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Technology and properties of low-pressure metalorganic vapour phase epitaxy grown InGaAs/AlInAs superlattice for quantum cascade laser applications

MIKOŁAJ BADURA[1*], KATARZYNA BIELAK[1], BEATA ŚCIANA[1], DAMIAN RADZIEWICZ[1], DAMIAN PUCICKI[1], WOJCIECH DAWIDOWSKI[1], KAROLINA ŻELAZNA[2], ROBERT KUDRAWIEC[2], MAREK TŁACZAŁA[1]

[1]Faculty of Microsystem Electronics and Photonics, Wrocław University of Science and Technology, Janiszewskiego 11/17, 50-372, Wrocław, Poland

[2]Faculty of Fundamental Problems of Technology, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370, Wrocław, Poland

[*]Corresponding author: mikolaj.badura@pwr.edu.pl

Quantum cascade laser is one of the most sophisticated semiconductor devices. The active region of the quantum cascade laser consists of hundreds thin layers, thus the deposition precision is the most crucial. The main technique for the fabrication of quantum cascade laser structure is molecular beam epitaxy, however, the prevalence of metalorganic vapour phase epitaxy techniques in the fabrication of semiconductor structures causes a perpetual work on the improvement production of the entire quantum cascade laser structure by the metalorganic vapour phase epitaxy. The paper presents technological aspects connected with the metalorganic vapour phase epitaxy growth of InGaAs/AlInAs low-dimensional structures for quantum cascade laser active region emitting ~9.6 μm radiation. Epitaxial growth of superlattice made of InGaAs/AlInAs lattice matched to InP was conducted at the AIXTRON 3x2″ FT system. Optical and structural properties of such heterostructures were characterised by means of high resolution X-ray diffraction, photoluminescence, contactless electroreflectance and scanning electron microscope techniques. Epitaxial growth and possible solutions of structure improvements are discussed.

Keywords: InGaAs, AlInAs, superlattice, metalorganic vapour phase epitaxy (MOVPE), quantum cascade laser (QCL).

1. Introduction

Quantum cascade laser (QCL) is one of the newest semiconductor sources of the light. In contrast to bipolar devices, it generates radiation by the intersubband transitions within conduction band of a semiconductor structure. As a source of mid-infrared to far-infrared coherent light QCL finds application in such fields as chemical and biological sensing, spectroscopy and telecommunication [1].

Active region of the QCL is generally designed as a multiple quantum well or superlattice structure [2]. The most popular material systems of those lasers are AlGaAs/GaAs and InGaAs/AlInAs/InP. However, only that InP-based allows to emit shorter wavelength light, up to 3 μm, mainly due to higher conduction band discontinuity [3].

Core of the QCL consists of hundreds of layers with thickness of just single nanometers. Such structure with overall thickness over a few micrometers is significantly sensitive to layers thickness and composition deviations. It is a big technological challenge to control those parameters and also to provide sharp and narrow interfaces. Due to this, for many years the molecular beam epitaxy (MBE) was the only technique capable of producing QCLs. Recently, there are papers describing the metalorganic vapour phase epitaxy (MOVPE) growth of quantum lasers, to make the mass production possible, and such issue is continuously under development and the number of paper focused on MOVPE growth is still growing. Present work describes the way of producing InGaAs/AlInAs/InP heterostructures for further QCL application. The influence of growth conditions on layers properties as well as its characterisation are discussed.

2. Experimental details

Epitaxial growth was made using AIXTRON 3×2″ FT CCS system at the 100 mbar pressure. The chemical elements precursors were: TMGa, TMIn, TMAl, PH_3 and AsH_3 as sources of gallium, indium, aluminium, phosphorus and arsenic, respectively. Growth temperature varied from 635 to 650°C. Pure H_2 acts as the carrier gas and InP:S (100) substrates were chosen for this experiment. V/III ratio varied from 220 to 333. Growth rate of InGaAs and AlInAs was maintained in the 1–3 μm/h range. InGaAs and AlInAs composition were controlled by the hydrogen flow through the TMGa and TMAl saturators, respectively, while TMIn flow was fixed. Samples of InGaAs/InP heterostructures were made with and without growth interruption to observe interfaces quality. Prepared samples were characterised by means of high resolution X-ray diffraction (HRXRD), photoluminescence (PL) at low and room temperature, contactless electroreflectance (CER) and scanning electron microscope (SEM).

