample current is then measured. The current during excitation reaches values of up to 0.1 mA, while the dark current drops to values of below 10 pA. It is desirable to measure the whole range without amplifier gain switching and with high dynamic range for precise analysis. Additionally, a signal bandwidth of around 1 MHz is desired to resolve processes with time constants in the order of 10 μs. As the photocurrent decays in an exponential way, a transimpedance amplifier with logarithmic response was chosen. Such amplifiers can be purchased as integrated circuits
for fibre optic applications. In this setup, an AD 8304 from Analog Devices was used. This amplifier is specified for an input current range from 100 pA to 10 mA, offers automatic bandwidth reduction at low signals and an active input guard driver.

![Connection scheme of the AD 8304 logarithmic transimpedance amplifier as it was used in the measurement setup discussed here.][89]

The current amplifier of our PICTS setup followed the suggestions of the manufacturer for the part values as shown in Figure 56. The exception was pin 1, VNEG, which was connected to a -0.5 V source to access the full dynamic range of the amplifier down to $2 \times 10^{-11}$ A. Figure 57 shows a typical PICTS transient, measured over a time of 10 s after the excitation pulse, decaying to a value below $2 \times 10^{-11}$ A, with the amplifier output bottoming out at the negative supply voltage. In the time range of $10^2$ s, a slight oscillation is visible, which is interference picked up by the system. This noise however does not represent a problem.
With signal amplitudes down of a few ten picoamperes, the measurement setup is extremely sensitive against electromagnetic interference (EMI) by surrounding equipment and RF radiation even of very low power. To isolate the system from low frequency noise 50 Hz line noise, the measurement amplifier and bias source was entirely operated by batteries. Also the inherent noise of the signal processing and acquisition electronics is of concern. In order to properly acquire these small signal transients, several shielding and filtering techniques are necessary. The different aspects are discussed in the following paragraphs.

7.3.3.1 Shielding of electronic components and cables

The most obvious approach to protect against RF interference is shielding, by enclosing the affected components inside of a metallic case and using cables with a braided or foiled screen. Such a metallic enclosure is capable of protecting against electric fields as well as against AC magnetic fields. No ferromagnetic case is necessary, as long as no DC or very low frequency magnetic fields have to be shielded. 50 Hz line noise is considered sufficiently high frequency for the use of nonferrous shielding material. Of course, an additional shield of mumetal or soft iron does not harm. In order to accomplish the expectations, the case needs to fulfil certain requirements. First, the case needs to be highly conductive around the full circumference, along all edges.
This is necessary for an effective shielding effect against both magnetic and electric fields. Electric fields are shielded, because the electric field inside of a conductor is zero. This is of course only true for an ideal conductor as soon as a current is flowing, so maximum conductivity is needed to minimize potential gradients. Shielding against magnetic fields also requires a high conductivity along all paths around the case. The shielding effect originates in the induction of eddy currents in the case walls, cancelling the field inside of the case. By using a massive case of high-conductivity material like an extruded aluminium case, or if necessary even a milled copper case, this is accomplished best. When using an aluminium case, the oxide layer of aluminium has to be removed immediately before assembly, as Al₂O₃ is an excellent insulator. Additionally, freshly stripped copper stranded wire can be inserted between the joint surfaces and protected from oxidation by contact grease. This stranded wire is then compressed by firmly tightening the case screws. An extruded aluminium case is an excellent EMI Shield if it is assembled the way described. The measurement amplifier and its batteries were installed in such a case. For cable shields, the same requirements apply, the conductivity should be as high as possible. Usually cables having both, foiled and braided shielding layers are superior to cables with only a braided shield. The cable shield should not be used as signal ground if possible, an individual signal ground connector inside of the shielding is beneficial as the shielding carries noise currents inherent to the shielding effect.

