Mid-infrared quantum cascade lasers: active medium and waveguide engineering

A dissertation submitted to
ETH ZÜRICH

for the degree of
Doctor of Sciences

presented by
ALFREDO BISMUTO
Dipl. Phys., Universitita’ degli studi Federico II Naples, Italy
born on February 23, 1983
Nationality: Italian

accepted on the recommendation of
Prof. Dr. Jérôme Faist, examiner
Prof. Dr. Dan Botez, co-examiner
Prof. Dr. Gottfried Strasser, co-examiner

2011
Abstract

Quantum cascade lasers are unipolar semiconductor devices in which laser action takes place between intersubband transitions in quantum wells. The lasing emission is determined through the layer sequence of the heterostructure and lasers can therefore be engineered to emit in most of the Mid-Infrared and Far-Infrared spectral regions. Primary goal of the present work is the optimization of high performance quantum cascade lasers in the Mid-Infrared range.

In order to reach this objective different aspects, that heavily influence laser performance, have been analyzed. In first place a key role is played by the optimization of the active region designs. A transport model developed inside our group has been used for this purpose to design new structures. Secondly the device fabrication process has been optimized. In particular a novel approach to the buried heterostructure process has been developed. The latter shows at the same time a better yield and a higher quality of the process and also is constituted by a reduced amount of processing steps.

Using both the above mentioned approaches to improve laser performance, a new laser structure has been designed and fabricated to obtain high performance and wide voltage tuning in the second atmospheric window. These devices show a maximum spectral coverage of more than 140 cm$^{-1}$ and together with the wide tuning show remarkable high performance. In particular, pulsed wallplug efficiencies up to 12.5 % and continuous wave emissions as high as 450 mW at room temperature are presented.

By the use of strain compensated epitaxial layers to increase the conduction band offset, laser designs have also been exploited in the first atmospheric window. Since interface roughness is know to be one of the main factors influencing quantum cascade laser performance in the Mid-Infrared, we present a study on the influence of the epitaxial growth temperature on the interface roughness parameters and consequently on laser performance. A non-monotonic behavior is observed with a clear maximum in the performance for a growth temperature of 515 °C. In this case, wallplug efficiencies up to 15 % are presented in pulsed operation and optical powers in continuous wave operation bigger than 600 mW are measured. Moreover a new active region design, based on a two-step composite injection barrier, is also introduced in order to reduce the parasitic current flowing before the structure alignment.
By the use of highly strained AlAs layers, laser emission in the 3-4 µm region is also presented. Both the development of a new active region design and the optimization of the epitaxial growth process result in the observation, for the first time, of room temperature emission at 3.3 µm using this material system. Watt-level powers are observed at room temperature in pulsed operation.

The last section of this work is dedicated to the waveguide engineering, rather than to the active region design. In the first part of it, high power quantum cascade laser are obtained using the principle of the diluted waveguide. In particular, the use of a quasi-rectangular mode profile does reduce the occurrence of detrimental effects as the vertical spatial hole burning, thus enhancing the efficiency of the lasers. Moreover the introduction of highly thermal conductive passive layers between the active stacks sensibly improve the thermal conductance of the structure. Peak powers up to 5 W were observed in this case in pulsed operation.

Preliminary work on the development of phase-locked buried heterostructure arrays of quantum cascade lasers is also shown. In particular narrowing of the farfield emission pattern is demonstrated.

In the end, some preliminary results are also presented on the fabrication of buried heterostructure photonic crystal quantum cascade lasers. Even though laser emission has not yet been observed, the development of these structures is of great interest for the fabrication of low power dissipation, uncooled devices with single mode spectral emission.
Abstract

I laser a cascata quantica sono dispositivi a semiconduttore omopolari in cui la transizione laser avviene tra differenti sottobande nelle quantum wells. L’energia dell’ emissione laser dipende dall’ eterostruttura e emissione laser può essere così ottenuta sia nel medio che nel lontano infrarosso. Lo scopo principale di questo lavoro è l’ottimizzazione delle performance nel caso di laser a cascata quantica nel medio infrarosso.

A questo scopo, differenti aspetti, che influenzano pesantemente le prestazioni dei laser sono stati analizzati in particolare dettaglio. In primo luogo, un ruolo fondamentale è giocato dall’ottimizzazione della sequenza di quantum wells che costituisce la regione attiva. Un modello di transporto quantistico, sviluppato all’interno del nostro gruppo, è stato utilizzato a tal fine. Fondamentale è anche l’ottimizzazione del processo di fabricazione dei dispositivi. In particolare, un nuovo approccio al processo buried heterostructure è presentato. Quest’ultimo approccio ha permesso lo sviluppo di un processo di fabbricazione che allo stesso tempo comporta un maggiore probabilità di successo e una maggiore qualità dei dispositivi ed inoltre ha permesso di ridurre il numero di fasi del processo.

Grazie allo sviluppo degli strumenti menzionati per ottimizzare le performance, una nuova struttura laser è stata disegnata e fabbricata al fine di ottenere alte performance e un’ampia accordabilità spettrale dell’emissione laser nella seconda finestra atmosferica. Questi dispositivi mostrano una copertura spettrale maggiore di 140 cm$^{-1}$ e, nonostante l’ampia tunabilità, alte performance sono osservate. In particolare, in pulsata, efficienze fino a 12.5 % e potenze ottiche in continua superiori a 450 mW sono state misurate a temperatura ambiente.

Utilizzando strain compensated InGaAs / AlInAs layers, in modo da aumentare la discontinuità in banda di conduzione, alcune strutture laser sono state sviluppate anche nella prima finestra atmosferica. Dal momento che la rugosità di interfaccia è nota essere uno dei principali fattori che limitano le performance dei laser nel medio infrarosso, uno studio dell’influenza della temperatura di crescita epitassiale sui parametri della rugosità di interfaccia e conseguentemente sulle performance dei laser è stata effettuata. Un andamento non monotono è stato in tal caso osservato, con una temperatura ottimale di crescita di circa 515 °C. In questo caso i dispositivi mostrano efficienze di wallplug fino a 15 % e potenze ottiche in continua maggiori di 600 mW a temperatura ambiente. Inoltre una nuova struttura, basata su
una barriera di iniezione composita, è presentata. Questa struttura presenta una riduzione della corrente parassita che percorre i dispositivi per voltaggi inferiori a quello di allineamento.

Attraverso l’utilizzo di highly strained AlAs layers, emissione laser nella regione compresa tra 3 e 4 µm è stata osservata. Sia lo sviluppo di una nuova regione attiva che l’ottimizzazione della crescita epitassiale hanno contribuito ad osservare, per la prima volta usando questi materiali, emissione laser a 3.3 µm a temperatura ambiente.


Lo sviluppo di phase-locked buried heterostructure arrays nei laser a cascata quantica viene inoltre presentato. Un restringimento del fascio laser in campo lontano è stato osservato.

Nell’ultima parte del lavoro, alcuni risultati preliminari sulla fabricatione di buried heterostructure cristalli fotonic nei laser a cascata verrano presentati. Anche se non è ancora stata osservata emissione laser, lo sviluppo di queste strutture è di cruciale importanza per la fabbricazione di dispositivi a basso consumo energetico a singolo modo spettrale e che non richiedano raffreddamento attivo.
To my family, who believed in me especially when I didn’t.
Acknowledgements

This PhD work has been first of all a great journey that has made of me a happy man. This would not have been possible without the continuous support of all the people around me.

First of all I would like to thank Prof. Jerome Faist, my "Doktorvater". This epithet can only partially describe the role that he had for me in the recent four years. It was a honor and a pleasure to have the opportunity to work under his supervision. He has been able not only to provide me with an overflow of excellent ideas, sometime even more than my brain could hold and grasp, but moreover he has always been able to provide me with his enthusiasm, especially when my own enthusiasm was fading away by the neverending "technical problems". I would also like to thank him for his unique ability to find always time to discuss with me, even when I could see that he was busy beyond repair.

I would also like to thank Prof. Gottfried Strasser to agree to co-advise my thesis and also Prof. Dan Botez, not only for the numerous and precious corrections he has suggested for my thesis, but also for all the moments we have shared in the cold winter of Madison Wisconsin, together with also Prof. Luke Mawst and Jeremy Kirch.

Looking back at the last four years, I do not know how to achieve to thank all the people that made this journey with me. I know I won’t manage to thank you all, but I hope that I achieved to express my gratitude in these years. In all the days spent to debug research problems and moreover for the nights that we spent drinking beer in order to forget them.

In particular I would like to thank Dr. Mattias Beck, for the all the time he has spent to provide me with high quality samples and for the all the help in understanding growth and regrowth related problems. I would also
like to thank Dr. Emilio Gini and Martin Ebnöther for all the MOVPE growths.

A special thank goes to Dr. Tobias Gresch, that introduced me in the "fantastic" world of Mid-IR quantum cascade lasers and of device fabrication. He also inoculated in me the idea that sleeping during processing is a vice that has to be eradicated, but I am not sure if I should thank him for that. I would also like to thank Dr. Laurent Nevou to bear my horrible French and for all the nice discussions, Dr. Giacomo Scalari for all the great advices, Dr. Fabrizio Castellano, Dr. Valeria Liverini, Prof. Keita Otani, Arun Mohan, Dr. Yargo Bonetti, Andreas Hugi and Dr. Milan Fischer for all the great moments. Special thanks reserve also my office colleagues during the years, for accepting the noise and the mess that meant having me in the office, Markus Geiser, Dr. Christoph Walther, Sabine Riedi and Dana Turcinkova. I would also like to thank an old colleague and friend, Dr. James Lloyd-Hughes for introducing me to the world of the single malt whiskey and also for forgiving me for missing his wedding to prepare my PhD defense. A special thank goes to thank Dr. Maria I. Amanti, we shared together so many good and bad moments that changed us, I hope in a better way. I would also like to thank all the friends and colleagues in the FIRST clean room for the support and for nice moments we had.

I would like also to thank the support of my Bachelor and Master supervisor Prof. Pasqualino Maddalena. He provided me with a lot of support and opportunities in spite of my young age, easing therefore the impact with the PhD studies.

All this journey would not have been possible without the unconditional love of my family, that supported and supports me in all the decisions I take.

In particular, my dad that taught me the love for the science and the research and that is responsible for taking me for the fist time in a lab, before I was five years old. My mom, that looking at me can always see a better man than I actually am and that, as every proper Italian Mom, would most probably carry me still in a stroller if only I would permit it!
In the end I want to thank my two Mousquetaires, Rosaria and Alessandro. My sister Rosaria, to be there always on my side and because I know that she will always be. My brother Alessandro, to keep me young inside and make me laugh even when we are sad. Looking at each other has always been a great way of growing up. Moreover I would like to thank both of them to take me shopping and tell me what I apparently MUST buy.

Grazie a tutti!
## Contents

List of Figures

List of Tables

1 Introduction

1.1 Motivation and organization of the work ............................................. 1

1.2 Mid-Infrared spectral range: Applications ............................................ 3

1.2.1 Trace gas sensing application .......................................................... 3

1.2.2 Breath analysis using Mid-IR sources .............................................. 5

1.2.3 Photoacustics .................................................................................. 6

1.2.4 Cavity-enhanced techniques .............................................................. 7

1.3 Quantum Cascade Laser ....................................................................... 8

1.3.1 Early studies ................................................................................... 8

1.3.2 First quantum cascade lasers ............................................................ 9

2 Quantum Cascade Lasers: Modelling ......................................................... 13

2.1 Quantum cascade laser ........................................................................ 13

2.2 Modelling in Quantum Cascade Lasers ............................................... 14

2.2.1 Rate equation model ....................................................................... 15

2.3 Density matrix approach ...................................................................... 16

2.3.1 Second-order coherence ................................................................. 21

2.4 Scattering processes ........................................................................... 23

2.4.1 Interface Roughness ....................................................................... 24

2.4.2 Alloy disorder ................................................................................ 25
CONTENTS

2.4.3 Ionized impurities .............................................. 26
2.4.4 LO-Phonons .................................................. 26
2.4.5 LA-Phonons .................................................. 27
2.5 Full Model ...................................................... 27
  2.5.1 Basis-selection .............................................. 28
  2.5.2 Model input parameters and outputs: ................... 29
    2.5.2.1 1/L measurement ..................................... 30
    2.5.2.2 Waveguide losses .................................... 31

3 Processing .......................................................... 35
  3.1 Introduction .................................................. 35
  3.2 Sample processing ............................................ 36
    3.2.1 Ridge process .......................................... 36
    3.2.2 Buried process ......................................... 37
    3.2.3 Inverted buried ......................................... 40
    3.2.4 Advantages .............................................. 41
  3.3 InP doping calibration: Iron and Silicon ................... 42
  3.4 Dry etching optimization .................................... 43
    3.4.1 Orthogonal matrix approach ............................ 46
    3.4.2 Optimized process for deep etching ................... 49
    3.4.3 Shallow etching process ................................ 49

4 Lattice matched quantum cascade lasers for wide tuning 53
  4.1 Electrical tuning in QCLs .................................... 53
  4.2 Active region design for wide tuning ....................... 55
    4.2.1 Process ................................................. 56
  4.3 Spontaneous emission tuning .................................. 56
  4.4 Laser performance and Spectral tuning ...................... 58

5 Short wavelength QCLs ............................................. 63
  5.1 Conduction band engineering ................................. 63
  5.1.1 Ternary compounds ...................................... 66
  5.2 Influence of interface roughness on performance in short wavelength QCLs 68
    5.2.1 Active region design ................................... 71
CONTENTS

5.2.2 Experimental results ........................................... 71
5.2.3 Failure of the model to calculate intrasubband broadening for large correlation lengths .................................. 75
5.2.4 Sample B (515 ° C) .................................................. 77
5.2.5 Radiative current .................................................... 80
5.3 Step quantum well design ........................................... 83
5.3.1 Active region design ............................................... 84
5.3.2 Simulated and Measured laser .................................. 86

6 QCLs in the 3-4 µm region ........................................... 91
6.1 Gas sensing in the 3-4 µm spectral range ........................ 92
6.2 Sources in the 3-4 µm range ........................................ 93
6.3 Material systems for short wavelength QCLs .................... 94
6.4 Growth optimization .................................................. 96
6.5 Active region design .................................................. 97
6.6 Growth characterization .............................................. 98
6.7 Laser performance .................................................... 100
6.8 Spectral control and continuous wave operation ............... 103

7 Waveguide Modelling: multielement laser arrays in Mid-IR 107
7.1 Introduction ............................................................ 107
7.2 Arrays types for QCLs ................................................. 108
7.3 Vertically coupled arrays ............................................. 108
7.3.1 Epitaxial growth and band structure .......................... 111
7.3.2 Ridge processing .................................................... 112
7.3.3 Fishbone design ..................................................... 114
7.3.4 Results of the fishbone process ................................. 116
7.4 Buried arrays ........................................................... 120
7.5 Evanescent-wave coupled buried arrays in Mid-IR QCLs ..... 121
7.5.1 Processing ............................................................ 122
7.5.2 Optical mode simulations ......................................... 122
7.5.3 Laser performance and farfield emission ...................... 123
7.5.4 Five-element array .................................................. 124
List of Figures

1.1 Absorption lines of the water molecule in the Mid-IR spectral range. The first and the second atmospheric windows are highlighted in shaded red. Source data are obtained from the HITRAN 08 database. (1) 4

1.2 Absorption lines of a selection of molecules that present resonances in the first and second atmospheric window. Source data are obtained from the HITRAN 08 database (1). 5

1.3 Typical experimental setup for photoacoustic measurement. The temperature gradient, generated by the light absorption inside the cavity, is indicated as light orange. 7

2.1 Conduction band diagram of a typical QCL design reprinted from Ref.(2). Fundamental period of the quantum structure is shown. 14

2.2 First(a) and second order (b) contribution to the tunneling process. 17

2.3 Two level system scheme described in the evolution equation (2.8). The energy levels on the states 1 and 2 in a tight binding picture are shown as dashed lines. 18

2.4 LO-phonon emission, with a wavevector $Q$, between a the state $i = |mk\rangle$ and $f = |nk\rangle$. LA-emission scattering process is also shown in the upper subband. 27

2.5 Full model: local bases are defined inside the active region and inside each base scattering is computed using a rate equation approach while transport between different basis is computed using sequential resonant tunneling. In the structure presented in figure, the basis is constituted by the fundamental period. 28
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>Energy band diagram of QCL design based on a double-phonon resonance, since</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>the structure presents a clear thicker extraction barrier the fundamental</td>
<td></td>
</tr>
<tr>
<td></td>
<td>period is divided in two zones: active region and injector region.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sequential resonant tunneling is used to compute the transport across the</td>
<td></td>
</tr>
<tr>
<td></td>
<td>injector and extraction barrier.</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Process flow for the standard heterostructure process in Mid-IR QCLs.</td>
<td>38</td>
</tr>
<tr>
<td>3.2</td>
<td>Process flow for the standard buried heterostructure fabrication in Mid-IR</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>QCLs.</td>
<td></td>
</tr>
<tr>
<td>3.3</td>
<td>Process flow for the inverted buried heterostructure process in Mid-IR QCLs.</td>
<td>41</td>
</tr>
<tr>
<td>3.4</td>
<td>n-doping profile of a test structure grown in the doping calibrations.</td>
<td>44</td>
</tr>
<tr>
<td>3.5</td>
<td>Top view of a deeply etched structure. In the right panel a close view of the</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>sidewalls roughness is shown.</td>
<td></td>
</tr>
<tr>
<td>3.6</td>
<td>Side-view of a shallow etching test, $\sim 40$ nm on a grating structure</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>defined using Deep-UV lithography. SiO$_2$ hard masking layer is also shown.</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>Conduction band diagram of a period of the active region at an average field</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>of 60 kV/cm. The moduli squared of the relevant envelop wavefunctions are</td>
<td></td>
</tr>
<tr>
<td></td>
<td>shown. Layer sequence is presented in the appendix A.1.1 (EV1140)</td>
<td></td>
</tr>
<tr>
<td>4.2</td>
<td>Measured and simulated intersubband electroluminescence spectra for an applied</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>field of 53 kV/cm. Peaks associated with the transitions (7)-(6), (7)-(5),</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(7)-(4) are labeled.</td>
<td></td>
</tr>
<tr>
<td>4.3</td>
<td>Simulated and measured spectral emission peaks as function of the electric</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>field. As already mentioned above, for high fields (bigger than 60kV) the</td>
<td></td>
</tr>
<tr>
<td></td>
<td>only relevant peak present both in the simulated and measured EL spectra is</td>
<td></td>
</tr>
<tr>
<td></td>
<td>the one attributed to the lasing transition.</td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>Fabry-perot spectra in function of the applied voltage measured in pulsed</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>mode.</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>Simulated and measured laser peak position as function of the electric field</td>
<td>59</td>
</tr>
</tbody>
</table>
4.6 Laser threshold as function of the inverse device length. Losses of $\sim 2.8\text{cm}^{-1}$ and differential gain of $g\Gamma = 4.4 \text{ kA}^{-1}\text{cm}^{-1}$ .......................... 61
4.7 Pulsed Power-Voltage-Current characteristic of a 3.9 mm long and 8.5 $\mu$m wide QCL. Total wallplug efficiency (%) is also shown(red squares). 61

5.1 Scheme of the effect of material strain on energy levels. For simplicity also here an average valence band is used instead of the three valence bands. ......................................................... 66
5.2 $\Gamma$-valley conduction band edges for unstrained (Ga,In)As, (Al,In)As, and Al(As,Sb) as function of the lattice constant with parameters from Refs. (3, 4). ......................................................... 67
5.3 $\Gamma$, $X$, $L$ conduction band edges for $In_{1-x}Ga_xAs$ and $In_{1-x}Al_xAs$ as function of the Gallium and Arsenic composition(3, 4). ................................. 67
5.4 $\Gamma$-valley conduction band edges for (Ga,In)As, (Al,In)As, and Al(As,Sb) pseudomorphically strained to a InP substrate as function of the lattice constant with parameters from Refs. (3, 4). As a comparison to better understand the stress effect, the energy positions of the unstrained binary compounds are shown as dots ........................................... 69
5.5 Inter-subband scattering times due to interface roughness, in an infinite quantum well with a 270meV transition energy, as function of the correlation length $\Lambda$, for various values of the in-plane energies, as indicated. 70
5.6 Simulated conduction band diagram of the diagonal three QWs design used for the study of the interface roughness. The structure is biased with an electric field of 79 kV/cm. Layer sequence in appendix A.1.6 (EV1299-1301) ................................................................. 71
5.7 Optical power (right axis) and applied bias (left axis) as a function of the injected current density for devices grown at different temperatures, as indicated ..................................................... 72
LIST OF FIGURES

5.8 a) Maximum current density $J_{\text{max}}$ (squares) and threshold current density $J_{\text{th}}$ (circles) simulated as function of the correlation length. b) Simulated slope efficiency per facet (triangles) and full-width-at-half-maximum (crosses) of the electroluminescence for a voltage of 14V are also plotted. Measured values for the samples A, B and C, were in both cases compared with simulated values using the values of the correlation length as a fit parameter. ......................................................... 73

5.9 Computed intersubband lifetimes for the upper(state 3) and lower(state 2) lasing levels for an applied field of 70 kV/cm as function of the correlation length $\Lambda$ ................................................................. 75

5.10 Computed populations, for the most relevant electronic energy levels, for selected correlation lengths. In the inset the laser population inversion as function of the correlation length is shown. ......................... 76

5.11 Intra-subband scattering times due to interface roughness, in an infinite quantum well with a 270 meV transition energy, as function of the correlation length $\Lambda$, for various values of the in-plane energies, as indicated. 77

5.12 Threshold current density as function of the inverse laser length. From linear regression values of waveguide losses and differential gain can be obtained: $\alpha_w = 3.1 \text{ cm}^{-1}$ and $g\Gamma = 3.3 \text{ cm/kA}$ ($T_{\text{growth}}=525 ^\circ \text{C}$) $\alpha_w = 2.8 \text{ cm}^{-1}$ $g\Gamma = 3.65 \text{ cm/kA}$ ($T_{\text{growth}}=475 ^\circ \text{C}$) $\alpha_w = 2.5 \text{ cm}^{-1}$ $g\Gamma = 3.62 \text{ cm/kA}$ ($T_{\text{growth}}=515 ^\circ \text{C}$) ................................................................. 78

5.13 Optical power per facet(left axis), applied bias(1-st right axis) and total wallplug efficiency(2-nd right axis) as function of the current for a 4.6 mm long and 8.5 $\mu$m wide device, grown at 515°C. Simulated curves are shown as dashed lines. ................................................................. 79

5.14 Comparison of the computed and experimental threshold current density as function of the temperature for a device shown in Fig. 5.13. .................. 79

5.15 Room temperature continuous wave operation for an uncoated device, 3 mm long, mounted epi-down on a diamond heat spreader. .................. 80
5.16 Top panel: Light-current-poser characteristic of two typical devices 8.5 \( \mu m \) wide and respectively 2.3 mm and 4.6 mm long. The current in the short device is scaled to the surface of the 4.6 mm long device. Due to the reduced mirror losses the longer device start lasing for a smaller current. The lasing threshold of the two devices is indicated by arrows on the voltage-current characteristic. The radiative current is highlighted in light blue. Bottom panel: Optical power estimated from the radiative current (blue), the power simulated using the transport mode (red) and the power measured using the calibrated powermeter (black). In order to account for the setup wiring and the waveguide cladding a series resistance of 0.65 \( \Omega \) has been considered.

5.17 The operating principle of the Step Well scheme is shown. In the left panel, for low applied fields the coupling of the injector state \( i \) to the next period is reduced. In the case of high electric fields, as shown in the right panel, the a good coupling is maintained between the injector state and the upper lasing state.

5.18 Conduction band diagram of the reference sample EV1326 (top panel) and the step well design (bottom panel) for an applied field of 85 kV/cm. Moduli squared of the relevant electronic wavefunctions are shown.

5.19 Conduction band diagram of the digital grading step well design. The layer sequence can be found in appendix (see EV1327 in A.1.4).

5.20 Simulated (top panel) and measured (bottom panel) injected currents (in logarithmic scale) as function of the voltage for typical devices (8.5 \( \mu m \) wide and 2.3 mm long) from the two designs.

5.21 Simulated (top panel) and measured (bottom panel) Light-current and Voltage-current curves for 2.3 mm long and 8.5 \( \mu m \) wide devices.

5.22 Threshold current densities as function of the laser inverse length for the reference (red) and the digital step well designs. Through linear fit, values of waveguide losses of 4.5 cm\(^{-1}\) and 4.1 cm\(^{-1}\) were respectively measured and differential gain values of 1.95 cm kA\(^{-1}\) and 2.95 cm kA\(^{-1}\).

6.1 Methane transmittance spectrum. Source *NIST Chemistry Webbook*. 

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.16</td>
<td>Light-current-poser characteristic of two typical devices</td>
</tr>
<tr>
<td>5.17</td>
<td>Operating principle of the Step Well scheme</td>
</tr>
<tr>
<td>5.18</td>
<td>Conduction band diagram of sample EV1326 and step well design</td>
</tr>
<tr>
<td>5.19</td>
<td>Conduction band diagram of digital grading step well design</td>
</tr>
<tr>
<td>5.20</td>
<td>Simulated and measured injected currents</td>
</tr>
<tr>
<td>5.21</td>
<td>Light-current and Voltage-current curves</td>
</tr>
<tr>
<td>5.22</td>
<td>Threshold current densities as function of laser inverse length</td>
</tr>
<tr>
<td>6.1</td>
<td>Methane transmittance spectrum</td>
</tr>
</tbody>
</table>

xiii
6.2 Γ-valley conduction band edges for the most used material systems for short wavelength QCLs. The energy levels as function of the lattice parameter are considered pseudomorphically strained to InP, a part for the case of the material system (1) InAs − AlSb that is considered as grown on InAs. ................................. 95

6.3 Rocking curves of the superlattice structures (100 period of 16 Å AlAs and 47 Å In₀.7Al₀.3As) grown for different growth temperatures (484 °C, 493 °C, 500 °C, 510 °C). From the insets a), b), one can easily see that the structure grown at 510 °C is already partially relaxed and already in the case of the structure grown at 500 °C, the peak intensity is reduced and a higher FWHM is observed. The two structures grown at 484 °C and 493 °C are almost equivalent. ................................. 96

6.4 Conduction band diagram of a period of the active region at an average field of 120 kV/cm. Moduli squared of the relevant envelop wavefunctions are shown. Light gray is used to show doped wells (6 × 10¹⁷ cm⁻³). The layer sequence is shown in the appendix A.1.6 (EV1517) ................................. 98

6.5 Measured and simulated XRD curves. The simulated curve is offset for clarity. Measured data fit well with the expected compositions InGaAs/InAlAs-AlAs. An average period thickness of 44.2nm can be derived in well agreement with the expected one(44.6 nm) ................................. 99

6.6 Pulsed Power-Voltage-Current characteristics of a HR coated 4.75 mm long and 18 µm wide laser for different heat-sink temperatures. ......... 100

6.7 Fabry-perot laser emission spectra; a tuning coefficient of 0.98 nm/K was found by linear fitting of the peak emission wavelength as function of the temperature. ................................. 101

6.8 Measured and simulated threshold current density as function the laser temperature. Assuming the usual exponential behavior, a characteristic temperature of 100 K is estimated for the measured values. Simulated values lead to an overestimation of the characteristic temperature that is expected to be almost 170 K. ................................. 101
6.9 Measured and simulated slope efficiencies as function the laser temperature. Assuming the usual exponential behavior, a characteristic temperature of 70 K is estimated for the measured values. Simulated values lead in this case to a characteristic temperature of 600 K, this value, completely unphysical for QCLs, is probably a symptom of the weakness of the model in this spectral range.

6.10 a) Threshold current densities as function of the laser inverse length for different temperatures (250K/265K/275K/285K/295K). Maximum current density value \( J_{\text{max}} \) is indicated as a dashed line. b) Waveguide losses (left axis) and differential gain (right axis) values as function of the temperature, estimated through linear fit from the left panel.

6.11 Peltier controller temperature (\( T_{\text{sub}} \)) as function of the active stack temperature (\( T_{\text{act}} \)) in a device with a thermal conductance of 1800 \( W \, K^{-1} \, cm^{-2} \) and using the characteristic temperature and current density measured in previous section (\( T_0 = 100K \) and \( J_0 = 210 \, A/cm^2 \)).

6.12 Room temperature EL spectrum for a 375 \( \mu m \) long device for an applied voltage of 14 V. The luminescence width, both at the 50 % level or the 75 % level of the central peak is shown.

7.1 Schematic representation of the basic types of phase-locked linear arrays. The traces correspond to refractive-index profiles. Based on a figure in the reference (5). (a) Leaky-wave array (b) evanescent wave array (c) Y-junction array.

