Optical spectroscopy studies of atom intermixing in the core versus growth temperature of the claddings in MOCVD-grown quantum cascade lasers

M Kurka1, M Badura1, D Dyksik1, K Ryczko1, J Kopaczecki, J Misiewicz1, B Ściana1, M Tłaczała2, I Sankowska3, K Pierściński3 and M Motyka1

1 Laboratory for Optical Spectroscopy of Nanostructures, Department of Experimental Physics, Faculty of Fundamental Problems of Technology, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, Wrocław 50-370, Poland
2 Faculty of Microsystem Electronics and Photonics, Janiszewskiego 11/17, Wrocław 50-372, Poland
3 Łukasiewicz Research Network—Institute of Electron Technology, Al. Lotników 32/46, Warszawa 02–668, Poland

E-mail: marcin.kurka@pwr.edu.pl

Keywords: quantum cascade lasers, optical spectroscopy, mid infrared, MOCVD, semiconductors, atoms interdiffusion

Abstract

Here we present optical spectroscopy studies to examine structural and optical properties of active region of quantum cascade lasers grown fully by MOCVD technique. The active part is InGaAs/AlInAs based multilayer structure nominally lattice matched to InP substrate. In this communication we study a set of structures with different growth temperature of the cladding layers and its influence on the properties of active core. The x-ray spectroscopy (XRD) allowed to determine the widths of constituent layers and compare obtained values with nominal ones. Fourier-transformed photoluminescence (FTPL) and photoreflectance (PR) measurements provided high signal to noise spectra, proving good optical and structural properties of investigated samples. A model of atoms interdiffusion processes was presented to explain observed small energy shifts of the transitions energies within the investigated multilayer structures.

1. Introduction

The spectral range of mid-infrared is of many important applications in optical gas sensing [1], such as medical diagnosis by means of analysis of exhaled air [2] for cancer markers [3] and also in industry for detection of hydrocarbons, such as methane [4], propane [3], acetylene [5] and formaldehyde [6]. Nowadays optical sensors for such applications utilize diode lasers (DLs) [8], quantum cascade lasers (QCLs) [9], and interband cascade lasers (ICLs) [10], in the III-V material system. Moreover, efforts have been made in order to achieve efficient light sources for the infrared range [11–13]. The latter are of particular importance for low electrical power consuming applications since they exhibit low threshold current densities and high wall-plug efficiency as well as tunability in broad temperature range and single-mode operation in cw mode. On the other hand, when high output optical power is the key factor, QCLs are of particular interest since they easily provide more than 1 W of optical power in the spectral range beyond 7 μm.

Typical QCL laser possess around 20 layer in one stage of the active core, whereas the number of stages varies from 20 to 70 for different designs. With such a complicated structure, high accuracy of width and composition of individual layers forming the complex multilayer structure is of paramount importance. As a result, the growth of QCLS has been historically realized by means of molecular beam epitaxy (MBE) technique, providing finest structural quality and accuracy. Another typical approach to reduce costs is to perform combined growth: MBE technique is used to grow the active core of the laser and metal organic chemical vapor deposition (MOCVD) to over-growth the active core with thick cladding layers. The complexity of the combined growth results from growing of the bottom cladding layer at first, transfer of the sample into the MBE reactor in order to deposit the active core, and finally the overgrowth of the active core with upper cladding in a MOCVD machine [14, 15]. In such a multi-step fabrication process the cladding’s temperature growth is the parameter of
importance, determining the structural and optical properties of the fully operational device. Recently, growth of both active core and claddings of QCLs by means of MOCVD\(^{[16]}\) was reported, greatly reducing production costs and growth times. With this respect, there is still plenty of room for further improvement of the growth procedure and subsequent optical and structural quality of the complex multilayer QCLs. Moreover, within this communicate, we additionally pay attention to small interdiffusion of atoms between the QW and barrier layers as a consequence of additional annealing of the core during the top cladding growth. Until now, such an analysis has not been applied for such multilayer full QCL’s designs. Some indication can be found in respect to asymmetric double quantum wells\(^{[17]}\) and symmetric InGaAsP multiple-quantum-wells\(^{[18]}\).