7.3.3.2 Grounding of instruments, cases and cables

Successful EMI shielding of an extended system, not fitting inside a single massive case requires proper grounding practices, otherwise the best case shields and cable screens are of little use. The purpose of grounding in EMI shielding is to ensure identical potentials of all individually shielded components. Electric field gradients lead to voltage gradients along the measurement system. These gradients have to be balanced by currents flowing between the components. Using only the cable shields as a balancing connection is often not sufficient as the conductivity is too low. The result is then a different ground potential in the two components affected, leading to common mode noise. To reduce this effect, all components have to be connected together, using large diameter copper cable or braided copper tape, ensuring low impedance. When designing a grounding concept, care has to be
taken not to introduce any ground loops by having several redundant ground paths to a single device. A ground loop picks up inductive noise, resulting in a circular current. Due to electrical resistances, a difference in ground potential results, introducing again common mode noise, defeating the purpose of the grounding. By using a tree-like or even better a star shaped ground topology, such currents cannot be induced. In some cases it is difficult to see ground loops, when they are formed by case protective earth (PE) connections on line-powered equipment like oscilloscopes, personal computers and alike. If two instruments are connected together with a shielded cable and another grounding connector, the cable shield should be connected only on one side, again to prevent a ground loop. The main grounding point should be as stable as possible compared to the surrounding potential. This is achieved best by using a large cross-section ground connection to the potential equalization of the building. In the case of this experiments, the PE conductor of the main power line to the laboratory was used with a 16 mm² copper cable connection, at the same point the floor ground for ESD protection of the laboratory was connected.

7.3.3.3 Cable selection

For low interference pickup, it is necessary to choose the proper cables for the measurement task at hand. Coaxial cables like RG58 are very popular in measurement setups, however they are not an optimum choice as long as the signal frequencies are low. They offer only a single signal conductor and require that the screen and signal ground are connected together. Additionally, they are susceptible to magnetic noise pickup [90], while the noise shielding is especially poor at low frequencies like 50 Hz line noise or interference from electric motors with variable frequency drives as they are used widespread.

Shielded foiled twisted pair cables (S-FTP) or star-quad as they are used in computer networks are superior in terms of noise pickup as long as the RF transmission properties of coaxial cables are not needed. Magnetic pickup is cancelled inside of the cable by the twisting of the signal carrying conductors. Additionally the signal ground is separated from the cable shield. If coaxial cables are used, the signal level should be held as high as possible and the connection impedance should be kept low. In some cases, coaxial cables are indispensable even under unsuitable conditions. The connection between the
sample head in the cryostat and the current amplifier in the PICTS measurement setup presented here is such a case. A bias voltage of 9V, signal return to the transimpedance amplifier, guard lead and a cable shield have to be realized with the lowest possible susceptibility to EMI as well as preventing leakage current from the bias source to signal return through the dielectric of the connection. To protect the signal return conductor from such parasitic influence, a guard conductor has to be used, what is not possible with twisted pair cables. Guarding is a technique to protect a highly sensitive current sensing input from leakage currents through the dielectric material. This is achieved by placing a conductor around the current return wire that is actively driven to the same potential as the current measurement input. This eliminates the electric field around the current measurement conductor, suppressing leakage currents in the dielectric. This potential control is accomplished by a guard driver, sensing the input potential and driving the guard to the same potential at low impedance. Such a guarded connection can be realized best using a triaxial cable. The electrical situation is again depicted in Figure 58.

![Diagram of guarded measurement connection using triaxial cable](image)

Figure 58: Implementation of a guarded measurement connection using triaxial cable. [91]
7.3.3.4 Signal filtering, antialiasing

Even by using the best shielding techniques and low noise electronics, EMI and noise at high frequencies cannot be avoided completely. A large portion of the noise lies outside of the frequency range of interest, like for example the prominent ISM frequency of 13.56 MHz that is used in high power plasma processing equipment. Strong pickup was noticed at this frequency. Being at such a high frequency, filtering is not a problem, the antialiasing filter will take care of it. A more serious problem is real statistical noise generated by the sample and the measurement electronics. At low signal levels, this is of course most prominent. The transient plotted in Figure 57 shows this behavior at lower signals. However, the noise does not increase as much as one would expect from the logarithmic response. The AD8304 amplifier performs an automatic bandwidth reduction at lower signal levels, eliminating high frequency noise. This is a very suitable behavior, as the processes observed at these low current levels do not contain any signal constituents of high frequency.

