Filling of In(Ga)P/GaInP quantum dot electron states detected by microphotoluminescence

A Yu Romanova¹,², K G Belyaev¹, P A Buriakov¹,², A S Vlasov³, N A Kalyuzhnyy⁴, S A Mintairov⁴, R Salić¹, D V Lebedev¹, M V Rakhlin¹, V I Smirnov¹,³, A A Toropov¹, A A Bogdanov³, S. Ramezanpour³ and A M Mintairov¹,⁴

¹ Ioffé Institute, St Petersburg 194021, Russia
² Peter the Great St. Petersburg Polytechnic University, St. Petersburg, 195251 Russia
³ ITMO University, Saint-Petersburg 197101, Russia
⁴ University of Notre Dame, Notre Dame, IN 46556 USA

e-mail: smershnajarukkola@gmail.com

Abstract. Microphotoluminescence (μPL) spectra of single In(Ga)P/GaInP quantum dots (QD) were investigated. Measurements were carried out at different optical pump power and at different electric field with constant optical pump. Filling of electron s-, p-, d-states was observed. Quantum confinement Stark effect (QCSE) was detected. Obtained PL life times of s-, p- electron states were 0.5 ns and 0.4 ns respectively. From spectra it is clearly seen that QDs have weak quantum confinement (ℏω~4-8meV).

1. Introduction
Self-organized InP quantum dots grown on GaInP (InP/ GaInP QDs) demonstrate unique properties which makes them a crucial element of ultralow threshold lasers [1, 2] and single photon-source [3, 4] structures for the visible range, 650 - 750 nm. Due to their weak quantum confinement (ℏω~5 meV) and large lateral size these QDs allow one to observe effects of electron-electron interactions, such as Wigner localization [5] and formation of whispering gallery electron modes [6].

It is known that QDs are often referred to as artificial atoms because of atomic-like (s, p, d, f) wavefunctions (shells) which correspond to its quantum levels. Charge carrier filling of these levels by electrical bias is well-known phenomenon of Coulomb blockade [7-9]. The majority of the works devoted to this subject discuss processes in QDs ensemble. In this work, shell filling of a single QD is observed with a help of microphotoluminescence (μPL) technique. Filling was achieved in two ways: by optical pumping and by electrical bias. Spectra of InP/GaInP QDs with injected electrons demonstrate appearance of the additional anti-Stokes lines which are related to recombination from QD occupied electron levels. From these spectra quantum confinement value (~4-8 meV) was obtained.

2. Experimental methodology
Samples were grown in AIX200/4 reactors by MOVPE epitaxy in Stranski-Krastanov mode. Structure design was as the following: GaAs substrate/GaAs 100 nm buffer layer/GaInP 60 nm/InP QDs /GaInP 40 nm. Growth temperature for QDs and GaInP layer was the same – 725⁰ C. Growth rate was 0.48 μm/h. Due to the fact that intermixing the Ga content in QD is 10-20% they will be denoted as
In(Ga)P. The resulting QDs have a lens-like shape with large lateral dimensions of about 150 nm and a thickness of about 20 nm. The Bohr radius in an InP/GaInP QD is 8.7 nm [10]. Due to this, weak confinement was manifested in the lateral plane.

To obtain information from a single dot structures with very low dot density (0.25 μm⁻²) were used. To measure the spectra at different optical pumping levels, we used a Cube 405-100C laser with a wavelength of 405 nm and a power of 100 mW. The dependence of the PL spectra on the change in the electric field was studied under constant optical pumping of 5 nW. For electrical measurements semi-transparent contacts Ti/Au with 20 nm thickness were deposited on the top. μPL measurements were carried out in continuous flow optical Janis cryostat at 10 K. To focus exciting laser beam on the mesa Mitutoyo objective 50x was used. Spectra were obtained with Princeton Instruments SP2500 monochromator coupled with Pylon CCD camera. To obtain photoluminescence lifetime Pilas pulse laser with a wavelength of 404 nm and a frequency of 60 MHz, a SPAD a TCSPCS Becker & Hickl were used.

3. Results and discussion
3.1. Quantum dot shell filling by optical pump

Single dot luminescence spectra at various pump power are presented in figure 1(a). It can be seen that increase of power results in appearance of additional peaks. It is known that intraband relaxation (~ ps) is much faster than luminescence lifetime (~ns). Thus, at low pump power radiative recombination occurs from the lowest S state. According to Pauli principle each energetic state may not contain more than two electrons. If photo-generation rate is faster than recombination rate, the state is being filled [11,12,13]. Thus, at the certain power it is possible to see not only the peak that corresponds to recombination from lowest state but also peaks that correspond to recombination from higher states. In other words, it becomes possible to see the structure of energy levels.