3. Results and discussion

One of the most important factors determining good quality of quantum structures, is their narrow interfaces. It is well-known that indium tends to segregate on the top of the grown layer, in the case of the multicomponent alloys [4–8]. Thus, the influence of the growth conditions on the InGaAs/InP heterostructures interfaces was firstly investigated. InP was chosen as a quantum wells barrier, as it is easier to analyze binary compound than ternary one. Samples P97 and P98 were grown at 635°C with V/III ratio equal to 333 and growth rate about 1 μm/h. Repeated 5 times InGaAs quantum well

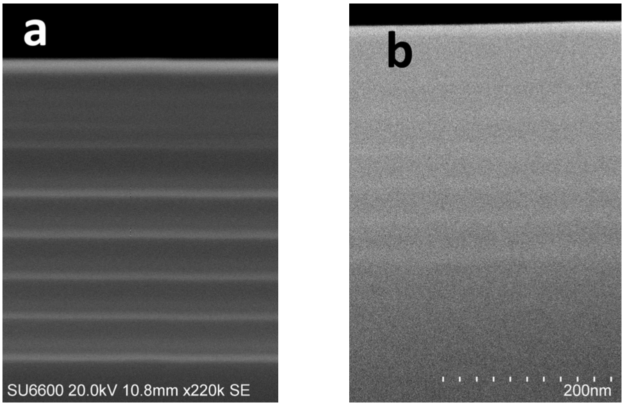

Fig. 1. SEM images of cross-sections of the P97 (**a**) and P98 (**b**) samples.

was about 10 nm thick, whereas InP was about 30 nm thick. In the case of P97 sample, growth of the layers was terminated after each of them for 5 s. It is one of the ways to improve interfaces, by evaporating the excess of the In from the surface during a short break [9].

However, even at SEM image of a cross-section of the P97 sample (Fig. 1**a**), a broad region of indeterminate interface is visible. Such feature appears only at the bottom of the quantum well. It can be explained by the competitive adsorption model proposed by NAKANO *et al.* [4]. They assumed that the reason of indium segregation is the difference in crystallization rate constants of In and Ga species. Concerning this, the bottom of the InGaAs layer could be poor in indium. Then, In concentration rises in the growth

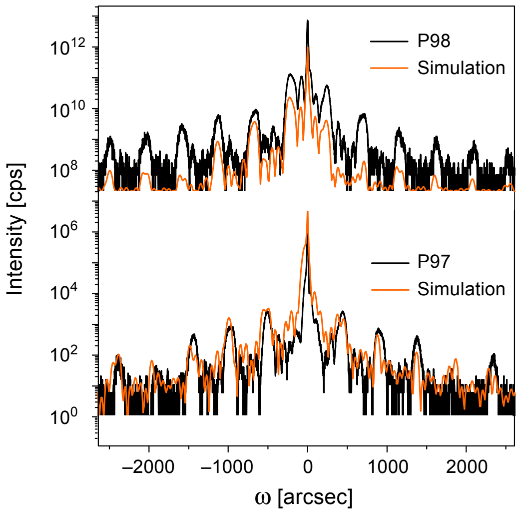

Fig. 2. HRXRD curves of the P97 and P98 samples (curves are shifted vertically for clarity).

direction to obtain a stable level after about 4 nm. Such assumption is confirmed by the HRXRD curves (Fig. 2). Simulation curve is the most appropriate for the 20–54.5% of In concentration gradient at the bottom sub-well region.

Then, to assure constant In distribution through the structure, constant TMIn flow was maintained during the whole growth process (sample P98). At the layers boundaries, TMGa flow was switched on/off, PH_3 and AsH_3 flows were switched. Time of that operations was equal to 0.5 s. It turned out that at SEM image, the boundary region is no longer visible (Fig. 1**b**). Both, quantum well and barrier layers are homogeneous. HRXRD analysis confirms that indium content is constant almost within all the quantum well. At the bottom of the well, there is In-reach region. However, this interface does not exceed 1 nm of thickness.

Photoluminescence spectra of samples P97 and P98 measured at 12 K are shown in Fig. 3. It is interesting that the peak corresponding to the P97 sample with broad developed interfaces is more sharp and narrow than P98 one. It is probably due to the fact that inhomogeneous interface reduced the effective thickness of the quantum well. Thus, due to quantum size effects, the emission peak shifted to a higher energy region and consequently FWHM was reduced. Broadening of the P98 correlated peak could be also caused by the top interface of the last deposited quantum well. As it was mentioned in [4], indium tends to accumulate at the top surface, independently from layer's thickness. As a result, the last quantum well could be influenced by its In-reach top surface.