If the signal is to be acquired digitally, an antialiasing low pass filter is mandatory before sampling of the data. Digital sampled data is capable of representing frequencies from 0 Hz up to $\frac{1}{2}$ of the sampling frequency, this limit is named Nyquist frequency. All frequencies higher than the Nyquist limit suffer from aliasing. These frequencies are transformed into a lower frequency range. There, they are mixed with the signal of interest, unrecoverable by digital filters. A low pass filter to prevent aliasing should be as steep as possible while having no pass band ripple to prevent the introduction of artifacts into the frequency response of the system. A passive LC filter with Butterworth response is suitable, offering a steep roll-off with a flat pass band as well as being low-noise using only passive components. In the experiment discussed here, a 5-pole Butterworth filter, designed for a source and sink impedance of 2000 ohms was used with a cut-off frequency of 500 kHz. The filter is of 5th order and offering a roll-off of 100 dB per decade. Figure 59 illustrates the circuit diagram of the filter with the necessary parts listed in Table 9. The filter was integrated into the signal connection from the measurement amplifier to the sampling hardware. Lengths of RG-58 cable were used as capacitors, allowing for tuning of the filter to the desired response. The inductances were inserted into the cable at suitable positions. RG-58 cable has a capacitance of around 85 pF/m. The terminal impedance of the filter has been designed to be
2000 Ohms to match available inductors while at the same time keeping the power consumption of the measurement amplifier acceptably low for battery operation.

![5-pole LC anti-aliasing filter](image)

**Figure 59:** 5 - pole LC anti-aliasing filter

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<table>
<thead>
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<tbody>
<tr>
<td>L1</td>
<td>1030 μH</td>
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<tr>
<td>L2</td>
<td>1030 μH</td>
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<tr>
<td>C1</td>
<td>98 pF</td>
</tr>
<tr>
<td>C2</td>
<td>318 pF</td>
</tr>
<tr>
<td>C3</td>
<td>98 pF</td>
</tr>
</tbody>
</table>

**Table 9:** Component values for Butterworth filter response

7.3.3.5 Data acquisition

The amplified and filtered analog data has to be digitized for successive processing. Digital sampling systems differ by the maximum possible sampling rate, the digital resolution in bits, the sampling noise and the capacity to handle large amounts of data and last but not least cost and software support. The requirements of the PICTS experiment were a sampling rate of at least 1 MSPS, a resolution of 16bits and the capability acquire at least one second of data. National instruments supplied the NI-PCI-6250 data acquisition card, which is capable of acquiring 1.25 MSPS with an accuracy of 16 bits. The control of the measurement system and data storage was done using a Matlab script.
7.4 Sample Preparation

As described in the theoretical part, PICTS measures the conductivity transient of the sample. In order to measure the conductivity, ohmic contacts to the quantum well are necessary. This is accomplished by alloying In-Sn contacts into the structure after etching a direct access to the layers to be measured. For PICTS analysis, samples of 3x3 mm² size were prepared. To allow for a direct access of the ohmic contacts to the quantum well, as well as to confine the analyzed region to the area of uniform excitation intensity, 0.5 mm wide ridges were etched into the surface.

Figure 60: Sample excitation and contacting scheme used for PICTS measurements. The contacts are InSn alloy, that is diffused into the structure.

After particle removal using Acetone:Water = 1:1 in 40 kHz ultrasonic for 2 minutes, the chips were dipped in NH₄OH(30%) solution for oxide removal, rinsed with DI water again and blown dry. An etch mask was manually applied, using AZ1518 photoresist and a size 0 paintbrush. A ridge of approximately 7.5 μm height was then etched on the samples using a sulfuric acid-based wet etch, suitable to form cleanly bevelled edges on GaAs [92]. The etching solution was H₂SO₄(96%):1H₂O₂(35%):5H₂O = 4:1:5 at room temperature. The etching time was 30 s. Figure 61 shows a cross-section of such an etched ridge. It is clearly visible that a metallic contact applied on top will contact all layers embedded in the 7.5 μm thick ridge.
Figure 61: SEM cross section of the edge of an etched ridge. The substrate is on the right side, while the left side is vacuum. The sidewalls are nicely beveled, exposing the quantum wells embedded in the structure to a metallization that will be applied on top.