7.2 Mode profile and refractive index along the growth direction. Active regions are represented by blue shaded areas. The effect of mode rectangularization due to the insertion of passive interstacks inside the active region stack is shown in the left panel compared to the right one.

7.3 Room temperature pulsed power-current-voltage curves for two different ridge widths. The narrower device, even if it is longer and consequently presents smaller waveguide losses, show sensibly smaller performance. Narrower devices, \( \sim 30 \, \mu m \) wide, did not show any lasing action at room temperature.
LIST OF FIGURES

7.4 Microscope image of the front facet of a device. Active region stacks are indicated using red arrows. .................................................. 113
7.5 Process flow for the fishbone process for multi-stack strucures. ........ 115
7.6 Left panel: Microscope picture of the fishbone process after the lateral active region etching. Active region stacks are indicated using green arrows. Right Panel: 2D simulated mode profile. .......................... 116
7.7 SEM of the ultimated fishbone process. In the zoomed picture the thin SiN layer (∼ 100 nm) deposited on sidewalls of the active region stacks is shown. ................................................................. 116
7.8 Influence of the lateral active region etching on the waveguide losses for different ridge widths. Losses, especially for the narrow stripes, tend to initially decrease with the increase of the lateral etching to reach then a nearly common value. ....................................................... 117
7.9 Power-Current-Voltage curve, in the 243 K - 300 K range, for a 5.4 mm long and 49 µm wide device ................................. 117
7.10 Average power in function of duty cycle, for the device shown in Fig.2. The figure inset shows the emitting spectrum at 300K, with a peak wavelength near 10.5 µm ................................................................. 118
7.11 Simulated thermal conductances for junction-up (red) and junction-down mounted devices (blue). Measured thermal conductances for junction up mounted devices (red dots) ................................................. 119
7.12 a) Measured farfield pattern for a 40 µm wide and 3 mm long device. 
   b) Simulated and measured farfield pattern in the growth (red) and lateral direction (blue) .......................................................... 120
7.13 a) Scanning electron microscope image of a typical two-elements array. 
   Active region structures(AR) are ∼ 7.5 µm wide. ....................... 122
7.14 Computed electric field in the vertical direction for a the two element array shown in Fig. 7.13. The most relevant optical modes are shown. 123
7.15 Room temperature pulsed Power-Voltage-Current characteristics of a two-elements array, 3.8 mm long. ................................. 124
7.16 Computed farfield emission patterns for the optical modes shown in the Fig. 7.14. ................................................................. 125
7.17 (a) Comparison of the measured farfield emission in lateral direction for the single element and the 2-elements array. Farfields were measured in pulsed operation at a current density of 3.5 kA/cm² at room temperature. (b) Simulated emission pattern for the fundamental mode of the single element ridge for the in-phase and out-of-phase modes of the 2-elements array. ................................................. 126

7.18 Simulated farfield emission along the lateral direction as function of the number of elements in the arrays for the in-phase mode. Narrowing of the far-field emission is observed up to a factor of 2 for the case of a 5-elements array. As mentioned already, the total active region width is kept constant to 15 µm for all the arrays. ................................. 127

7.19 (a) Scanning electron microscope image of a buried 5-elements array. Each active element is ∼ 3 µm and is identified by the label AR. .... 127

7.20 Simulated optical mode and farfields for the 5-element array ........ 128

7.21 Measured farfield emission pattern for 5 elements array (Experiment) compared with the simulated farfield emission (Mode (a) and (d)). .... 129

7.22 TM Photonic band structure for a square array of columns with a radius of r = 0.375 a. The active medium squared columns are surrounded by insulating InP. In the left inset a cross-sectional view of the dielectric function is shown. The right inset shows the the Brillouin zone, with the irreducible zone in shaded red. ................................. 131

7.23 a) Zoom of the photonic crystal band diagram shown in Fig. 7.22 near the Γ-point. b) Ratio of the optical mode energy inside the pillars to the pillar area as function of the pillar ratio (r/a) for the third band. In the top-inset, the optical mode of the third band at the Γ-point is shown. 132

7.24 SEM images of the photonic crystal structure pattern defined by deep-UV lithography and SiO₂ plasma etching. ................................. 133

7.25 SEM images of the photonic crystal structure after the ICP plasma etching and before the selective InP regrowth. ................................. 133

7.26 SEM images of the photonic crystal structure after the regrowth of the insulating InP layer (a) and after the n-contact InP cladding layer (b). 134
LIST OF FIGURES

7.27 Illustration of the buried heterostructure photonic crystal QCL, surface emission is indicated by the arrows on the side of the top metalization layer. ................................................. 134

7.28 Illustration of the buried heterostructure photonic crystal QCL. The InGaAs layer, 20 nm thick, that separates the two epitaxial InP regrowths is shown. A possible leakage path at the structure boundaries is shown. 135
List of Tables

3.1 SEM images of front facet of lasers fabricated with the standard buried heterostructure (left panel) and the inverted buried (right panel) processes. The sample produced using the inverted buried process shows a higher etching uniformity. ................................................................. 42

3.2 SEM images of top of lasers fabricated with the standard buried heterostructure (left panel) and the inverted buried (right panel) processes. ................................................................. 42

3.3 List of the orthogonal matrices to be used as function of the number of parameters and levels. ................................................................. 47

3.4 Application of the $L_4$ matrix to a problem where 4 variables ($A, B, C, D$) can be varied over 3 levels (1, 2, 3). In this case only 9 tests are necessary in order to fully characterize the system. In the first test all the parameters are kept at the 1 level setting, in the second one all a part from one are varied to the second level setting, etc. ................. 47

3.5 Average etch rate $E_{press}$ and selectivity $S_{press}$ as function of the chamber pressure. ................................................................. 49
Chapter 1

Introduction

1.1 Motivation and organization of the work

This work describes the work performed by the author at the ETH Zürich, under the supervision of Prof. Jérôme Faist on the optimization of high performance quantum cascade lasers (QCLs) in the Mid-IR spectral region.

In this introductory chapter, some of the potential applications of QCLs in the Mid-IR will be introduced, with special attention to the spectroscopic applications. In the second part of this chapter a brief historical overview of the main results obtained in quantum cascade laser since their first demonstration will be presented.

In the second chapter, the basic theory of the principal processes that are behind quantum cascade laser operation will be discussed. In particular, a new transport model based on a density matrix formalism will be described. This model implements both coherent transport with sequential resonant tunneling and direct scattering by LO-phonons, interface roughness, alloy disorder and ionized dopants(6). Using this model, laser behavior, as light-current-voltage characteristic as well as gain and luminescence spectra, can be simulated.

In the third chapter, an overview of the different QCL fabrication processes is presented. In particular, a novel approach to the buried heterostructure process is presented. This new process is characterized by a reduced amount of fabrication steps and also a reduced amount of crystal defect introduced by the InP regrowth steps. In addition a more uniform current injection in the active region stack is obtained.
1. INTRODUCTION

In the second part of the third chapter, the method of the orthogonal matrices for process optimization will be described and applied in particular to the optimization of the plasma etching process. This technique is of general interest and can be used for any processing step and allows to reduce the number of test runs necessary for a multi-parameter optimization.

In the fourth chapter the development of widely tunable quantum cascade lasers in the second atmospheric window will be used. As material system InGaAs and AlInAs are used, both lattice matched to InP and high optical powers are observed both in pulsed and in continuous wave operation. The lasers, with emission frequency at $\sim 8.5 \ \mu m$, are processed as Fabry-perot cavities and a maximum spectral coverage of $\sim 140 \ \text{cm}^{-1}$ was observed.

The fifth and the sixth chapters are focused on the development of lasers in the first atmospheric window (3-5 $\mu m$).

In particular, in the fifth chapter, design of efficient quantum cascade lasers, based on $\text{InGaAs/AlInAs}$ strain compensated to InP, emitting 4-5 $\mu m$ spectral range will be analyzed. A brief survey of the effect of material strain on the band offset discontinuities will be presented in the first part of the chapter. Subsequently, using a design emitting at 4.6 $\mu m$, the effect epitaxial growth temperature on the interface roughness parameters and consequently on laser performance will be presented. In the final part of the chapter a new laser design will be introduced especially designed in order to reduce the parasitic current flowing in the structure before structure alignment.

The sixth chapter is dedicated to the development of extremely short wavelength quantum cascade lasers emitting in the 3-4 $\mu m$ spectral range, based on the $\text{InGaAs/AlInAs-AlAs}$ material system, strain compensated to InP. Due to the high strain introduced by the individual AlAs layers, growth optimization was performed in order to avoid crystal relaxation of the structure.

The seventh chapter is particularly dedicated to the waveguide engineering instead than on the active region optimization. In particular the implementation of phase locked arrays of Mid-IR QCLs is presented.

In the initial part of the chapter a multi-section quantum cascade laser waveguide for high peak power operation at 10.5 $\mu m$ is presented and in the second part the development of buried heterostructure phase locked arrays emitting at 8.2 $\mu m$ is presented.
1.2 Mid-Infrared spectral range: Applications

In the final part of the chapter, preliminary results on the fabrication process of buried second-order photonic crystal will be introduced.

1.2 Mid-Infrared spectral range: Applications

Coherent sources in the Mid-IR spectral range are of great interest due to the large number of scientific and industrial applications in this spectral range, e.g. frequency metrology, high resolution spectroscopy, industrial control, clinical diagnostic.

In fact, in the Mid-IR spectral region, that can be defined as the wavelength range between 3 and 20 $\mu$m, numerous molecules have strong absorptions fingerprints. These resonances can be orders of magnitude bigger than the ones in the NIR spectral range. In particular for many application, e.g. pollution control, detection of water contaminants and breath analysis, two distinct regions of the Mid-IR spectral range are particularly important. They are usually referred as the first and the second spectral windows and they lie respectively in the 3-5 $\mu$m and in 8-13 $\mu$m ranges and they are characterized by the absence in these regions of water resonances. In the Fig. 1.1, the absorption lines of the water molecule in the Mid-IR are shown.

In the next sections some of the possible applications of the QCL for spectroscopy will be presented.

1.2.1 Trace gas sensing application

Laser sources in the Mid-IR spectral range provide a an unique tool for the gas sensing applications. In the Fig. 1.2 some of the most relevant substances that have resonances in the first and second atmospheric window are shown. Some of the possible gas sensing applications of laser spectroscopy in the Mid-IR spectral region are:

- **Urban and Industrial Emission Measurements**
  - Industrial Plants
  - Combustion Sources and Processes
  - Automobile and Aircraft Emissions

- **Rural Emission Measurements**
  - Agricultural and Animal Facilities
1. INTRODUCTION

![Absorption lines of the water molecule in the Mid-IR spectral range. The first and the second atmospheric windows are highlighted in shaded red. Source data are obtained from the HITRAN 08 database.](image)

**Figure 1.1:** Absorption lines of the water molecule in the Mid-IR spectral range. The first and the second atmospheric windows are highlighted in shaded red. Source data are obtained from the HITRAN 08 database. (1)

- **Environmental Gas Monitoring**
  - Atmospheric Chemistry
  - Volcanic Emissions

- **Chemical Analysis and Industrial Process Control**
  - Pharmaceutical, Food & Semiconductor Industry

- **Biomedical and Clinical Diagnostics**
  - Breath analysis

Some of these applications have been in the last years limited by the availability of compact, efficient and tunable laser sources in this region and nowadays, with the reached maturity of the quantum cascade lasers, a new renaissance in the field is taking place.

Most of this applications are based on the detection in different condition of the same molecules, e.g. NO, CO etc., and moreover the same spectroscopic techniques are generally used for the different purposes, e.g. photoacoustics. For this reason, in the
next section only one of this application will be described in deeper details, i.e. breath analysis and then some of the spectroscopic techniques will be described.

**Figure 1.2:** Absorption lines of a selection of molecules that present resonances in the first and second atmospheric window. Source data are obtained from the HITRAN 08 database (1).

### 1.2.2 Breath analysis using Mid-IR sources

In this subsection, the merits connected to the use of Mid-IR sources for biomedical diagnosis will be discussed.

Particular attention will be given to the key role of these sources for the real time
breath analysis (7, 8, 9, 10). This diagnostic technique provides important informations regarding the health status of the subject and it has numerous advantages compared to the classical methods as the direct measurement of the metabolites from the blood exams. In fact the analysis of the exhaled breath provides a simple, non-invasive technique capable of online measurements and therefore it also allows to obtain additional information on the different phases of the exhalation process (11).

The main constituents of the exhaled human breath are obviously nitrogen, oxygen and water. In addition to these, various volatile metabolites can be found that are formed inside the organism. Carbon dioxide is the main metabolite present in the breath and, even though it is not itself a disease marker, it has an important role for breath testing in the case of breath testing when $^{13}$C-labeled pharmaceuticals are used (12, 13).

Among the disease markers a prominent role is played by Nitric oxide. The presence of endogenous NO in the exhaled breath correlates in fact with the presence of various lung diseases as for example asthma (14, 15).

Over the last 20 years carbon monoxide (CO) has been used in order to identify current and passive smokers or to determine the bilirubin production especially in the new born babies (16, 17).

Compounds as the methane and the sulfur compounds are instead originated from the gastro-intestinal tract and can help monitoring the food metabolization. The latter has also a relevant impact on the veterinary diagnostic cause of the minimal disturbance on the animal.

In conclusion, the analysis of the exhaled breath will most probably play an important role in the future and the use of optical spectroscopy using Mid-IR sources, as QCLs, is one of the most promising technique to pursuit this goal.

### 1.2.3 Photoacoustics

One of the most used optical techniques based on the direct absorption is the photoacoustic spectroscopy (PA) (18, 19). A typical example of a photoacoustic detection scheme is shown in Fig. 1.3. The gas of interested is inserted inside an acoustic cavity.

If the laser light is tuned on an absorbing molecular transition of the gas, it will excite the gas molecules that will transfer some of the acquired energy to the surround-
1.2 Mid-Infrared spectral range: Applications

ing molecules by collision. This will generate a thermal gradient inside the cavity that will translate into periodic pressure changes. The induced sound is then recorded by a microphone and measured using a lock-in amplifier.

If the chopping frequency of the laser source matches the acoustic resonance of the cavity, then the whole structure will act as an organ-tube and the generated sound wave can amplified resulting in an enhancement of the sensitivity of the system. The

![Figure 1.3: Typical experimental setup for photoacoustic measurement. The temperature gradient, generated by the light absorption inside the cavity, is indicated as light orange.](image)

PA signal can be written as (20) (21):

\[
S(\lambda) = s \cdot \sigma(\lambda)N P(\lambda)
\]  

(1.1)

where \(\sigma\) is the absorption cross-section, \(P\) is the laser power and \(N\) is the concentration of the molecules. The sensitivity coefficient \(s\) depends on the construction of the acoustic cavity design and can reach values up to \(\sim 10^4\) using electromechanical resonances (22).

1.2.4 Cavity-enhanced techniques

Cavity-enhanced spectroscopy is one of the most versatile and precise techniques to measure low absorption lines using high finesse cavities. Sensitivities obtained can be much higher than the ones obtained using the standard multi-pass technique since effective absorption pathlengths can be as long as few km. There are several different schemes that can be used, but among these an important role is surely played by Cavity
1. INTRODUCTION

Ring-Down spectroscopy (CRDS) that provides not only high selectivity but also short measurement times. The measurement is done monitoring the light that leaks out of one of the cavity mirrors. A minimum detectable absorption of $10^{-10}$ cm$^{-1}$ was observed with 1 s integration time.\(^{(23, 24)}\)

1.3 Quantum Cascade Laser

1.3.1 Early studies

Quantum cascade lasers (QCLs) are unipolar semiconductor laser based on intersubband transition in heterostructures. These transitions occur between confined electronic states inside the conduction band.

In 1971 Kazarinov and Suris for the first time proposed that population inversion could be obtained between electronic subbands in semiconductor superlattices and the proposed to use biased superlattice structures to obtain stimulated emission \(^{(25)}\).

In the following years, superlattices and resonance tunneling through double-barrier heterostructures were studied intensively \(^{(26, 27, 28)}\) and the existence of discrete states in semiconductor quantum wells was proven by absorption measurements \(^{(29)}\).

One of the main contribution to the field of the heterostructures was certainly given by A.Y. Cho and J.R. Arthur at the Bell Laboratories with the introduction of the molecular beam epitaxy (MBE) \(^{(30, 31, 32)}\).

In fact in comparison with the other epitaxial techniques present at the time, liquid phase epitaxy (LPE) and vapor phase epitaxy (VPE), in the MBE the growth is performed in an ultra-high vacuum environment.

Starting from 1985, the group led by F. Capasso and A. Cho at the Bell Labs started working on the resonant tunneling in heterostructures \(^{(33, 34)}\). Based on these works, and on the early proposal by Kasarinov and Suris, H.C. Liu from the National Research Council in Ottawa, proposed a novel superlattice infrared source based on intersubband transitions and resonant tunneling phenomena in a finite superlattice\(^{(35)}\) that constituted a big leap to the actual design of quantum cascade structures.

One of the first experimental results toward the actual realization of the quantum cascade laser was the observation, by J. Faist et Al. at Bell Labs, of the electroluminescence emission from coupled quantum wells with a graded injector design \(^{(36)}\).
1.3 Quantum Cascade Laser

Unfortunately, the measured emission spectra were much wider (~ 60 meV) than expected.

Nevertheless only few months later, J. Faist obtained a sensitive narrowing, of roughly a factor of 2, in the emission only by removing the Si-doping from the active region while increasing the doping in the injector region (37).

1.3.2 First quantum cascade lasers

The realization that the removal of Si-doping from the active region wells produced a narrowing in the EL spectra, opened finally the route to the realization of the first QCL.

In fact in the 1994, shortly after the demonstration of the electroluminescence narrowing, J. Faist et Al. showed for the first time lasing emission in a quantum cascade structure (38).

The structure was grown using the InGaAs/AlInAs material system lattice matched on InP. Lasing emission at 4.2 µm was observed up to a maximal temperature of 90 K in pulsed operation.

The active region design consisted of a 3-coupled wells design, where the lasing transition occurs between the states 3 and 2 and the energy spacing between the state 2 and the state 1 is resonant with the longitudinal phonon energy, in order to minimize the depopulation time out of the lower lasing state.

Moreover, in order to increase the non radiative scattering time between the states 3 and 2, the spatial overlap between the two wavefunction was reduced and laser action was based on a diagonal transition. In the years subsequent to the first observation of lasing action in a QC structure, laser performance have been steadily improved both due to new design schemes and also due optimization of the growth process and device fabrication process.

Even thought it is impossible to report all the results obtained, in this section some of the major achievements will be described.

In 1995, Faist et al. introduced a new injector design, in order to reduce the carrier escape in the continuum, that would act as a bragg reflector for the electrons in the upper lasing state (39, 40). Scamarcio et Al. in 1997 proposed also a new class of designs based on miniband transitions in superlattices (41). This design, in which the
1. INTRODUCTION

population inversion is guaranteed by the long interminiband lifetime compared to the intraminiband ones, demonstrated for the first time the possibility of obtaining high peak powers using QCLs. Unfortunately the high doping used in this design to obtain flat minibands did limit sensibly the performance.

The introduction of a chirped superlattice design by Treducucci et al., allowed to overcome this problem and for the first time high power pulsed operation up to 325 K was obtained\(^{(42)}\). In the same year Sirtori and Al. demonstrated the first QCL structure based on the GaAs/Al\(_x\)Ga\(_{1-x}\)As material system \(^{(43)}\). Even though laser performance using this material system in the Mid-IR never reached the performance obtained using InGaAs/AlInAs on InP, it set the basis that lead to the demonstration of the first THz quantum cascade laser \(^{(44)}\).

In 1998, Faist and Al. also demonstrated the first QCLs emitting at short wavelengths, 3.4 \(\mu\)m, using strain compensated In\(_{0.7}\)Ga\(_{0.3}\)As/Al\(_{0.6}\)In\(_{0.4}\)As on InP in order to increase the conduction band discontinuity \(^{(45)}\). This laser held the record of the short wavelength in a QCL for almost 10 years.

Since then, a lot work was done on the development of new lasing schemes for high temperature operation. Among these, it is important to mention two of the nowadays most used quantum cascade laser designs: the bound-to-continuum and the two-phonon resonance designs, both introduced by the group of J. Faist et Al. at University of Neuchatel. \(^{(46)}\).

The same year, Beck et Al. obtained for the first time continuous laser operation at room temperature using a two-phonon resonance design \(^{(47)}\).

This result can be considered as the benchmark defining the beginning of the maturity phase for Mid-IR quantum cascade lasers.

The origins of this impressive result can be mainly attributed to the use of a buried heterostructure process in which the active region was buried in InP, improving the laser thermal conductance while at the same time reducing the optical losses due to the smaller absorption of insulating InP compared to the standard insulating layers used for ridge processes as SiN or SiO\(_2\).

Another important factor that contributed to obtain continuous wave operation was the epi-down mounting of the device on a diamond heat-spreader.

The result obtained by Beck et Al. triggered a rapid development in the field of the buried heterostructure Mid-IR QCLs for continuous wave operation. In particular
impressive results were obtained both from the group of Prof. Razeghi at the Nordwest university and by Agilent Technologies in collaboration with the group of Prof. Capasso at Harvard University, see for example \((48, 49, 50, 51, 52, 53, 54)\) and more recently by Pranalitica \((55, 56, 57, 58)\).

Nowadays continuous wave operation, multi-watt emission is observed in several portion of the Mid-IR range and more and more applications are being developed based on QCLs sources.

Nevertheless a lot of work is still to be done in the laser optimization, especially on the active region and waveguide design and on the fabrication process, in order to achieve stable sources with high performance in all the Mid-IR range.
1. INTRODUCTION
Chapter 2

Quantum Cascade Lasers: Modelling

In this chapter, a basic introduction of the different transport models used in the case of quantum cascade lasers will be presented. The principal intersubband scattering mechanism will be discussed in the section 2.4. Among the various models, special attention will be given to the density matrix approach and in particular to a novel model, implemented in our group, that accounts for both coherent transport with sequential resonant tunneling and direct scattering by LO-phonons, interface roughness, alloy disorder and ionized dopants (6). This model can be used to predict current-voltage and current-light behavior of the structures without any fitting parameter.

2.1 Quantum cascade laser

As already mentioned in the previous chapter, a quantum cascade laser is an homopolar semiconductor device and laser behavior is full determined by intrasubband transitions in the conduction band. This peculiar property of quantum cascade lasers gives rise to their unique design flexibility.

By the use of epitaxial growth techniques, a series of quantum wells is defined and radiation emission takes place due to electron transition between the various energy states of the quantum wells. For this reason, emission frequency for these devices is completely defined by the size of the quantum wells involved and can be widely adjusted.
2. QUANTUM CASCADE LASERS: MODELLING

Obviously also the population inversion and an efficient electron transport have to be properly engineered in order to obtain stimulated emission. For this reason, since their first demonstration, it has been clear that in the case of QCLs the implementation of accurate transport models was necessary to obtain good laser performance.

Figure 2.1: Conduction band diagram of a typical QCL design reprinted from Ref.(2). Fundamental period of the quantum structure is shown.

2.2 Modelling in Quantum Cascade Lasers

Quantum cascade lasers have been modeled in different ways along the years, starting from the most elementary rate equation approaches\(^{(59, 60)}\) to the fully quantum mechanical approaches \(^{(61)}\). Due the large number of degrees of freedom, it is clear that the improvement of laser performance is bound to the development of a model that has good predictive capabilities, while maintaining the computational lightness necessary in order to perform fully automatic design optimization.
2.2 Modelling in Quantum Cascade Lasers

2.2.1 Rate equation model

A quantum cascade laser is constituted by the repetition of a fundamental sequence (period) of quantum wells. Electron are transfered by one period to the subsequent one through resonant tunneling. One of the easiest and qualitatively accurate approaches to model quantum cascade laser structures is to write the rate equations for the relevant states inside the period. Considering the Hamiltonian for a carrier inside the structure:

$$H = \frac{\hbar^2}{2m} + V_{\text{crystal}} + V_{\text{het}} + V_{\text{field}} + H_{\text{phot}} + H_{\text{scat}}$$  \hspace{1cm} (2.1)

where $V_{\text{crystal}}$ is the crystal potential, $V_{\text{het}}$ is the potential generated by the heterostructure, $V_{\text{field}}$ is the field applied to the structure, $H_{\text{phot}}$ is the interaction of the electron with the photons and $H_{\text{scat}}$ includes all the relevant scattering terms, e.g. electron-phonon interaction, interface roughness, alloy disorder, phonon-assisted scattering. This Hamiltonian can obviously not be treated exactly, but it is necessary to use a perturbative approach:

$$H = H_0 + H' = \frac{\hbar^2}{2m} + V_{\text{crystal}} + V_{\text{het}} + V_{\text{field}} + H_{\text{phot}} + H_{\text{scat}}$$  \hspace{1cm} (2.2)

The system can then be solved finding the eigenstates $|\Psi\rangle$ of the unperturbed Hamiltonian $H_0$ and the interaction Hamiltonian $H'$ simply induces transitions between the unperturbed states. In that way the problem can be written as a set of rate equations for each energy level, e.g for the 3 level system:

$$\frac{dn_3}{dt} = \frac{J}{q} - \frac{n_3}{\tau_3} - Sg_c(n_3 - n_2)$$  \hspace{1cm} (2.3)

$$\frac{dn_2}{dt} = \frac{n_3}{\tau_{32}} - \frac{(n_2 - n_{2\text{therm}})}{\tau_2} + Sg_c(n_3 - n_2)$$  \hspace{1cm} (2.4)

$$\frac{dS}{dt} = \frac{c}{n_{\text{refr}}} \left[ (g_c(n_3 - n_2) - \alpha_{\text{tot}})S + \frac{\beta n_3}{\tau_{sp}} \right]$$  \hspace{1cm} (2.5)

Where $J$ is the current density inside the structure, $q$ is the electron charge and $g_c$ is the peak gain cross section, $n_{2\text{therm}}$ is the thermal population of the level 2, $\tau_3$ and $\tau_2$ are the lifetimes of the levels 3 and 2, $\tau_{32}$ is the non-radiative relaxation time from the level 3 to level 2 and $S$ is the photon flux per unit width of the active region.
and per period. The total losses $\alpha_{tot}$ are the sum of the mirror losses at the facets $(\alpha_{mi} = -(1/2L)\ln(R_i))$ and the waveguide losses $\alpha_m$. Even though the rate equation model allows us to have clear insight of the qualitative behavior of intraperiod dynamics and to obtain expressions both for the current and the slope efficiency at the threshold, it is oversimplified and has important limitations. First of all, in the way it has been written, the number of carriers inside the structure $(J/q)$ is set by hand and moreover an unitary injection efficiency inside the upper lasing state is supposed.

A first step to overcome this limitation and also estimate the current in our model, is the use the periodicity of the system to compute the current self-consistently as the net rate between the different periods (59).

$$J_{tot} = J_{next} - J_{prev}$$ (2.6)

The previous model has been used to calculate electron transport in various cascade structures (60), unfortunately this model cannot account for mechanisms as the dephasing of the electron wavefunctions. Consequently artifacts, as the anticrossing between states with a large spatial separation, are observed.