Secondly, after elaboration of proper properties of InGaAs quantum well growth, InP barriers were replaced by the AlInAs ones. In order to provide high quality of AlInAs/InGaAs heterostructures, growth temperature of such structures should be higher than 635°C [10], used for earlier InGaAs/InP growth. Higher temperature increases indium length of segregation within InGaAs layers, on the other hand it is necessary for defect-free AlInAs growth. Finally, growth temperature was established at 650°C while V/III ratio was equal to 220. The epitaxial growth of the nanometers thick

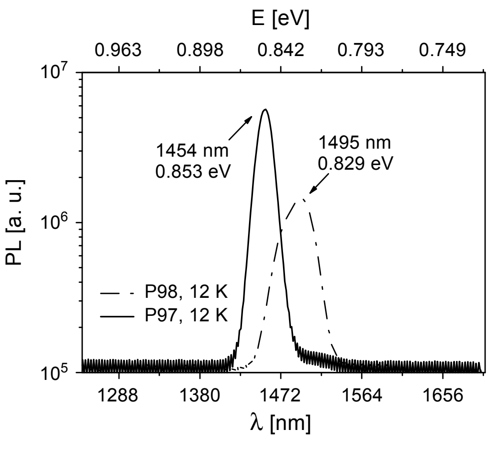

Fig. 3. PL spectra at 12 K of the P97 and P98 samples.

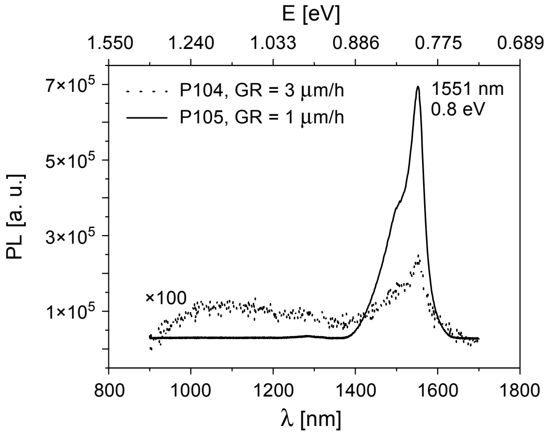

Fig. 4. Room temperature PL spectra of the P104 and P105 samples (GR – growth rate).

layers requires a high precise control of the growth process. The reduction of the growth rate provides a precise determination of the film thickness. A low growth rate has also a positive impact on the crystalline quality – during slow epitaxial growth less point defects formed in the structure. During our researches, we have reduced the growth rate from 3 µm/h (sample P104) to 1 µm/h (sample P105 and further). The structure P105 that grew slower shows more intensive response to optical excitation at room temperature (Fig. 4), what corresponds to investigations made by Jasik *et al*. [11]. Subsequent processes are carried out under conditions to obtain growth of 1 µm/h.

Then, the influence of the wells thickness on the energy states was investigated. Sample P104 was deposited as a 10 nm thick InGaAs well whereas P105 was a 5 nm thick InGaAs well sandwiched between 30 nm AlInAs barriers. Theoretical calculations of energy levels within those quantum structures were carried out. Material parameters [12] were corrected as for strained heterostructures according to Pikus–Bir Hamiltonian, similar to assumptions included in [13]. Subsequently, Schrödinger equations were solved numerically.

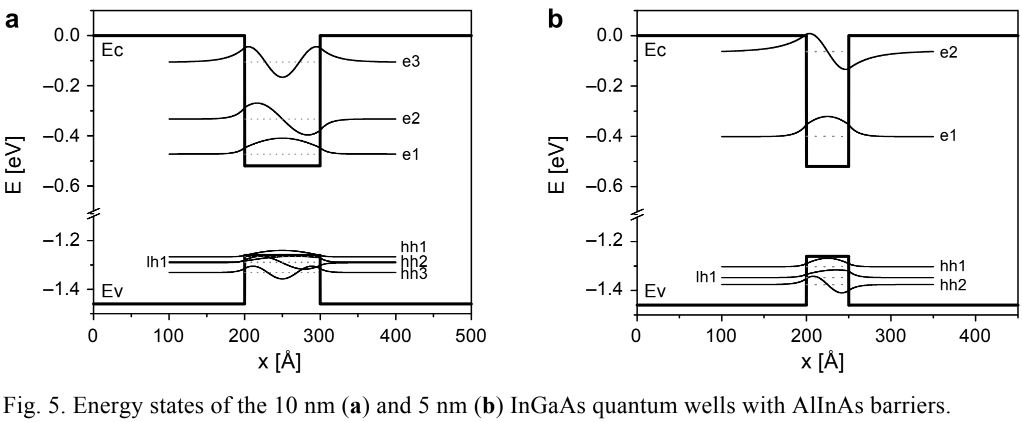

Fig. 5. Energy states of the 10 nm (**a**) and 5 nm (**b**) InGaAs quantum wells with AlInAs barriers.

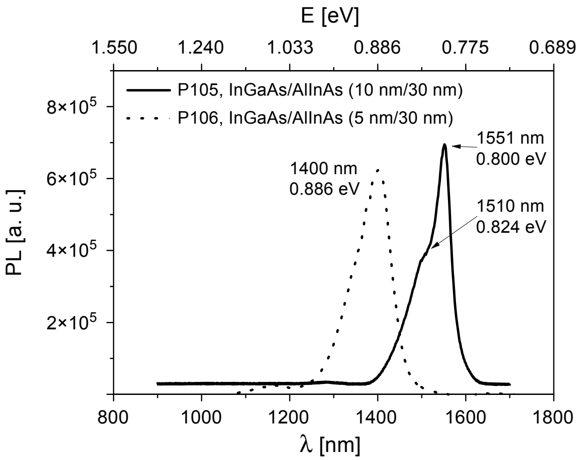

Fig. 6. Room temperature PL spectra of the P105 and P106 samples.