Small pieces (around 0.5 x 0.5 x 0.1 mm) of InSn alloy were cut and placed onto the freshly etched samples. Using a microscope slide, the contact metal was pressed firmly onto the sample surface to securely attach it. Subsequently the samples were then annealed at 250°C for 5 minutes under low-pressure nitrogen atmosphere in the RTA furnace.

The samples were then inserted into the PICTS measurement setup and checked at room temperature for dark conductivity as well as conductivity under laser excitation to ensure proper contacting.

7.5 Data analysis

The logarithmic current signal acquired by the sampling card is first filtered. As the significant frequency components of the signal are lower with longer times, adaptive low pass filtering is applied to reduce noise in the
acquired transient. Spline fitting of the measured curve on a log-log scale has proven to be most effective and time efficient. This was accomplished by the Matlab function csaps. Using these signal condition techniques, a signal-to-noise ratio sufficient for analysis by inverse Laplace transformation was obtained. Figure 62 shows a typical transient curve as acquired after averaging and the corresponding rate spectrum at 80 K of a GaInNAs SESAM test structure.

![Figure 62](image.png)

**Figure 62:** a) Current transient curve, measured on a GaInNAs SQW test structure b) resulting emission rate spectrum after inverse Laplace transform

Such transients were then recorded on the complete temperature range from 320K down to 80K in intervals of 1K. The temperature was ramped down during the successive transient acquisitions, in order to prevent an influence by frozen carriers that are freed upon heating. Plotting these spectra two-dimensionally, logarithmic emission rate divided by $T^2$ vs. inverse temperature results in an Arrhenius plot of the defects in the material, responsible for the measured current decay curve as already discussed in the theoretical introduction. In literature, PICTS spectra are usually not isothermal rate spectra, but the signal plotted versus temperature at a given emission rate. This results from the classical method used in DLTS. A hardware double boxcar correlator was used for analysis, tuned to a certain mission rate. The sample was then swept through the measurement temperature range. For a better
comparability to literature, such spectra were also plotted also from the acquired data.

7.6 Results and discussion

The PICTS method was applied to InGaAs SESAMs as well as to GaInNAs SESAM and VECSEL test structures. The objective was to find a correlation between the directly measurable effects of deep level defects to their energetic position and concentration, and find also a correlation to the growth- and annealing process applied to the structure to find a tentative identification of the defects responsible for the measured optical properties. Literature reports a few studies performed on GaInNAs of different composition, mainly using DLTS on lattice matched solar cell material, only Erol [86] and Mazzucato [93] used PICTS on undoped strained QW samples. Table 10 summarizes results from literature.

<table>
<thead>
<tr>
<th>Author</th>
<th>material</th>
<th>Trap activation energies, meV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balcioglu [94]</td>
<td>Ga$<em>{0.93}$In$</em>{0.07}$N$<em>{0.03}$As$</em>{0.97}$</td>
<td>230, 270, 450, 770</td>
</tr>
<tr>
<td>Kaplar [95]</td>
<td>Ga$<em>{0.925}$In$</em>{0.075}$N$<em>{0.025}$As$</em>{0.975}$</td>
<td>200, 340, 360, 710, 820</td>
</tr>
<tr>
<td>Jackrel [96]</td>
<td>Ga$<em>{0.94}$In$</em>{0.06}$N$<em>{0.015}$As$</em>{0.985}$</td>
<td>50-60, 120, 590, 610</td>
</tr>
<tr>
<td>Erol [86]/Mazzucato[93]</td>
<td>Ga$<em>{0.8}$In$</em>{0.2}$N$<em>{0.015}$As$</em>{0.985}$</td>
<td>160, 330</td>
</tr>
</tbody>
</table>

Table 10: Deep level defects found in GaInNAs structures of different compositions using DLTS and PICTS methods.