### 2.3 Density matrix approach

A more effective way to model the transport in QCLs and, account for phenomena as resonant tunneling, is the use of a density matrix formalism. In this section at first simple model, slight modification of the model originally proposed by Kasarinov and Suris(62, 63), will be presented. As a result of the approximations made in this model, scattering intersubband conserves the in-plane momentum and therefore no second-order effects in the transport or gain are taken into account. In the second part of the section, a more sophisticated transport model, developed by Willemberg and al. (64) will be presented. In this case, the second order effect in tunneling are considered, i.e. electrons can tunnel from one subband to another without momentum conservation by means of a virtual intermediate state. As it can be seen in Fig. 2.2, while the first order contribution to the tunneling is conservative in the wave vector space, the second-order one is conservative in the energy space but not in the wave vector one.(65) For sake of simplicity let’s consider a two level system, as shown in Fig. 2.3, where periodic
2.3 Density matrix approach

boundary conditions are applied and the injector level of one period is connected with the upper level of the next one through a barrier with a coupling strength $\Omega$. The Hamiltonian of the tunneling mechanism can be written as:

$$H_0 = \begin{pmatrix} E_1 & \hbar \Omega \\ \hbar \Omega & E_2 \end{pmatrix}$$  \hspace{1cm} (2.7)

The evolution of the complete system is then simply described by the Liouville-Von Neumann equation:

$$i\hbar \frac{d\rho}{dt} = \mathcal{L}_0(\rho) + \mathcal{L}'(\rho)$$  \hspace{1cm} (2.8)

where Liouville superoperator $\mathcal{L}_0$ corresponds to the tunneling process and $\mathcal{L}'$ is relative to the loss of coherence in the scattering processes between states 2 and 1 inside the
Figure 2.3: Two level system scheme described in the evolution equation (2.8). The energy levels on the states 1 and 2 in a tight binding picture are shown as dashed lines.

period. The density matrix elements $\rho$ can be written as:

$$\rho = \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{12}^* & \rho_{22} \end{pmatrix}$$

(2.9)

where the terms $\rho_{11}$ and $\rho_{22}$ account for the electron populations in the states 1 and 2 and the $\rho_{12}$ and $\rho_{21}$ are the polarization terms. The Liouville operators can be written as:

$$\frac{\mathcal{L}_0}{i\hbar} = \begin{pmatrix} 0 & i\Omega & -i\Omega & 0 \\ i\Omega & -i\Delta & 0 & -i\Omega \\ -i\Omega & 0 & i\Delta & i\Omega \\ 0 & -i\Omega & i\Omega & 0 \end{pmatrix}$$

(2.10)

$$\frac{\mathcal{L}'}{i\hbar} = \begin{pmatrix} -\frac{1}{\tau_1} & 0 & 0 & \frac{1}{\tau_2} \\ 0 & -\frac{1}{\tau_1} & 0 & 0 \\ \frac{1}{\tau_1} & 0 & 0 & -\frac{1}{\tau_2} \end{pmatrix}$$

(2.11)

where $\Delta = (E_1 - E_2)/\hbar$ is the energy detuning. The Liouville superoperator $\mathcal{L}'$ can be separated into a part that acts on the diagonal terms, i.e. level populations, and depends on the level lifetimes $\tau_1$ and $\tau_2$ and the non-diagonal terms that depend on the dephasing time $\tau_\parallel$ and only act on the polarization terms ($\rho_{12}$, $\rho_{21}$). Writing explicitly
2.3 Density matrix approach

by components the evolution of the density matrix in time we obtain:

\[
\frac{d\rho_{11}}{dt} = -i\Omega(\rho_{21} - \rho_{12}) - \frac{\rho_{11}}{\tau_1} + \frac{\rho_{22}}{\tau_2} \quad (2.12)
\]

\[
\frac{d\rho_{22}}{dt} = i\Omega(\rho_{21} - \rho_{12}) + \frac{\rho_{11}}{\tau_1} - \frac{\rho_{22}}{\tau_2} \quad (2.13)
\]

\[
\frac{d\rho_{12}}{dt} = -i\Omega(\rho_{22} - \rho_{11}) - i\Delta \rho_{12} - \frac{\rho_{12}}{\tau_\parallel} \quad (2.14)
\]

\[
\frac{d\rho_{12}}{dt} = i\Omega(\rho_{22} - \rho_{11}) + i\Delta \rho_{21} - \frac{\rho_{21}}{\tau_\parallel} \quad (2.15)
\]

In order to solve this equation system in the steady state \(\frac{d\rho}{dt} = 0\), we need still to impose the charge conservation condition inside the system \(\rho_{11} + \rho_{22} = 1\).

One of the main advantages in the use of the density matrix formalism is that the time evolution of any operator can be computed by simply considering the commutator of the Hamiltonian with the operator itself. A current operator can then be defined as:

\[
\hat{J} = q_0 \frac{dZ}{dt} = q_0 [H, Z] \quad (2.17)
\]

and the expectation value of the current density is simply the trace of the operator \(\langle Tr(\hat{J})\rangle\) divided by the distance between the centroids of the electron wavefunctions \((z_{11} - z_{22})\):

\[
j = \imath n_s q_0 \Omega(\rho_{21} - \rho_{12}) = q_0 n_s \frac{2\Omega^2 \tau_\parallel \frac{\tau_1}{\tau_1 + \tau_2}}{1 + \Delta^2 \tau_\parallel^2 + 4\Omega^2 \tau_\parallel \frac{\tau_1 - \tau_2}{\tau_1 + \tau_2}} \quad (2.18)
\]

where \(n_s\) is the total sheet electron density inside the structure. In the case the backscattering is neglected \((\tau_1 \to \infty)\) leads to the well known Kazarinov and Suris formula (62):

\[
j = q_0 n_s \frac{2\Omega^2 \tau_\parallel}{1 + \Delta^2 \tau_\parallel^2 + 4\Omega^2 \tau_\parallel \tau_2} \quad (2.19)
\]

The previous equation allows to clearly define two different transport regimes of transport through a barrier as shown by (63). In fact if the lifetimes \(\tau_\parallel\) and \(\tau_2\) are much smaller than the inverse of the coupling \((\Omega^2 \tau_\parallel \tau_2 \ll 1)\), the broadening of the levels exceeds the energy splitting due to the resonant tunneling process. In this
2. QUANTUM CASCADE LASERS: MODELLING

case, also called weak-injection coupling regime, the transport is mostly dominated by incoherent tunneling. On the other side, if $\Omega^2 \tau_1 \tau_2 \gg 1$ than the transport works in the strong coupling regime and then maximum current obtained at resonance is only dominated by the upper state lifetime and is independent from the coupling strength $\Omega$:

$$J = q_0 n_s \Omega^2 \tau_1$$  \hspace{1cm} \text{(Weak coupling regime)} \hspace{1cm} (2.20)

$$J = \frac{q_0 n_s}{2 \tau_2}$$  \hspace{1cm} \text{(Strong coupling regime)} \hspace{1cm} (2.21)

Even though, it is clear that in the case of a quantum cascade structure a strong injection is beneficial to insure a fast tunneling of the electrons inside the upper lasing state, the actual amount of coupling necessary to obtain best laser performance has been longly debated. In fact, while a too low value of $\Omega$ will limit the maximum current inside the structure, at the same time with the increase of the coupling $\Omega$ also the non-resonant injection into other states will be enhanced and injection efficiency will be lowered. A way to obtain a good compromise between the two regimes, is to adjust the coupling in order to obtain a splitting comparable to the broadening induced by dephasing.

Unfortunately it is not easy to measure the dephasing time inside a quantum cascade laser; for a long time the width on the luminescence spectrum has been considered as a good indirect measurement of this lifetime. Based on this assumption and using a model similar to what is shown here, but based on a 3 level system, Khurgin et al. (66) found that the maximum of gain is obtained when $\Omega \sim \left( \frac{\Omega}{\tau_1 \tau_2} \right)^{1/4}$, where the 3 and 2 are the upper and lower lasing states and 1 is the injector state. In that case good laser performances were observed especially at low temperatures. Recent studies have questioned the assumption of the proportionality between dephasing time and electroluminescence linewidth in the case of mid-IR quantum cascade lasers, where the interface roughness is the dominant scattering mechanism. This point will be further addressed in the following sections.
2.3 Density matrix approach

2.3.1 Second-order coherence

As already mentioned, in this section the ideas behind the implementation of the second order effects in the transport and the gain modeling for a QCL will be briefly introduced. Nevertheless, the full derivation goes beyond the scope of this section and a more detailed treatment can be found elsewhere (6, 64, 67, 68).

In the model previously presented the electrons tunnel through a barrier conserving their in-plane vector. While it appears clear that second-order scattering plays a key role in the case of gain without inversion, due to scattering optically-assisted transition (69), recently it was proven that also trying to compute the transport in quantum cascade structures, the second-order effects cannot be neglected (70).

In introducing scattering-assisted tunneling inside the model, we can take advantage of the fact that the most relevant scattering process, for mid-IR quantum cascade lasers, is the interface roughness. Since this scattering mechanism is energy-conserving, the additive component in the Hamiltonian can be considered purely diagonal.

The Hamiltonian of the tunneling process (2.7) can then be rewritten as a super-matrix with an explicit dependence on the wave vector:

\[ H_{0}^{kk'} = H_{0}^{k} \delta_{kk'} + V_{kk'} \]

where \( H_{0}^{k} \) term is diagonal in the k-space and conserves the momentum, while the second term is diagonal in the energy space.

\[ H_{0}^{k} = \begin{pmatrix} E_{1}^{k} & \hbar \Omega \\ \hbar \Omega & E_{2}^{k} \end{pmatrix}, \quad V^{kk'} = \begin{pmatrix} V_{11}^{kk'} & 0 \\ 0 & V_{22}^{kk'} \end{pmatrix} \]

thus electrons can tunnel from the state \( |1k\rangle \) by means of the \( \hbar \Omega \) term to a virtual intermediate state \( |2k\rangle \) and then scatter to the final state \( |2k'\rangle \) using an intrawell relaxation process \( V^{kk'} \). Analogously to what was done in the last section, the evolution of the system can then be written for the components of the density matrix. In this case, since only elastic scattering has been considered, we can separate the evolution of the diagonal and non-diagonal terms and once solved for the stationary state the
current density can be derived as:

\[ j = \frac{2q_0n_s d|\hbar \Omega|^2}{\hbar} \sum_k \gamma^k_i (f^{k}_{11} - f^{q+}_{22}) + (\gamma^k_i (f^{q-}_{11} - f^{k}_{22}) \right) + (\gamma^k (\gamma^k + \gamma^k)^2) + (\gamma^{k+})^{2} \]

(2.24)

where \( q^\pm = h^{-1} \sqrt{2m^*(E_k \pm \hbar \Delta)} \) is the in-plane momentum of the final state, \( d = z_{11} - z_{22} \) is the spatial separation between the centroids of the wavefunctions and \( \gamma^k_i \) is the scattering induced broadening of the state \( i \) at the wave vector \( k \). The carrier distributions at the wave vector \( k \), in the subbands \( i \), are \( f^{k}_{ii} \) and are obtained as steady-state values of the diagonal terms of the density matrix, through a Laplace limit (71).

From the previous equation, a possible formulation of the Kazarinov and Suris current expression can be retrieved, if \( q^\pm \) is set equal to \( k \) and if a constant broadening \( \gamma \) is assumed:

\[ j = \frac{2q_0n_s d|\hbar \Omega|^2}{\hbar} \frac{2\gamma(n_2 - n_1)}{(\hbar \Delta)^2 + (2\gamma)^2} \]

(2.25)

An easier expression for (2.24) can be obtained, that still accounts for the second-order component of the current, if we consider that the low electron density is classically distributed in each subband with the same electronic temperature and that an uniform scattering potential can be considered, resulting in a constant broadening \( \gamma \):

\[ j = \frac{q_0n_s d|\hbar \Omega|^2}{\hbar} \frac{2\gamma}{(\hbar \Delta)^2 + (2\gamma)^2} \left( \theta(\Delta)(n_2 - e^{-\beta \hbar |\Delta|} n_1) + \theta(-\Delta)(n_2 e^{-\beta \hbar |\Delta|} - n_1) \right) \]

(2.26)

where the \( \delta(x) \) is the Heaviside function, with \( \Delta(x^-) = 0, \Delta(x^+) = 1 \) and \( \Delta(0) = 1/2, \beta = 1/kT \). As we can see in the equation (2.26), the current density is driven by an effective population difference term. The presence of this term is not only responsible for the typical dispersive shape of the current, in the case of equally populated subbands (69) important in the case of Bloch gain analysis, but explains also the asymmetry of the current as function of the detuning in the case where one of the two subband is empty. As shown already by Terazzi et al (70), this component of the current in QCLs is not negligible and should be taken into account in the modeling.
2.4 Scattering processes

Treating electron dynamics up to this point, the physical nature of the scattering processes hasn’t been yet analyzed. In this section the most relevant scattering processes for quantum cascade lasers will be introduced based on the model developed by Unuma et al (72). Particular attention will be given to interface roughness scattering, considered one of the most relevant scattering processes for Mid-IR QCLs.

The general theory of the intersubband absorption was firstly formulated by Ando et al (73, 74). Considering two subbands, and supposing all the electrons to be initially in the ground state, the inter-subband and intra-subband broadening can be then written as:

\[
\Gamma_{\text{intra}}(E) = 2\pi \sum_{k'} |\langle 0 k' | H_1 | 0 k \rangle - (1 k' | H_1 | 1 k) |^2 \delta[\epsilon(k) - \epsilon(k')]_{\epsilon(k)=E} \tag{2.27}
\]

\[
\Gamma_{\text{inter}}(E) = 2\pi \sum_{k'} |\langle 0 k' | H_1 | 1 k \rangle |^2 \delta[\epsilon(k) - \epsilon(k') + E_{10}]_{\epsilon(k)=E} \tag{2.28}
\]

where \(E_{10}\) is the intersubband energy separation, \(\epsilon(k) = \hbar^2 k^2/2m^*\), and \(m^*\) is the electron effective mass and \(H_1\) is the Hamiltonian of the scattering process. The \(\langle \ldots \rangle\) denotes the average on the distribution of scatterers.

Considering the most important causes of scattering in the case of intersubband transitions: interface roughness (IFR), LO phonons (LO), alloy disorder (AD) and ionized impurities (ION), the total broadening will simply be given by:

\[
\Gamma^{\text{TOT}}_{\text{intra}}(E) = \Gamma^{\text{IFR}}_{\text{intra}}(E) + \Gamma^{\text{LO}}_{\text{intra}}(E) + \Gamma^{\text{AD}}_{\text{intra}}(E) + \Gamma^{\text{ION}}_{\text{intra}}(E) \tag{2.29}
\]

\[
\Gamma^{\text{TOT}}_{\text{inter}}(E) = \Gamma^{\text{IFR}}_{\text{inter}}(E) + \Gamma^{\text{LO}}_{\text{inter}}(E) + \Gamma^{\text{AD}}_{\text{inter}}(E) + \Gamma^{\text{ION}}_{\text{inter}}(E) \tag{2.30}
\]

In the next subsections, the broadening calculation for each of these scattering mechanisms will be explored.
2. QUANTUM CASCADE LASERS: MODELLING

2.4.1 Interface Roughness

In order to give a statistical description of the fluctuations in the epitaxial layers widths, we introduce a Gaussian distribution for the roughness height:

\[ \langle \Delta(r)\Delta(r') \rangle = \Delta^2 \exp\left(-\frac{|r-r'|^2}{\Lambda^2}\right) \]  

(2.31)

where \( \Delta \) is the mean height of the roughness and \( \Lambda \) is the correlation length. The scattering matrix element between the initial state in the band \( m \), with momentum \( k' \), to the band \( n \) and a momentum \( k \) is:

\[ \langle mk' | H_1 | nk \rangle = \int d^2r F_{nm} \Delta(r) e^{iq \cdot r} \]  

(2.32)

with \( F_{nm} \) being:

\[ F_{nm} = V_0 \psi_m(-L/2)\psi_n(-L/2) \]  

(2.33)

proportional to the wavefunction at the material interface \((-L/2)\).

Since the interface roughness is equivalent to local fluctuation in well width, the previous equation can be equivalently written as:

\[ F_{nm} = \sqrt{\frac{\partial E_m}{E_m} \frac{\partial E_n}{E_n}} \]  

(2.34)

In the case of an infinite barrier the previous expression is proportional to \( L^{-3} \). Substituting (2.34) in to the (2.27), we find:

\[ \Gamma_{FR_{\text{intra}}}(E) = m^* \Delta^2 \Lambda^2 \left( F_{00} - F_{11} \right)^2 \int_0^\pi d\theta e^{-q^2 \Lambda^2/4} \]  

(2.35)

\[ \Gamma_{FR_{\text{inter}}}(E) = m^* \Delta^2 \Lambda^2 F_{01}^2 \int_0^\pi d\theta e^{-q^2 \Lambda^2/4} \]  

(2.36)
where the scattering vectors \( q \) and \( \tilde{q} \) are given by:

\[
q^2 = 2k^2(1 - \cos \theta) \tag{2.37}
\]
\[
\tilde{q}^2 = 2k^2 + \frac{2m^*E_{10}}{\hbar^2} - 2k \sqrt{k^2 + \frac{2m^*E_{10}}{\hbar^2} \cos \theta} \tag{2.38}
\]

It is important to mention that even though the equations (2.35) have some similarities, e.g. are both proportional to \( \Delta^2 \) and to \( \Lambda^2 \) for small \( \Lambda \), the term \( \Gamma_{\text{IF R}}^{\text{intra}} \) diverges in the case of large \( \Lambda \). In fact while its prefactor grows as \( \Lambda^2 \), the integral decreases only as \( \Lambda \). This result is obviously unphysical and does show the failure of this model to predict the intrasubband broadening in the case of long correlation lengths. This topic will be analyzed in a more detailed fashion in the fourth chapter, with particular focus on the effect of epitaxial growth temperature on the interface roughness and consequently on laser performance.

### 2.4.2 Alloy disorder

When the epitaxial layers are composed by a ternary material \( A_xB_{1-x}C \) such as \( \text{In}_x\text{Ga}_{1-x}\text{As} \) and \( \text{In}_x\text{Al}_{1-x}\text{As} \), electrons can be scattered by variations in the alloy composition that involve fluctuation in the conduction band offset.

The scattering element in this case can be written as (72):

\[
\langle mk' \mid H_1 \mid nk \rangle = \frac{a^3(\delta E_c)^2x(1-x)}{4} \int dz (\psi_{m}(z)\psi_{n}(z))^2 \tag{2.39}
\]

where \( a \) is the lattice constant and \( \delta E_c \) is the difference in conduction band minima for the binary compounds AC and BC. Substituting (2.39) into (2.27), it is possible to obtain the broadening relative to alloy disorder as done previously in the case of interface roughness.

The alloy disorder can indeed be seen as a kind of roughness scattering. In fact, while interface roughness leads to a broadening of energy levels, due to fluctuations in the grown quantum well widths, in a similar way alloy disorder introduces variations in the quantum well heights, therefore also inducing a broadening of the energy levels.
2. QUANTUM CASCADE LASERS: MODELLING

2.4.3 Ionized impurities

In quantum cascade laser Si doping is generally inserted in the structure to control the electron density. When the dopant atoms are ionized, the electrons can be scattered by their Coulomb potential. The scattering element due to an impurity placed at the position $Z$ is given by:

\[
\langle mk' | H_1 | nk \rangle = \frac{e^2}{2\epsilon_0 k_0 q} \int dz (\psi_m(z) \psi_n(z)) e^{-q|z-Z|}
\]  

(2.40)

It is important to mention that even if impurity scattering is the crucial factor limiting the low temperature mobility, in the case of quantum cascade lasers in the Mid-IR it has a limited impact due to the low doping levels, high electron energies and the high operational temperature.

2.4.4 LO-Phonons

Optical phonon scattering is surely the most efficient scattering mechanism when the energy separation between the subbands is bigger than the one of a phonon. As phonons are vibrational waves they have a two fold effect on the structure potential. They tend to on one hand to induce a deformation potential due to the displacement of the atoms. At the other hand, they generate also a piezoelectric potential. If the latter term is dominant and the optical phonons can be assumed monoenergetic, the approach developed by Price et al (75) can be used. The scattering rate can then be written as:

\[
\langle mk' | H_1 | nk \rangle = \frac{m^* e^2 \omega_{LO}}{2\hbar \epsilon_p} \int d\theta \left( \frac{I^{mn}(Q)}{Q} \right)
\]

(2.41)

\[
I^{mn} = \int dz \int dz' \psi_m(z) \psi_n(z)e^{-Q|z-z'|} \psi_n(z') \psi_m(z')
\]

(2.42)

where $\epsilon_p^{-1} = \epsilon_{\infty}^{-1} - \epsilon_s^{-1}$ and $\epsilon_{\infty}$ and $\epsilon_s$ are the high frequency and static dielectric functions and $Q$ is the wavevector of the emitted optical phonon:

\[
Q = \sqrt{k_m^2 + k_n^2 - 2k_mk_n \cos \theta} \quad k_f^2 = k_i^2 + \frac{2m^*}{\hbar^2} (E_i - E_f - \hbar \omega_{LO})
\]

(2.43)
2.5 Full Model

In this chapter a survey of some of the transport models in quantum cascade laser, together with a brief introduction of the scattering mechanisms was given in order to introduce the model, developed in our group \((6, 67)\), that has been used in this work in order to predict laser behavior.

As mentioned, the scattering processes considered in the computation are:

- LO-phonon scattering
- Interface roughness
- Alloy disorder
- Impurity scattering

Figure 2.4: LO-phonon emission, with a wavevector \(Q\), between a the state \(i = \mid m k \rangle\) and \(f = \mid n k \rangle\). LA-emission scattering process is also shown in the upper subband.

2.4.5 LA-Phonons

Interaction of the electrons with the LA-phonons can be calculated using a deformation potential approximation for details see \((76)\). Due to the inefficiency of these processes it has a marginal effect in mid-IR quantum cascade lasers and it is not included in the transport model used in this work.
LA-phonon scattering and electron-electron scattering have not yet been implemented, but in the case of Mid-IR quantum cascade lasers at high temperature, they both seem to have a marginal effect.

This model stands halfway between a full quantum such mechanical model and a simple scattering model. In fact, it can predict typical quantum mechanical effects as second-order tunneling current and Bloch gain, while it maintains the computational lightness necessary to perform fast and effective design optimization. In order to do that this model combines the use of a simple rate equation model to compute the scattering inside a local base, but the transport between different bases is modeled using sequential resonant tunneling (Fig. 2.5).

![Figure 2.5: Full model: local bases are defined inside the active region and inside each base scattering is computed using a rate equation approach while transport between different basis is computed using sequential resonant tunneling. In the structure presented in figure, the basis is constituted by the fundamental period.](image)

### 2.5.1 Basis-selection

As mentioned already, the model allows the arbitrary definition of different local basis inside the fundamental laser period. The number of different basis in each period can be varied accordingly to the structure design. As an example, while in Fig. 2.5 the base coincides with the fundamental period, in the laser design, shown in the Fig. 2.6, a clear extraction barrier can be observed and consequently the basis should be divided into two basis. The first one is constituted by the active region zone where the lower lasing
state is depopulated using a double phonon resonance, the second base is constituted by the injector region.

![Energy band diagram of QCL design based on a double-phonon resonance](image)

**Figure 2.6**: Energy band diagram of QCL design based on a double-phonon resonance, since the structure presents a clear thicker extraction barrier the fundamental period is divided in two zones: active region and injector region. Sequential resonant tunneling is used to compute the transport across the injector and extraction barrier.

### 2.5.2 Model input parameters and outputs:

As already mentioned, the model analyzed in this chapter is able to predict not only the electron transport, i.e. voltage-current characteristic, but also the laser performance, i.e. light-current characteristic. In particular, it is important to stress that the model does not comport any fitting parameters and that therefore has unique predictive capabilities. It is nevertheless true, that some of the parameters connected to the scattering processes, e.g. interface roughness correlation length, are difficult to be directly measured.

In order to fix the parameters that could not be measured directly, the model predictions over a large amount of active region designs in different spectral ranges where observed and these parameters were adjusted in order to obtain the best agreement, in a model validation phase. An example of that will be shown in the case of the interface roughness in the next chapters. After the model validation was performed
these parameters are kept constant and are not used as fitting parameters in order to obtain a better agreement for each structure. Even though the model does not need any fitting parameter, it does predict the absolute values for the current or the optical power emitted by the device. For this reason, since these quantities do not only depend on the active region design but also on the laser fabrication process and on the laser dimensions, the only input parameters that need to be inserted in the model each time we run a new simulation are:

- mirror losses
- waveguide losses
- laser ridge width

The first and last ones are simply related to the geometry of the actual device, i.e. length, width and facet reflectivities. Concerning waveguide losses, they can be measured in different ways; one of the simpler and mostly used technique is the measurement of the variation of the threshold current as function of the device length (1/L measurement). Even if this measurement leads to high relative errors, it provides a preliminary and fast approximation of the waveguide losses that can be used as a starting point for the structure simulations.

### 2.5.2.1 1/L measurement

This measurement technique is based on simplest expression for the threshold condition in a laser:

\[
\alpha_m + \alpha_w = J_{th} g \Gamma \tag{2.44}
\]

where \( g \) is the differential gain of the structure, \( \Gamma \) is the 2D overlap factor of the optical mode with the active region and \( \alpha_m \) are the total mirror losses, that can be written as:

\[
\alpha_m = \frac{- \ln R_1 R_2}{L} \tag{2.45}
\]

where \( R_1 \) and \( R_2 \) are the reflectivity at the laser facets. Using a linear fit of the threshold current density as function of the inverse length of the devices, the differential gain and
the waveguide losses can then be measured:

\[ J_{th} = -\ln \frac{R_1 R_2}{1 - \Gamma} \left( \frac{\alpha_w}{q\Gamma} \right) + \frac{\alpha_w}{q\Gamma} \]  

(2.46)

### 2.5.2.2 Waveguide losses

Waveguide losses in a quantum cascade laser have a crucial impact on the laser performance. For this reason, the goal of this subsection will be to analyze in deeper details their physical origin.

The waveguide losses (\(\alpha_w\)) can be written as:

\[ \alpha_w = \Gamma \alpha_{nonres} + (1 - \Gamma - \Gamma_{lossy}) \alpha_{FC} + \alpha_{lossy} \Gamma_{lossy} + \alpha_{scat} + \alpha_{BF} \]  

(2.47)

- The *non resonant* losses (\(\alpha_{nonres}\)) include the losses due to the absorption spectrum of the active region structure for all the energies but the lasing one. Contributions to these losses come mainly from the absorption between states inside the injector region for small energies and to the continuum of states above the injector region for higher energies.

- The *free carrier* losses (\(\alpha_{FC}\)) are due to the presence of doped cladding layers above and below the active region stack. In order to minimize these losses, the cladding doping is generally reduced in proximity of the active medium, where the optical mode intensity is still relevant.

- The *absorption in the lossy layers* term (\(\alpha_{lossy}\)) accounts for the losses induced by lossy insulating layers and metallic layers in the top of the waveguide. In the case of QC lasers processed in a ridge configuration, as will be described in section 3.2.1, the overlap of the optical mode with the metallic layer is practically irrelevant. On the contrary the insulating layers, of SiN or SiO\(_2\), deposited on the ridge side walls contribute sensibly to the total waveguide losses. There are different ways of reducing these losses, e.g. by engineering the waveguide design as described in the section 7.3.3 or by the use of a buried heterostructure process, described in section 3.2.2 (*standard buried*) and 3.2.3 (*inverted buried*). As we
2. QUANTUM CASCADE LASERS: MODELLING

will see, the former one reduces the overlap of the mode with the insulating layers, while the second one does completely remove the insulating layers.

- The scattering losses ($\alpha_{\text{scat}}$) are due to light-scattering processes inside the cavity, e.g. side walls roughness, and are completely dependent of the actual fabrication process and their minimization plays a crucial role in the development of high performance lasers in the Mid-IR.

- The back-filling ($\alpha_{\text{BF}}$) losses term is due to the thermally activated back-filling of carriers from the injector states to the lower lasing state of the lasing transition that lowers the population inversion. It can be expressed as:

$$\alpha_{\text{BF}} = n_s \exp\left(-\frac{\Delta_{\text{inj}}}{k_B T}\right)$$

where $n_s$ is the sheet carrier density and $\Delta_{\text{inj}}$ is the injector’s quasi-Fermi energy.

In the previous subsection we have see that the total waveguide losses can be estimated through the variation of the threshold current as function of mirror losses. If one is only interested in the total optical losses, neglecting the thermal back-filling, a similar technique can be used. The ratio of slope efficiency between an uncoated device and the same device after the application of a facet back HR coating. In that case the total optical losses can be written as (49):

$$\alpha_{\text{opt}} = \frac{-2 \ln R_u + \ln R_u R_c \cdot \eta_{u/c}}{2L(\eta_{u/c} - 1)}$$

where $\eta_{u/c}$ is the ratio of the slope efficiency between the coated and uncoated device.
It is important to mention that some authors (e.g. (49)) use a different notation concerning the losses, defining the threshold current as:

\[ J_{th} = \frac{\alpha_m + \alpha_w}{g_c \Gamma} + J_{tr} \]  

(2.50)

where the term \( J_{tr} \), denoted as transparency current, includes the non radiative losses inside the active region, while the \( \alpha_w \) are not anymore the total waveguide losses but only the waveguide losses external to the active region.
2. QUANTUM CASCADE LASERS: MODELLING

1
Chapter 3

Processing

In the previous chapter, the basic theory of intersubband transition and in particular of quantum cascade lasers has been discussed. In the following sections, the methodology toward the actual realization of high performance Mid-IR QCL devices is presented.

Particular attention will be drawn to the fabrication of buried heterostructure (BH) quantum cascade lasers. After introducing the standard BH process, the implementation of a simplified BH process will be shown. In addition to a sensible reduction in the number of fabrication steps, this process shows also a diminished amount of crystal defects originated from the burying regrowth steps and a more uniform current injection in the structure.

In the final sections the optimization of dry etching technique for highly anisotropic structures will be presented. In describing the dry etching process optimization, particular attention will be given to the use the use of the orthogonal arrays design for process optimization (77, 78). This technique is of general interest and can be used for the optimization of any process step with multiple variables and merit factors in order to reduce the number of necessary test runs.

