Molecular-beam epitaxy of 7-8 μm range quantum-cascade laser heterostructures

A V Babichev\textsuperscript{1,2}, D V Denisov \textsuperscript{1}, A V Filimonov \textsuperscript{1}, V N Nevedomsky \textsuperscript{2}, A S Kurochkin \textsuperscript{1}, A G Gladyshev \textsuperscript{1}, L Ya Karachinsky\textsuperscript{1,2,3}, G S Sokolovskii \textsuperscript{2}, I I Novikov\textsuperscript{1,2,3}, A Bousseksou \textsuperscript{4}, A Yu Egorov \textsuperscript{1,3*}

\textsuperscript{1}Connector Optics LLC, 194292 St. Petersburg, Russia
\textsuperscript{2}Ioffe Institute, 194021 St. Petersburg, Russia
\textsuperscript{3}ITMO University, 197101, St. Petersburg, Russia
\textsuperscript{4}Centre for Nanoscience and Nanotechnology (C2N Orsay), CNRS UMR9001, Univ. Paris Sud, Univ. Paris Saclay, 91405, Orsay, France

E-mail: anton.egorov@connector-optics.com

Abstract. The method of molecular beam epitaxy demonstrates the possibility to create high quality heterostructures of quantum cascade lasers in a spectral range of 7-8 μm containing 50 quantum cascades in an active region. Design based on the principle of two-phonon resonant scattering is used. X-ray diffraction and transmission electron microscopy experiments confirm high structural properties of the created heterostructures, e.g. the identity of the composition and thickness of epitaxial layers in all 50 cascades. Edge-emitting lasers based on the grown heterostructure demonstrate lasing with threshold current density of 2.8 kA/cm\textsuperscript{2} at a temperature of 78 K.

1. Introduction
Quantum-cascade lasers (QCL) emitting in a spectral range of 7-8 μm can effectively be used for remote gas analysis and various medical applications [1]. In particular, lasers with a wavelength of 7.5 μm are used for detection of SO\textsubscript{2} [2] and trinitrotoluene [3]. The application of laser radiation with wavelength near 7.8 μm provides the detection of methane concentration [4], and can be used for remote monitoring of leaks in pipelines and at chemical plants.

The implementation of QCL can be done in different ways. The results of studies of QCL in the range of 7-8 μm published so far were based on structures with two- [5] or three-phonon resonance scattering [6], on superlattice [7], on structures with transitions between a bound state and continuum, based on the strained heteropairs [8] and on non-resonance escape of charge carriers [9].

Basic technologies to create QCL heterostructures are metal-organic vapour-phase epitaxy (MOVPE) and molecular beam epitaxy (MBE). MOVPE allows one to create heterostructures with a greater growth speed. MBE allows implementation of lasers with higher quantum efficiency [10]. Additional improvement of quantum efficiency of QCL is possible to achieve by implementing multi-cascade QCL heterostructures containing up to 100 cascades [11]. Manufacturing of such multi-cascade QCL heterostructures requires maintaining of high identity of chemical composition and cascade layer thickness throughout the whole long process of epitaxy [12]. The utilization of industrial
MBE system satisfies these requirements, which was demonstrated by a number of research groups [13-15]. The use of state of the art multi-substrate industrial MBE systems such as Riber 49-7000, Veeco Gen 200-2000 and Oxford VG Semicon V80H-V150 substantially increases the overall yield.

2. Experimental
QCL heterostructures were grown by Connector Optics LLC using MBE system - Riber 49, equipped with a solid-state source of arsenic of cracker type and ABI 1000 cells for gallium and indium metals. ABI 1000 source has a cylindrical crucible and a dual-zone heater and specially designed to ensure high stability of metal flow during a long epitaxy process. ABI 1000 requires no temperature correction while it is emptied, e.g. during the depletion of the metal loaded in the cells. To create QCL heterostructure on InP substrate of (001) orientation doped with sulphur up to 3×10^{18} cm^{-3}, a 2 μm buffer layer was grown with the level of Si doping of 1×10^{17} cm^{-3}. The next layer of In0.53Ga0.47As having the thickness of 0.5 μm was doped up to level 5×10^{16} cm^{-3}. Next, the heterostructure active area was grown. The layout of the single quantum cascade is presented in Table 1. To obtain photons of 0.025±0.001 eV energy we implemented the design, which provides the transition from the top- to the lower-level of 5.3 nm quantum well (Layer 17, Table 1). Depletion of the lower-level was achieved by means of two-phonon resonance scattering with emission of two longitudinal optical (LO) phonons [5]. Here with the electron from the lower-level of the first quantum well (Layer 17, Table 1) is scattered emitting LO-phonon to another lower discrete level of the neighboring quantum well (Layer 15, Table 1), from which it scatters again emitting LO-phonon to another lower discrete level of the following quantum well (Layer 13, Table 1) and then it is released into the injector. To ensure the scattering with LO-phonon emission, the energy gap between levels in neighboring quantum wells should be close to LO-phonon energy, which is 0.035 eV in this case. The final QCL heterostructure includes 50 such quantum cascades (QC) and is formed using of broadband, Al0.49In0.52As, and narrowband, In0.53Ga0.47As, solid alloys, matched to the lattice parameter of InP substrate.