These studies listed above were all done using a small set of samples, not suitable for statistical evaluation of the results. The interpretation of Arrhenius plots from PICTS and DLTS is often difficult and the spectra suffer from low peak resolution. This leads to scattering of the data beyond any usability to identify the defects. Additionally, every researcher uses his own nomenclature for the features found. We postulate that only data from the same research group using the same equipment is comparable. However, PICTS spectra or Arrhenius colourplots are a suitable means to compare the data by eye and identifying identical features in different samples for interpretation. The
combination of activation energy and axis intercept of the Arrhenius line is also a reliable qualifier for identical defects when plotted two-dimensionally.

7.6.1 Sample overview

GaInNAs and InGaAs single and multiple quantum well samples with different growth conditions were analyzed. These samples show large differences in wavelength, PL efficiency and recombination kinetics in pump probe experiments. The different deep-level defects are plotted in Figure 63. The trap parameter plotted on the y axis is $\ln(\gamma\sigma)$, containing information on the capture cross section of the defect and the effective mass of the involved carrier.

![Figure 63](image.png)

Figure 63: Defects observed in InGaAs and GaInNAs test structures, grown under different conditions.

It is clearly seen that the most prominent defects are grouped at 200, 300 and 320 meV. These defects were identified in most samples. Other defects are scattered among the experimentally available parameter space, however not observed with a sufficient certainty for discussion. It is interesting to note, that the signature of these defects dominating the PICTS spectra are not dependent on the band gap of the material, as they are found in InGaAs as well as in
GaInNAs at the same energetic position. They also do not depend on the presence of nitrogen in the sample.

7.6.2 Influence of nitrogen

In order to detect the influence of nitrogen on the occurrence of certain deep-level defects, InGaAs and GaInNAs structures, only differing in nitrogen content were compared. To be comparable with the published results in literature, PICTS spectra versus temperature were plotted. Erol et al. [86] claimed to see GaInNAs specific deep-levels, labeled Psi1 and Psi2 in their study. In order to verify the occurrence of the same defects in our samples, we measured PICTS spectra with comparable identical emission rates as used in Figure 64.

Figure 64: GaInNAs PICTS results of Erol et. al, as published in [86]. The traces PITS 1 to 5 represent rate windows of 4/40, 8/80, 16/160 32/320 and 64/640 ms representing carrier emission rates of 250, 125, 63, 31 and 16 s⁻¹ a conversion is given in [97].

As our measurement configuration only provided reliable data at temperatures above 120K, an additional trace at an emission rate of 5000/s is
shown, where the features otherwise hidden in the low temperature range are shifted into the observable range. Figure 65 shows the PICTS spectra for both samples. It is evident that our results show the same defects as they were observed in GaInNAs samples in literature. However, also the nitrogen-free samples contain exactly the same defects at the same energetic positions, although with different signal magnitude.

![Figure 65: PICTS spectra of a GaInNAs and a comparable nitrogen-free InGaAs test structure. The same features as in the results of Erol et. al. are seen. The emission rates of the traces were chosen at identical values, and additionally 5000 /s.](image)

For a better illustration of this identity of detected defects, Arrhenius plots of a In$_{0.35}$Ga$_{0.65}$As and a In$_{0.35}$Ga$_{0.65}$N$_{0.015}$As$_{0.085}$ structure are overlaid in Figure 66. Within experimental precision, the observed defects are identical for GaInNAs and InGaAs as it can be seen by the double lines in the Arrhenius plot.
Figure 66: Overlay of two Arrhenius plots for a In$_{0.35}$Ga$_{0.65}$As test structure with an identical nitrogen containing structure. The observed features are the same and in identical energetic position, seen by double lines.

