Optical study of GaAs quantum dots embedded into AlGaAs nanowires

2012 Semicond. Sci. Technol. 27 015009

(http://iopscience.iop.org/0268-1242/27/1/015009)

Semicond. Sci. Technol. **27** (2012) 015009 (5pp) doi:10.1088/0268-1242/27/1/015009

Optical study of GaAs quantum dots embedded into AlGaAs nanowires

V N Kats[1], V P Kochereshko[1,2], A V Platonov[1], T V Chizhova[1], G E Cirlin[1,3], A D Bouravleuv[1,3], Yu B Samsonenko[1,3], I P Soshnikov[1,3], E V Ubyivovk[2], J Bleuse[4] and H Mariette[4]

[1] A F Ioffe Physical-Technical Institute, 194021, St Petersburg, Russia
[2] Physical Department, St Petersburg State University, Ulyanovskaya 1, Peterhof, 198504 St Petersburg, Russia
[3] St Petersburg Academic University of the RAS, Khlopina 8/3, 195220 St Petersburg, Russia
[4] CEA-CNRS group 'Nanophysique et Semiconducteurs', CEA, INAC/SP2M, and Institut Néel, 17 rue des Martyrs, F-38054 Grenoble, France

E-mail: alexei.platonov@mail.ioffe.ru

Received 15 June 2011, in final form 9 November 2011
Published 7 December 2011
Online at stacks.iop.org/SST/27/015009

Abstract
We report the photoluminescence characterization of GaAs quantum dots embedded in AlGaAs nanowires. Time-integrated and time-resolved photoluminescence was measured for both arrays and single quantum dot/nanowires. The optical spectroscopy data show the influence of growth temperature on the distribution of diameters and the presence of different crystalline phases in the AlGaAs nanowires. By means of scanning and transmission electron microscopy and photoluminescence we observed that the growth temperature has a strong influence on the homogeneity of the nanowires, in size and density. In photoluminescence spectra of a single quantum dot, spectral diffusion was observed in the exciton line. Formation of various crystalline phases in the AlGaAs nanowires leads to very long decay times for the nanowire luminescence, around 20 ns.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Free-standing semiconductor nanowires (NWs) are promising one-dimensional nanostructures for applications in nanoelectronics [1] and nanophotonics [2]. Much effort has been devoted to optimizing the growth parameters [3–7] and to providing a theoretical background for the growth technology [8–10]. A very interesting recent development has been the demonstrations that one or several quantum dots (QDs) can be embedded in a NW [11, 12].

Modern epitaxial techniques enable one in principle to control the sizes and the positions of NWs at the nanometer scale, making them very attractive for applications. The most important task in this area is to obtain highly homogenous ensembles of NWs that have a small distribution of sizes and well-determined spatial positions for use in nanoelectronics. It was established that the growth temperature can play an important role in fabrication of homogeneous arrays of NWs [13–17]. Despite very impressive progress in NW fabrication, many aspects of growth are not completely understood. In particular, it is very important to determine growth procedures (especially temperature, but also flux rates and other inter-dependent parameters) that can yield homogenous NW ensembles. In this paper, we report on the growth and the characterization by time-integrated and time-resolved photoluminecence (PL) spectroscopy of GaAs QDs embedded in AlGaAs NWs grown at different temperatures.

2. Experiment

We study AlGaAs NWs with embedded GaAs QDs. The NWs were grown on GaAs (111)B semi-insulating substrates in an EP1203 MBE system equipped with solid sources supplying Ga and Al atoms and an As effusion cell producing arsenic tetramers. The chosen substrate orientation yields the growth of NWs which are mostly oriented perpendicular to the surface.