3.1 Introduction

For the fabrication of the QCLs analyzed in this work, two different epitaxial techniques were used.
3. PROCESSING

The active region sequences are growth by molecular beam epitaxy (MBE), while laser claddings layers and the insulating burying layers were grown by metalorganic vapor phase epitaxy (MOVPE). Both the equipments are located in the FIRST Center for Micro- and Nano-technology of the Swiss Federal Institute of Technology (ETH) in Zürich, where also all the other fabrication steps are performed.

The MBE samples were grown by Dr. Mattias Beck and Mr. Milan Fischer using a solid-source MBE (V80H) from VG Semicon, dedicated to growth of mid-IR and Far-IR quantum cascade lasers structures on InP and GaAs substrates.

The MOVPE growths were performed by Dr. Emilio Gini and Mr. Martin Ebnöther.

3.2 Sample processing

Since the first demonstration of a room temperature Mid-IR quantum cascade laser operating in continuous wave, it has been clear that laser performance are not only influenced by a proper active region design engineering but they are strongly affected by the thermal properties and the optical losses introduced by the fabrication process.

In this section the most used laser fabrication processes, for Mid-IR QCLs, will be described.

3.2.1 Ridge process

The ridge process (Fig. 3.1) is traditionally considered the most simple and most used process in Mid-IR QCLs. Unfortunately, due to its low thermal conductance and high optical losses, it is not well suited for high power, continuous wave lasers. Since most of the optical losses take place at the ridge sidewalls, by the use of wide ridges, the influence of the optical losses on the laser performance can be mitigated at the price of an even lower thermal conductance, in this way high peak power can be obtained in pulsed operation using low duty cycle pulses.

The principal steps of this process are the following:

(a) after MBE growth of the active region structure, the samples are transferred to the MOVPE and the cladding planar regrowth is performed (b), then a layer of SiO₂ is deposited by Plasma Enhanced Vapor Deposition (PECVD) as an hard masking layer (c). Using a thin photoresist and standard UV photolithography, the patterning of the
laser waveguides is defined (d) and the pattern is then transferred to the SiO$_2$ layer by Reactive Ion Etching (RIE), using a Ar/CHF$_3$ chemistry (e) and the resist layer is then stripped away. In order to remove polymer residuals an O$_2$ plasma process is then performed (f) [79]. The use of an hard masking layer is necessary due to the incompatibility of the used InP etching solution, HCl-based, with standard soft masking layers (resist). A strongly anisotropic HCl:CH$_3$COOH (1:3) solution is used for InP etching, in order to obtain vertical sidewalls and reduce the undercutting (g).

The active region is then etched using an isotropic HBr:HNO$_3$:H$_2$O (1:1:10) (h) solution. Being the latter nearly uniform for all the the etched materials (InP, AlInAs, InGaAs) a smooth surface is obtained after etching. Unfortunately, due to the isotropic behavior of the used solution, the etched structures show an undercut larger than the vertical etching depth ($\text{undercut} \sim 1.2 \times \text{etch depth}$).

Once the etching of the active stack is performed the hard mask layer is removed by HF etching and an insulating layer is deposited by PECVD on the etched structure (i). The relevant overlap of the optical mode with this layer is one of the most important sources of optical losses in this waveguide configuration, therefore in order to minimize the losses Silicon Dioxide or Silicon Nitride are used as insulation materials, depending on the laser spectral range. Using optical lithography and RIE etching the insulating layer is opened on the ridge head. An ohmic contact is then deposited (Ti/Pt/Au, 5 nm/40 nm/100 nm) by e-beam evaporation on the opening using standard lift-off (k). Finally electroplated gold pads is deposited (m) and the substrates are thinned to $\sim 150\mu$m in order to reduce thermal resistance. Back ohmic contact are finally deposited on the wafer bottom side (Ge/Au/Ni/Au, 15 nm/50 nm/10 nm/150 nm) (n).

### 3.2.2 Buried process

In the case of standard buried heterostructure design (Fig. 3.2), processing steps up to the active region wet etching (a)-(h), are identical to the ridge process.

After that, an insulating InP layer (Fe doped) is grown using selective regrowth in MOVPE on the side of the etched structure. The etching mask, SiO$_2$, is also used as the masking material for the selective regrowth step. After stripping the masking layer, by HF etching, an SiN insulating layer is then deposited using PECVD (j). In
3. PROCESSING

Figure 3.1: Process flow for the standard heterostructure process in Mid-IR QCLs.

In this case, since the optical mode is far from the insulating layer, its influence on the waveguide losses is irrelevant and consequently only SiN is used due to its slightly higher thermal conductance compared to SiO$_2$. Steps between (j)-(p) are analogous to the ridge process.

As already mentioned, using the buried heterostructure process Beck et al. (47) obtained the first room temperature, continuous wave quantum cascade laser in the Mid-IR. This result can be attributed to the low absorption coefficient and the high thermal conductance of Fe-doped InP compared to SiN and SiO$_2$. This process has
3.2 Sample processing

Figure 3.2: Process flow for the standard buried heterostructure fabrication in Mid-IR QCLs.

nevertheless some important drawbacks that this limit laser performance.

Firstly, due to the high total etch depth (active region + cladding), wet etching generates a big undercut in the structures and consequently, a highly not uniform active region width is observed along the vertical direction \(\text{undercut} \sim 1.2 \times \text{etch depth}\), leading to pumping inhomogeneities in the different active region periods (see Fig. 3.1). Moreover the thick selective regrowth step, needed to planarize (i), tends also to favor the creation of InP spikes. Due to their high surface volume ratio, the growth rate of
3. PROCESSING

these defects is much higher and structures as high as 10-20 µm can be observed. In some cases, an additional photolithographic and etching steps are needed in order to regain the planarity of the structure. In addition thermal conductance of the fabricated devices, even though much higher than in the case of a normal ridge process, is still limited by the SiN insulating layer that acts also as a thermal barrier between the laser cladding and the gold layer. This effect is particularly relevant in the case of devices mounted epide-side-down.

3.2.3 Inverted buried

Starting from an idea of Dr. Beck, a modified buried heterostructure process was developed in this work, in order to overcome the limitations of a standard buried process and at the same time reduce the total number of steps in the buried process making it easier and faster.

As shown in Fig. 3.3, after the MBE active region growth (a), a SiO$_2$ is deposited by PECVD as a masking layer (b), and, after the waveguide patterning (c) and after RIE etching (d) and O$_2$ plasma for resist stripping (e), the active region layers are etched using the HBr:HNO$_3$:H$_2$O solution. Differently from standard buried heterostructure process, in this case the total etching depth is constituted only by the active region and is generally between 2 – 3 µm instead of 5 – 7 µm.

After the etching, the structure is planarized using selective growth of InP:Fe in MOVPE. After the SiO$_2$ layer is removed and only then the n-doped InP cladding is grown over all the structure (h). An Ohmic contact is then deposited over all the structures with no additional lithographic step (i). Electroplating, lapping and backcontacting are then performed as for the standard buried process.

In conclusion in this modified version of the buried heterostructure process, the active region etching is performed before the cladding regrowth and the sequence of the two epitaxial regrowths is inverted resulting in a much thinner InP:Fe regrowth. For this reason in the following section we will refer to this process as the inverted buried process. Moreover the total number of process steps and in particular of optical lithographies is reduced to a maximum of three resulting in a easier and faster process.
3.2 Sample processing

Figure 3.3: Process flow for the inverted buried heterostructure process in Mid-IR QCLs.

3.2.4 Advantages

The effect of the smaller etching depth in active region profile is clearly showed in Fig. 3.1 were the waveguide profile is shown both for the standard and the modified buried process. In the left panel the waveguide profile obtained using the standard buried process is shown. Between the top and the bottom of the active region stack, a difference in the waveguide width $\Delta w \sim 5 \, \mu m$ is observed for an etching depth of $\sim 4 \, \mu m$ ($\Delta w \sim 1.2 \times (etch\ depth)$) as described for the standard ridge process. In the case of the inverted buried process (right panel) a $\Delta w \sim 1.5\mu m$ for a $\sim 2.8\mu m$ etching depth, resulting in $\Delta w \sim 0.5 \times (etch\ depth)$.

As mentioned above, another advantage of a thinner regrowth is the reduced amount of defects due to the selective growth of insulating InP. In the Fig. 3.2, we present as a comparison the optical image of the top of the laser ridges for the two kinds of processes.
3. PROCESSING

Table 3.1: SEM images of front facet of lasers fabricated with the standard buried heterostructure (left panel) and the inverted buried (right panel) processes. The sample produced using the inverted buried process shows a higher etching uniformity.

In the left panel the ridges are clearly recognizable even after planarization and InP crystallites can be observed on the side of the laser ridge. In the right panel, for the inverted buried process, a red rectangle was drawn in order to guide the eye to the top of the buried laser ridge that is not anymore clearly visible after the planarization.

Table 3.2: SEM images of top of lasers fabricated with the standard buried heterostructure (left panel) and the inverted buried (right panel) processes.

3.3 InP doping calibration: Iron and Silicon

It is clear that, in order to fabricate QCLs in BH configuration, an accurate control of the doping concentration is needed, both for the insulating (Iron doped) and the conductive layers (Silicon doped).

In order to characterize the Si- and Fe- doping concentration in the layers grown a
Capacitance-Voltage measurement (CV) was performed using a commercial instrument (CVP21).

CV profiling technique is a well reliable technique used to analyze the doping profiles in semiconductor devices. Using a Schottky barrier at the semiconductor interface, a depletion region is created and due to the ionized charges it behaves as a capacitor. By varying the voltage applied, the depletion width is modified and the surface doping concentrations can be determined. By the use of a shallow progressive etching (HCl 0.1 M), the doping profile across the all growth sequence is measured.

A test structure is grown periodically, generally twice in a year, by MOVPE to control doping levels. In table 3.3 the growth sequence, of a typical test structure, with the expected doping levels is shown. The growth is started using a nominal Si doping of $1.2 \times 10^{17} \text{ cm}^{-3}$ and a nominal Fe doping of $4 \times 10^{16} \text{ cm}^{-3}$.

In the second layer the Fe-level is lowered to $8 \times 10^{15} \text{ cm}^{-3}$, while the Si doping is kept constant. Finally in the last layer, only Si is used for doping($1.2 \times 10^{17} \text{ cm}^{-3}$) and no Iron is incorporated. The structure is grown on an heavily Sulfur doped InP substrate($4 \times 10^{18} \text{ cm}^{-3}$).

An example of the measured doping profile is presented in Fig. 3.4. From the layer III, one can see that the silicon doping is actually slightly higher($1.65 \times 10^{17}$) that the expected value.

Using the levels I and II, then also the Iron level is measured and found to be also higher than expected, e.g. in the layer III the value is $5.5 \times 10^{16}$ instead of $4 \times 10^{16}$. Using these values the gas fluxes can be periodically recalibrated.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness</th>
<th>Si concentration</th>
<th>Iron Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>InP</td>
<td>410 nm</td>
<td>$1.2 \times 10^{17}$</td>
</tr>
<tr>
<td>II</td>
<td>InP</td>
<td>410 nm</td>
<td>$1.2 \times 10^{17}$</td>
</tr>
<tr>
<td>III</td>
<td>InP</td>
<td>410 nm</td>
<td>$1.2 \times 10^{17}$</td>
</tr>
</tbody>
</table>

3.4 Dry etching optimization

In the previous sections we pointed out that by the use of the inverted BH process, the undercut of the etched structures could be strongly reduced. Nevertheless in the case of strongly anisotropic structures, plasma etching techniques are beneficial in order to obtain vertical sidewalls. Wet-etching techniques still have considerable advantages,
3. PROCESSING

![Graph showing n-doping profile](image)

**Figure 3.4:** n-doping profile of a test structure grown in the doping calibrations.

principally in terms of side walls roughness, and after dry-etching an additional shallow wet-etching process is always beneficial.

An Inductively Coupled Plasma system (OXFORD Intruments ICP 180) was used (80, 81) for the dry etching. In order to obtain the best results on InP-based materials, Cl₂ and CH₄ were used as the etching gases. In fact, even though fast and smooth etching can be obtained on GaAs using only Cl₂ based chemistries, in the case of In-based materials the etching efficiency is strongly limited by the low volatility of the InClₓ layer formed on the exposed surface during the etching process (82).

To overcome this problem, methane can be used as an additional etching gas, since the In(CH₃)ₓ-compounds have a much higher volatility. One of the main drawbacks in using the CH₄ is its tendency to deposit polymers on the surface. If not removed these polymers will eventually stop the etching process. For this reason, in the etching processes discussed in this work, the etching steps are kept smaller than 2 µm and in the case thicker etchings are necessary they are interlayered with O₂ plasma etching steps. Never the less the number on the interruptions in the etching process has to be kept also low, since it tends to enhance the sidewalls roughness.
3.4 Dry etching optimization

In order to minimize the polymer production, high sample temperature has to be maintained during the etching process, either through the use of high power plasmas or through sample heating.

Using this plasma chemistry, methane acts as the main etching gas and, while chlorine act also as a secondary etching gas, but its main role is the sidewalls passivation, in order to reduce structure undercut.

Higher \( \frac{Cl_2}{CH_4} \) ratios reduce the structure undercut but increase the polymer deposition eventually stopping the etching process. The etch rate is both dependent on the ICP and the RIE power, but for too high RIE powers the etching selectivity toward the hard mask is affected. Another important parameter in the optimization of a plasma process is the amount of neutral gases in the plasma (83). Neutral gases, as Ar and H\(_2\), inside the process help not only to produce an high density plasma, but also to enhance the desorption of the etch products by to physical etching.

From the previous arguments, it appears clear that the number of parameters influencing the quality of the etch process is relatively large, e.g.:

- RIE power
- ICP power
- Etching gases fluxes
- Neutral gases fluxes
- Chamber pressure
- Sample temperature

All these parameters have an impact on the process outcome and no principal factor can easily be distinguished, moreover the effect of these parameters cannot be considered independent. In addition, no single merit factor can easily be identified to judge the dry etching quality. Therefore the optimization of the etching process requires the simultaneous adjustment of multiple, non independent variables and merit factors. For this reason, in order to minimize the number of necessary tests, an orthogonal array approach was used (77). The basic principles of this technique will be briefly introduced in the next paragraph.
3. PROCESSING

3.4.1 Orthogonal matrix approach

Supposing to have a system with a number \( m \) of variables and that each of these can assume \( l \) different values (levels) and that we want to find the best combination of the parameters in order to optimize the outcome.

The simplest method for process optimization is given by the one-dimensional search. In this case, all the parameters, except one, are fixed and, varying the remaining one, the level that corresponds to the best relative output is then selected and fixed. The second parameter is then varied until process is again maximized and then fixed. This procedure is repeated for all the parameters. This approach requires a number of tests equal to the product of the number of levels and the number of variables (\( m \times l \)).

This method as the advantage of being extremely easy to follow and, in the case of independent input parameters, it can lead to accurate results. Nevertheless, this process does completely fail in the case the different parameters have cross effects on each others. In order to include all the possible effects due to non-independent variables, a full dimensional search could be used as in the case of factorial designs (84).

Factorial designs were introduced for the first time by R.A. Fischer in 1920. In this case all the possible combinations of level setting are analyzed for all the input parameters. Unfortunately, the number of tests necessary in this method is \( l^m \) and the application of a full factorial model for a more than two variables is generally discarded.

In order to overcome this problem, Dr. Genicchi Tagushi in 1950 developed a new kind of fractional factorial design. Based on orthogonal matrices, this method permitted to perform accurate process optimization, with a number of tests much smaller then the two methods above discussed. In fact instead of testing all the possible combinations, orthogonal designs uses just certain representative combinations. The relevant combinations to be tested are defined to form a basis of orthogonal arrays. These can be derived using linear algebra (85) or found in literature. (depending on the number of input parameters and number of levels of each parameter a different orthogonal matrix has to be used ( as listed in the Table 3.3). For example if the process to be optimized has 4 distinct variables (\( A, B, C, D \)) with three possible levels (1, 2, 3) the matrix \( L_4 \) (shown in Table 3.4) has to be used: We can see that in this
3.4 Dry etching optimization

<table>
<thead>
<tr>
<th>Number of parameters</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>L₄</td>
<td>L₄</td>
<td>L₈</td>
<td>L₈</td>
</tr>
<tr>
<td>3</td>
<td>L₉</td>
<td>L₉</td>
<td>L₉</td>
<td>L₁₈</td>
</tr>
<tr>
<td>4</td>
<td>L₂₅</td>
<td>L₂₅</td>
<td>L₂₅</td>
<td>L₂₅</td>
</tr>
</tbody>
</table>

Table 3.3: List of the orthogonal matrices to be used as function of the number of parameters and levels.

<table>
<thead>
<tr>
<th>Variables</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>III</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>IV</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>V</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>VI</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>VII</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>VIII</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>IX</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.4: Application of the L₄ matrix to a problem where 4 variables (A, B, C, D) can be varied over 3 levels (1, 2, 3). In this case only 9 tests are necessary in order to fully characterize the system. In the first test all the parameters are kept at the 1 level setting, in the second one all a part from one are varied to the second level setting, etc.

case, only 9 experimental runs are necessary, instead of the 81 tests that would be needed in a full factorization analysis.

To understand the application of the orthogonal design approach in the case of the plasma etching, we can apply for example the matrix L₄ to the case of the ICP etching of a semiconductor, where the parameters of interest are the ICP power, RIE power, etching gas flux and chamber pressure. In this example each of these parameters has 3 possible levels as shown in Table 3.4.1 and the matrix L₄ can then be used in order to optimize this process.
3. PROCESSING

<table>
<thead>
<tr>
<th>Level setting</th>
<th>ICP Power</th>
<th>RIE Power</th>
<th>Chamber Pressure</th>
<th>Cl₂ flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1200 W</td>
<td>100 W</td>
<td>3 mTorr</td>
<td>6 sccm</td>
</tr>
<tr>
<td>2</td>
<td>1500 W</td>
<td>115 W</td>
<td>4 mTorr</td>
<td>7 sccm</td>
</tr>
<tr>
<td>3</td>
<td>1800 W</td>
<td>130 W</td>
<td>5 mTorr</td>
<td>8 sccm</td>
</tr>
</tbody>
</table>

Once defined the number of variables and levels to be optimized, the control parameters (merit factors) have to be defined. For example in the case of plasma etching InP etch rate and SiN to InP selectivity could be used to start. Additional merit factors could be the etching uniformity or the sidewalls slope and the sidewalls roughness.

As shown in Table. 3.4 the first parameter, i.e. in this case the ICP power is kept constant in the tests I-III, IV-VI and VII-IX. Averaging the results from these tests an average etching rate and selectivity as function of the ICP power can be defined as follows:

\[
E_{ICP}(1200 \text{ W}) = \frac{1}{3} (E_{test(I)} + E_{test(II)} + E_{test(III)})
\]
\[
E_{ICP}(1500 \text{ W}) = \frac{1}{3} (E_{test(IV)} + E_{test(V)} + E_{test(VI)})
\]
\[
E_{ICP}(1800 \text{ W}) = \frac{1}{3} (E_{test(VII)} + E_{test(VIII)} + E_{test(IX)})
\]
\[
S_{ICP}(1200 \text{ W}) = \frac{1}{3}(S_{test(I)} + S_{test(II)} + S_{test(III)})
\]
\[
S_{ICP}(1500 \text{ W}) = \frac{1}{3}(S_{test(IV)} + S_{test(V)} + S_{test(VI)})
\]
\[
S_{ICP}(1800 \text{ W}) = \frac{1}{3}(S_{test(VII)} + S_{test(VIII)} + S_{test(IX)})
\]

where \(E_{ICP}\) and \(S_{ICP}\) are the average etch rate and the selectivity as function of the ICP power. \(E_{test}\) and \(S_{test}\) are the etch rate and the selectivity for the different test runs.

In a similar manner, the etch rates and the selectivities as function of the other parameters can be found (RIE power and pressure and etching gases ratio). In order further clarify the method, the results obtained for the etch rate and the selectivity as function of the pressure in the chamber are plotted in Fig. 3.5 \((E_{pres}, S_{pres})\).

Examining the etch rates and the selectivities for all the others parameters we can optimize the process to obtain, for example, the highest selectivity and etch rate in the process.
3.4 Dry etching optimization

3.4.2 Optimized process for deep etching

In the previous section, we have described the method used in order to optimize the etching process. The actual optimized process was obtained by subsequent application of the mentioned technique in order to optimize also additional parameters, as for example the inert gas ratio.

Deep etching of InP/InGaAs/AlInAs

<table>
<thead>
<tr>
<th>Cl₂</th>
<th>Ar</th>
<th>CH₄</th>
<th>H₂ Pressure</th>
<th>ICP power</th>
<th>RIE Power</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>7 sccm</td>
<td>2 sccm</td>
<td>6 sccm</td>
<td>4mTorr</td>
<td>1800 W</td>
<td>120 W</td>
<td>60 °C</td>
</tr>
</tbody>
</table>

The final process shows an etch rate of 1.1 \( \mu \text{m/min} \) for InP and 0.8 \( \mu \text{m/min} \) for the active region stack (InGaAs/AlInAs). The hard mask etching is \( \sim 100 \text{ nm/min} \). The top view of a typical etched structure is shown in the Fig. 3.5. One can see that sidewalls roughness induced by the etching process is of the order of tens of nanometers.

3.4.3 Shallow etching process

In the previous section we presented the process used in the case deep structure etching are needed. In the case of shallow etching, less than 100nm, e.g. grating etching, a different etching process used. This process only uses Methane as an etching gas and in order to keep the etching rate low only the RIE power is used. The process parameter are listed in the table 3.4.3.
A side view of a shallow etching test is shown in Fig. 3.6 in which a \( \sim 40 \) nm grating is etched inside the semiconductor. The grating is defined by Deep-UV lithography and a SiO\(_2\) layer is used as hard masking layer.

<table>
<thead>
<tr>
<th>Cl(_2)</th>
<th>Ar</th>
<th>CH(_4)</th>
<th>H(_2) Pressure</th>
<th>ICP power</th>
<th>RIE Power</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 sccm</td>
<td>2 sccm</td>
<td>48 sccm</td>
<td>30 mTorr</td>
<td>0 W</td>
<td>250 W</td>
<td>30 °C</td>
</tr>
</tbody>
</table>
3.4 Dry etching optimization

Figure 3.6: Side-view of a shallow etching test, \( \sim 40 \text{ nm} \) on a grating structure defined using Deep-UV lithography. SiO\(_2\) hard masking layer is also shown.
3. PROCESSING
Chapter 4

Lattice matched quantum cascade lasers for wide tuning

In the previous chapters both the modeling and the device fabrication that lead to high performance QCLs in the MId-IR, have been analyzed.

In this chapter both these tools will be used for the development of widely tunable quantum cascade lasers in the second atmospheric window. As material system, InGaAs well and AlInAs barriers are used, both lattice matched to the InP substrate.

4.1 Electrical tuning in QCLs

We gave see in the introduction that tunable Mid-IR sources are highly desirable for many applications, e.g. free space communication, remote sensing and high resolution spectroscopy. For many of these purposes not only high power and good beam quality are required, but wide spectral tuning is also a key factor. Electrical tuning is the most direct and robust method to obtain spectral tunability and it permits tuning speeds much higher than in the case of temperature tuning.

Since the pioneering work of Kazarinov and Suris, it was noted that intersubband transitions between two states, with an energy distance of $E_{21}$, can be effectively tuned by a change of an electric field of value $\Delta F$ via a first-order Stark effect, with the tuning
4. LATTICE MATCHED QUANTUM CASCADE LASERS FOR WIDE TUNING

range being equal in a good approximation to

\[ \Delta E_{21} = (z_{22} - z_{11}) \Delta F q_0 \] (4.1)

where \( z_{22} \) and \( z_{11} \) are the expectation values of the position operator for the upper and lower states, respectively. This effect, small for vertical transitions, can be engineered to be high by the use of diagonal transitions in coupled quantum wells.

In quantum cascade lasers, a laser transition based on a pair of states characterized by a large value of \( z_{22} - z_{11} \) has also often been used, as it offers a large value of the upper state lifetime as well as an improvement of the injection efficiency. Wide tuning of the spontaneous emission from such structures was indeed observed(86, 87, 88, 89).

However, somewhat paradoxically, devices that exhibited the largest value of the static dipole showed little or no tuning above threshold. The reason is that in these devices, because of the combination of a very large ratio of upper to lower state lifetime and the absence of resonant tunneling injection, the transport above threshold was completely dominated by photon-assisted tunneling, driving the differential resistance to very low values and preventing the voltage tuning of the transition.

One of the used ways to overcome this problem is the use of multi-section laser cavities in which the different sections are differently biased (88).

In general, such a "locking" of the bandstructure above threshold is expected for devices that combine a large ratio of upper to lower state lifetime with an injector in the strong coupling regime. Since these features are also usually the ones implemented in devices with high efficiency, the capability of electrical tuning seemed incompatible with high performance operation. In ref (90), voltage tuning of almost 100 cm\(^{-1}\) was obtained using a structure based on an anticrossed diagonal transition. Unfortunately in that case, especially for low applied fields, reported results suffer from inherent leakage paths in the structure. Most likely they are due to electron escape from the coupling level in the last well of the injector, to the lower lasing states.

These do strongly limit laser performances, in particular threshold current.
4.2 Active region design for wide tuning

In this chapter we will see that, with a proper active region engineering, a large electrical tuning can be achieved without limiting the laser performance.

In order to obtain that, in addition to the large value of $z_{22} - z_{11}$, such a design should exhibit a large range of operating field $\delta F$ above threshold in order to limit the voltage locking that prevents tuning by first-order Stark effect.

As shown in Fig. 4.1, where the schematic band structure of the device is reported, the design is based on a bound-to-continuum scheme with a relatively short and wide miniband. Carriers are injected in the upper lasing state through a relatively short injector. The relatively broad linewidth of the laser transition combined with the presence of the last quantum well of the injector, thermally populated at low bias enables significant current injector even before the resonant bias.

The combination of short upper state lifetime ($\tau_7 \approx 40 fs$ at high optical fields) and relatively large relative dephasing between the injector state and the upper state of the laser transition(66) insures that the injector does not operate in the strong coupling

Figure 4.1: Conduction band diagram of a period of the active region at an average field of 60 kV/cm. The moduli squared of the relevant envelop wavefunctions are shown. Layer sequence is presented in the appendix A.1.1 (EV1140)
4. LATTICE MATCHED QUANTUM CASCADE LASERS FOR WIDE TUNING

regime($\Omega_c\tau_1^{1/2}/\tau_\perp^{1/2} \approx 0.2$).

A low active region doping and low waveguide losses minimize the threshold current and insure a large dynamical range. The above discussion assumed that the field would not be screened by the electron density in the active region. Such screening effects are kept to a low value through two key features: first, the use of a low doping in the active region, as well as a short active region period, insures that such screening field would be minimum. Moreover, as the difference between the upper and lower state population remains approximatively constant with applied field because of the locking of the gain to its threshold value, one expects such screening effect to remain very small. In contrast to that, some designs, such as photon-tunneling assisted ones (88), present a significant increase in the oscillator strength with applied field causing a very strong negative effect on the tuning, since in this case the upper state population is expected to decrease with applied field, creating an effective screening of the applied electrical field. The structure presented in this work has been simulated using the transport model introduced in the second chapter.

4.2.1 Process

The structure was grown by solid-source molecular beam epitaxy (MBE). In order to reduce the free carrier absorption inside the substrate the structure was grown on a low doped InP substrate (Si doping $2 \cdot 10^{16}$ cm$^{-3}$). Fifty periods of the active region(see A.1.1) were grown sandwiched in two InGaAs layer, 100nm thick, in order to improve the optical mode confinement. The lasers were processed using a the inverted buried process with ridge widths ranging between 6-9 $\mu$m. On the top of the InGaAs confinement layer a 4.4 $\mu$m thick InP cladding was grown by metallorganic-vapor-phase epitaxy(MOVPE). In order to provide a good electrical contact the growth was terminated by 80 nm of highly doped InGaAs ($3 \cdot 10^{19}$ cm$^{-3}$).

4.3 Spontaneous emission tuning

To measure the electroluminesce spectra (EL), short lasers (750 $\mu$m) were cleaved along the waveguide and light emission was measured orthogonally to the ridge using a Fourier-transform IR spectrometer and a cooled HgCdTe detector. Fig. 4.2 shows a
4.3 Spontaneous emission tuning

comparison between simulated and measured electroluminescence spectra for an applied field of 53 kV/cm.

As it can be seen, for this field, the spontaneous emission shows 3 relevant peaks. The first one, placed at 140 meV, can be attributed to the lasing transition (7)-(6), while the other two, respectively at 166 meV and 200 meV, are relative to the transition from the upper lasing state(7) to the two lower states(5),(4). A good agreement is shown between the simulated and measured curves also for the spontaneous emission. The

![Figure 4.2: Measured and simulated intersubband electroluminescence spectra for an applied field of 53 kV/cm. Peaks associated with the transitions (7)-(6), (7)-(5), (7)-(4) are labeled.](image)

model also predicts accurately the field dependence of these peaks, as shown in Fig. 4.3. The importance of the two latter peaks, relevant at low fields (40-55 kV/cm), decreases at higher bias (55-80 kV/cm), where, both in the simulations and in the measurements, they are not recognizable anymore as their dipole matrix element progressively vanish.