This observation suggests that PICTS is not suitable to detect any nitrogen-induced defects in GaInNAs. At least not within the parameter space accessible in the actual spectrometer. Despite these results, we expected to see an influence of the growth parameters on the concentration of these defects and possibly find a correlation to growth parameters, as well as to macroscopically observable properties like PL efficiency and carrier recombination time. In order to find such relations, two sets of samples were analyzed. First InGaAs SESAM structures, with very different pump probe responses, and second a set of GaInNAs growth optimization samples, grown at different temperature and III/V ratio, compared before and after annealing which showed large variations in PL efficiency and were already well characterized during growth optimization studies for the 1.3 μm VECSEL.

7.6.3 Results and discussion of measured results

Two different InGaAs SESAM structures were compared, one grown at 300°C, another at 450°C. It was expected to find a difference in the defect concentration in both cases, lower growth temperature samples contain generally more defects. The results given in Figure 67 follow these expectations.
Results of a comparative measurement of two InGaAs SESAMs. The signal intensity if every detected defect is plotted versus its activation energy. The peak intensity represents the concentration of the respective defect in arbitrary units.

These SESAMs were previously characterized by pump probe measurements, which resulted in a very fast recovery time for the sample grown at 450°C, while the 300°C grown structure showed considerably slower recovery dynamics. These results are counterintuitive and not expected from the overall defect concentration measured. Figure 68 illustrates the temporal response of the SESAMs.

Pump probe response of the two InGaAs SESAM samples analyzed by PICTS measurements.
Similarly, the GaInNAs structures analyzed by PICTS did not show a statistically significant correlation between any growth parameters and measured deep level defect concentration. Only a general reduction of the measured defect concentration was observed upon RTA. The magnitude of this reduction was only about a factor of 2, compared to the change in PL intensity on a scale of orders of magnitude. Thus, the concentration of observed defects in GaInNAs does not determine the PL intensity observed.

This result is disappointing on the first view, as a correlation between deep-level defects and temporal response of SESAMs and PL efficiency of laser gain structures is beyond any doubt. Apparently PICTS is insensitive to this kind of deep level defects, which are highly efficient recombination centers. Figure 53 in the introduction shows the path of such a recombination. This kind of defect is an equally good trap for electrons and holes with a large capture cross-section. For a defect to produce a measurable PICTS signal, it is necessary to emit trapped carriers into the conduction or valence band. If the trapped carriers recombine with a complementary electron or hole instead of being emitted, no signal is measurable. Lifetime-determining defects are expected to behave like that, and being not detectable in PICTS. The only technique known to us so far that is directly capable of probing such fast recombination channels is ODMR [13]. This method relies on the effect that recombination is spin selective. Selective modification of the spin of trapped carriers by magnetic resonance influences then the recombination rate. However, such experiments are very specialized research projects on their own and beyond the scope of this project.

A major drawback of thermal spectroscopy methods like PICTS and DLTS was the long measurement time needed to achieve a sufficient SNR for Laplace transform methods or the low resolution obtained by the classical correlation method [97]. These measurements have demonstrated that high-resolution PICTS measurements on single quantum wells are possible by using a direct digital approach, sampling a logarithmic analog signal over many orders of magnitude and applying the Gaver-Stehfest algorithm for signal processing. We found three different deep-level defects that did not change their energetic position with the band gap of the material and were present in InGaAs as well as in GaInNAs. The observed activation energies were 200, 300 and 320 meV.
Pure MBE grown GaAs however did not show a signal in this activation energy range. Measurements using variable excitation wavelengths, as well as variable excitation intensity indicated that the observed defects reside in the quantum well, not in the surrounding barriers.
8. Conclusions and outlook

During this project, we demonstrated the versatility of GaInNAs to be used either as an absorber in SESAMs as well as an active material in VECSELs. The combination of both functions has lead to the first modelocked VECSEL at 1.3 μm wavelength. The growth process of active and passive GaInNAs material was investigated in detail and a stable fabrication process was established. Extensive studies of the different growth parameters have led to an understanding of the resulting effects.