The substrate surface was first deoxidized at 630 °C. Then a 100 nm thick GaAs buffer layer was grown at

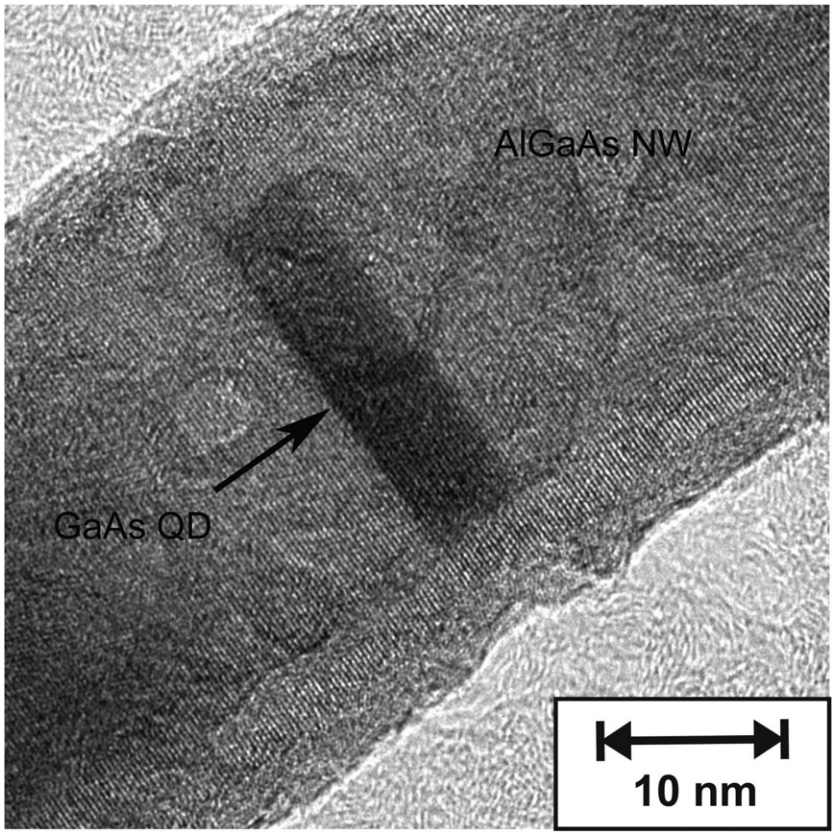

Figure 1. TEM image of an AlGaAs NW with an embedded GaAs QD.

600 °C to achieve an atomically flat surface. By means of the Au effusion cell installed directly in the III–V growth chamber, an amount of gold equivalent to a 1 nm layer was deposited, without V-group flux, at 550 °C. Deposition was followed by a 1 min waiting time to achieve better homogeneity of the droplets.

During the subsequent NW growth, the As_4/(Ga+Al) flux ratio was set at ∼1. Decreasing this value leads to metal-stabilized growth conditions and formation of large metal droplets on the surface. On the other hand, higher flux ratios produce a broader NW size distribution. For the NW growth, the substrate temperature was set at 550 °C or 580 °C. Substrate temperatures lower than this range yield only poor material quality not suitable for optoelectronics, whereas too high substrate temperatures suppress the formation of NWs.

Our preparation procedure induces the formation of droplets containing Au alloyed with the substrate constituents. The droplet sizes range between 40 and 50 nm. Growth of NWs on the droplets was initiated by opening the Al, Ga and As sources, simultaneously. For the samples discussed here, the nominal growth rates, i.e. the equivalent growth rates that would be obtained on a clean, gold-free surface, were set to 1 monolayer (ML) s^{-1} for GaAs and 0.4 ML s^{-1} for AlAs. The resulting $Al_xGa_{1-x}As$ growth rate was 1.4 ML s^{-1} corresponding to an Al content in the solid solution of $x = 0.285$, for growth of a planar layer. Since the Al content in a NW could be different from that in a planar layer, the NW composition was measured by Raman spectroscopy. We have found that the alloy composition in our NWs is $x = 0.24$–0.26.