Here we present results of spectroscopic studies performed on the active parts of QCLs designed for emission at 9 \(\mu\)m, completely grown by MOCVD on InP substrate. We studied the influence of different growth temperatures of the top cladding with respect to the growth temperature of the core part. The structure under investigation consists of the active core made of InGaAs/AlInAs multilayers structure and InP claddings, both grown during the same process.

2. Materials and methods

The samples were grown by MOCVD technique using AIXTRON 3 \(\times\) 2 CCS system. The TMIn, TMGa, TMAl were used as the sources of indium, gallium and aluminium, whereas PH\(_3\) and AsH\(_3\) act as the sources of phosphorus and arsenic elements, respectively. In-situ control of deposited epilayers was performed by the LayTec EpiTT device capable of two channels reflectometry and true temperature pyrometry measurements of the samples. The active region of the lasers was of four-well two-phonon resonance design\(^{[19]}\). The layer sequence of one period of the structure, in nanometers, starting from the injection barrier is: 4.0, 1.9, 0.9, 5.8, 0.9, 5.0, 2.2, 3.4, 1.4, 3.3, 1.3, 3.2, 1.5, 3.1, 1.9, 3.0, 2.3, 2.9, 2.5, 2.9 nm. The AlInAs layers are denoted in bold. Laser structure consists of 20 segments. The structure layout was based on a design shown in\(^{[19]}\). Growth temperature of the active region was 645 \(°C\) (reference sample). Claddings were formed by 1.5 \(\mu\)m thick InP layers and deposited in 600 (Sample A), 645 (Sample B) and 680 \(°C\) (Sample C). Growth pressure was equal 100 mbar for whole structure. Growth rate was kept at the level of 0.3 nm /s for core and over 4.4 \(\mu\)m/h in case of claddings.

The structural investigations were performed by means of HRXRD measurements. Figure 1 shows the rocking curves for four structures under investigation. The obtained results show that all samples exhibit flat and sufficiently sharp interfaces between epilayers forming the barriers and quantum wells. The satellite peak SL0 indicates that the lattice mismatch of strained periodic structure to the substrate is equal to 1967 ppm. The FWHM and intensity of higher order satellite peaks stay at constant level for every growth temperature, what may indicate that there is no significant material intermixing at the interfaces even for top cladding deposition temperature higher than active core one. The summarizing information about samples’ layers sequence and widths is presented in figure 2.
In order to measure the FTPL spectra we used a Bruker Vertex 80 v spectrometer operating in a step-scan mode, together with an external chamber for experiments with an additional modulated beam [20]. In this case liquid-nitrogen cooled InSb photodiode detector was used. In all measurement configurations the pump beam was provided by the 660 nm line of a semiconductor laser diode, which was mechanically chopped at a frequency of 275 Hz. Phase sensitive detection of the optical response was performed using a lock-in amplifier. In order to probe the excited optical transitions the modulated reflectivity spectra in the so-called bright configuration of a photoreflectance (PR) setup have been measured [21, 22]. This modulation spectroscopy has been proven to be sensitive to almost any optical transition occurring in the structure, including those with small oscillator strength as well as the nominally forbidden ones or such being indirect in the real space. To calculate the energy states of a QW, we solved the Schrödinger equation by taking into account a particle with a parabolic dispersion curve [23].

3. Results

Figure 3 presents the conduction and valence band edges calculated in accordance with the layer widths obtained from XRD spectra. Black solid (red dashed) curves denote the wave function probability densities of ground (excited) states within the respective bands of InGaAs/InAlAs multilayer structure. It is worth noting the maximum of the probability density for states e1, e2, h1, h2 (see figure 3) is located in the wider triple QWs. Gray parallel lines stand for the ladder of possible energy states in the respective multi quantum wells. In this picture the ground direct transition in the gamma point of the Brillouin zone occurs between the first electron e1 and the first heavy hole h1 states at 809 meV, whereas the transition between first excited states (between second electron e2 and second heavy hole h2 states) equals to 850 meV.