The model of exciton photo-generation processes in QDs was created by authors [11,14]. It should be taken into account that probability of exciton generation on the higher level depends on the lower level filling. When QD is photoexcitated by a CW light source ground state condition is achieved. In this case with the increase in pump power the intensity of each peak saturates at the certain power. For peaks corresponding to high energy states this value is higher than that for lower energy peaks. This is confirmed by an additional figure 1(b), which shows the dependence of the intensities s-, p-, d- and f-peaks on the applied excitation power. It can be seen that saturation for s-states already occurs at 5 mkW, and with the increase of the level number the saturation power increases.
One can see (figure 1(a)) that at power level 1 μW state filling starts. With power increasing –D and –F peaks appear. For –S and –P peaks time resolved experiments were carried out (figure 2). The PL dynamics was measured at wavelengths of 702 nm (p-state) and 704 nm (s-state). Emission decay times determined from this curves are the following: τ=0.5 ns and τ=0.4 ns. Peak intensities demonstrate tendency to saturation for S and P – peaks which is in accordance with the model [11]. The ratio of values at saturation condition is proportional to its recombination rates:

\[ \frac{\gamma_1}{\gamma_0} = \frac{2}{g！！i！！l_0/l_i} \]

where \( \gamma \) is recombination rate, \( g \) – level degeneration, i- denotes shell number, 0- ground state (S -shell). Putting luminescence decay values (\( \tau=\gamma^1 \)) and \( g=6 \) (P state) into the equation results in intensity ratio of 3.75, which is higher than observed in experiment. This may point out that P state does not reach saturation at used power level. Another explanation may be that there are additional non-radiant processes which were not considered in the model.

The difference in peak positions is about ~6 meV. This difference is constant for all states which points out that QD have a weak confinement with parabolic potential.

3.2. Quantum dot shell filling with electrical field

Generally, applying electric bias to QDs results in carrier injection [8]. However, barrier potential should be overcome for QDs that already contain charge carriers. The barrier is created by piezoelectric field induced by atomic ordering of GaInP [15]. Otherwise, if there are no charge carriers in the QDs charge injection is determined solely by its capture mechanism. One of the possible ways to inject carriers into QD is with electrical bias. It affects single dot luminescence drastically because of two factors: a) Coulomb interaction between the host electrons and photo-excited electron-hole and b) quantum confinement Stark effect (QCSE). It should be noted that injected carriers occupy lowest shell levels so the shell filling is achieved.

In figure 3 single dot luminescence spectra are presented. To avoid filling of p-, d-, f-states by optical pumping experiments were carried out at pump power 5 nW. It can be seen that the increase of electrical bias results in two main observed effects: shift of main peak corresponding to S electronic shell to lower energies and appearance of additional peaks with low intensity. In work [16] it is shown that applying of external field results in shifts of InP QD excited states \( E(V) \) due to QCSE. The shift value obtained in this work is about 3 meV per 1 V which is comparable with that obtained by authors [16].

Based on the results of works devoted to QDs which contain residual electrons [5,6] it can be concluded that additional carriers should interact with each other and photoexcited e-h pair. Photoexcited hole appears in Hartree-Fock potential of \( N+1 \) electrons, thus its single-particle states (–S, –P, –D) mix. So radiant transitions from occupied levels become possible. There are two peaks on single dot emission spectrum with no electrical field. One peak is related to s-shell. The probability of p-state filling at such low power is very small. From the analysis of different spectra from single dots we suppose that other peak could be related to recombination with light holes. At 1V the \( P \)-shell is filled leading to appearance of the corresponding peak in the spectrum. The electron number in the dot (\( N+1 \)) should not exceed 8 (2S and 6P) because of Pauli principle. Thus, such QDs may contain 2-7 residual electrons. 2 V bias results in appearance of third peak. This clearly points out that filling of \( D \) electron shell starts. So it can be concluded that QD under 2V bias contain 8 residual electrons and photoexcited electron captured by \( D \)- shell.
Figure 2. Luminescence decay of peaks corresponding to different electronic shells of In(Ga)P QD.

Figure 3. Single dot emission spectra of In(Ga)P QD at different electric field bias. Dotted line represents S peak position versus electric field bias.

The values of peak difference are presented in the table 1. They are close to values obtained with optical pumping.

Table 1. Difference in luminescence peak positions.

| Voltage applied to sample, V | Difference between peak positions, meV |
|------------------------------|---------------------------------------|
|                              | ΔS,P  | ΔP,D  |
| 0                            | -     | -     |
| 1                            | 6     | -     |
| 2                            | 8     | 4     |
| 3                            | 7     | 4     |

4. Conclusion
In this work, shell filling of a single QD was observed with the help of µPL technique. Spectra demonstrate complicated structure under high optical power because of complicated occupation of the electron levels. The same behavior was detected by applying electrical field. Difference of shell peak positions is ~4-8meV which shows weak quantum confinement.

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