To produce AlGaAs/GaAs/AlGaAs QDs, NW growth was started with 15 min of AlGaAs and then the Al source was closed for 5 s in order to form a GaAs slice in each NW. Growth of AlGaAs was then continued to produce a core–shell structure. (We did not perform any growth interruption at the heterointerfaces.) In principle, by repeating this procedure, it is possible to get QD molecules consisting of a pair of coupled QDs or even a QD superlattice. The growth was completed with 2 min deposition of GaAs at 530 °C to avoid possible oxidation of the AlGaAs shell layer.

Before the optical experiments, the samples were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). A TEM image of a single AlGaAs NW containing a slice of GaAs is shown in figure 1. The dark area seen at the centercenter of the NW corresponds to a single GaAs QD. It is seen that the interfaces along the growth axis and across the radius are rather sharp. The GaAs QD looks like a disc surrounded by the wide-gap semiconductor AlGaAs. The diameter of the NWs in our samples was 25–50 nm, the length was 500 nm and the thickness of the QD was several atomic monolayers, i.e. 2–5 nm.

Continuous wave and time-resolved PL measurements were performed on a set of samples in the temperature range from 5 up to 250 K and for various optical excitation densities. The samples were excited by either the second harmonic of an Nd:YAG laser or a doubled Ti:Sapphire laser with 100 fs pulse duration and 70 MHz repetition frequency. The average power of the lasers was about 10 μW and the spot diameter was

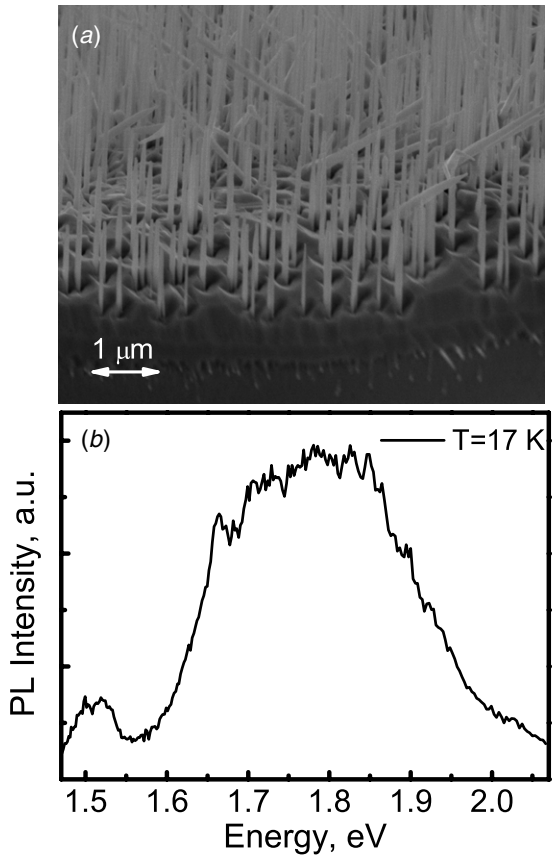

Figure 2. (*a*) SEM image of a sample grown at 550 °C. (*b*) PL spectrum taken for this sample.