After growing the 50 QCs we consequently formed the layers of In0.53Ga0.47As with n-doping level of 1×10^{17} cm^{-3} and 1×10^{19} cm^{-3}, having the thickness of 0.1 μm and 0.02 μm, respectively. The level of layer doping was calibrated on the test epitaxial layers of In0.53Ga0.47As and InP. The precise calibration of the chemical composition of epitaxial layers and growth speeds of In0.53Ga0.47As and Al0.49In0.52As solid alloys was carried out by growing of a special test heterostructure based on 10 pairs of alternating layers of Al0.48In0.52As /In0.53Ga0.47As, each of 10 nm thick. All samples were grown under the same equivalent pressure of arsenic flow (As4) equal to 1×10^{-5} Torr and the same growth speed of 0.2 nm/s. QCs were grown at a substrate temperature of 480°C. During the growing of the doped layers of In0.53Ga0.47As and InP, the epitaxy temperature was lowered to 450-460°C. To ensure better uniformity of thickness of epitaxial layers in all QCs during their epitaxy, we increased rotation speed of the substrate holder up to 24 rpm. The rotation speed was chosen in such a way that during the growth of the thinnest layer in the quantum cascade (layer Al0.48In0.52As of 1 nm thickness) the substrate holder have been made two full rotations.

3. Results and discussion
The thickness of QCL heterostructure layers was controlled using transmission electronic microscopy (TEM) and X-ray diffraction. TEM measurements were made using the transmission electron microscope JEM2100F. The samples in cross-sectional geometry were prepared using a standard technique by plane cleavage of the structure (1-10) and their further polishing [16]. In the final stage the samples were narrowed by Ar+ ion etching with energies of 3–4 keV. The images were made at the acceleration voltage of 200 kV. To define the interfaces between the layers, we plotted the image intensity profile, which was orthogonal to the layer interfaces. The averaging width was 20 nm. The location of the edges between the layers was taken by the half-height of transitional contrast from one layer to the other. The cross-sectional TEM image of a QCL heterostructure is shown in Figure 1. The
total thickness of one period was equal to 532 Å. The thickness of the cascade according the TEM measurements and taking into account full errors, was 532±50 Å.

Figure 1. TEM image of a QCL heterostructure cross-section. The lighter layers correspond to InGaAs, darker layers to AlInAs.

Figure 2 shows the calculated (according to specification) and experimental X-ray diffraction curves of a QCL heterostructure. The X-ray diffraction measurements with high resolution were made in the vicinity of a symmetric reflex (004) of InP using PANalytical XPertPro diffractometer in a parallel X-ray beam geometry. The 6 kW X-ray source was represented by a tube with a rotating copper anode (λ=0.15406 nm). FWHM of the primary beam was below 12”, which was provided by using a fourfold Ge (220) monochromator. Figure 2 shows characteristic peaks of X-ray diffraction from InP substrate and periodic QCL heterostructure. There is a complete match between the zero peak of the satellite structure and the position of the peak of InP substrate. This fact proves the exact correspondence between the chemical composition of the epitaxial layers and the values in the growth specification. In addition, this figure shows 13 satellites, resulting from the periodic structure of quantum cascades. Satellites, located to the left of the substrate peak, have FWHM of 26±5”, and the ones located to the right are slightly widened. When calculating the total thickness of the quantum heterostructure cascade, we took into account the angular position of the peaks with clear maxima. The calculated thickness of the QC for the experimental curve was 526±7 Å. Thus, there was an exact matching between the thickness of the quantum cascade measured in experiment with the cascade thickness determined using the specification (see Table 1). Furthermore, it should be noted that satellites have a distinct shape with one maximum. In the case of non-optimized parameters of the epitaxial process, the splitting of the satellite peaks could appear and several maxima could emerge, which is associated with fluctuations of the composition and thickness of epitaxial layers in different heterostructure cascades [16]. This result indicates a significantly better flow stability of Group III elements when using ABI 1000 cell with a cylindrical crucible, comparing to a general ABN 700 cell with a conical crucible [16].
To prove the optical quality of the grown QCL heterostructure and to study its optical properties, we processed the laser diodes in ridge geometry with width of 20 microns. The lasing spectrum is shown in the Figure 3a. The maximum of stimulated radiation intensity corresponds to a wavelength of 7.6 μm. A typical linewidth of lasing spectra (FWHM) is about 2.8 nm. Typical light-current and voltage-current characteristics of the QCL laser diode measured at a temperature of 78 K are shown in Figure 3b. Threshold current of 0.9 A (which corresponds to the threshold current density of 2.8 kA/cm²) was obtained. The clear diode type voltage-current dependence without parasitic current flow channel was observed.