Figure 4 shows room (panel a) and 77 K (panel b) temperature FTPL spectra of reference sample (dashed black curve), sample A (red curve), sample B (black curve), and sample C (blue curve). The room temperature spectra (panel a) for all investigated samples exhibit a high signal to noise ratio providing the first indication of high optical quality of the MOCVD-grown samples. Two maxima, labeled H1e1 and H2e2, are visible, corresponding to the calculated parity-allowed interband optical transitions related to the first and second electron and heavy hole states (see. Figure 3). The measured transition energies correspond well with the calculated values. The obtained spectra do not exhibit energy shift due to the variation of the growth temperature of the cladding layers, whereas a clear influence of the temperature on the intensity of the obtained spectra is visible. The highest value of PL peak intensity, obtained for the reference sample, results from the absence of the cladding layer. As a result the excitation laser is not diffused on the relatively thick cladding layer, leading to enhanced electron-hole pair generation and higher PL yield. We can clearly see that the highest intensity is for the same cladding temperature as the InP lower cladding. The temperature of 645 °C was chosen as it is the
optimal temperature for InP growth in terms of optical properties [24]. Then, the visible change of PL intensity is caused by increased roughness of the InP cladding and local distortions of crystallinity, which account for increased dissipation of the signal. The PL spectra measured at 77 K is dominated by the fundamental transition (H1e1), while the H2e2 transition could not be seen due to the sensitivity decrease in the detector shorter wavelength region of the experimental setup. Although PL peak intensities behave in the same manner as the room temperature spectra, we notice the fluctuation of the PL peak energy while the growth temperature of the cladding layer is altered.

Figure 3. Calculated energy band diagram of one period at 300 K of the core layers in investigated samples, together with wave functions of the first two electron and hole states.

Figure 4. Room temperature (panel a) and 77 K (panel b) FTPL spectra of the investigated samples.
Figure 5 presents the photoreflectance spectra measured for reference sample (panel a), sample A (panel b), sample B (panel c), and sample C (panel d), respectively. For all samples under investigation the PR spectra exhibits a number of optical features connected with fundamental and excited interband transitions. Such a behavior in PR spectra proves the high optical quality of the investigated samples.

4. Discussion

Although the obtained PR spectra exhibits a high level of complexity (many overlapping transitions), three (four) optical transitions H1e1, H2e2, L1e1 (H3e3) have been identified (see figure 5, panel a), due to the sufficient energy separation between them. The oscillations above 1 eV originate from the transition between high-energy states forming the ladder within both conduction and valence bands (see figure 3). Since the energy separation between the states in the ladder is of the order of 10 meV, and the PR setup possess finite resolution (not possible to distinguish transition separated by less than 10 meV) the obtained spectra possess visible oscillations. Similarly to low temperature PL spectra we observe the energy shift of the ground optical transition while the growth temperature of the cladding layer is altered. Moreover, for sample C, where the highest growth temperature of the cladding layer was used (680 °C) we noticed reduction of the signal to noise ratio. Such a situation might be explained as a small reduction of the interface sharpness between layers, being a result of small atoms interdiffusion between QWs and barriers, also changing strain. Assuming Fick’s law and concentration-independent interdiffusion coefficient (D), the composition profile of groups III and V in the QW is given by:

\[
 w(z) = w_2 - \frac{w_2 - w_1}{2} \left[ \text{erf} \left( \frac{L + 2z}{4Ld} \right) + \text{erf} \left( \frac{L - 2z}{4Ld} \right) \right],
\]  

(1)
where $w_1$ and $w_2$ are the initial concentrations of atoms in the well and in the barrier, respectively, $L$ is the as-grown nominal width of the QW, $z$ is the quantization direction, $L_d$ is (in our approach) the diffusion length. We assume here that interdiffusion concern the group-III atoms - Aluminum and Gallium.

We theoretically investigated this structure-design utilizing the Schrödinger’s equation to the Ben Daniel-Duke’s equation [25]. The model includes strain effects for both the valence and conduction bands. For solving the Schrödinger equation and deriving the confined levels energies and related wave functions for electrons and holes we use the finite difference [26]. All the material parameters are taken from [27].