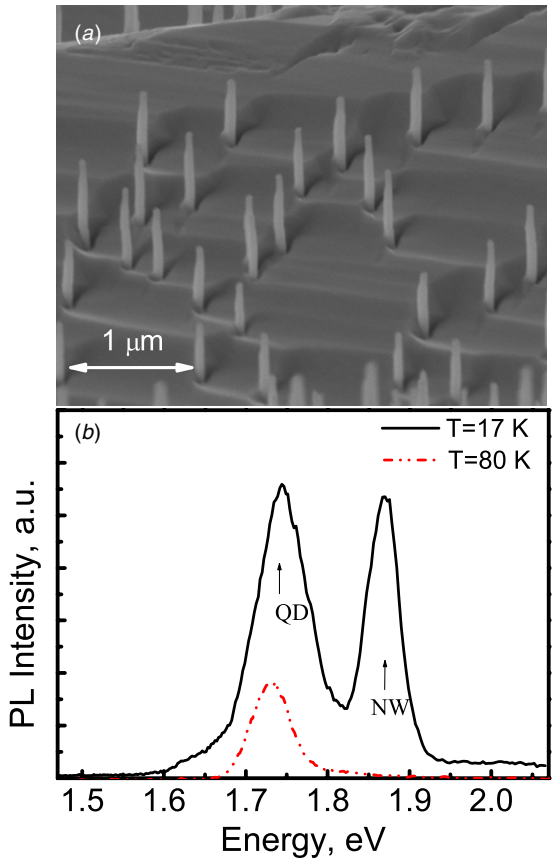

Figure 3. (*a*) SEM image of a sample grown at 580 °C. (*b*). PL spectra taken at two temperatures for this sample .

15 μm. A Jobin–Yvon 30 cm monochromator with an avalanche photodiode detector was used to acquire the spectra.

3. Results

Figure 2(*a*) shows an STM image of a sample grown at 'low' temperature (550 °C). It is seen that the NWs are strongly inhomogeneous as concerns diameter and position on the substrate.

The diameters range between 100 and 500 Å, and the diameter can even change considerably along a given wire. Most of the wires are perpendicular to the substrate, but some of them are tilted, i.e. there is orientation inhomogeneity, and some of them are detached from the substrate. It is clear that this sample is strongly inhomogeneous.

A PL spectrum from this type of sample is shown in figure 2(*b*). The emission is very broad, spreading from 1.65 to 1.95 eV, without any reproducible structure. This band is a mixture of recombination emission coming from NWs and from the QDs embedded in them, and the two contributions cannot be separated.

In contrast, for samples grown at higher temperature (580 °C), a much better homogeneity is obtained, for both the diameters and the lengths of the NWs, see figure 3(*a*). For example, we can estimate from this figure that the spread of NW diameters does not exceed 15%. Additionally, the diameter is relatively constant along the length of a wire.

The PL spectrum taken from this structure at temperature 10 K is given by the solid trace in figure 3(*b*). Two intense lines at energies 1.73 and 1.87 eV dominate the spectrum. We attribute these lines to carrier recombination in the QDs and in the NWs, respectively.

Indeed, the NW material, $Al_xGa_{1-x}As$ with $x \approx 0.25$–0.3, has a bandgap of $E_g^{AlGaAs} = 1.8$–1.9 eV, and the bandgap of the QD material is $E_g^{GaAs} = 1.519$ eV, at helium temperatures. Consequently, the energy position of the PL peak for the QDs ranges between $E_g^{GaAs} = 1.519$ eV, for very large dots and $E_g^{AlGaAs} = 1.8$ eV, for very small dots. More precisely, the position of the PL line for a QD with the thickness of about 20 A and diameter of 200 Å will lie approximately 200 meV higher than the GaAs bandgap, i.e. at about 1.7 eV. The PL line of a NW lies higher: it should not normally be lower in energy than the $Al_{0.25}Ga_{0.75}As$ bandgap, $E_g^{AlGaAs} = 1.8$ eV (but see later). In contrast to the results shown in figure 2(*b*), the width of these PL lines evidences the much narrower distribution of NW diameters, which does not exceed 15%.

The difference in the nature of the two lines shown in figure 3(*b*) is confirmed by the temperature dependence of the recombination emission. The dashed trace in figure 3(*b*) is the PL spectrum taken at 77 K: the intensity of the NW line completely disappears at this higher temperature, whereas the intensity of the QD line drops by only a factor of 3. At low temperature, carriers can become localized in the AlGaAs