The intersubband emission of the grown structure does indeed show voltage tuning and that the main optical transition peak position can tune over almost 20 % of its value. Moreover the simulated tuning is in good agreement with the measured one, showing that, as expected, carrier screening effects are marginal. Nevertheless, as
4. LATTICE MATCHED QUANTUM CASCADE LASERS FOR WIDE TUNING

Figure 4.3: Simulated and measured spectral emission peaks as function of the electric field. As already mentioned above, for high fields (bigger than 60kV) the only relevant peak present both in the simulated and measured EL spectra is the one attributed to the lasing transition.

As mentioned above, spontaneous emission tuning over a large range was already shown in the past by (86, 87, 88) with limited results in term of lasing emission tuning.

4.4 Laser performance and Spectral tuning

Laser emission spectra for a typical uncoated Fabry-perot device, 2.3 mm long and 8.5 µm, in pulsed operation as function of the voltage is presented in Fig. 4.4. The laser emission is indeed continuously tuned in a field range between 50 kV/cm and 85 kV/cm. Laser peak tuning of 80 cm⁻¹ is shown and a maximum spectral coverage over more than 140 cm⁻¹ is reported. The peak of the laser emission was also consequently calculated in function of the applied field and in Fig. 4.5 a comparison between simulated and measured data is reported and shows an excellent agreement.

We have shown that, differently from the designs proposed in the past, the presented structure is characterized by a continuous laser tuning with voltage and the
4.4 Laser performance and Spectral tuning

**Figure 4.4:** Fabry-perot spectra in function of the applied voltage measured in pulsed mode.

**Figure 4.5:** Simulated and measured laser peak position as function of the electric field.
laser emission is observed for voltage ranges between $\sim 12$ V to $\sim 19$ V, denoting a very reduced voltage clamping of the structure above threshold. In Fig. 4.7 a typical light-current-voltage characteristic is shown for a laser uncoated, 3.9 mm long and 8.5 $\mu$m wide. One can easily notice, that the decrease of the differential resistance at threshold is not as strong as in conventional designs. This can be attributed to the short injector, which allows an efficient carrier injection inside the upper lasing state for a wide range of fields. In fact, while for high electric fields the injection from the state (0) is dominating, in the case of lower electric fields the states (1), (2), (3) play a relevant role. Nevertheless this non resonant injection does not seem to limit laser performance, in fact observing the optical power versus current characteristic a threshold current density of 1.5 kA/cm$^2$ is obtained at 300 K in pulsed operation as well as a slope efficiency of 1.4 W/A per facet. Total wallplug efficiencies up to 11.5% were measured in pulsed operation.

Simulated curves for the voltage, the optical power and the wallplug are plotted in Fig. 4.7 as dashed lines. A really good agreement is found in the case of the current-voltage characteristic. Predicted curves for the wallplug efficiency and the optical power show only a small underestimation of the threshold current value. Nevertheless values like slope efficiency and peak wallplug seem to be well reproduced by our model. As mentioned in the second chapter, describing the model, the only parameters inserted in the model were: the laser dimension and the waveguide losses. No fit parameter were used in the simulation and total waveguide losses were estimated using the dependence of the threshold current density with the reciprocal cavity length (1/L - measurement) (Fig. 4.6). Losses were determined to be around 2.8 cm$^{-1}$, a particularly low value for QCLs in this frequency range, where free carrier absorption starts to play an important role.

To measure the laser performance in continuous wave operation some of the devices we mounted epide-side-down on a diamond submount. In this case a total power of 450 mW, was measured.

In conclusion we have seen that even though the QCL structure was designed with the purpose of obtaining the largest spectral tuning, its lasers performance are comparable with the best ones present in literature for this wavelength (91).

In particular from literature survey it seems that wallplug efficiency and continuous-wave power are the highest observed for this wavelength.
4.4 Laser performance and Spectral tuning

**Figure 4.6:** Laser threshold as function of the inverse device length. Losses of $\sim 2.8 \text{ cm}^{-1}$ and differential gain of $g\Gamma = 4.4 \text{ kA}^{-1}\text{ cm}^{-1}$

**Figure 4.7:** Pulsed Power-Voltage-Current characteristic of a 3.9 mm long and 8.5 $\mu$m wide QCL. Total wallplug efficiency (%) is also shown (red squares).
4. LATTICE MATCHED QUANTUM CASCADE LASERS FOR WIDE TUNING
Chapter 5

Short wavelength QCLs

In the following chapter the design of efficient quantum cascade lasers, based on strain compensated to InP, emitting in the 4-5 µm spectral range will be analyzed.

In the first section a brief survey of the effect of material strain on conduction band discontinuity will be given.

In the second section, using a design emitting at 4.6 µm, the effect of growth temperature on interface roughness parameters and consequently on laser performance will be presented. A comparison with curves predicted using the transport model presented in the second chapter will also be given.

In the last part of the chapter, the use of the developed model to design of a new structure will be presented. In particular a new active structure will be presented designed to reduce the current leakage before structure alignment.

5.1 Conduction band engineering

In the previous chapter the development of high performance quantum cascade lasers using InGaAs / AlInAs layers lattice matched to InP has been analyzed.

Using this material system the best performance is obtained for QCLs emitting in the second spectral window (8 – 14µm). Unfortunately, since the conduction band discontinuity for this material system is only 520 meV as the photon energy increases, the amount of carriers that escape in the level continuum dramatically increases.
5. SHORT WAVELENGTH QCLS

As general guideline given two materials, with a conduction band discontinuity of \( \Delta E_c \), the maximal photon energy that can be reached is \( \sim \frac{1}{2} E_c \).

In the case of lattice matched InGaAs/AlInAs, the shortest emission wavelength obtainable should then be \( \sim 4.8 \mu m \). Using laser designs based on diagonal transition, this value could be still slightly reduced.

Nevertheless even though laser emission could be obtained for short wavelengths using this material system, laser performance would still suffer from severe carrier leakage\(^{(92)}\) in the energy continuum.

Since the beginning of epitaxial growth techniques, it was noticed that thin epitaxial layers could be grown with a lattice constant slightly different than the one of the used substrate. As we will see in the next sections, the possibility of introducing stress inside the grown layers provides an additional tool to tailor the emission wavelength in QCLs.

The grown interface between the mismatched layers, so called pseudomorphic, is characterized by an uniform in-plane lattice constant, that remains the same through all the structure, and the lattice mismatch can be accommodated by an uniform lattice strain if the thickness of each layer does not exceed a critical thickness above which the layer relaxes and its in-plane lattice constant reaches back the its bulk value.

Changing the amount of strain does modify sensibly the band structure and consequently the material conduction band offset can be tuned accordingly to the needs. The knowledge of the conduction band discontinuities is essential for the design of quantum cascade lasers, however this parameter is difficult to measure and experimental values exist only for a limited number of material system.

In this section we will introduce a simple model developed by \(^{(3)}\) that provides an useful tool to determine the band offset for a wide number of materials. It is important to point out that this theory assumes all the interfaces to be ideal and the atomic structure of each semiconductor to be maintained up to the interface.

Considering a system constituted by two layers, of thicknesses \( h_1 \) and \( h_2 \), and denoting with \( a_\parallel \) the in-plane lattice constant of the system and \( a_{\perp i} \) the lattice constant of the layer \( i \) in the perpendicular direction, the strain inside this pseudomorphic system can be computed minimizing the elastic energy, and the parallel and perpendicular
5.1 Conduction band engineering

components of the ε strain tensor can be written:

\[ a_{\parallel} = \frac{a_1 G_1 h_1 + a_2 G_2 h_2}{G_1 h_1 + G_2 h_2} \quad (5.1) \]

\[ \epsilon_{\parallel} = \frac{a_{\parallel}}{a_i} - 1 \quad (5.2) \]

\[ a_{\perp i} = a_i \left(1 - D_i \left(\frac{a_{\parallel}}{a_i} - 1\right)\right) \quad (5.3) \]

\[ \epsilon_{\perp i} = \frac{a_{\perp i}}{a_i} - 1 \quad (5.4) \]

where \( a_i \) are the equilibrium lattice constants and \( G_i \) is the shear module:

\[ G_i = 2 \left(\frac{c_{i11}^\parallel}{c_{i11}^\parallel} + 2 \frac{c_{i12}^\parallel}{c_{i11}^\parallel}\right)(1 - D_i/2) \quad (5.5) \]

and the constants \( D_i \) can be calculated starting from the elastic constants depending from the lattice orientation. In the case of the orientation (001)

\[ D_i^{001} = \frac{2c_{i12}^\parallel}{c_{i11}^\parallel} \quad (5.6) \]

From the equation (5.1) we can clearly see that in the case of thin layers deposited on a substrate, i.e. \( h_1 >> h_2 \), \( a_{\parallel} \) is simply equal to \( a_1 \).

The effect of the hydrostatic deformation potential on the valence band and the conduction band can be then expressed as:

\[ \Delta E_{v,av} = a_v \frac{\Delta \Omega}{\Omega} \quad (5.7) \]

\[ \Delta E_c = a_c \frac{\Delta \Omega}{\Omega} \quad (5.8) \]

\[ \Delta E_{c,ind} = a_{c,ind} \frac{\Delta \Omega}{\Omega} \quad (5.9) \]

where \((\Delta \Omega)/\Omega = Tr(\epsilon) = (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})\) is the fractional volume change inside the structure and \( \Delta E \) are the relative changes of the position of respectively the valence band, the conduction band and the indirect valleys in the conduction band. It is important to point out that one of the main advantages of the Model-Solid theory is that not only allows the generation of an accurate band structure but it also permits to align this structure on an absolute scale. In fact all the energy levels are referred to
5. SHORT WAVELENGTH QCLS

a "vacuum level" calculated modelling the solid as a superposition of neutral atoms.

In the case of the valence band, the strain and the spin-orbit interaction generate three separate bands, light hole band, heavy hole band and split-off band, but only the average value is computed in the equation (5.7). In the Fig. 5.1 the qualitative effect of compressive and tensile strain is shown for a material for which $a_v > 0$ and $a_c < 0$, e.g. GaAs.

![Figure 5.1](image)

Figure 5.1: Scheme of the effect of material strain on energy levels. For simplicity also here an average valence band is used instead of the three valence bands.

5.1.1 Ternary compounds

In the previous section, the effect of the strain on semiconductor materials as been described. Using this theory the band shifts for most of the binary semiconductors can be calculated. Unfortunately, in most of the cases of interest, ternary compounds $A_{1-x}B_xC$ are used and the needed parameters have to be computed starting from the respective binary compounds $AC$ and $BC$.

The variation of the composition ($x$) inside a ternary compound has a two fold effect on the electronic structure. First of all the energy and the lattice constant of the compound have to be determined as function of the composition, secondly the effect of strain inside the structure have to be considered and the elastic coefficients for the ternary compound have to be determined.

While the lattice constant is simply obtained as linear interpolation, for the calcu-
5.1 Conduction band engineering

Figure 5.2: \( \Gamma \)-valley conduction band edges for unstrained (Ga,In)As, (Al,In)As, and Al(As,Sb) as function of the lattice constant with parameters from Refs. (3, 4).

Figure 5.3: \( \Gamma, X, L \) conduction band edges for \( \text{In}_{1-x}\text{Ga}_x\text{As} \) and \( \text{In}_{1-x}\text{Al}_x\text{As} \) as function of the Gallium and Arsenic composition(3, 4).

The conduction band In the case of III-V semiconductors the bowing parameter is

\[
E(A_{1-x}B_xC) = (1 - x)E_{AC} +xE_{BC} - x(1 - x)c'
\]  

(5.10)

where the bowing parameter \( c' \) accounts for the deviation from the linear interpolation. The conduction band In the case of III-V semiconductors the bowing parameter is
5. SHORT WAVELENGTH QCLS

generally positive resulting in a band gap smaller. Using the above described model and the parameters from Refs. (3, 4), in the Fig. 5.2 the conduction band edges for the Γ-valleys of unstrained (Ga,In)As, (Al,In)As, and Al(As,Sb) as function of the lattice constant are shown. For the case of the $In_{1-x}Ga_xAs$ and $In_{1-x}Al_xAs$ also the indirect valleys position is plotted respectively as function of the Gallium and Arsenic composition (Fig. 5.3). In the previous graphs we considered only the effect of the different composition on the conduction bands, but as mentioned above the growth of these material on a substrate introduces an additional constraint, uniform in-plane lattice constant, and consequently further modify the position of the conduction bands. In order to estimate this effect also the elastic constants of the ternary compounds have to be evaluated.

The elastic coefficients can be interpolated using the lattice constants as weighting parameters:

$$c^{A_1-xB_xC} = \frac{(1-x)a_i^{AC} + xa_j^{BC}}{\delta_k^{A_1-xB_xC}}$$ (5.11)

Once all the parameters are derived the position of the energy bands can be calculated on any substrate, in a similar way as for binary compounds. In Fig. 5.4 the Γ-conduction band offset for the same materials shown in Fig. 5.2 are now shown pseudomorphically strained to a InP substrate. From the previous figure one can see that inserting small stress levels in the grown $In_{1-x}Ga_xAs$ and $In_{1-x}Al_xAs$, the conduction band offset can be more than doubled and high performance short wavelength QCLs can be produced using this material system.

5.2 Influence of interface roughness on performance in short wavelength QCLs

In the second chapter a brief analysis of the most relevant scattering mechanisms in Mid-IR quantum cascade laser was done. As the transition energy is completely defined by the width of the quantum wells, it was very early noted that the performances of quantum cascade lasers should be very dependent on the quality of the interfaces between the epitaxial layers. For this reason, in this section we will describe in deeper
5.2 Influence of interface roughness on performance in short wavelength QCLs

Figure 5.4: \( \Gamma \)-valley conduction band edges for (Ga,In)As, (Al,In)As, and Al(As,Sb) pseudomorphically strained to a InP substrate as function of the lattice constant with parameters from Refs. (3, 4). As a comparison to better understand the stress effect, the energy positions of the unstrained binary compounds are shown as dots.

details the influence of interface roughness on the performance in quantum cascade lasers.

It was shown early that interface roughness scattering was the key factor that determined the width of the intersubband absorption (93). As described in the section 2.35, a model that assumed interfaces with steps with an Gaussian distribution \( \langle \Delta(r)\Delta(r') \rangle = \Delta^2 \exp(-\frac{|r-r'|^2}{\Lambda^2}) \), characterized by an average step height \( \Delta \) and a correlation length \( \Lambda \), was shown to correctly predict the temperature dependence of the intersubband emission broadening (94). Early studies, mostly performed on devices operating at relatively long wavelengths \( \lambda \approx 9 \mu m \) have focused on the prediction and minimization of the emission broadening parameter (66, 95), as the threshold current density of quantum cascade lasers should be proportional to the latter. Recent work have shown however that some devices, with an extremely wide gain bandwidth, have at the same time record wallplug efficiencies, as shown by (2, 96). In fact, the situation for lasers operating at relatively short wavelengths is more complex, as one expects not only the broadening but also the intersubband lifetime to be influenced by the interface roughness scattering. To better clarify the previous statement, the model for the inter-
face roughness, described in the section 2.35, was used to calculate the intersubband and intrasubband scattering times for an infinitely deep quantum well. The width of the quantum well has been selected in order to obtain an intersubband transition corresponding to a wavelength $\lambda = 4.6 \, \mu m$. In the Fig. 5.5 the intersubband lifetime is plotted in this case for different initial electron kinetic energies ($E_k$). This time shows a non-monotonic behavior as a function of the correlation length and is minimum for roughly $\Lambda = 30 \, \AA$. This minimum in the scattering time corresponds to the resonance condition $q\Lambda \approx 1$, where $q$ is the exchanged wavevector during the intersubband transition process. Later in the chapter the behavior of this model also for the intrasubband lifetime will be investigated and in particular the failure of the model to estimate the intrasubband lifetime for long correlation length.

![Figure 5.5](image)

**Figure 5.5:** Inter-subband scattering times due to interface roughness, in an infinite quantum well with a 270meV transition energy, as function of the correlation length $\Lambda$, for various values of the in-plane energies, as indicated.

Trying to explore experimentally the dependence of the laser performance on interface roughness, a way to systematically vary interface roughness inside a quantum cascade laser has to be found. In this work, the performances of strain-balanced quantum cascade lasers operating at a wavelength of $\lambda \approx 4.6 \, \mu m$ are investigated as a function of the substrate temperature during epitaxial growth. Although a quantitative dependence of the correlation length on the growth temperature goes beyond the scope of this work, we assumed that the enhanced mobilities of the atoms on the
5.2 Influence of interface roughness on performance in short wavelength QCLs

surface, due to the higher substrate temperature, would increase the value of the IFR correlation length \( \Lambda \) monotonically while leaving the step height essentially unchanged.

5.2.1 Active region design

The devices are based on a three wells active region shown in the inset of Fig. 5.6, already presented elsewhere\(^\text{(97)}\). The diagonal nature of the laser transition makes these devices especially sensitive to the effect of interface roughness and therefore well suited for this study.

![Figure 5.6: Simulated conduction band diagram of the diagonal three QWs design used for the study of the interface roughness. The structure is biased with an electric field of 79 kV/cm. Layer sequence in appendix A.1.6 (EV1299-1301)](image)

5.2.2 Experimental results

The strain-balanced \( \text{In}_{0.62}\text{Ga}_{0.38}\text{As/In}_{0.4}\text{Al}_{0.6}\text{As} \) structures have been grown by molecular beam epitaxy (MBE) on n-doped InP. The three different samples have been grown, in sequential runs, with growth temperatures of respectively 475 °C, 515 °C and 525 °C.
In order to minimize the influence of device fabrication in the layers comparison the laser structures have been processed in a single processing run. As described in the section 3.2.3 an inverted buried-heterostructure process was used, with ridge widths ranging between 6 and 9 $\mu$m. For each layer, the thirty-five active region periods were sandwiched between two InGaAs confinement layers, 200 nm thick, in order to improve mode confinement. A 3.2 $\mu$m thick InP cladding was grown by metalorganic-vapor-phase epitaxy (MOVPE), followed by a layer 80 nm thick of highly doped InGaAs ($3\times10^{19}$ cm$^{-3}$), in order to provide an uniform current injection in the lasers. For pulsed operation devices were cleaved and mounted epi-side up on copper submounts and measured on a Peltier cooler.

The typical light-current-voltage characteristics of three otherwise identical devices grown at the three different substrate temperatures are compared in Fig. 5.7. One can easily see that small changes in growth temperature strongly influence laser performance and that the device B, grown at 515 °C, exhibits the best performance in terms of threshold current density and slope efficiency. Note also that the same device shows the largest change in differential conductance at threshold, sign of an excellent injection efficiency.

In order to gain further insight and try to relate growth temperature and interface
5.2 Influence of interface roughness on performance in short wavelength QCLs

Figure 5.8: a) Maximum current density $J_{\text{max}}$ (squares) and threshold current density $J_{\text{th}}$ (circles) simulated as function of the correlation length. b) Simulated slope efficiency per facet (triangles) and full-width-at-half-maximum (crosses) of the electroluminescence for a voltage of 14V are also plotted. Measured values for the samples A, B and C, were in both cases compared with simulated values using the values of the correlation length as a fit parameter.
roughness parameters, using the transport model described in the second chapter, the
luminescence linewidth, threshold current, slope efficiency and maximum current at the
roll-over point were simulated as function of the interface roughness correlation length.

Comparing then the values measured for the different growth temperatures with the
curves simulated as function of the correlation length, a relation between the correlation
length and the growth temperature could be found. As mentioned above, this compari-
son is based on the assumption that the growth temperature does in first approximation
mainly influence the interface roughness correlation length. In modeling the electron
transport, in contrast to our previous work on longer wavelength devices (6), where
the best predictions were achieved by assuming the electron temperature to be equal
to the lattice one, we could only predict correctly our maximum operation current by
assuming a non-negligible electron heating, computed assuming a kinetic balance be-
tween electron cooling and heating and a uniform temperature for all subbands. We
observed this behavior for all the strain-compensated devices, which is in agreement
with the experimental measurements of electron heating by photoluminescence (98).

A comparison between the experimental results and the theoretical prediction is
shown in Fig. 5.8. A good agreement can be achieved for the slope efficiency as well as
for threshold and the maximum current densities if one assumes a value of the correlation
length of $\Lambda = 55, 85, 185 \text{ Å}$ for the growth temperatures of $T = 475, 515, 525 \text{ °C}$
respectively. Best performances are achieved at a growth temperature of $515\text{°C}$, where
the correlation length $\Lambda = 85 \text{ Å}$ is close to the optimum value predicted by the com-
puter model $\Lambda = 100\text{Å}$. In agreement with this interpretation, optimum performances
are achieved for a correlation length corresponding approximatively to the resonance
condition $q\Lambda \approx 1$ for the momentum exchange expected for the interlevel transitions of
the injector with a characteristic transition energy of $E \approx 34 \text{ meV}$.

The non-monotonic behavior of the predicted performance as a function of the
correlation length $\Lambda$ is the result of a complex interplay between the transport and
gain mechanisms. After studying the different contributing factors, we believe that a
key contribution originates from the change in the upper and lower state lifetimes as
a function of $\Lambda$. As shown in Fig. 5.9, for short values of $\Lambda$, the upper state lifetime
is quenched, reducing the population inversion and driving up the threshold current
density. In contrast, too large values of the correlation length yields to a reduction of
the extraction from the lower state, reducing the population inversion and limiting the
maximum current. The electron populations as function of energy as shown in Fig. 5.10 for selected values of the correlation length. In the inset the population inversion for the lasing transition is plotted as function of the correlation length.

![Image](image_url)

**Figure 5.9:** Computed intersubband lifetimes for the upper(state 3) and lower(state 2) lasing levels for an applied field of 70 kV/cm as function of the correlation length Λ

In conclusions we have shown that the model achieves to well estimate laser parameters as the threshold current density, the slope efficiency and the maximum current density, however it systematically overestimates the broadening of the ISB luminescence (Fig. 5.8a) by ≈ 20 – 30%. In addition, it predicts an intersubband linewidth that increases monotonically with correlation length, a feature not observed in our case. In order to understand the origin of this discrepancy, in the next section the calculation of the intersubband and intrasubband scattering times for an infinite QW is presented.

5.2.3 Failure of the model to calculate intrasubband broadening for large correlation lengths

Aim of this section is to try to better understand how the model developed by Ando et Al. (99), presented in section 2.35, does fail predicting just the luminescence linewidth that has historically been the only parameter used to estimate the interface roughness in a QCL. We attribute this discrepancy to the unphysical feature of the model,
that predicts a diverging of the *intrasubband* scattering rate with increasing correlation length. In fact recalling the expressions for the intersubband and intrasubband broadenings induced by interface roughness:

\[ \Gamma_{\text{intra}}(E) = \frac{m^* \Delta^2 \Lambda^2}{\hbar^2} \left( F_{01} - F_{10} \right)^2 \int_0^\pi d\theta e^{-2k^2(1-\cos \theta)^2 \Lambda^2/4} \]  

\[ \Gamma_{\text{inter}}(E) = \frac{m^* \Delta^2 \Lambda^2}{\hbar^2} F_{01}^2 e^{-\frac{2m^* F_{01}}{h^2} \Lambda^2} \int_0^\pi d\theta e^{-\left( 2k^2 \Lambda^2 - 2k \sqrt{k^2 + \frac{2m^* F_{01}}{h^2} \Lambda^2} \cos \theta \Lambda^2 \right)/4} \]  

The intrasubband broadening is diverging due to the contribution to the scattering by the small-angle scattering \((q \Lambda \approx 0)\), whereas we would expect physically a transition to an inhomogenous broadening whose broadening would be roughly independent on \( \Lambda \) in the limit \( \Lambda \to \infty \). This unphysical behavior of the model did not appear in past studies because only the product \( \Delta \Lambda \) and not the individual terms was taken as the parameter to be adjusted to the experiments \((94)\).

Note that this limitation of the model does not appear for the *intersubband* lifetime, key to the transport properties, because the latter involves transitions at finite exchanged wavevector \(q\), i.e. the intersubband term is cut due to the exponential term in red in the eq. \((5.12)\). To better show this behavior of the intrasubband scattering...
5.2 Influence of interface roughness on performance in short wavelength QCLs

time, we can again consider the example of the infinitely deep QW presented at the beginning of the section. The intrasubband scattering time in this case is presented in Fig. 5.11 and one can see that for long correlation length this lifetime reaches unphysical values in the sub-fs range.

![Intra-subband scattering times due to interface roughness](image)

**Figure 5.11:** Intra-subband scattering times due to interface roughness, in an infinite quantum well with a 270 meV transition energy, as function of the correlation length Λ, for various values of the in-plane energies, as indicated.

5.2.4 Sample B (515 ° C)

In the previous section, we showed that the transport model presented in the second chapter is able to correctly predict laser properties as slope efficiency, threshold current and maximum current. In this section we want to show in bigger details the simulations for the best sample.

As described in the second chapter already, in order to simulate the laser characteristics, the waveguide losses, dependent on the laser fabrication process, have to be measured and then used as input parameter of the transport model. In first approximation the losses can be calculated from a linear regression from the threshold current density dependence from the inverse laser length, (1/L measurement). In the Fig. 5.12 the losses and the differential gain are then calculated for the samples grown at different growth temperature. We can see that, even if the slightly smaller losses are observed for the sample B, the losses values are comparable as expected due to the
common fabrication process. Using these values for the waveguide losses, the character-

\[ \alpha_w = 3.1 \text{ cm}^{-1} \text{ and } g\Gamma = 3.3 \text{ cm}\cdot\text{kA} \left(T_{\text{growth}} = 525 \degree\text{C}\right) \]
\[ \alpha_w = 2.8 \text{ cm}^{-1} \text{ and } g\Gamma = 3.65 \text{ cm}\cdot\text{kA} \left(T_{\text{growth}} = 475 \degree\text{C}\right) \]
\[ \alpha_w = 2.5 \text{ cm}^{-1} \text{ and } g\Gamma = 3.62 \text{ cm}\cdot\text{kA} \left(T_{\text{growth}} = 515 \degree\text{C}\right) \]

Figure 5.12: Threshold current density as function of the inverse laser length. From linear regression values of waveguide losses and differential gain can be obtained: \( \alpha_w \) and \( g\Gamma \). Simulated curves are shown as dashed lines. One can easily see that a part from small discrepancies for high current density the simulated performances follow well the measured ones. A threshold current density of 1.5 kA/cm\(^2\), peak power per facet of 1.8 W/A were measured at 300 K in pulsed operation corresponding to a total wallplug efficiency of 14.5 %. Finally, the temperature dependence of the laser threshold was also simulated and compared to the experimental values in Fig. 5.14. The usual temperature dependence of the threshold current \( J_{\text{th}} = J_0 \exp(T/T_0) \) was assumed. Simulated values of \( T_0 = 143 \) K and \( J_0 = 214 \) A/cm\(^2\) are in really good agreement with measured values of \( T_0 = 147 \) K and \( J_0 = 220 \) A/cm\(^2\). For continuous-wave measurements, the lasers are mounted on a diamond submount using an evaporated In/Au. 

In Fig. 5.15 the total c.w. optical power emitted from an uncoated device, mounted epide-side-down on a diamond holder is presented. Even though a maximum power of 600
5.2 Influence of interface roughness on performance in short wavelength QCLs

Figure 5.13: Optical power per facet (left axis), applied bias (1st right axis) and total wallplug efficiency (2nd right axis) as function of the current for a 4.6 mm long and 8.5 \( \mu \text{m} \) wide device, grown at 515°C. Simulated curves are shown as dashed lines.

Figure 5.14: Comparison of the computed and experimental threshold current density as function of the temperature for a device shown in Fig. 5.13.

\( \text{mW} \) is observed, comparing the previous value with the peak power emitted in pulsed, it is clear that a better optimization of the episide-down mounting process has to be done.
In this section an alternative way of measuring the optical power is presented. This method does only rely on current-voltage measurements and has the advantage of not being subjected to any collection efficiency factor.

We have seen that one of the peculiar property of electron transport in QCLs is the change of the differential resistance in the current-voltage characteristic when laser threshold is reached. It is well known that this effect is due to the photon driven contribution to the current, i.e. the upper lasing state lifetime is quenched by due to the stimulated emission contribution and more electrons pass through the structure for the same electric field.

We tried to use the measurement of this \textit{radiative current} in order to estimate of the number of photons present inside the optical cavity and therefore the optical power emitted by the laser. This method does only rely on current-voltage measurements and therefore has the advantage of not being subjected to any collection efficiency factor and moreover does not require any photo-detection.