The project added to the knowledge about the fabrication of GaInNAs in the community, and documented sufficient stability and reproducibility of the growth process, as required for a future commercial application.

Optimum absorber material is obtained at a growth temperature of 450°C, with an indium concentration of 35% and a growth rate of 1.25 μm/h. The quantum well thickness was 10 nm and the V/III BEP ratio was fixed to 24. The absorption wavelength is adjusted solely by the nitrogen content in a range of 1100 to 1600 nm. GaInNAs SESAMs grown under these conditions showed very low saturation fluences in antiresonant structures. Slight annealing up to 600°C for 1 minute can be used for absorption edge tuning and reduction of the nonsaturable losses in SESAMs. This treatment, however, results in an increased recovery time, especially in 1.3 μm wavelength SESAMs. A controlled nitrogen flux exposure of the wafer surface before growth of the quantum well results in an absorber, that can be tuned by annealing without losing the fast recombination time.

Active material for laser gain structures is obtained by using 410°C growth temperature at a growth rate of 1.25 μm and the minimum permissible V/III BEP ratio and an indium content of 35%. For process stability, a V/III BEP ratio of 24 is recommended, however, it might be reduced to half the value if a stable arsenic flux can be guaranteed. An incorporation of approximately 1.8% of
nitrogen is necessary. To improve the radiative efficiency, a MBE in-situ high-temperature annealing step of 700°C for 5 minutes under arsenic overpressure is necessary. These conditions result in high-efficiency laser gain material that demonstrated a record-high slope-efficiency for optically pumped 1.3 μm GaInNAs VECSELs.

We performed PICTS measurements in order to find a better understanding on the formation of deep-level defects depending on the used growth conditions, as well as their influence on macroscopically measurable properties such as absorber recovery time and PL efficiency. Contrary to the expectations, no correlation between the observed deep levels and macroscopic properties could be found. Even if some publications show promising results, PICTS has proven to be an unsuitable method to identify the defects responsible for the nitrogen-dependent carrier recombination observed in GaInNAs. Further work using methods like ODMR is necessary for a definitive identification of the relevant recombination channels.