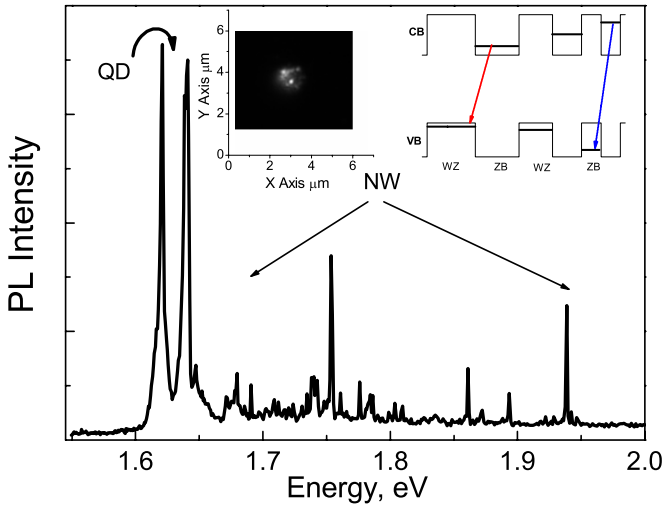

Figure 4. A micro-PL spectrum taken at $T = 6$ K for a GaAs/AlGaAs QD/NW sample. Left: spatially resolved PL intensity of the area under study. Right: bandgap schema of the effective type-II 'superlattice' formation in a mixed-phase AlGaAs NW.

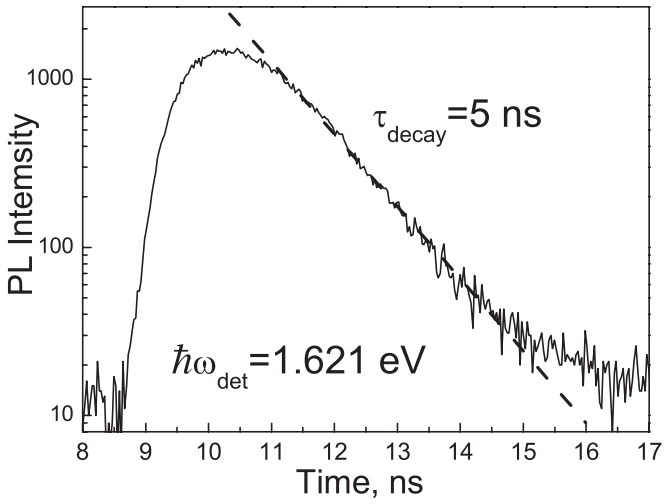

Figure 5. Time dependence of the PL maximum for the lowest QD peak of figure 4.

barriers by fluctuations of the alloy composition. So they recombine in the barriers before they can be captured into the QDs. With increasing temperature, the carriers delocalize and their collection into a QD becomes more efficient. This is why the intensity of the PL from the barriers falls relative to that of the PL from the QDs. This is similar to the effect of temperature seen for a quantum well inserted in a superlattice [18].

Comparing the results shown in figures 2 and 3, we can conclude that a narrow distribution of NW diameters can be obtained by adjusting the growth conditions.

Having optimized the growth process to obtain a homogeneity of the NW diameters, we performed an optical study (PL spectra and time-resolved spectroscopy) on a single QD and single NW. For this purpose, a strongly magnified image of the sample surface was projected onto the slit of the spectrometer. As a result, only the signal coming from a very small number of NWs is collected. The spatial resolution of the objective was about 1.5 μm, and the average distance between NWs was about 0.8 μm. Thus the photodetector may collect a signal coming from several NWs, containing QDs of slightly different sizes.

The emission spectrum shown in figure 4 corresponds to three NWs having a diameter 250 Å, which is nearly 50 Å bigger than the NWs of the sample presented in figure 3. (The inset in figure 4 is the PL intensity image over the area including these NWs.) There are two groups of lines in this spectrum: three relatively wide lines in the energy range 1.6–1.65 eV and many irregularly distributed narrow lines at higher energy (1.75–1.95 eV).

The line at 1.62 eV and the doublet at 1.64 eV are attributed to the PL from three single QDs embedded in three NWs. This interpretation is confirmed by time-resolved PL measurements, as shown in figure 5. The decay time for all three lines was found to be the same and equal to 5 ns. This is a little longer than the decay times observed for the exciton recombination in similar self-assembled (Stranski–Krastanov) InAs/GaAs QDs, but is notably shorter than the decay times measured for all the other lines in this spectrum (20 ns).