Table 1. Design of a QCL cascade.

| No | Layer material | Layer thickness according to specification (Å) | Layer thickness determined by TEM analysis (Å) |
|----|----------------|-----------------------------------------------|-----------------------------------------------|
| 1  | In₀.₅₃Ga₀.₄₇As | 24                                            | 24                                            |
| 2  | Al₀.₄₈In₀.₅₂As | 24                                            | 21                                            |
| 3  | In₀.₅₃Ga₀.₄₇As | 26                                            | 24                                            |
| 4  | Al₀.₄₈In₀.₅₂As | 21                                            | 22                                            |
| 5  | In₀.₅₃Ga₀.₄₇As | 26                                            | 24                                            |
| 6  | Al₀.₄₈In₀.₅₂As | 18                                            | 25                                            |
| 7  | In₀.₅₃Ga₀.₄₇As | 27                                            | 24                                            |
| 8  | Al₀.₄₈In₀.₅₂As | 16                                            | 31                                            |
| 9  | In₀.₅₃Ga₀.₄₇As | 29                                            | 26                                            |
| 10 | Al₀.₄₈In₀.₅₂As | 17                                            | 24                                            |
| 11 | In₀.₅₃Ga₀.₄₇As | 31                                            | 31                                            |
| 12 | Al₀.₄₈In₀.₅₂As | 25                                            | 18                                            |
| 13 | In₀.₅₃Ga₀.₄₇As | 44                                            | 43                                            |
| 14 | Al₀.₄₈In₀.₅₂As | 12                                            | 19                                            |
| 15 | In₀.₅₃Ga₀.₄₇As | 52                                            | 42                                            |
| 16 | Al₀.₄₈In₀.₅₂As | 12                                            | 25                                            |
| 17 | In₀.₅₃Ga₀.₄₇As | 53                                            | 31                                            |
| 18 | Al₀.₄₈In₀.₅₂As | 10                                            | 26                                            |
| 19 | In₀.₅₃Ga₀.₄₇As | 17                                            | 25                                            |
| 20 | Al₀.₄₈In₀.₅₂As | 43                                            | 27                                            |
| Total thickness of the cascade | 527 | 532 |
Figure 2. X-ray diffraction curves of QCL heterostructure. The experimental curve is shown in the top, the calculated counterpart is shown in the bottom.

Figure 3. (a) The lasing spectrum measured at 78 K; (b) voltage-current curve (left vertical axis) and light-current curve (right vertical axis) of a QCL laser ridge measured at a temperature of 78 K.

4. Conclusions
We have studied the parameters of the epitaxy for 7-8 µm optical range multi-cascade QCL heterostructures grown using the industrial multi-substrate MBE system - Riber 49 equipped with ABI 1000 cells. To achieve QCL lasing in the specified spectral range we used the cascade design based on two-phonon resonant scattering. Using X-ray diffraction and transmission electron microscopy, we investigated structural properties of QCL heterostructures and confirmed their high structural perfection, e.g. the identity of their compositions and thicknesses of epitaxial layers in all 50 cascades and full compliance with the numerical specification. The heterostructures were used for
manufacturing of stripe lasers with 20 µm stripe width. Laser ridges demonstrated the lasing at a wavelength of 7.6 µm and threshold current density of 2.8 kA/cm² at a temperature of 78 K.

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