For a commercial success of GaInNAs lasers, the efficiency needs to be improved further. An optimized nitrogen incorporation process, leading to less defects by ion damage or by incorporation of nitrogen in unwanted configurations is a possible approach. Also the usage of surfactants like antimony during growth, has shown to be successful in the development of 1.5 μm GaInNAsSb lasers [98]. When GaInNAs material continues to increase in performance and reliability, many future applications are possible: For example GaAs based PICs for high-speed telecom applications and a broad wavelength range of VECSEL sources, optically, as well as electrically pumped, cw and mode-locked.
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<th>Description</th>
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<tr>
<td>ΔR</td>
<td>Modulation depth</td>
</tr>
<tr>
<td>ΔRₙₙₛ</td>
<td>Nonsaturable losses</td>
</tr>
<tr>
<td>AlAs</td>
<td>Aluminium arsenide</td>
</tr>
<tr>
<td>AlGaAs</td>
<td>Aluminium gallium arsenide</td>
</tr>
<tr>
<td>BEP</td>
<td>Beam equivalent pressure</td>
</tr>
<tr>
<td>BFM</td>
<td>Beam flux monitor</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge coupled device</td>
</tr>
<tr>
<td>CF</td>
<td>Conflat</td>
</tr>
<tr>
<td>CPU</td>
<td>Central processing unit</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of thermal expansion</td>
</tr>
<tr>
<td>cw</td>
<td>Continuous wave</td>
</tr>
<tr>
<td>DBR</td>
<td>Distributed bragg reflector</td>
</tr>
<tr>
<td>DFB</td>
<td>Distributed feedback</td>
</tr>
<tr>
<td>DLP</td>
<td>Digital light processor (R) Texas Instruments</td>
</tr>
<tr>
<td>DLTS</td>
<td>Deep-level transient spectroscopy</td>
</tr>
<tr>
<td>DRS</td>
<td>Diffuse reflectance spectroscopy</td>
</tr>
<tr>
<td>DWDM</td>
<td>Dense wavelength division multiplexing</td>
</tr>
<tr>
<td>EMI</td>
<td>Electromagnetic interference</td>
</tr>
<tr>
<td>EOM</td>
<td>Electro optic modulator</td>
</tr>
<tr>
<td>ERGO</td>
<td>Erbium ytterbium glass laser</td>
</tr>
<tr>
<td>ESD</td>
<td>Electrostatic discharge</td>
</tr>
<tr>
<td>Fₛₙₙₙₛ</td>
<td>Saturation fluence</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full-width at half-maximum</td>
</tr>
<tr>
<td>GaAs</td>
<td>Gallium arsenide</td>
</tr>
<tr>
<td>GaAsP</td>
<td>Gallium arsenide phosphide</td>
</tr>
<tr>
<td>GaInNAs</td>
<td>Gallium indium arsenide nitride phosphide</td>
</tr>
<tr>
<td>GaNAs</td>
<td>Gallium nitride arsenide</td>
</tr>
<tr>
<td>GDD</td>
<td>Group delay dispersion</td>
</tr>
<tr>
<td>HRXRD</td>
<td>High resolution X-ray diffraction</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively coupled plasma</td>
</tr>
<tr>
<td>InGaAs</td>
<td>Indium gallium arsenide</td>
</tr>
<tr>
<td>InGaAsP</td>
<td>Indium gallium arsenide phosphide</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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</tr>
<tr>
<td>InP</td>
<td>Indium phosphide</td>
</tr>
<tr>
<td>ISM</td>
<td>Frequency for industrial, scientific and medical use</td>
</tr>
<tr>
<td>LCD</td>
<td>Liquid crystal display</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>ML</td>
<td>Monolayer</td>
</tr>
<tr>
<td>MOSFET</td>
<td>Metal oxide semiconductor field effect transistor</td>
</tr>
<tr>
<td>MOVPE</td>
<td>Metal organic vapor phase epitaxy</td>
</tr>
<tr>
<td>MQW</td>
<td>Multiple quantum well</td>
</tr>
<tr>
<td>ODMR</td>
<td>Optically detected magnetic resonance</td>
</tr>
<tr>
<td>OPO</td>
<td>Optical parametric oscillator</td>
</tr>
<tr>
<td>PBN</td>
<td>Pyrolytic boron nitride</td>
</tr>
<tr>
<td>PE</td>
<td>Protective earth</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma-enhanced chemical vapour deposition</td>
</tr>
<tr>
<td>PIC</td>
<td>Photonic integrated circuit</td>
</tr>
<tr>
<td>PICTS</td>
<td>Photoinduced transient spectroscopy</td>
</tr>
<tr>
<td>PID</td>
<td>Proportional-integral-derivative</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly methyl methacrylate</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
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<tr>
<td>QW</td>
<td>Quantum well</td>
</tr>
<tr>
<td>RBW</td>
<td>Resolution-bandwidth</td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>RHEED</td>
<td>Reflection high energy electron diffraction</td>
</tr>
<tr>
<td>ROC</td>
<td>Radius of curvature</td>
</tr>
<tr>
<td>RTA</td>
<td>Rapid thermal annealing</td>
</tr>
<tr>
<td>SESAM</td>
<td>Semiconductor saturable absorber mirror</td>
</tr>
<tr>
<td>SiGe</td>
<td>Silicon-germanium</td>
</tr>
<tr>
<td>SNR</td>
<td>Signal to noise ratio</td>
</tr>
<tr>
<td>SQW</td>
<td>Single quantum well</td>
</tr>
<tr>
<td>TSC</td>
<td>Thermally stimulated current</td>
</tr>
<tr>
<td>VCSEL</td>
<td>Vertical cavity surface emitting laser</td>
</tr>
<tr>
<td>VECSEL</td>
<td>Vertical external cavity surface emitting laser</td>
</tr>
<tr>
<td>VGF</td>
<td>Vertical gradient freeze</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
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