Note that the QD lines cannot be interpreted as exciton and biexciton lines, because the energy distance between the single and double lines is 20 meV, whereas the biexciton binding energy for QDs similar to ours is only about 8 meV [19].

The full-width at half-maximum of the emission line of a single QD was found to be relatively large (about 2 meV). This linewidth is not lifetime limited, implying that it is not an intrinsic property of the QDs, but an effect of their local environment. One possible explanation of the linewidth is fluctuating Stark shifts induced by photoexcited charge carriers. Effects of this kind, termed '*spectral diffusion effects*', were already reported [20–22] for lattice-matched QDs like GaAs/AlGaAs. The PL line of a single QD 'jumps' from one energy to another at a frequency which increases with optical excitation intensity so that the line appears broad at high excitation.

Another contribution to the large linewidth could come from the center-of-mass quantization of the exciton in the transverse direction of the NW: indeed, QDs in our samples have a disc shape, with thicknesses of about 20–50 Å and diameters of 200–500 Å. The electron quantization energy in such discs is tens and even hundreds of meV for quantization along the NW axis, but nearly 100 times less for 'transverse' quantization. As a result, many energy levels of the transverse quantization will be associated with the fundamental level of the longitudinal quantization. The allowed optical transitions for this case will appear as an array of narrow lines of smaller intensity broadening the main line. At high enough optical excitation, all these closely situated levels are populated by carriers. This could contribute to the large observed linewidth and to the increase of the PL decay time up to 5 ns from typical for such structures 1 ns. Unfortunately, it was not possible in our experiments to decrease the excitation density to a value small enough without losing the signal detected by the system. However, by increasing the photoexcitation power, these lines clearly become broader.

In summary, the optical data for the low energy lines are consistent with the emission coming from highly populated QDs in the NWs.

We attribute the set of irregularly distributed lines at higher energies (1.75 –1.95 eV) to carrier recombination in the NWs. As mentioned before, the effective bandgap of a NW cannot be smaller than the bandgap of bulk $AlGa_{(1-)}As$—the NW material. However, in our spectrum (figure 4) the strong line at 1.75 eV lies at about 50 meV lower than the bandgap energy of AlGaAs with $x = 25\%$. The decay time of the PL for this line is long—20 ns, and it disappears at temperature of 77 K as is typical for PL coming from carriers in a NW.

We propose that these irregularly distributed lines in the range 1.75–1.95 eV are related to a mixture of wurtzite (WZ) and zinc-blende (ZB) phases in our wires (see inset to figure 4): spontaneous crystalline phase transitions from the cubic ZB to the hexagonal WZ structure are known to occur in such NWs [23, 10, 24]. Because of the band structure difference between ZB and WZ AlGaAs, the alternation in crystalline structure leads to the formation of an effective type-II 'superlattice' along the growth direction (see the inset of figure 4), inducing a quantization of the carriers along the wire axis. The effective bandgap in a mixed ZB–WZ phase is of order 100 meV less than that of ZB AlGaAs, i.e. it should be about 1.7–1.75 eV [24].

Consequently, the NW carrier states become quasi-zero-dimensional rather than the one-dimensional states of a perfectly homogeneous, long, AlGaAs wire. The quantization energies depend on the thickness of the ZB and WZ layers in the wire, which are uncontrolled in our growth procedure, so we obtain a random distribution of the electron and hole energy states, as illustrated in the inset of figure 4.

The long decay time, typically 20 ns, measured for all the lines from 1.75 eV–1.95 eV, confirms such an interpretation, namely that these lines are related to the spatially indirect recombination in type-II structures.

4. Conclusion

Photoluminescence (PL) from single QDs embedded in NWs has been measured. It has been shown that by adjusting the growth procedure one can obtain good homogeneity as concerns the QD and NW sizes. Micro-PL spectroscopy shows emission lines corresponding to carrier recombination both in QDs and in NWs. For recombination in a QD, the linewidth and decay time values are larger than those observed for self-assembled QDs, which could be due not only to spectral diffusion but also to some influence of the transverse quantization. The emission lines coming from the NWs are attributed to recombination between electrons in zinc-blende (ZB) AlGaAs layers and holes in wurtzite (WZ) AlGaAs layers. The long decays obtained for the latter transitions strongly support the interpretation involving the formation of a type II superlattice between ZB and WZ phases.