In order to measure the radiative current, we would need to modify the total losses and then quantify the difference in current for the same applied field in the two cases: lasing on and lasing off. One of the possible ways to do that is to use two devices of two
5.2 Influence of interface roughness on performance in short wavelength QCLs

![Graph showing light-current-characteristic of two typical devices](image)

**Figure 5.16:** Top panel: Light-current-characteristic of two typical devices 8.5 µm wide and respectively 2.3 mm and 4.6 mm long. The current in the short device is scaled to the surface of the 4.6 mm long device. Due to the reduced mirror losses the longer device start lasing for a smaller current. The lasing threshold of the two devices is indicated by arrows on the voltage-current characteristic. The radiative current is highlighted in light blue. Bottom panel: Optical power estimated from the radiative current (blue), the power simulated using the transport mode (red) and the power measured using the calibrated powermeter (black). In order to account for the setup wiring and the waveguide cladding a series resistance of 0.65 Ω has been considered.

Different lengths, that in first approximation differ only by the mirror losses. In order to measure this photon-driven current, in Fig. 5.16 (top panel) the voltage characteristics of two different devices, respectively 2.3 mm and 4.6 mm are shown. To compare the two curves for the same current densities, the current flowing in the shorter device has
5. SHORT WAVELENGTH QCLS

been normalized for the surface of the 4.6 mm long device. Due to the higher value of mirror losses the shorter device will start lasing for a bigger current density.

From the comparison of the two curves it appears evident the change of differential resistance that corresponds to the lasing threshold in the longer (red arrow) and in the shorter device (blue arrow). The radiative current flowing into the longer device is then obtained by subtracting the currents in the two devices for the same voltage:

\[ I_{\text{rad}}(V) = I_{4.6\text{mm}}(V) - I_{2.3\text{mm}}(V) \]  

(5.14)

The total optical power in the cavity \( P_{\text{cavity}} \) will then simply be the product of the photon-driven current for the photon energy \( h\nu \) and the active period number \( N_p \).

The power out-coupled \( P_{\text{out}} \) will be:

\[ P_{\text{out}} = P_{\text{cavity}} \cdot \frac{\alpha_{m1}}{\alpha_{tot}} = I_{\text{rad}} \cdot N_p \cdot \frac{h\nu}{e} \cdot \frac{\alpha_{m1}}{\alpha_{tot}} \]  

(5.15)

where \( \alpha_{m1} \) are the mirror losses of the front facet and \( \alpha_{tot} \) are the total waveguide losses \( \alpha_{tot} = \alpha_{m1} + \alpha_{m2} + \alpha_w \).

In Fig. 5.16 (bottom panel), the optical power predicted using the above mentioned technique is compared with the optical power measured using a calibrated thermopile detector and with the optical power simulated using our transport model; a really good agreement is found. As already pointed out, the power estimated using this method does not require the accurate measurement of setup-dependent factors like the collection efficiency and the use of properly calibrated detectors.
5.3 Step quantum well design

In the previous section, the importance of the interface roughness and in particular of the growth conditions on the laser performance has been analyzed. Another key parameter, that can strongly influences laser performance, is the injection efficiency of the carriers in the upper lasing state.

In the case of the short wavelength QCLs, the high electric field necessary to align the injector state with the upper lasing state results generally in a relevant parasitic current flowing through the structure already for low electric fields. Is well known that a possible way to improve this filtering is to increase the thickness of the injector barrier but at the same time it will limit the maximal current flowing in the structure.

A possibility to reduce this parasitic current, while maintaining an efficient coupling of the injector with the upper lasing state, is to introduce the principle of composite barrier for the injection barrier. In this case, as shown in Fig. 5.17, the coupling of the injector state with the lower lasing state is reduced for low electric fields, while maintaining an efficient coupling of the injector state with the upper lasing state at the structure alignment. This injection scheme, already presented by Becker et al. (100) in the GaAs/AlGaAs material system, is here applied to a InP-based quantum cascade laser emitting at 4.8 μm.

![Figure 5.17: The operating principle of the Step Well scheme is shown. In the left panel, for low applied fields the coupling of the injector state i to the next period is reduced. In the case of high electric fields, as shown in the right panel, the a good coupling is maintained between the injector state and the upper lasing state 3.](image-url)
5. SHORT WAVELENGTH QCLS

5.3.1 Active region design

![Conduction band diagram of the reference sample EV1326 (top panel) and the step well design (bottom panel) for an applied field of 85 kV/cm. Moduli squared of the relevant electronic wavefunctions are shown.](image)

Figure 5.18: Conduction band diagram of the reference sample EV1326 (top panel) and the step well design (bottom panel) for an applied field of 85 kV/cm. Moduli squared of the relevant electronic wavefunctions are shown.

In order to compare the effect of the new injection scheme, we started from a laser a reference laser design and, using the transport model introduced in the second chapter, a new injector zone was designed. The reference active region is presented in the top
5.3 Step quantum well design

Panel of the Fig. 5.18 and is based on a bound-to-continuum design emitting at 4.8 $\mu$m with a total strain of 2%, using In$_{0.666}$Ga$_{0.334}$As/In$_{0.365}$Al$_{0.635}$As.

For the optimized structure the same compositions are used in all the active region but in the injector barrier, where a composite barrier should be used with a step of $\sim$ 0.3 eV. In the Fig. 5.18 a comparison of the two designs is shown for an applied field of 85 kV/cm. In the optimization of the structure not only a composite barrier was inserted, but as we can see, also the laser extraction as been modified by making the structure look as having a three-phonon resonance depopulation scheme for the lower laser level. Moreover the dipole moment of the lasing transition benefits from the substitution of the first active region barrier with a composite barrier.

Unfortunately, for the growth of the actual structure, the MBE used did not permit the growth of the composite barrier, since the use of an additional aluminum cell would have been necessary. In order to overcome this problem, the 0.3 eV barrier has been substituted by a digital grading (in the following referred as digital step well design). As we can see comparing the simulated electronic wavefunctions in the Fig. 5.17 and 5.19, the two structures are theoretically equivalent. In the reality, the digital grating makes the structure more sensitive to the interface roughness, but due to the growth optimization done, partially shown in the previous sections, we expect the its presence not to sensibly limit laser performance.

Figure 5.19: Conduction band diagram of the digital grading step well design. The layer sequence can be found in appendix (see EV1327 in A.1.4).
5. SHORT WAVELENGTH QCLS

5.3.2 Simulated and Measured laser

In order to compare the efficiency of the new injection scheme, both the digital grading step well and the reference sample were grown in MBE in sequential runs and processed together, using the inverted buried process. As described in the section

![Graph](image)

**Figure 5.20:** Simulated (top panel) and measured (bottom panel) injected currents (in logarithmic scale) as function of the voltage for typical devices (8.5 µm wide and 2.3 mm long) from the two designs

3.2.3 an inverted buried-heterostructure process was used, with ridge widths ranging between 7 and 10 µm. Both wafers are constituted by thirty-five active region period
repetitions. A 3.2 \mu m thick InP cladding was grown by MOVPE, followed by a layer
80 nm thick of highly doped InGaAs (3 \times 10^{19} \text{cm}^{-3}), in order to provide an uniform
current injection in the lasers. In Fig. 5.20 the injected current (in logarithmic scale)
as function of the voltage is shown for typical devices (8.5 \mu m wide and 2.3 mm long)
from the two designs. Simulated values are presented in the top panel of the figure,
while measured values are shown in the lower panel. For these curves, one can easily
notice that: the simulated curves and the measured ones show exactly the same trend
and therefore the simulation program achieved to correctly predict the effect of the new
design on the electron transport. Secondly, the impact of the new injector design on
the parasitic current before alignment can be observed both in the simulated and in the
measured curves. The new design shows indeed a much smaller parasitic current before
the structure alignment. Moreover the new design does also show a much larger change
of differential resistance at the threshold, sign of the improved injection efficiency. In
the Fig. 5.21 the optical power(right axis) and voltage(left axis), as function of the
current are shown, for the same two different designs. As in the Fig. 5.20 simulated
curves are presented in the top panel, while the measured data are shown in the bottom
one. Simulated power-current curves show that indeed the step well design is expected
to present a bigger dynamical range and higher gain. Indeed, from measured values, the
new design clearly shows clearly better performance, e.g. for the two uncoated devices
shown in the figure, the threshold current is reduced from 5.3 kA/cm^2 to 3 kA/cm^2 and
the slope efficiency per facet increases from 800 mW/A to 1.2 W/A. Unfortunately, one
can easily see that according to the simulations, both for the reference design and the
step quantum well, the measured performance are sensibly worse than the one expected
from the simulation.

We attribute this discrepancy to a contamination in the process, since the same
design had been already already grown and processed (101) and laser performance
were in that case in accord with the simulated ones. The idea of a contamination is
supported by the measurement of the waveguide losses (Fig. 5.22), where values of
4.5 cm^{-1} and 4.1 cm^{-1} are obtained. These values are in fact a factor of two higher
than the values expected in this wavelength range and measured in the past for designs
identical to the one of the reference sample(\sim 2.5 cm^{-1}).

It is clear that a new fabrication run is necessary to prove that the origin of the
limited performance were due to a process contamination. Nevertheless it was shown in
this section that the use of a digital grading step well reduced the amount of parasitic current while at the same time improving laser performance.
5.3 Step quantum well design

Figure 5.22: Threshold current densities as function of the laser inverse length for the reference (red) and the digital step well designs. Through linear fit, values of waveguide losses of 4.5 cm$^{-1}$ and 4.1 cm$^{-1}$ were respectively measured and differential gain values of 1.95 cm kA$^{-1}$ and 2.95 cm kA$^{-1}$. 
5. SHORT WAVELENGTH QCLS
Chapter 6

QCLs in the 3-4 μm region

In this chapter, the development of quantum cascade lasers with emission wavelength in the 3-4 μm range will be described.

In particular in the section 6.1 the application of sources in this spectral range for environmental sensing will be briefly discussed. In the in the section 6.3, the different material systems used for QCLs emitting in this spectral range will be introduced with a brief survey of the performance obtained using each of them. In the section 6.4 the optimization of the MBE growth process in the case of high strained materials will be discussed. In the section 6.5, a new active region structure, designed to emit at 3.3 μm will be presented. Finally in the section 6.7, laser performance obtained at 3.3 μm will be shown.

In the recent years, with the stricter regulations in environmental monitoring, the analysis of trace level of gases has become crucial. That triggered the need for compact sensors capable of real-time concentration monitoring. Among the different possibilities, optical gas sensors present numerous advantages, especially regarding high sensitivity measurements, e.g. industrial monitoring. As seen in the introduction, the first atmospheric spectral window, in the band between 2.9 μm and 5.3 μm, is of great interest for these applications due to the large number of molecules (e.g. NO, CO, CO2, CH2O) that show characteristic absorptions in this band. Inside this spectral region, the 3-4 μm range is specially significant since the fundamental C-H, N-H and O-H stretching modes have resonances in this region(102, 103) and these absorption lines can be several orders of magnitude stronger than the overtone and combination
bands in the NIR, permitting the measurement of extremely low concentrations using compact and relatively simple systems (104, 105, 106).

### 6.1 Gas sensing in the 3-4 µm spectral range

Among the gases that present resonances in the 3-4 µm spectral range, methane is clearly one of the most interesting (107). In the Fig. 6.1, the transmittance spectrum of the CH$_4$ in this spectral range is shown. Methane is one of the most important greenhouse gases, third after CO$_2$ and H$_2$O and it is estimated that roughly 50 % of the global methane emission is due to human-related activities. The control of the methane emission is particularly important, due to the big impact that it can have in the planet climate changes. In fact, methane has a high "Global warming potential". The *global warming potential factor* (GWP) is a measure of the amount of heat that a greenhouse gas can trap in the atmosphere. GWP is generally calculated over a specific time interval, e.g. 20, 50, 100 years, accounting also for the atmospheric lifetime of the gas and is expressed as function of the GWP of the CO$_2$, that is conventionally taken as unitary. The methane has a GWP of 56 in 20 years, meaning that compared to the same amount of carbon dioxide, methane can trap fifty-six times more of heat in the atmosphere. The control of the methane emission is therefore crucial both in the air but also near the sources, e.g. near landfills.

![Graph showing methane transmittance spectrum](image)

**Figure 6.1:** Methane transmittance spectrum. Source NIST Chemistry Webbook.
Among the other substances that present resonances in this spectral range it is important also to mention butane and propane and formaldehyde. The first two are used as fuels, chemical feedstocks and propellants, while the latter is one of the major component of the resins used in wood-based materials.

Formaldehyde is one of the most dangerous toxins that can be found in the living species (108). The World Health Organization has set a minimum risk level for this substance to 0.08 ppmV in the indoor environment. Up to date, photoacoustic techniques are the only ones able to reach the necessary sensitivity without preliminary molecule-specific separation steps.

6.2 Sources in the 3-4 \( \mu \text{m} \) range.

Over the last decade, amazing developments have been made in semiconductor laser production in this energy range. Advances have been made in particular in the field of interband cascade lasers (ICLs) (109) and QCLs (110, 111) and room temperature lasing emission has been observed for both systems. An alternative way for laser light generation in this spectral range lies obviously in the use of non-linear wavelength conversion strategies as quasi-matched difference frequency generation using for example Periodically Poled Lithium Niobate (PPLN). Nevertheless this last option requires more complicated optical systems and obtained peak optical powers are generally small (fractions of mW).

Up to date, best performance in this spectral range are obtainable using ICLs, that achieve room temperature continuous wave operation (109). These sources are characterized by low threshold current densities and low power consumption. Nevertheless, they are also characterized by extremely low characteristic temperatures (\( T_0 \) and \( T_1 \) are much smaller than 50 K) and increases in the device temperature cause a strong degradation of both the slope efficiency and the threshold current. Relatively low slope efficiency values are also observed, in comparison to QCLs in the same spectral range. Moreover, due to the material systems used, e.g. AlSb/GaAs/InAs/AlInSb on GaSb substrate, the growth optimization is really crucial and the device fabrication is not compatible with most of the processes developed for high performance laser operation.

As seen in the previous chapter, in case of the QCLs, the ability to tailor the photon energy is limited, on the high energy side, on the size of the conduction band discon-
6. QCLS IN THE 3-4 $\mu$m REGION

Discontinuity $\Delta E_c$ between the two materials. As a matter of fact, to achieve good laser performances at room temperature, the edge of the conduction band should lie much higher in energy than the upper lasing lever, in order to inhibit the thermally activated escape of carriers in the continuum. Furthermore lasers designs emitting at these wavelengths not only need large band discontinuities, but also narrow wells, requiring a proper control of the interface roughness during the epitaxial growth. Another limitation to short wavelengths is the energy separation between the $\Gamma$ and the X and L valleys in order to minimize the intervalley scattering processes.

### 6.3 Material systems for short wavelength QCLs

The leading contender material systems for quantum cascade lasers emitting in the 3 – 4 $\mu$m spectral range are:

1. InAs-AlSb on InAs(112),
2. InGaAs-AlInSb on InP(111)
3. InGaAs-AlAs on InP(113)

As shown in the Fig. 6.2, the InAs – AlSb material system (violet arrow) has the great advantage of having the largest band discontinuity. It also has a relatively large $\Gamma$-L valleys separation ($\sim 0.7$ eV) (113). Unfortunately InAs band-gap is comparable with the emission energy, thus band-edge absorption constitutes the main limitation for these sources (114).

QCLs based on InGaAs – AlInSb lattice matched to InP do also show a large conduction band discontinuity (1.7 eV) (red line in Fig. 6.2). Short wavelength emission in this material system is limited by the InGaAs X- and L-valleys that lie ($\sim 0.5$ eV) above the X-valley.

In the case of InGaAs – AlAs strain compensated to InP, the largest possible band-offset discontinuity ($\sim 1.5$ eV) could be achieved using the InAs wells and AlAs barriers pseudomorphically strained to InP. However the growth of InAs layers is particularly challenging, due to its tendency to form three dimensional nanostructures as for example S-K dots. More reliable growth conditions can be achieved using strained
6.3 Material systems for short wavelength QCLs

InGaAs/InAlAs-AlAs that nevertheless provides a relatively high band offset discontinuity (∼1.4 eV). Moreover, as shown in Fig. 6.2, the compositional dependence $E_c(x)$ for the $Ga_{1-x}In_xAs$ is not as pronounced as for the $Al_{1-x}In_xAs$ and consequently the use of $InGaAs$ wells, instead of $InAs$, does not affect particularly the $\Delta E_c$.

The $InGaAs – AlAs$ material system has the main advantage of being the most mature material systems for Mid-IR QCLs. For this reason, the use of advanced device fabrication techniques, as for example buried heterostructure technique described in the third chapter, can be applied with no need for further optimization.

Unfortunately up to date, no QCL with an emission wavelength shorter than 3.6 $\mu$m was demonstrated in this material system in a temperature range accessible by thermoelectric cooling (45, 115).

In the next sections, the development of a room temperature quantum cascade laser emitting at 3.3 $\mu$m based on $InGaAs – AlAs$ system will be analyzed. Particular attention will be given to the epitaxial growth optimization and on the active region design.

---

Figure 6.2: Γ-valley conduction band edges for the most used material systems for short wavelength QCLs. The energy levels as function of the lattice parameter are considered pseudomorphically strained to InP, a part for the case of the material system (1) $InAs – AlSb$ that is considered as grown on InAs.
6.4 Growth optimization

![Figure 6.3: Rocking curves of the superlattice structures (100 period of 16 Å AlAs and 47 Å In₀.₇Al₀.₃As) grown for different growth temperatures (484 °C, 493 °C, 500 °C, 510 °C). From the insets a), b), one can easily see that the structure grown at 510 °C is already partially relaxed and already in the case of the structure grown at 500 °C, the peak intensity is reduced and a higher FWHM is observed. The two structures grown at 484 °C and 493 °C are almost equivalent.](image)

In the growth of strained QCLs, a higher growth temperature results in a reduced background doping and increased species mobility on the surface. At the same time the critical thickness, above which the structure relaxes, of the individual strained layers is reduced by a temperature increase. In order to determine the optimal growth condition for the highly strained AlAs layers, InAlAs/AlAs superlattices (16 ÅAlAs and 47 ÅIn₀.₇Al₀.₃As) have been grown for different temperatures. High-resolution X-
6.5 Active region design

ray diffraction has been used to analyze strain balance and crystalline quality of grown structures. In the Fig. 6.3 the rocking curves of the superlattices are shown. One can easily see that the structure grown at 510 °C (red in figure) is partially relaxed. In the case of the structure grown at 500 °C (violet in the figure), a reduction of the peak intensity and a broadening of the peaks can be observed. The two structures grown at 484 °C and 493 °C appear to be almost equivalent and in order to reduce the background doping a growth temperature of 493 °C has been selected for our active region structure.

6.5 Active region design

As already mentioned, also in the case of \( \text{InGaAs} - \text{AlAs} \), a relatively high band offset discontinuity can be obtained by the use of highly strained AlAs barriers. It has been pointed out in the previous section that the thickness of each layer has to be smaller than the critical thickness. In addition to that, the global structure strain has also to be compensated. In our case, the a strain of the 3.54 % is due to the AlAs barriers while the \( \text{In}_{0.72}\text{Ga}_{0.28}\text{As} \) wells have a strain of \(-1.34\%\). It is clear that the compensation of the total strain does introduces an important constraint on the laser design and it is not possible to tune independently the thicknesses of the barriers and the wells, i.e. the total thickness of the AlAs system would be bound to be \( \sim \frac{1}{3} \) of the total InGaAs thickness.

This limitation affects in particular the design of an efficient carrier injection in the upper lasing state. As already presented by Semtsiv et Al.(115), this problem can be overcome by the use of composite barriers. With the use of two component barriers (InAlAs/AlAs) the barrier thickness and the strain can be tuned almost independently. Using this material system (InGaAs-InAlAs/AlAs on InP) we tried to design a QCL emitting at 3.3 \( \mu \text{m} \).

In Fig. 6.4, the conduction band diagram of laser structure at an applied field of 120 kV/cm is presented. The laser design is based on a classical bound-to-continuum scheme, where particular care has been taken to enlarge the lower miniband in order to obtain an efficient carrier extraction. Moreover to reduce the resonant reabsorption from the extractor levels, we tried to increase the energy of the upper miniband, pushing its levels toward the continuum. In addition, even though in the previous section we
Figure 6.4: Conduction band diagram of a period of the active region at an average field of 120 kV/cm. Moduli squared of the relevant envelop wavefunctions are shown. Light gray is used to show doped wells ($6 \times 10^{17}$ cm$^{-3}$). The layer sequence is shown in the appendix A.1.6 (EV1517)

have showed that AlAs thicknesses below 16 Å should not lead to relaxation, for the laser design due to the major complexity of the structure, the concept of composite barriers was used to maintain the AlAs layer thicknesses below 10 Å to avoid excessive strain in the individual barriers.

6.6 Growth characterization

Fig. 6.5 compares the experimental and simulated rocking curves of the strain-compensated heterostructure over an Ω scanning range of 10 degrees in the (004)InP reflection. The high degree of crystal quality and thickness homogeneity is visible from more than 70 well defined satellite peaks with full-width at half-maximums (FWHM) of 18-30 arcsecs (FWHM of the InP substrate is 19 arcsecs). From the spacing between the satellite peaks an average period thickness of 44.8 nm is extracted with a deviation smaller than half a percent from the designed value of 44.6 nm. The 0th-order satellite peak is slightly separated from the substrate peak by 165 arcsec indicating that the strain
is not perfectly balanced between the 3.5 % compressive strained AlAs and the 1.3 % tensile strained InGaAs layers (in respect to InP), but the overall strain still being less than 0.1 %. The active region of the lasers is composed of 30 period repetitions, sandwiched by two 200nm thick InGaAs \((10^{16} \text{ cm}^{-3})\) confinement layers. A cladding consisting of a 2 \(\mu\)m thick and a 1 \(\mu\)m thick InP n-type layers\((2 \times 10^{17} \text{ cm}^{-3} \text{ and } 8 \times 10^{18} \text{ cm}^{-3})\) was grown by MOVPE as in ref.(116), followed by 100 nm of a highly doped InGaAs \(6 \times 10^{18} \text{ cm}^{-3}\). The grown structures have been processed in a standard ridge configuration, with 10-20 \(\mu\)m large waveguides using wet etching techniques. A 350 nm thick SiO\(_2\) layer has then been deposited to provide electrical insulation. For pulsed operation devices were cleaved and mounted epide side up on copper submounts and measured on a Peltier cooler.

Figure 6.5: Measured and simulated XRD curves. The simulated curve is offset for clarity. Measured data fit well with the expected compositions InGaAs/InAlAs-AlAs. An average period thickness of 44.2nm can be derived in well agreement with the expected one(44.6 nm)
6. QCLS IN THE 3-4 µM REGION

6.7 Laser performance

In Fig. 6.6 the emitted optical power and the applied voltage as function of the current are shown for a typical 18 µm wide and 3.8 mm long laser. An high reflection (HR) coating, consisting of 250 nm of Al₂O₃, 10 nm of Ti and 100 nm of Au, was applied on the laser back facet. Watt-level emission was observed at room temperature and the laser performance is comparable to what was observed for Sb-containing QCLs(111). Laser emission spectra for temperatures between 250 K and 350 K are shown in Fig. 6.7. Measuring the peak wavelength position as function of the temperature a tuning coefficient of 0.98 nm/K was obtained. In order to better explore the influence of thermally activated carrier leakage on laser behavior, in figures 6.8 and 6.9 the dependence of the threshold current density and of the slope efficiency are plotted as function of the heat sink temperature. Assuming the usual exponential trend \( J = J_0 \exp(T/T_0), \frac{dP}{dI} = (dP/dI)_0 \exp(-T/T_1) \), characteristic temperatures of 100 K and 70 K were measured for \( T_0 \) and \( T_1 \) respectively in the 250 K - 300K temperature range. The measured characteristic temperatures are comparable with what is observed in Sb-containing QCLs in this spectral range. In the figures 6.8 and
6.7 Laser performance

Figure 6.7: Fabry-perot laser emission spectra; a tuning coefficient of 0.98 nm/K was found by linear fitting of the peak emission wavelength as function of the temperature.

Figure 6.8: Measured and simulated threshold current density as function the laser temperature. Assuming the usual exponential behavior, a characteristic temperature of 100 K is estimated for the measured values. Simulated values lead to an overestimation of the characteristic temperature that is expected to be almost 170 K.

6.9 also simulated threshold current density and slope efficiency values are shown. As one can see, differently from what seen in the previous chapters, in the other spectral ranges, the transport model in this case does fail the estimation of the characteristic temperatures, and the effect of carrier leakage(92) in this energy range is not well accounted. In order to also estimate waveguide losses and differential gain for our lasers, threshold current density as function of the laser inverse length is shown in Fig. 6.10a for different currents. Waveguide losses and differential gain were obtained through
Figure 6.9: Measured and simulated slope efficiencies as function the laser temperature. Assuming the usual exponential behavior, a characteristic temperature of 70 K is estimated for the measured values. Simulated values lead in this case to a characteristic temperature of 600 K, this value, completely unphysical for QCLs, is probably a symptom of the weakness of the model in this spectral range.

Figure 6.10: a) Threshold current densities as function of the laser inverse length for different temperatures (250K/265K/275K/285K/295K). Maximum current density value $J_{\text{max}}$ is indicated as a dashed line. b) Waveguide losses (left axis) and differential gain (right axis) values as function of the temperature, estimated through linear fit from the left panel.

linear fit analysis. In Fig. 6.10b these two quantities are plotted as function of the heat sink temperature. As expected, waveguide losses are nearly constant in the analyzed temperature range and they are comparable with the free-carrier absorption expected in this spectral range (smaller than 1 cm$^{-1}$), suggesting that resonant intersubband
reabsorption does not play a relevant role for the shown active region design in contrast with what shown in ref (116). In addition, as described in the section 2.5.2.2, the ratio of the slope efficiencies of coated and uncoated devices allows us to calculate the non-thermal losses. Values between 0.5-0.6 cm$^{-1}$ have been measured for the different devices. At the same time, Fig. 6.10b shows also that the differential gain does steadily decrease with temperature, and that the low differential gain is probably in this case the most important limiting factor to laser performance.

6.8 Spectral control and continuous wave operation

The devices presented up to now are based on a wide ridges process and due to their poor thermal conductance, continuous wave operation is prevented. In this paragraph we will try to estimate the maximum temperature that could be obtained in continuous wave operation if a narrow ridge, inverted buried process would be used. In a quantum cascade laser, the temperature of the active region stack ($T_{act}$) can be defined as:

\[ T_{act} = T_{sub} + \Delta T \]  

(6.1)

![Figure 6.11: Peltier controller temperature ($T_{sub}$) as function of the active stack temperature ($T_{act}$) in a device with a termal conductance of 1800 W K$^{-1}$ cm$^{-2}$ and using the characteristic temperature and current density measured in previous section ($T_0 = 100K$ and $J_0 = 210$ A/cm$^2$).](image)
where $T_{\text{sub}}$ is the nominal temperature defined by the laser cooling system and $\Delta T$ is the temperature difference generated in the active region stack by the dissipated electrical power. Therefore

$$T_{\text{act}} = T_{\text{sub}} + \frac{P_{\text{electr}}}{G_{\text{th}}} \quad (6.2)$$

where $P_{\text{electr}}$ is the electrical power density dissipated in the system and $G_{\text{th}}$ is the specific thermal conductance of the system.

$$T_{\text{act}} = T_{\text{sub}} + \frac{V_0 J_0 e^{T_{\text{act}}/T_0}}{G_{\text{th}}} \quad (6.3)$$

where the exponential trend of the current density has been used. From the previous expression we can plot the temperature of the controller has function of the active region temperature. The values of the thermal conductance measured typically in the case of narrow ridges (4 $\mu$m) produced using the inverted buried processes, reach more than 1800 $W K^{-1} cm^{-2}$.

![Figure 6.12: Room temperature EL spectrum for a 375 $\mu$m long device for an applied voltage of 14 V. The luminescence width, both at the 50 % level or the 75 % level of the central peak is shown](image)

The characteristic characteristic temperature ($T_0$) measured for this layer assumes
values around 100 K. As we can see in Fig. 6.11 that curve does present a clear maximum that denotes a good estimation of the maximum temperature in c.w. operation. The maximum value obtained for $T_{\text{sub}}$ in this case is $\sim 310$ K and therefore with the use of a narrow ridges BH process, for the first time room temperature c.w. operation should be observable in QCLs in this spectral range.