Following the calculations presented in Fig. 5**a**, concerning a 10 nm thick well (P105), energies 0.794 and 0.816 eV stand for e1-hh1 and e1-lh1 transitions, respectively. PL spectrum of P105 sample, recorded at room temperature (Fig. 6), reveals two components of the luminescence peak. Their energies are slightly higher than calculated ones. That may point at a thinner well than assumed. It was calculated that transitions observed at PL spectrum correspond to a 9.3 nm thick well, which composition was determined from simulations of HRXRD curves. In the case of a 5 nm thick quantum well (sample P106), PL peak is significantly blue-shifted. Its energy equal to 0.886 eV corresponds to the e1-hh1 transition within a 4.9 nm thick InGaAs well. Those measurements and calculations prove that deposited structures have parameters very close to the intended values.

The above-described studies were used to develop the technology of InGaAs/AlInAs superlattice. The process parameters were chosen as: $T = 650°C$, V/III ratio = 220,

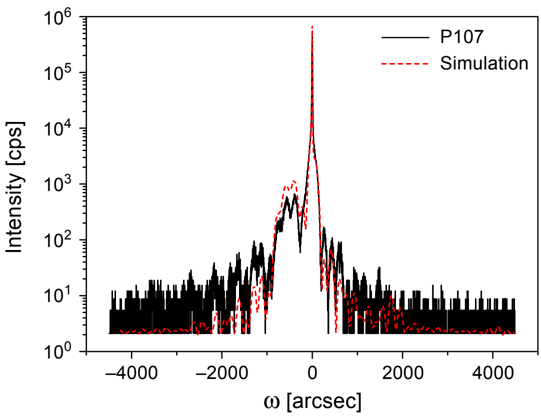

Fig. 7. HRXRD curve of the InGaAs/AlInAs (5 nm/3 nm) superlattice.

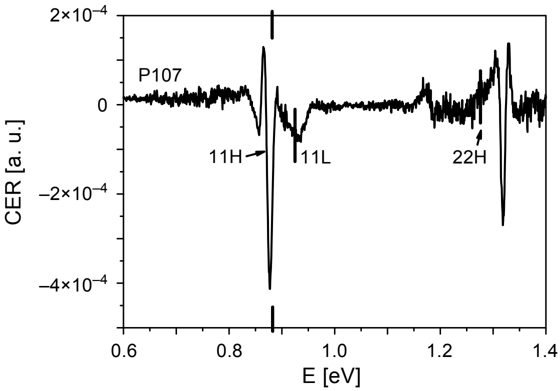

Fig. 8. CER spectrum of the InGaAs/AlInAs (5 nm/3 nm) superlattice. Theoretically calculated transition energies are marked by the black vertical lines.

GR = 1 μm/h (GR – growth rate), and $p = 100$ mbar. As a result, the sequence of $Al_{0.48}In_{0.52}As/In_{0.53}Ga_{0.47}As$ layers with thicknesses of 3 and 5 nm, respectively, were obtained. The high crystalline quality of the obtained superlattice was confirmed by HRXRD measurements – diffraction curve is presented in Fig. 7. The contactless electroreflectance spectrum (Fig. 8) shows distinctly two e1-hh1 and e1-lh1 optical transitions, whereas the e2-hh2 transition lies within InP substrate oscillation. The energies of these transitions are equal to 0.882, 0.926, 1.292 eV, respectively. These values are correlated with theoretical calculations of a 5 nm thick quantum well illustrated in the energy diagram in Fig. 5**b**.

4. Summary

In this work, the authors show the elaboration process of InGaAs/AlInAs superlattice made by low-pressure metalorganic vapour phase epitaxy (LP-MOVPE). To provide good interfaces, deposition sequences were changed. Surprisingly, better interfaces were obtained without any growth interruptions. In contrast, the process with brakes necessary to evaporate In from the surfaces gave a broad indefinite interface of InGaAs/InP heterostructure. Then, it was stated that a lower growth rate is better in the case of quantum structures. Samples grown at a growth rate of about 1 μm/h have better optical and structural properties than samples grown at 3 μm/h. In addition, the numerical modelling was used as a tool to confirm measurement results as well as a feedback determining one of the variables, *e.g.*, thickness of the well, when the rest of the variables are fixed. As a result, InGaAs/AlInAs superlattice was fabricated with parameters proper for further improving and application in quantum cascade lasers.

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