Acknowledgments

This work was supported in part by grants of the Presidium RAS, the Russian Federal Agency for Science and Innovation (contract no 02.740.11.0383), by several RFBR grants and by the program of cooperation between the RFBR and the CNRS. The authors are grateful to Ronald Cox for their help in preparing this text.

References

[1] Bryllert T, Wernersson L E, Lowgren T and Samuelson L 2006 *Nanotechnology* **17** S227
[2] Gradecak S, Qian F, Li Y, Park H G and Lieber C M 2005 *Appl. Phys. Lett.* **87** 173111
[3] Seifert W *et al* 2004 *J. Cryst. Growth* **272** 211
[4] Dubrovskii V G, Cirlin G E, Soshnikov I P, Tonkikh A A, Sibirev N V, Samsonenko Yu B and Ustinov V M 2005 *Phys. Rev.* B **71** 205325
[5] Harmand J C, Patriarche G, Péré-Laperne N, Mérat-Combes M N, Travers L and Glas F 2005 *Appl. Phys. Lett.* **87** 203101
[6] Plante M C and LaPierre R R 2006 *J. Cryst. Growth* **286** 394
[7] Dubrovskii V G, Sibirev N V, Cirlin G E, Harmand J C and Ustinov V M 2006 *Phys. Rev.* E **73** 021603
[8] Glas F and Harmand J C 2006 *Phys. Rev.* B **73** 155320
[9] Persson A I, Fröberg L E, Jeppesen S, Björk M T and Samuelson L 2009 *J. Cryst. Growth* **311** 2123
[10] Dubrovskii V G *et al* 2009 *Phys. Rev.* B **80** 205305
[11] Borgström M T, Zwiller V, Müller E and Imamoglu A 2005 *Nano Lett.* **5** 1439
[12] Renard J, Songmuang R, Bougerol C, Daudin B and Gayral B 2008 *Nano Lett.* **8** 2092
[13] Jabeenet F, Rubini S and Martelli F 2009 *Microelectron. J.* **40** 442
[14] Wu Z H, Sun M, Mei X Y and Ruda H E 2002 *Appl. Phys. Lett.* **81** 5177
[15] Chan S K, Cai Y, Wang N and Sou I K 2007 *J. Cryst. Growth* **301–302** 866
[16] Fang F, Zhao D X, Zhang J Y, Shen D Z, Lu Y M, Fan X W, Li B H and Wang X H 2008 *Mater. Lett.* **62** 1092
[17] Chang Y-L, Feng L, Fatehi A and Zetian M 2009 *Nanotechnology* **20** 345203
[18] Kop'ev P S, Suris R A, Uraltsev I N and Vasiliev A M 1989 *Solid State Commun.* **72** 401
[19] Heinrich J, Huggenberger A, Heindel T, Reitzenstein S, Hofling S, Worschech L and Forchel A 2010 *Appl. Phys. Lett.* **96** 211117
[20] Kuroda K, Kuroda T, Sakoda K, Kido G and Koguchi N 2007 *J. Lumin.* **122–123** 789
[21] Neuhauser R G, Shimuzu K T, Woo W K, Empedocles S A and Bawendi M G 2000 *Phys. Rev. Lett.* **85** 3301
[22] Plakhotnik T, Fernee M J, Littleton B, Rubinsztein-Dunlop H, Potzner C and Mulvanry P 2010 *Phys. Rev. Lett.* **105** 167402
[23] Shtrikman H, Popovitz-Biro R, Kretinin A and Heiblum M 2009 *Nano Lett.* **9** 215
[24] Spirkoska D *et al* 2009 *Phys. Rev.* B **80** 245325