Due to the big number of the sensing applications in this spectral range, not only high performance, but also good spectral control and in particular single spectral mode operation are key parameters in the implementation of laser sources. For the above mentioned reasons, the next steps in this research line will involve both the use of 1-st order DFB gratings to obtain spectral control and buried narrow ridges to obtain room temperature c.w. operation. In order to obtain an idea of wavelength range accessible, either in an external cavity configuration or by the use of DFB gratings, the electroluminesce of the structure is shown in Fig. 6.12 for an applied voltage of 14 V. The luminescence width, both at the 50 % level (3.05 – 3.8 $\mu$m) and at the 75 % level (3.15 – 3.6 $\mu$m) is shown. Therefore with the aid of an accurate control over the facet reflectivities a wide tuning could be obtained in external cavity configuration. Measurements in this direction are starting to be performed. Moreover DFB grating have also been written, using holographic technique, and the fabrication process is in progress to produce single spectral mode, narrow stripes lasers.
6. QCLS IN THE 3-4 μM REGION
Chapter 7

Waveguide Modelling:
multielement laser arrays in Mid-IR

In the previous chapters, the attention was focused on the active region engineering and process optimization in order to enhance laser performance. The goal of the next sections will be analysis of the waveguide design. In particular the implementation of phase-locked arrays in QCLs will be discussed.

In the section 7.2, an analysis of the basic array types that could be used for Mid-IR QCLs is presented. In section 7.3 vertically coupled arrays emitting at 10.5 µm will be presented, while in the section 7.4 laterally coupled arrays processed in an inverted buried configuration will be shown. In the last section (7.6), preliminary results on the fabrication of buried second-order photonic crystal will be introduced.

7.1 Introduction

For many of the QCL applications, large peak and average optical powers as well as a good beam quality are necessary. Recently outstanding improvement has been carried out on narrow stripe buried heterostructure quantum cascade lasers and multi watt-level optical emission has been reached in continuous wave operation(55, 91). Unfortunately,
conventional narrow stripe lasers are intrinsically limited by the relevant optical power density on the facet. Moreover the sub-wavelength confinement of the optical mode results in a low beam quality. By the use of large aperture devices, high peak powers with narrow emission could be obtained in pulsed operation. However, wide stripe lasers show poor thermal performance and the increase of optical field inhomogeneities in the gain medium gives rise to detrimental effects, as for example, spatial hole burning.

In the case of interband lasers, one solution to the above mentioned problems has been the development of buried heterostructure phase locked arrays. In fact these devices combine the narrow emission, typical of wide aperture devices, with the high thermal conductance, typical of BH narrow stripe devices. For these devices extremely high powers and efficiencies were obtained in a narrow beam.

### 7.2 Arrays types for QCLs

In Fig. 7.1 the basic types of arrays, used for interband diodes and that could be easily implemented for Mid-IR QCLs, are shown. In the case of leaky-wave-coupled arrays (a), the fundamental lasing mode has major peaks in the low index regions and gain medium is placed in these regions. For the evanescent-wave coupled array (b), electric field has instead peaks only inside the high-index regions, where gain medium is placed, and the optical mode is guided using dielectric confinement. Also y-junction coupled arrays (c) are based on the dielectric confinement and the in-phase operation is guaranteed in this case by the interference at of the different elements, that is constructive only for the in-phase mode.

### 7.3 Vertically coupled arrays

Before proceeding to the development of BH QCL arrays, in this section the development of QCL structures with multiple active core stacks is presented for high pulsed powers at 10.5 μm. The waveguide is constituted by four active cores separated along the growth direction by passive InP layers. As will be shown in deeper details in this section, the InP stacks help at the same time to improve thermal conductance in the structure and to maximize slope efficiency.
7.3 Vertically coupled arrays

In quantum cascade lasers, electrons are injected from period to period emitting ideally a photon at each step. For this reason, scaling of the power with the number of periods in the active region has been already demonstrated\footnote{119}. Unfortunately, with the increase in the number of periods, large optical field inhomogeneities across the active region will result, leading to detrimental effects as the increase of the vertical hole burning effect. Consequently, saturation of the gain medium will naturally occur only for periods of the active region that are in the peak of the optical mode. As already shown by Gresch et al.\footnote{120}, in a waveguide where the overlap factor is constant over all the periods, the onset of the gain medium saturation occurs at larger optical powers than in the case of a tightly confined waveguide; in ref. \footnote{120}, the ratio of saturation

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7_1.png}
\caption{Schematic representation of the basic types of phase-locked linear arrays. The traces correspond to refractive-index profiles. Based on a figure in the reference \footnote{5}. (a) Leaky-wave array (b) evanescent wave array (c) Y-junction array.}
\end{figure}
7. WAVEGUIDE MODELLING: MULTIELEMENT LASER ARRAYS IN MID-IR

Intensity between these two waveguides was estimated to be a factor of 2.

In order to estimate the detrimental effect of vertical spatial hole burning on the slope efficiency, we can consider once more the rate equation model (see section 2.2.1) for the period $i$ of the QCL. It can be written, neglecting spontaneous emission as:

$$\frac{dn^i_3}{dt} = \frac{J}{e} - \frac{n^i_3}{\tau_3} - Sg_c(n^i_3 - n^i_2)$$  \hspace{1cm} (7.1)

$$\frac{dn^i_2}{dt} = \frac{n^i_3}{\tau_{32}} - \frac{n^i_2}{\tau_2} + Sg_c(n^i_3 - n^i_2)$$  \hspace{1cm} (7.2)

$$\frac{dS}{dt} = \frac{c}{n_{ref}} \left[ \sum_{i=1}^{N_p} \Gamma_i g_c(n^i_3 - n^i_2)S + \alpha_{tot} \right]$$  \hspace{1cm} (7.3)

where $N_p$ is the total number of periods and $\Gamma_i$ is the overlap factor of the optical mode with the active region period $i$.

Imposing the steady-state condition for the photon flux and neglecting the lower state population ($n^i_2 = 0$), the equation (7.3) can be written as

$$\alpha_{tot} = \sum_{i=1}^{N_p} \Gamma_i g_c n^i_3$$  \hspace{1cm} (7.4)

Solving the equation (7.1) for the $n^i_3$ and inserting it into the (7.4) we obtain that the current density can be written as:

$$J = \frac{q\alpha_{tot}}{g_c} \frac{1}{\sum_{i=1}^{N_p} \Gamma_i \frac{1}{\tau_3} + g_c \Gamma_i S}$$  \hspace{1cm} (7.5)

If we assume $\tau_3 g_c \Gamma_i S << 1$, we can expand the (7.5) to the first order and write the photon density as:

$$S = \frac{g_c J \tau_3 \sum_{i=1}^{N_p} \Gamma_i - q\alpha_{tot}}{g_c^2 J \tau_3^2 \sum_{i=1}^{N_p} \Gamma_i^2}$$  \hspace{1cm} (7.6)

Deriving the previous equation in the current and substituting the current density
7.3 Vertically coupled arrays

expression (7.5), the slope efficiency at threshold \( S = 0 \) can be written as:

\[
\left. \frac{dS}{dj} \right|_{S=0} = \frac{1}{q\alpha_{tot}} \left( \sum_{i=1}^{N_p} \Gamma_i \right)^2 \sum_{i=1}^{N_p} \Gamma_i^2
\]  

(7.7)

In the previous equation the effect of vertical spatial hole burning on the slope efficiency is shown and one can easily see that the slope efficiency in a QCLs is expected to be maximum in the case of constant overlap factor in each period (rectangular optical mode). For a more detailed description we refer to the work of Gresch(121).

In conclusion, we have seen that a rectangular mode profile would have the effect of maximizing the slope efficiency and therefore we want to design the waveguide in order to obtain such a mode profile.

One of the possible ways to obtain such a quasi-rectangular mode profile is by dividing the gain medium in different cores and separate them by passive buffer layers. In Ref. (120) structures with 3 active region cores (InAlAs/InGaAs), separated by two InGaAs buffer layers, were presented. Although these lasers, operating in the 4.5-5.2 \( \mu \text{m} \) spectral range, led to record peak power, average powers were limited strongly by the poor thermal conductance of the structure.

To improve the thermal resistance of the structure, InP could be used instead of InGaAs in the buffer layers since InP presents a thermal conductance almost 20 times bigger than InGaAs.

7.3.1 Epitaxial growth and band structure

In the this section, we present a new waveguide design in which four active region stacks are separated by InP inter-layers. The effect of the multi-stack design on the optical mode compared with a classical single active region stack waveguide of the same thickness is shown in Fig. 7.2. One can easily see the effect of rectangularization of the optical mode due to the multi-stack design.

In order to grow the InP inter-layers and the active region design at the same time the growth was performed by MOVPE, at AL Technologies GmbH in Darmstadt, Germany. The 4 active region cores are based on a AlInAs/InGaAs bound-to-continuum design, emitting at 10.5 \( \mu \text{m} \) and the fundamental period sequence can be found in appendix A.1.5 (D121).
To reduce the free carrier absorption, that has a nearly $\sim \lambda^2$ dependence (122), low doping has been used inside the gain medium ($1.3\times10^{16}$ cm$^{-3}$) and the InP layers ($2\times10^{16}$ cm$^{-3}$). Growth starts with a 500nm thick InP buffer layer ($n=4\times10^{16}$ cm$^{-3}$) and is followed by a 440nm thick InGaAs layer ($n=2\times10^{16}$ cm$^{-3}$) for the optical mode confinement. Then four active region cores, each composed of 15 pairs of active and injection regions, are grown separated by three InP interstacks. The first and the third InP layers are 1 $\mu$m thick, while the central one is 1.6 $\mu$m thick. After the fourth active region an upper InGaAs confinement layer (450nm, $n=2\times10^{16}$ cm$^{-3}$) and a 4 $\mu$m thick InP cladding layer were grown. The growth is terminated with a 550nm thick InGaAs contact layer ($n=6\times10^{18}$ cm$^{-3}$).

### 7.3.2 Ridge processing

Laser devices were processed in a standard ridge configuration, using SiN on the sidewalls to provide electrical insulation. Laser ridges were etched using the solution of HBr:HNO$_3$:H$_2$O, as described in the third chapter, with widths between 30 and 50 $\mu$m. Wide ridges were used in order to reduce the waveguide losses introduced by the SiN insulation layer, particularly high in these spectral range.

In the Fig. 7.3, the laser performance of two lasers with ridge widths of respectively 48 $\mu$m and 40 $\mu$m, are compared. One can clearly see that laser performance at this wavelength are strongly influenced by laser width, showing that waveguide losses are

![Figure 7.2: Mode profile and refractive index along the growth direction. Active regions are represented by blue shaded areas. The effect of mode rectangularization due to the insertion of passive interstacks inside the active region stack is shown in the left panel compared to the right one.](image-url)
still a major issue. Narrower ridges, $\sim 30 \mu m$ wide, did not show lasing action at room temperature.

Figure 7.3: Room temperature pulsed power-current-voltage curves for two different ridge widths. The narrower device, even if it is longer and consequently presents smaller waveguide losses, show sensibly smaller performance. Narrower devices, $\sim 30 \mu m$ wide, did not show any lasing action at room temperature.

In Fig. 7.4 a microscope picture of the front facet can be observed. One can easily see that, due to the use of an isotropic wet etchant and the relevant thickness of the structure (thicker than 10 $\mu m$), big fluctuations of the laser width across the different stacks can be observed. This effect reflects also into the voltage versus current characteristic observed in Fig. 7.3, where non-uniform electron injection can be observed.

Figure 7.4: Microscope image of the front facet of a device. Active region stacks are indicated using red arrows.
7. WAVEGUIDE MODELLING: MULTIELEMENT LASER ARRAYS IN MID-IR

7.3.3 Fishbone design

In the previous section, lasing emission at 10.5 µm was obtained using a multi-stack structure. Unfortunately, laser performances are still strongly limited from the waveguide losses introduced by the SiN insulating layer deposited on the laser sidewalls as demonstrated by the heavy dependence of laser performance on ridge width. Moreover, the use of an isotropic wet etchant solution does not guarantee uniform electrical injection inside the active medium stacks.

In this section a new fabrication process, designed to overcome the above mentioned problems, will be described (Fig. 7.5).

Firstly, as described in the third chapter, undercut problems can be solved by the use of plasma etching that guarantees nearly vertical sidewalls and uniform pumping in the structure.

More difficult is the minimization of the losses introduced by the SiN insulating layer. In order to reduce these ones, a lateral selective wet etching of the active region stacks (step (g) in Fig. 7.5) is performed after the dry etching of the complete structure (f).

A solution of H$_2$SO$_4$:H$_2$O$_2$:H$_2$O (4:1:20) has been used for this purpose. This solution does provide an uniform InGaAs/AlInAs lateral etching of $\sim$ 1µm/minute while not attacking the InP layers. A picture of the etched structure is shown in Fig. 7.6. By the use of the lateral active region etching the overlap of the optical mode, maximum in the active region stacks, with the insulation layers is strongly reduced.

In the Fig. 7.8 the effect of the lateral etching on the simulated waveguide losses is shown for structures with ridge widths of 20-30-40-50 µm. Optical simulations show that, for 20 to 50 µm wide waveguides, optical losses drop sensibly for active region narrowings up to $\sim$2 µm, reaching successively a plateau. For this reason further lateral etching would not considerably reduce optical losses while compromising the mechanical stability of the structure. For an overall undercut of 2.0 µm, waveguide losses are expected to be $\sim$ 2.5 cm$^{-1}$.

In case of no undercut, additional losses up to 3 cm$^{-1}$ have been estimated for the widest considered ridges (50 µm). Obviously this calculation does not take in account the additional losses coming from sidewalls roughness, also supposed to be reduced by the lateral etching process step.
Ideally using this additional etching step, the SiN deposition on the active region sidewalls should be prevented. Unfortunately, due to the intrinsic non-directionality of the PECVD, used to deposit the 400nm thick SiN insulation layer, it is not possible to completely prevent SiN deposition inside the laterally etched regions. By SEM inspection, thickness of the penetrated layer is estimated to be $\sim 100\text{nm}$ (Fig. 7.7). In computing the waveguide losses, the presence of the thin lossy layer on the side of the active regions has been taken in account. After the selective etching step, only $O_2$ plasma cleaning was used as additional precaution in order to avoid contamination inside the laterally etched regions. Post processing inspection showed that these areas were clean from residuals. For a lateral under-etching up to 5 $\mu\text{m}$ a maximal 0.5% reduction is expected for the overlap of the optical mode with the active region.
7. WAVEGUIDE MODELLING: MULTIELEMENT LASER ARRAYS IN MID-IR

Figure 7.6: Left panel: Microscope picture of the fishbone process after the lateral active region etching. Active region stacks are indicated using green arrows. Right Panel: 2D simulated mode profile.

Figure 7.7: SEM of the ultimted fishbone process. In the zoomed picture the thin SiN layer (~ 100 nm) deposited on sidewalls of the active region stacks is shown.

7.3.4 Results of the fishbone process

In Fig. 7.9 pulsed (1% duty) power-current-voltage curves are shown for a 5.4 mm long and 49 µm wide device. Peak powers of 7.8 W and 4.7 W and slope efficiencies of 1.7 W/A and 1.3 W/A were measured at 243 K and 300 K, respectively. Threshold current densities were 1.15 kA/cm² at 243 K and 1.58 kA/cm² at 300 K. Fitting the exponential decay of the threshold current density with temperature \( J = J_0 e^{\frac{T}{T_0}} \) yields a \( T_0 \) of 180 K and a \( J_0 \) of 300 A cm².

At 300 K, in the case of shorter and narrower devices (l=3 mm, w=30-40 µm), slope efficiencies up to 1.6 W/A were measured. The threshold current density ranges
7.3 Vertically coupled arrays

Figure 7.8: Influence of the lateral active region etching on the waveguide losses for different ridge widths. Losses, especially for the narrow stripes, tend to initially decrease with the increase of the lateral etching to reach then a nearly common value.

Figure 7.9: Power-Current-Voltage curve, in the 243 K - 300 K range, for a 5.4 mm long and 49 µm wide device.
between 1.6-1.7 kA/cm², the peak powers between 1.5 W and 4 W.

As explained in the section 2.5.2.2, the total waveguide losses of our structures were derived from the threshold current density of a coated and an uncoated device(123). Assuming a facet reflectivity of R=0.27, our devices show waveguide losses ranging from 6 to 7.5 cm⁻¹.

The ratio of the slope efficiencies of uncoated and coated devices can be used in order to estimate the non-resonant losses. Losses ranging between 1.3 and 2 cm⁻¹ were observed. This value is in good agreement with the expected value of 2.7 cm⁻¹. Pulsed wall-plug efficiencies of our devices at 300 K are measured to be 4-4.3%. At 243 K efficiencies up to 7.3% were observed(124).

In Fig. 7.10 the average power, for the device shown in Fig. 7.9, is presented as a function of the duty cycle. Maximum average powers of 310 mW at 300 K, 470 mW at 273 K and 580 mW at 258 K were measured. At 300 K maximum power was obtained with a duty cycle of 12%. In the case of Ref. (120), where InGaAs buffer layers were used, thermal rollover occurred at 4% duty cycle.

In Fig. 7.11 comparison between simulated and measured thermal conductances is shown as a function of the active region width. Thermal conductance of our devices was measured using the drift of the threshold current with temperature and duty cycle.

Figure 7.10: Average power in function of duty cycle, for the device shown in Fig.2. The figure inset shows the emitting spectrum at 300K, with a peak wavelength near 10.5 µm.
Specific thermal conductances of 200-260 W·K⁻¹cm⁻² were estimated for junction up devices, which agrees well with the values obtained from thermal simulations. Also shown in Fig. 7.11 are simulated thermal conductances in the case of junction down devices, mounted on diamond heat spreaders; in this case thermal conductances up to 850 W·K⁻¹cm⁻² are expected for narrow (∼12 µm) and from 400-600 W·K⁻¹cm⁻² for 20-50 µm wide ridges.

In Fig. 7.12 measured farfield pattern (a) of a 40 µm wide and 3 mm long laser is also shown. For farfield emission, assuming a gaussian profile, full-widths at half-maximum of 18.7° and 39.8° were fitted, respectively in the growth and perpendicular direction. As shown in Fig. 7.12 (b), these values are in good agreement with performed 2D optical simulations that predict a FWHM of 17.8° and 39°. A good agreement with simulations is present also in the case of 30 µm ridges, where measured FWHM are 24° and 39.8° and simulated ones are 22.4° and 39°. This values are sensibly smaller than the ones measured in the case of traditional waveguides (43°x67°)(49). Measurement of the farfield emission pattern as a function of increasing current revealed no change and thus, no beam-steering effect was observed.
7. WAVEGUIDE MODELLING: MULTIELEMENT LASER ARRAYS IN MID-IR

![Figure 7.12: a) Measured farfield pattern for a 40 µm wide and 3 mm long device. b) Simulated and measured farfield pattern in the growth (red) and lateral direction (blue)](image)

7.4 Buried arrays

In the previous section, we have shown that using vertically coupled quantum cascade lasers, high peak powers could be achieved in a single beam. Waveguide losses are still nevertheless limited by the waveguide losses introduced by the SiN insulating layer, since, due to the unidirectionality of the PECVD deposition, a thin layer layer is deposited on the active medium stack sidewalls. In addition the thermal conductance of the structure is still too low to reach high powers in continuous-wave operation.

For this reason, in this section we will describe the implementation of buried het-
Considering the arrays types shown in the section 7.2 and their application in QCLs, the tree array principle using several Y-junction was already shown by (125) in a non-buried configuration. Unfortunately, this array class has intrinsically a poor fill factor of the optical mode and in a buried heterostructure configuration radiation losses would even increase, due to the smaller dielectric confinement typical of buried lasers. Moreover, the geometrical design of the structure makes it extremely sensitive to inhomogeneities coming from the epitaxial regrowth.

In the case of interband lasers, for array with a high number of elements, the best performance was obtained using leaky-wave arrays (126). In fact in the leaky-wave coupled arrays, differently from the evanescent-wave ones, parallel coupling between all the elements can be obtained, leading to a higher intermodal selectivity. Nevertheless, leaky-wave arrays are not based on dielectric confinement and the average refractive index in the interelement needs to be bigger than the one of the active elements. For this reason they require a more complicate interelement design.

On the contrary for evanescent-wave coupled array, the interelement can be constituted completely by insulating InP, resulting in an immediate transfer from the developed buried heterostructure process. Moreover for the few-element arrays, leaky-wave modes play a minor role since they are very lossy.

For the above mentioned reasons, in this work we decided to start exploiting the possibility of combining elements in a buried heterostructure for a QCL, starting with a reduced number of elements, evanescently coupled. It is nevertheless clear that in order to obtain high powers, the next step is the development of leaky-wave coupled array with large number of elements.

7.5 Evanescent-wave coupled buried arrays in Mid-IR QCLs

As already mentioned, in this section some preliminary results in Mid-IR QCLs lasers will be shown. In particular, the results obtained on two elements arrays and five-elements arrays will be presented. It is important to mention that all for all the arrays mentioned in the next section the total active region width has been kept constant to 15 μm, e.g. in the case of the five-element array the single element width is reduced to $\sim 3 \, \mu m$. 

121
7. WAVEGUIDE MODELLING: MULTIELEMENT LASER ARRAYS IN MID-IR

7.5.1 Processing

Figure 7.13: a) Scanning electron microscope image of a typical two-elements array. Active region structures (AR) are \(\sim 7.5 \, \mu m\) wide.

The quantum cascade structure used in this work has been grown by molecular beam epitaxy (MBE) and has an emission wavelength of 8.2 \(\mu m\). The active region design used for this structure is similar to what was already presented in ref. (2) (Layer sequence in appendix A.1.1 (EV1096)). Array elements were defined by plasma etching to reduce the undercut but in this case, an additional pure H\(_2\)SO\(_4\) etching is necessary in order to guarantee a complete polymer removal and prepare the structure for the epitaxial regrowth.

A 4 \(\mu m\) thick InP:Si layer \((n=1 \times 10^{17} \, cm^{-3})\) was grown on the top of the structure as cladding. In Fig. 7.13 an SEM image for a two elements array is shown, active regions (AR) are clearly recognizable surrounded by InP.

7.5.2 Optical mode simulations

In the Fig. 7.14, the computed electric field distribution of most relevant modes of the two-element array are presented. The array elements have been designed in order to maximize the overlap of the in-phase mode (a) with the active medium and to provide coupling between the elements via the evanescent field.

Finite element simulations, in the case of an infinitely long structure, show that it is possible to design the array in order to select the operational mode by losses discrimination.
7.5 Evanescent-wave coupled buried arrays in Mid-IR QCLs

Figure 7.14: Computed electric field in the vertical direction for a the two element array shown in Fig. 7.13. The most relevant optical modes are shown.

7.5.3 Laser performance and farfield emission

In Fig. 7.15, the emitted optical power and the applied voltage as function of the current are shown for a 2-elements array, each element 7.5 µm wide and 3.8 mm long, and with an interelement spacing of 3.5 µm. In order to show that the in-phase component was predominant, in the laser emission pattern was measured and compared with the farfield emission extracted from the near-field simulations (Simulated farfield emissions for the modes in Fig. 7.14 are shown in Fig. 7.16). In the Fig 7.17a, a cut of the measured farfield emission along the lateral direction is shown for the case of a single and a double elements array. The emission of the 2-elements array is a factor 1.5 narrower than the emission coming from the single element laser. To better show that, in the Fig 7.17a the lateral cut of the simulated farfield emission patterns are shown for the fundamental mode of the single element laser and for both the in-phase (a) in Fig. 7.14 and the out-of-phase mode (b) in Fig. 7.14 of the two elements array. The out-of-phase mode
does clearly show a multi-lobed emission pattern while a good agreement between the measurements and the simulations is shown both for the 1-element and the 2-elements lasers if considering the fundamental modes.

It is important to notice that no beam steering has been observed in the lasers for the different applied biases.

To show the narrowing of the emission with the number of array elements, in the Fig. 7.18 the simulated far-field patterns along the lateral dimension for the in-phase optical mode as function of the number of elements in the array. As it can be seen, already with the use of a 5-elements array farfield emission in the lateral direction can be sensibly narrowed up to a factor of more than 2.

7.5.4 Five-element array

In the Fig. 7.19, the SEM picture of a five-element array is shown. An interelement spacing of $\sim 2.5 \mu m$ is used to separate the $3 \mu m$ wide active elements. In the Fig. 7.20, the most relevant optical modes inside the 5-element array are shown. For each of them, the simulated farfield pattern is extracted by the near field. In the Fig. 7.21 the measured 2-dimensional farfield emission for a 5-elements array is shown.
emission pattern shows a narrow central spatial emission but two lateral modes are clearly visible showing an out-of-phase component of the optical mode. Considering the simulated emission pattern shown in Fig. 7.20, we believe that the observed farfield emission is due to a combination of the in-phase mode((a) in Fig. 7.20) with an out-of phase component ((c) in Fig. 7.20).

In addition, laser performance of multi-element array are not yet as good as performances of the single ridge, standard BH process and in particular in the case of the 5-elements array no room temperature laser emission was observed.

We attribute this effect mainly to two different effects. Firstly the choice of a constant total width for the active region for the different arrays does imply that for example in the 5-elements arrays the single element width is reduced to 3 µm and the influence of the sidewalls roughness plays a relevant role. This technological issues can surely be minimized by process optimization and increasing the single element width. Secondly as
Figure 7.17: (a) Comparison of the measured farfield emission in lateral direction for the single element and the 2-elements array. Farfields were measured in pulsed operation at a current density of 3.5 kA/cm$^2$ at room temperature. (b) Simulated emission pattern for the fundamental mode of the single element ridge for the in-phase and out-of-phase modes of the 2-elements array.

already mentioned with the increase in the number of elements the modal discrimination for evanescently coupled arrays is reduced and increases the array tendency to work on an out-of-phase mode.

In conclusion in this section we presented the implementation of buried heterostruc-
7.5 Evanescent-wave coupled buried arrays in Mid-IR QCLs

Figure 7.18: Simulated farfield emission along the lateral direction as function of the number of elements in the arrays for the in-phase mode. Narrowing of the far-field emission is observed up to a factor of 2 for the case of a 5-elements array. As mentioned already, the total active region width is kept constant to 15 \(\mu\)m for all the arrays.

Figure 7.19: (a) Scanning electron microscope image of a buried 5-elements array. Each active element is \(\sim 3\ \mu\)m and is identified by the label \(AR\).
Figure 7.20: Simulated optical mode and farfields for the 5-element array structure quantum cascade lasers based on evanescent-wave coupling between the elements. Narrowing of the farfield emission pattern is shown. Unfortunately, due to the intrinsic poor modal discrimination of evanescently coupled arrays, leaky waves arrays arrays
Figure 7.21: Measured farfield emission pattern for 5 elements array (Experiment) compared with the simulated farfield emission (Mode (a) and (d)).

are necessary already in the case of 5-elements arrays.
7. WAVEGUIDE MODELLING: MULTIELEMENT LASER ARRAYS IN MID-IR

7.6 Second-order PhC

In this section, the development of surface-emitting Mid-IR QCLs, based on a buried heterostructure photonic crystal resonators will be treated. The devices are designed to operate on band-edge modes of the photonic crystal structure. Unfortunately, due to technological issues, no working device was yet observed. Nevertheless simulation results and preliminary fabrication data will be presented.

7.6.1 Introduction

In the Mid-IR and Far-IR spectral regions, photonic crystals-based quantum cascade structures were already demonstrated (127, 128, 129, 130, 131, 132, 133, 134). The application of photonic-crystal technology is particularly appealing because it allows the achievement of simultaneous spectral and spatial mode engineering. Impressing results were also obtained in the Mid-IR spectral range using second-order grating on disk lasers (135, 136, 137).

Unfortunately, none of the structures presented up to date made use of the buried heterostructure technology. We believe that the development of photonic-crystal buried heterostructure quantum cascade lasers is a key issue in the fabrication of low dissipation sources in the Mid-IR.

Moreover in the photonic crystal based structures presented in the past, the active region is directly sandwiched between the substrate and the top metalization layer that at the same time acts as a surface plasmonic layer and enables electric current injection. Such plasmonic waveguides are known to induce high ohmic losses and sensibly limit laser performance. In addition in all the structures presented in the past in the Mid-IR the photonic crystal was defined by a series of holes in the active medium, in order to allow electrical injection in the structure. This led to the electrical pumping of zones in which the electric field amplitude is low, with a consequent higher current flowing into the device.

In a buried heterostructure PhC device, an uniform electric injection can be guaranteed through a conductive cladding layer and a photonic crystal resonator based on active region columns rather than holes can be used, reducing the amount of pumped surface.
7.6.2 Band structure

Two-dimensional photonic crystal waveguides can be divided into two main categories: defect mode cavities and band-edge mode cavities (138). The first ones require a full bandgap of the photonic structure and are obtained by the introduction inside this gap of a defect that supports localized modes. Band-edge mode cavities operate instead in regions with a low group velocity (139). The latter resonators have the advantage of not needing a gap inside the band-structure and moreover the spatial delocalization of the optical mode, typical of these resonators, is beneficial to reduce detrimental effects as spatial hole burning and at the same time improve light extraction efficiency.