More details can be found in ref. [28–30]. In our case we reduced problem of hundreds of layers to those connected with section responsible for emission (main four QWs). After interdiffusion, the atomic composition of the structure gradually changes from an abrupt interfaces to a graded profile and an InGaAlAs alloy structure is formed. Figure 6, shows the calculated shape electron confinement profile, the calculated energies and the density probabilities of ground state of electron. In particular, there can be observed the influence on band alignment by atom’s interdiffusion. For small diffusion (figure 6(a)) the interdiffusion results in a negligible change in the confinement potential profiles for electron and we don’t see significant difference in comparison to fully rectangular band alignment. We have a different situation for $L_d = 2$ Å (figure 6(b)) and $L_d = 5$ Å (figure 6(c)). In the case of $L_d = 2$ Å the potential build-up is significantly modified by the atoms of group-III interdiffusion. This is very visible in the area of barriers, and in particular it will provide the thinnest barrier. The interdiffusion process affects not only the average thickness of such a barrier, but also the value of the potential in its area. At the same time, the interdiffusion process causes that electron ‘feels’ an effective increase in the width of the well, and moves to lower energy values. This has impact spatially for barriers and first thinner QW, what can be seen in wave function evolution across multilayer structure. Due to unintentional doping of the samples we assume that changes in carrier concentration that may affect the confining potential are negligible. We calculated couple of transition energies (including light holes transitions) as a function of diffusion length (see figure 7). In this graph $\Delta E$ denotes energy difference between those obtained for rectangular shape and those

**Figure 6.** Calculated wave function (black) and band profiles at 77 K for different diffusion length $L_d = 0.05$ nm (panel a), $L_d = 0.2$ nm (panel b) and $L_d = 0.5$ nm, respectively.
dependent on the profile change influence by diffusion. We see that increasing diffusion allows for reduction of the transition energies ($\Delta E < 0$) but after $L_d = 2 \text{ Å}$ $\Delta E$ became positive (which means increase of the transition energy in comparison to nominal situation). For high diffusion $L_d = 5 \text{ Å}$ energy difference might reach more than 10 meV. Also, the light hole related transition seems to be more sensitive for this changes reaching higher values of $\Delta E$ in comparison to transitions connected with heavy holes. By comparing transition energy difference obtained by PL measurements (see inset figure 7.), we were able to determined possible diffusion length in our samples, which is maximally around 1.5 Å (obtained for sample C). Taking into account, that thinnest layer is 7 Å, we have to conclude, that application of higher growth temperature might activate small diffusion process, which in influence optical properties of the core part of the structure. This is important, since XRD spectra didn’t show critical differences between investigated samples.

5. Conclusions

In this paper we have shown Fourier-transformed photoluminescence and photoreflectance studies performed on a set of InGaAs/AlInAs samples capped by InP cladding, grown with the same or different growth temperatures between core part and cladding, examined previously by means of HR-XRD measurements. High correspondence between calculated optical transition values and measured features was obtained. Moreover, we presented a simple model to explain processes that lead to deterioration of the structure. The results of the analysis of the optical spectra coming from emission and absorption measurements allow to conclude, that core part and cladding should be grown in the same temperature, even if samples have to be transferred between different MBE or MOCVD chambers. Generally, one should try to keep growth temperature of the top cladding lower than the growth temperature of the core part, in order to avoid so-called post growth annealing effects, i.e. atoms interdiffusion between layers in core part, as well as growing InP out of optimal temperature values.

Acknowledgments

This work was supported by the project SENSE, founded by National Centre for Research and Development TECHMAT-STRATEG1/347510/15/NCBR=2018. This work was partially financed in a form of a scholarship from the means granted to the Faculty of Fundamental Problems of technology from the Ministry of Science and Higher Education in 2018 for the purpose of scientific research and development, and related tasks serving the purpose of development of young scientists and participants of doctoral studies. In addition, this work was co-financed by Wrocław University of Science and Technology statutory grants. Finally, M D acknowledges the financial support from the Foundation for Polish Science (FNP) within the START fellowship.
Competing interests statement

The authors have no competing interest to declare.

ORCID iDs

M Kurka https://orcid.org/0000-0003-0143-6765
J Kopacze https://orcid.org/0000-0003-4851-9568
B Ściana https://orcid.org/0000-0001-8771-3545
M Motyka https://orcid.org/0000-0002-0886-2356

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