![Figure 7.22: TM Photonic band structure for a square array of columns with a radius of $r = 0.375 \, a$. The active medium squared columns are surrounded by insulating InP. In the left inset a cross-sectional view of the dielectric function is shown. The right inset shows the Brillouin zone, with the irreducible zone in shaded red.](image)

Resonators presented in this section, square lattice of active region rods in InP, are based on band-edge modes and due to the low index contrast ($\frac{n_{AR}}{n_{InP}} \sim 1.1$), no band gap is observed neither in TE or in TM polarization; the minimum index ratio for obtaining a gap in TM polarization being in this case $\frac{n_{AR}}{n_{InP}} \sim 1.7$ (140).

The photonic band diagram for the TM-polarized light is presented in Fig. 7.22. In the left inset a cross-sectional view of the dielectric function is shown, the use of rods with squared base is simply due to technical constraints in writing lithographic masks.
7. WAVEGUIDE MODELLING: MULTIELEMENT LASER ARRAYS IN MID-IR

with circular structures of these dimensions. The right inset shows the the Brillouin zone, with the irreducible zone in shaded red. Since we were interested in surface-emitting devices, modes at the Γ points were considered. In particular in the Fig. 7.23 a), a zoom of the band diagram around the Γ-point is shown. One can easily see that the third band as an almost flat dispersion, indicating a low mode group velocity and higher gain. For these reason our resonators were designed to lase on this band. The optical mode corresponding to the third band at the Γ-point is shown in the top-left inset of the Fig. 7.23 (b). The pumping efficiency for the third band as function of the pillar radius to period ratio is shown is Fig. 7.23 (b).

The pumping efficiency is defined in this case as the ratio between the energy inside the pillar divided by the pillar cross-section area. One can see that the pumping efficiency tends to saturate for ratios bigger than 0.35, resonators with radius-to-period radius between 0.3 and 0.4 were then designed.

![Figure 7.23](image-url)

**Figure 7.23**: a) Zoom of the photonic crystal band diagram shown in Fig. 7.22 near the Γ-point. b) Ratio of the optical mode energy inside the pillars to the pillar area as function of the pillar ratio \( r/a \) for the third band. In the top-inset, the optical mode of the third band at the Γ-point is shown.

### 7.6.3 Processing

In the following section, the fabrication process of buried heterostructure PhC will be described. The structure is defined using simple Deep-UV lithography, with features as small as 350 nm, without the need for expensive and time consuming electron beam
Figure 7.24: SEM images of the photonic crystal structure pattern defined by deep-UV lithography and SiO\(_2\) plasma etching.

lithography. A SiO\(_2\) hard mask is then etched by RIE, as already described in the inverted buried process section (Fig. 7.24). The pillars are then defined using deep plasma etching (Fig. 7.25) and then insulating InP is deposited around the pillars by selective growth in MOVPE (Fig. 7.26 a)). After hard mask stripping a thin InP cladding is deposited on the structure (Fig. 7.26 a)). In the surface emitting PhC structures, the top metalization layer deposited is smaller than the actual PhC structure and provides at the same time absorbing losses at the boundaries and guarantees also light extraction. An illustration of the final device is shown in Fig. 7.27. From the (Fig. 7.26), we can immediately recognize that mayor issues are present in the regrowth steps and that in particular in the first InP regrowth. In fact, the faster growth rate on the top of the pillars leads to the creation of crystallites that eventually prevent
7. WAVEGUIDE MODELLING: MULTIELEMENT LASER ARRAYS IN MID-IR

a) after Insulating InP growth

Figure 7.26: SEM images of the photonic crystal structure after the regrowth of the insulating InP layer (a) and after the n-contact InP cladding layer (b)

b) after InP n-contact growth

Figure 7.27: Illustration of the buried heterostructure photonic crystal QCL, surface emission is indicated by the arrows on the side of the top metalization layer.

the InP growth in the bottom of the structure creating holes in the layer (Fig. 7.26 b)). Moreover devices fabricated up to now showed current leak paths that prevented current injection inside the active region.
Even though no conclusive explanation has been proved, we do believe that the current leaks originate from the etch rate difference, in the ICP, between the boundaries and the active region pillars.

In fact, the material extraction between the pillars during the etching process is much slower than the one on the structure boundaries. Consequently the etch depth on the boundaries is so elevated that the insulating InP regrowth doesn’t achieve to cover sufficiently the structure sidewalls and conducting InP is then deposited at the boundaries of the structure producing leakage paths. This conclusion was reached due to the InGaAs layer (20 nm thick) that we use at the end of the regrowth of insulating InP, in order to label the separation between the regrowths. In the Fig. 7.28 appears clear that this InGaAs layer is well below the beginning of the active region layer, instead of being above the end of the active stack. The etch rate difference in the different points of the structure cannot be controlled, therefore, in order to remove the leakage paths, a new etch step will have to be introduced in the process flow that etches at the boundaries, where there is no gold contact, also the n-contact layer. Moreover since, as mentioned, light extraction is expected on the surface at structure boundaries the etching of the n-contact in also beneficial in order to reduce the optical losses.

Using this additional etching step, we are confident to obtain working devices.
7. WAVEGUIDE MODELLING: MULTIELEMENT LASER ARRAYS IN MID-IR
Chapter 8

Conclusions and Outlook

In this work the development of high performance quantum cascade lasers in the Mid-IR spectral range was presented.

In order to reach this objective, four distinct aspects that heavily influence performance in QCLs have been analyzed. First of all, the optimization of the active region design, in order to insure efficient carrier injection in the upper lasing state and extraction out of the lower lasing state. Secondly the epitaxial growth optimization in order to obtain high quality layers even in the case of heavily strained structures and also to reduce scattering mechanisms that can limit laser performance. Thirdly, the optimization of the fabrication process, that is crucial to reduce optical losses and improve the laser thermal conductance. Last, but not least, the engineering of the waveguide design, crucial both for high power and spectral control.

In the early part of the work, the optimization of the fabrication process methods has been carried out. A new buried heterostructure process has been developed where the total number of fabrication steps has been sensibly reduced, in particular the photolithographic steps can be reduced up to only two (ridge definition and electroplating pads). At the same time this process insures a better control of the active stack profile insuring a more uniform current injection. Moreover since the thickness of the InP lateral regrowth is reduced by a factor of two, the total amount of defects is reduced. In the new process flow the temporal sequence of the two InP epitaxial regrowths (Cladding and Insulating layer) has been inverted, therefore the process has been referred in the text as inverted buried process (Insulating layer, Cladding).
8. CONCLUSIONS AND OUTLOOK

At the same time the validation of a new transport model has been carried out, in order to obtain predictive information about laser performance. Several structures have been grown over all the Mid-IR spectral range and simulations have been compared with the measured values.

Using the optimized process and the transport model, a new laser structure has been designed and processed in order to obtain high performance and wide voltage tuning in the second atmospheric window. The design is based on a bound to continuum scheme, in which the relatively thin injector region insures carrier injection over a wide range of electric fields. In the case of Farbry-Perot devices, a maximum spectral coverage of over $140 \text{ cm}^{-1}$ is obtained by only voltage tuning at room temperature, corresponding to $\sim 12 \%$ of the central wavelength. In spite of the wide tuning, high laser performance were also observed. In particular, threshold currents as low as $1.5 \text{ A/cm}^2$ and slope efficiencies per facet as high as $1.4 \text{ W/A}$. Wallplug efficiencies as high as $12.5 \%$ were observed in pulsed operation. In order to measure the performance in cw, some devices were mounted epi-side down on a diamond heat spreader and powers as high as $450 \text{ mW}$ were observed at room temperature.

In the case of quantum cascade lasers emitting in the first atmospheric window, the use of strained $\text{InGaAs}/\text{AlInAs}$ on $\text{InP}$ has been necessary in order to increase the band offset discontinuity. To optimize laser performance in this spectral range, a study of the influence of the growth temperature on interface roughness and consequently on laser performance has been carried out. In particular a non-monotonic behavior of the performance as function of the growth temperature has been observed, with a clear maximum in our case for temperatures around $515 \, ^{\circ} \text{C}$. Comparing simulated and measured laser performance, a correspondence between the growth temperature and the interface roughness could be retrieved and a correlation length of $\sim 85 \, \text{Å}$ was associated with a growth temperature of $515 \, ^{\circ} \text{C}$. Moreover, the failure of the model to predict the electroluminescence linewidth for long correlation lengths has been analyzed. The latter being the only parameter used in the past to estimate the interface roughness. In the case of a growth temperature of $515 \, ^{\circ} \text{C}$, total wallplug efficiencies as high as $15 \%$ were measured. Room temperature continuous wave powers up to $600 \, \text{mW}$ were measured for devices mounted epi-side down.

A new active region, emitting at $\sim 4.8 \, \mu\text{m}$, was also designed in order to reduce the parasitic current flowing in the active region before structure alignment. With
this aim, a two-step composite barrier (step well) has been used as an injector barrier. Due to the unavailability of an additional Al cell in the used MBE, the growth of the two-step barrier has been substituted with an equivalent digital grating. Measured voltage-current characteristic show indeed a reduction of the parasitic current but, unfortunately, the laser performance of both the new design and the reference sample are lower than expected from simulations. The low laser performance is attributed to process contamination and in order to confirm this supposition a new fabrication process will have to be performed on the same structures.

By the use of highly strained AlAs layers, QCLs in the 3-4 µm range have also been developed. Growth optimization as been carried out also in this case in order to prevent layer relaxation. Using the principle of the composite barrier (AlInAs/AlAs), in order to tune independently both the layer thicknesses and the total net strain of the structure, a new active region has been designed. Room temperature emission at 3.3 µm was for the first time observed in this material system and laser emission up to 350 K was demonstrated. At room temperature, watt-level emission was observed in pulsed operation, using wide ridges. Wide ridges were also the reason of the limited thermal conductance of the devices. Using the measured characteristic temperature $T_0$ of the devices and the expected thermal conductance of narrow ridges BH lasers, a maximal continuous temperature of 310 K is previsioned. The use of first order distributed feedback gratings, defined using holography, will be also used in order to obtain single mode emission.

In the first part of the section dedicated to the waveguide engineering, high peak power quantum cascade lasers have been produced using a diluted waveguide. The active region stack has been in fact separated in the growth direction in 4 different stacks and interlayed by passive InP stacks. These stacks have at the same time the effect of improving the thermal conductance of the structure while at the same time guarantees a quasi-rectangular optical mode; using the rate equation model, we have shown that in a QCL structure slope efficiency is maximized if the overlap factor is constant in each active period (rectangular mode). Peak powers up to 5 W are measured in pulsed operation at room temperature and average powers up to 300 mW. In order to reduce the thermal resistance of the structure and obtain high powers also in continuous wave, the same structure will be processed in narrower ridges in a BH configuration. Averages powers of over a Watt are expected in this case.
8. CONCLUSIONS AND OUTLOOK

Preliminary work on the implementation of high power, BH phase locked arrays has been carried out. Narrowing of the farfield emission pattern had been demonstrated both for two- and five-elements arrays. In order to better compare the different arrays, the total active region width was kept constant to 15 $\mu$m in all the devices. Nevertheless the degradation of the laser performance with the increasing number of elements, especially for the 5-elements arrays, shows on one side the necessity to better control the sidewall roughness and moreover the presence of an anti-phase component is a symptom that antiguide based arrays have to be used in order to insure in-phase operation.

In order to obtain spectral control of laser emission and at the same time obtain low dissipation and narrow surface-emission, some preliminary results on the development of buried heterostructure photonic crystal based QCLs. Laser emission has not yet been observed due to technical problems but, due to the reduced amount of electrically pumped surface, this resonators could be crucial in the development of single mode, low power consumption (less than 1 W), uncooled devices. Since the latest technical problems seem to be simply connected the over etching of the structure, we expect to obtain the first results on the lasing emission already in the next fabrication run.
Appendix A

Processing

A.1 Active region designs

A.1.1 EV1096, EV1140: Wide tuning

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness [Å]</th>
<th>Doping [cm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlInAs</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>31</td>
<td>1.2×10¹⁷ cm⁻³</td>
</tr>
<tr>
<td>AlInAs</td>
<td>34</td>
<td>1.2×10¹⁷ cm⁻³</td>
</tr>
<tr>
<td>InGaAs</td>
<td>29</td>
<td></td>
</tr>
</tbody>
</table>
## A. PROCESSING

### A.1.2 EV1299-1301: Three QWs design

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness [Å]</th>
<th>Doping [cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlInAs</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>22</td>
<td>$1.2 \times 10^{17} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>AlInAs</td>
<td>19</td>
<td>$8.1 \times 10^{16} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>InGaAs</td>
<td>21</td>
<td>$1.2 \times 10^{17} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>AlInAs</td>
<td>21</td>
<td>$8.1 \times 10^{16} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>InGaAs</td>
<td>20</td>
<td>$1.2 \times 10^{17} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>AlInAs</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>
### A.1.3 EV1326: Step Well

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness [Å]</th>
<th>Doping [cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlInAs</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>20</td>
<td>$1.85 \times 10^{17}$ cm$^{-3}$</td>
</tr>
<tr>
<td>AlInAs</td>
<td>18</td>
<td>$1.06 \times 10^{17}$ cm$^{-3}$</td>
</tr>
<tr>
<td>InGaAs</td>
<td>20</td>
<td>$1.85 \times 10^{17}$ cm$^{-3}$</td>
</tr>
<tr>
<td>AlInAs</td>
<td>20</td>
<td>$1.06 \times 10^{17}$ cm$^{-3}$</td>
</tr>
<tr>
<td>InGaAs</td>
<td>19</td>
<td>$1.85 \times 10^{17}$ cm$^{-3}$</td>
</tr>
<tr>
<td>AlInAs</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>20.5</td>
<td></td>
</tr>
</tbody>
</table>

### A.1.4 EV1327: Step Well

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness [Å]</th>
<th>Doping [cm$^{-3}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlInAs</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>15</td>
<td>$1.5 \times 10^{17}$ cm$^{-3}$</td>
</tr>
<tr>
<td>InGaAs</td>
<td>19</td>
<td>$2.6 \times 10^{17}$ cm$^{-3}$</td>
</tr>
<tr>
<td>AlInAs</td>
<td>22</td>
<td>$1.5 \times 10^{17}$ cm$^{-3}$</td>
</tr>
<tr>
<td>InGaAs</td>
<td>18</td>
<td>$2.6 \times 10^{17}$ cm$^{-3}$</td>
</tr>
<tr>
<td>AlInAs</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>16</td>
<td></td>
</tr>
</tbody>
</table>
A. PROCESSING

A.1.5 D121 : Bound to continuum at 10.5 $\mu$m

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness [Å]</th>
<th>Doping $[cm^{-3}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlInAs</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>62</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>37</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>18 $\times 10^{16} \ cm^{-3}$</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>35 $\times 10^{16} \ cm^{-3}$</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>20 $\times 10^{16} \ cm^{-3}$</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>34 $\times 10^{16} \ cm^{-3}$</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>33</td>
<td></td>
</tr>
</tbody>
</table>
### A.1 Active region designs

#### A.1.6 EV1517-8

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness [Å]</th>
<th>Doping [cm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlAs</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>31</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>4</td>
<td>6 × 10¹⁷ cm⁻³</td>
</tr>
<tr>
<td>AlInAs</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>19</td>
<td>6 × 10¹⁷ cm⁻³</td>
</tr>
<tr>
<td>AlInAs</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>18</td>
<td>6 × 10¹⁷ cm⁻³</td>
</tr>
<tr>
<td>AlInAs</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>17</td>
<td>6 × 10¹⁷ cm⁻³</td>
</tr>
<tr>
<td>AlInAs</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>12</td>
<td>6 × 10¹⁷ cm⁻³</td>
</tr>
<tr>
<td>AlInAs</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>AlAs</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>AlInAs</td>
<td>13</td>
<td></td>
</tr>
</tbody>
</table>
### A. PROCESSING

#### A.2 Cladding recipes

##### A.2.1 EV1140: Wide tuning

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness [µm]</th>
<th>Si Doping [cm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>InGaAs</td>
<td>0.3</td>
<td>$6 \times 10^{18} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>InP</td>
<td>4.4</td>
<td>$5 \times 10^{16} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>InGaAs</td>
<td>0.3</td>
<td>$6 \times 10^{16} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td><strong>Active region</strong></td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>0.2</td>
<td>$6 \times 10^{16} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>InP</td>
<td>150</td>
<td>$2 \times 10^{16} \text{ cm}^{-3}$</td>
</tr>
</tbody>
</table>

##### A.2.2 EV1299-1301

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness [µm]</th>
<th>Si Doping [cm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>InGaAs</td>
<td>0.08</td>
<td>$6 \times 10^{18} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>InP</td>
<td>0.7</td>
<td>$7 \times 10^{18} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>InP</td>
<td>2.5</td>
<td>$2 \times 10^{16} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>InGaAs</td>
<td>0.1</td>
<td>$6 \times 10^{16} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td><strong>Active region</strong></td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>0.1</td>
<td>$2 \times 10^{16} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>InP</td>
<td>150</td>
<td>$2 \times 10^{17} \text{ cm}^{-3}$</td>
</tr>
</tbody>
</table>

##### A.2.3 EV1326-1327

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness [µm]</th>
<th>Si Doping [cm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>InGaAs</td>
<td>0.08</td>
<td>$6 \times 10^{18} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>InP</td>
<td>0.7</td>
<td>$7 \times 10^{18} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td>InP</td>
<td>2.5</td>
<td>$2 \times 10^{16} \text{ cm}^{-3}$</td>
</tr>
<tr>
<td><strong>Active region</strong></td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>InP</td>
<td>150</td>
<td>$2 \times 10^{17} \text{ cm}^{-3}$</td>
</tr>
</tbody>
</table>
### A.2 Cladding recipes

#### A.2.4 EV1517

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness $[\mu$m]</th>
<th>Si Doping $[cm^{-3}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>InGaAs</td>
<td>0.08</td>
<td>$6 \times 10^{18} , cm^{-3}$</td>
</tr>
<tr>
<td>InP</td>
<td>1.0</td>
<td>$8 \times 10^{18}$</td>
</tr>
<tr>
<td>InP</td>
<td>2.0</td>
<td>$2 \times 10^{17} , cm^{-3}$</td>
</tr>
<tr>
<td>InGaAs</td>
<td>0.2</td>
<td>$6 \times 10^{16} , cm^{-3}$</td>
</tr>
<tr>
<td><strong>Active region</strong></td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>0.1</td>
<td>$6 \times 10^{16} , cm^{-3}$</td>
</tr>
<tr>
<td>InP</td>
<td>150</td>
<td>$2 \times 10^{17} , cm^{-3}$</td>
</tr>
</tbody>
</table>

#### A.2.5 D121: Bound to continuum at 10.5 $\mu$m

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness $[\mu$m]</th>
<th>Si Doping $[cm^{-3}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>InGaAs</td>
<td>0.55</td>
<td>$6 \times 10^{18} , cm^{-3}$</td>
</tr>
<tr>
<td>InP</td>
<td>4.0</td>
<td>$4 \times 10^{16} , cm^{-3}$</td>
</tr>
<tr>
<td>InGaAs</td>
<td>0.45</td>
<td>$2 \times 10^{16} , cm^{-3}$</td>
</tr>
<tr>
<td><strong>Active Region</strong></td>
<td>1.1</td>
<td>$1.3 \times 10^{16} , cm^{-3}$</td>
</tr>
<tr>
<td>InP</td>
<td>1.0</td>
<td>$2 \times 10^{16} , cm^{-3}$</td>
</tr>
<tr>
<td><strong>Active Region</strong></td>
<td>1.1</td>
<td>$1.3 \times 10^{16} , cm^{-3}$</td>
</tr>
<tr>
<td>InP</td>
<td>1.6</td>
<td>$2 \times 10^{16} , cm^{-3}$</td>
</tr>
<tr>
<td><strong>Active Region</strong></td>
<td>1.1</td>
<td>$1.3 \times 10^{16} , cm^{-3}$</td>
</tr>
<tr>
<td>InP</td>
<td>1.0</td>
<td>$2 \times 10^{16} , cm^{-3}$</td>
</tr>
<tr>
<td><strong>Active Region</strong></td>
<td>1.1</td>
<td>$1.3 \times 10^{16} , cm^{-3}$</td>
</tr>
<tr>
<td>InGaAs</td>
<td>0.44</td>
<td>$2 \times 10^{16} , cm^{-3}$</td>
</tr>
<tr>
<td>InP</td>
<td>0.5</td>
<td>$4 \times 10^{16} , cm^{-3}$</td>
</tr>
<tr>
<td>InP</td>
<td>200</td>
<td>$1 - 2 \times 10^{18} , cm^{-3}$</td>
</tr>
</tbody>
</table>
A. PROCESSING

A.2.6 Thin cladding for surface emitting PhC

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness [µm]</th>
<th>Si Doping [cm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>InGaAs</td>
<td>0.01</td>
<td>6 × 10¹⁸ cm⁻³</td>
</tr>
<tr>
<td>InP</td>
<td>0.6</td>
<td>1 × 10¹⁷ cm⁻³</td>
</tr>
<tr>
<td>InGaAs</td>
<td>0.3</td>
<td>4 × 10¹⁶ cm⁻³</td>
</tr>
<tr>
<td>Active region</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>InGaAs</td>
<td>0.2</td>
<td>4 × 10¹⁶ cm⁻³</td>
</tr>
<tr>
<td>InP</td>
<td>150</td>
<td>2 × 10¹⁶ cm⁻³</td>
</tr>
</tbody>
</table>

A.2.7 Doping calibration

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness [µm]</th>
<th>Si Doping [cm⁻³]</th>
<th>Fe Doping [cm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>InP</td>
<td>0.4</td>
<td>4 × 10¹⁶ cm⁻³</td>
<td></td>
</tr>
<tr>
<td>InP</td>
<td>0.4</td>
<td>2 × 10¹⁶ cm⁻³</td>
<td>2 × 10¹⁶ cm⁻³</td>
</tr>
<tr>
<td>InP</td>
<td>0.4</td>
<td>2 × 10¹⁶ cm⁻³</td>
<td>2 × 10¹⁶ cm⁻³</td>
</tr>
<tr>
<td>InP</td>
<td>300</td>
<td>1 − 2 × 10¹⁸ cm⁻³</td>
<td></td>
</tr>
</tbody>
</table>

A.3 Stress compensated SiN mask for plasma etching

As already described in the third chapter, SiN (PECVD) was used as hard mask for plasma etching.

In the case of deep etching, e.g. the fishbone design described in the paragraph 7.3.3, a thick masking layer has to be developed. Unfortunately, for thicknesses bigger than 1 µm standard SiN deposited on InP shows an excessive stress and the hard masking layer tends to crack during the ICP etching damaging the structure.

The main component of this stress is the thermal stress and it is due to the difference in the expansion coefficients of the hard mask and the semiconductor and to the big difference between deposition temperature and characterization temperature (in our case is ∼ 300 °C). One of the most common way of reducing the stress induced in to the deposited layer is the use of dual-frequency plasma excitation.

In our case two sources at 13 MHz and 130 kHz are used.
A.3 Stress compensated SiN mask for plasma etching

When a high frequency source is used to excite the plasma a compressive strain is induced while if the low frequency component is used a tensile strain is observed.

Therefore varying the duty cycle of the two source a zero-stress layer can be deposited.

In order to measure the strain inside the deposited layer a Tencor Stress Meter has been used. This machine allows to measure a curvature as long as to 20 km in the measured layers.

The optimized process is listed here and over a full two-inch wafer a radius of curvature bigger that 1 km is observed. This value indicates a sensibly lower stress than in the initial case, only high frequency on, where curvatures smaller than 100 m were measured.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>25</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>HF Pulse time [s]</td>
<td>LF Pulse time [s]</td>
<td>Pressure [mTorr]</td>
<td>rate [nm/min]</td>
</tr>
<tr>
<td>13</td>
<td>4</td>
<td>650</td>
<td>20</td>
</tr>
</tbody>
</table>

Appendix B

Curriculum vitae

Personal information

Name: Alfredo Bismuto

Address: Institute of Quantum Electronics
          ETH Zurich HPT-F10
          Wolfgang-Paulistrasse 16
          8093 Zurich
          Switzerland

Phone: +41(0)44 633 65 77

Email: bismuto@phys.ethz.ch

Date of birth: February 23, 1983, Naples, Italy

Nationality: Italian
B. CURRICULUM VITAE

Education

Jul. 07 – Sept. 11 Ph.D. student Quantum OptoElectronics group at the Institute of Quantum Electronics ETH Zürich Switzerland under supervision of Prof. J. Faist.

Research activity: Mid-infrared quantum cascade lasers: active medium and waveguide engineering. This work includes the optimization of the active region design using electron transport models and fabrication process of the laser sources using clean room facilities for III-V semiconductor systems. It concerns also the modeling of the waveguides using simulation software and the activity in the laboratory with cryogenic systems, FTIR and different optical and electronic systems for infrared radiation.

Jan. 11 Visiting Research Assistant at the University of Wisconsin-Madison, USA.

Apr. 07 – Jun. 07 PhD studies at the Mesoscopic Physics Group, University of Neuchâtel, Switzerland under the supervision of Prof. J. Faist.

Nov. 06 – Mar. 07 Research assistant at the Quantum Device Lab at the Institute of Solid State Physics ETH Zurich Switzerland under the supervision of Prof. A. Wallraff.

Research activity: High RF frequency measurements in a pulse tube cooler for applications in quantum computing using superconducting junctions.


Final note: 110/110 cum laude

Thesis title: Optical characterization of nanostructures for chemical sensing.

Research activity: Study of time-resolved recombination dynamics in nanostructures. Particular attention was given to the analysis of the effects that the surrounding ambient factors (gas, temperature) produces on the luminescence dynamics in view of the possible application of these materials in purely optical sensing devices. The investigated samples, were either nanowires fabricated by
thermal evaporation of ZnO and SnO$_2$ powders or silica skeletons of marine diatoms.

**Sept. 01 – Oct. 04** Bachelor studies: "Laurea Triennale" in Physics at Universita’ degli studi Federico II, Naples, Italy.

Final note: **110/110 cum laude**

Thesis title: **Time resolved photoluminescence on tin dioxide nanobelts.**

**Sept 96 – Jul. 01** High school studies: Scientific Lyceum- Liceo scientifico F. Sbordon, Naples, Italy.

Final Note: **100/100.**

**Languages**

**Italian** Mother tongue.

**English** fluent, spoken and written.

**French** good spoken and basic written.

**German** Basic.
Appendix C

Publications

Peer-reviewed journal papers

As primary author


C. PUBLICATIONS


As contributing author


**Invited talks**

1. **A. Bismuto**, R. Terazzi, M. Beck, and J. Faist. *Room temperature, watt-level emission at 3.3m in Sb-free InGaAs-AlAs quantum-cascade lasers*, Joint Annual Meeting of the Swiss and Austrian Physical Societies Lausanne (Switzerland), June 15, 2011.

**Conference contributions (only when first author or presenter)**


5. **A. Bismuto**, R. Terazzi, M. Beck, and J. Faist. *High power, broad gain quantum cascade lasers emitting at 8.5 µm*. International Conference on Intesubband Transitions in Quantum Wells (ITQW 09), Montreal (Canada), September 6–11, 2009. (Poster)


Bibliography


quantum cascade lasers,” *New Journal of Physics*, vol. 12, p. 033045, 2010. 1, 13, 21, 27, 74


[68] J. Faist, Quantum Cascade Lasers. To be published. 21


166


[97] Q. Yang, R. Losch, W. Bronner, S. Hugger, F. Fuchs, R. Aidam, and J. Wagner, “High peak power strain-compensated GaInAs/AlInAs quantum cascade lasers (λ ~ 4.6 μm) based on a slightly diagonal active region design,” *Applied Physics Letters*, vol. 93, no. 25, p. 251110, 2008. 71


[101] A. Bismuto. 87


[111] J. P. Commin, D. G. Revin, S. Y. Zhang, A. B. Krysa, K. Kennedy, and J. W. Cockburn, “High peak power at 3.3 and 3.5 \(\mu\)m InGaAs/AlAs(Sb) quantum cascade lasers operating up to 400 K,” *Applied Physics Letters*, vol. 97, no. 3, p. 031108, 2010. 93, 94, 100


[115] M., M. P. Semtsiv, M. Ziegler, S. Dressler, G. N. Masselink, W. T., T. Dekorsy, and Helm, “Above room temperature operation of short wavelength (\(\lambda= 3.8\ \mu\)m) Strain-Compensated in\(_{0.73}\)Ga\(_{0.27}\)AsAlAs Quantum-Cascade lasers,” *Applied Physics Letters*, vol. 85, no. 9, 2004. 95, 97


171


172


