Dependence of the band-gap pressure coefficients of self-assembled InAs/GaAs quantum dots on the quantum dot size

C. Kristukat, A. R. Goñi, K. Pötschke, D. Bimberg, and C. Thomsen

1 Institut for Solid State Physics, Technical University Berlin, PN 5-4, Hardenbergstr. 36, 10623 Berlin, Germany
2 ICREA Research Professor, ICMAB-CSIC, Esfera UAB, 08193 Bellaterra, Spain

Received 3 July 2006, revised 7 September 2006, accepted 7 September 2006
Published online 27 November 2006

PACS 62.50.+p, 78.55.Cr, 78.67.Hc, 81.07.Ta

We report on low-temperature photoluminescence experiments on self-assembled InAs/GaAs quantum dots under high hydrostatic pressure up to 8 GPa using a diamond anvil cell. The sample exhibits a multimodal size distribution of the quantum dots, which gives rise to a characteristic emission profile displaying up to nine clearly separable peaks attributed to the ground-state recombination from each quantum dot subensemble with different size. Structural analysis revealed that their size differs in entire monolayer steps. The measured pressure coefficients for each subensemble show a linear dependence on their zero-pressure emission energy ranging from 65 meV/GPa for the largest dots to 112 meV/GPa for the smallest ones. Pressure dependent strain simulations based on an atomistic valence-force field yield that the pressure coefficient of the InAs band-gap is strongly reduced when InAs is embedded in a GaAs matrix. Taking into account confinement effects within the envelope function approximation, the calculated pressure coefficients are in good agreement with the experimental findings.
Dependence of the band-gap pressure coefficients of self-assembled InAs/GaAs quantum dots on the quantum dot size

C. Kristukat, A. R. Goñi, K. Pötschke, D. Bimberg, and C. Thomsen

1 Institut für Solid State Physics, Technical University Berlin, PN 5-4, Hardenbergrstr. 36, 10623 Berlin, Germany
2 ICREA Research Professor, ICMAB-CSIC, Esfera UAB, 08193 Bellaterra, Spain

Received 3 July 2006, revised 7 September 2006, accepted 7 September 2006
Published online 27 November 2006

PACS 62.50.+p, 78.55.Cr, 78.67.Hc, 81.07.Ta

We report on low-temperature photoluminescence experiments on self-assembled InAs/GaAs quantum dots under high hydrostatic pressure up to 8 GPa using a diamond anvil cell. The sample exhibits a multimodal size distribution of the quantum dots, which gives rise to a characteristic emission profile displaying up to nine clearly separable peaks attributed to the ground-state recombination from each quantum dot subensemble with different size. Structural analysis revealed that their size differs in entire monolayer steps. The measured pressure coefficients for each subensemble show a linear dependence on their zero-pressure emission energy ranging from 65 meV/GPa for the largest dots to 112 meV/GPa for the smallest ones. Pressure dependent strain simulations based on an atomistic valence-force field yield that the pressure coefficient of the InAs band-gap is strongly reduced when InAs is embedded in a GaAs matrix. Taking into account confinement effects within the envelope function approximation, the calculated pressure coefficients are in good agreement with the experimental findings.

1 Introduction

The pressure dependence of the recombination energy of self-assembled InAs/GaAs quantum dots [1] (QD) has been studied by many groups in the last two decades. The considerable low pressure coefficients and their large variation observed in different samples has been addressed in several publications. Here we present the results from photoluminescence experiments on a sample of coefficients of the transition energies as it exhibits up to nine QD subensembles, each with a different size. Only recently Luo et al. [2] reported results from empirical pseudopotential calculations for many different dot geometries and found an almost linear dependence between the emission energy, which is a function of the dot size, and the pressure coefficients. Those are, however, heavy numerical calculations, where the physical origin of the observed effects is difficult to trace back. We will show in the following that it is possible to explain qualitatively the variation of the pressure coefficients simply by using strain calculations together with bulk deformation potentials and considering quantum confinement within the effective mass approximation.

* Corresponding author: e-mail: kristukat@physik.tu-berlin.de, Phone: +49 30 314 22083, Fax: +49 30 314 277051
2 Experiment

The sample was grown by metalorganic chemical vapor deposition on a GaAs \{001\} substrate. A 300 nm thick GaAs buffer layer was followed by a 60 nm AlGaAs diffusion barrier and 90 nm GaAs. Then 1.9 monolayers (MLs) InAs were deposited with a subsequent growth interruption to allow QD nucleation and formation before being capped by 5 nm GaAs. Further details about the sample growth can be found in Ref. [3].

The sample had to be cleaved and thinned down to a thickness of around 30 \(\mu\)m to fit into a diamond anvil cell for high-pressure experiments. Photoluminescence (PL) measurements were performed at different temperatures in a helium-bath cryostat. The samples were excited using the 514 nm line of an Argon laser. The excitation intensity was always below 5 mW/cm\(^2\) to ensure that luminescence from excited states is negligible. The emitted light was dispersed by a 90 cm single-grating spectrometer and detected by a cooled Si-diode using lock-in techniques. Helium was used as pressure medium and pressure changes were performed well above the melting point of He to assure hydrostatic conditions. The pressure calibration was done by means of the ruby luminescence method [4, 5] with temperature corrections according to Ref. [6].

3 Experimental results

Figure 1a shows a series of low-temperature photoluminescence spectra for different pressures. Spectra exhibit at low pressure a multimodal distribution of the ground-state optical transition energies, which spans the range from 1.05 to 1.35 eV at ambient pressure. Calculations based on an eight band \(k\cdot p\) model [7, 8] and a structural analysis demonstrate that this distribution originates from a discrete, stepwise variation of the size of the QDs [3]. The InAs QDs have the shape of a truncated pyramid, differing in height and base length in multiples of a monolayer. The eight peaks marked in the bottom spectrum of Fig. 1a) relate to quantum dots of 2–9 monolayers in height. They can be well fitted with Gaussians, yielding a FWHM of about 30 meV for each peak and an increasing peak separation with decreasing QD height. Centered at 1.49 eV a sharp feature is observed, which originates from the recombination of carriers confined in the wetting layer. In addition, there are two small peaks on each side of the WL one, where the lower is attributed to its LO-phonon replica and the higher is due to the free exciton recombination of bulk GaAs.

With increasing pressure all observed peaks shift to higher energies, which is a clear indication that the observed transitions are direct in \(k\)-space and occur at the Brillouin zone center [9]. At 3.1 GPa a ninth peak appears on the high energy side of the QD emission band. Its energy and shape suggest that it is due to recombination within the next smaller ensemble of dots, i.e. a dot of only one monolayer height. As shown below, the conduction band offset (CBO) significantly increases with rising pressure. A confined state which is energetically very close to the top potential edge, will lower its energy with respect to the potential edge as the CBO increases. Thus, a state with a very small localization energy at ambient pressure would become confined, as the pressure increases. Therefore, with increasing pressure such electrons would be finally able to recombine with the holes. At 6.3 GPa the width of the whole QD emission band has reduced considerably. The sharp wetting layer peak and the upper four of nine peaks related to the QDs have disappeared. A shoulder on the high energy tail of peak five corresponds to the onset of the sixth line. A new feature appears at about the WL energy, denoted as \(\Gamma\), which is very weak and broader than the WL peak. These observations indicate that a crossing of the \(\Gamma\)-states with an X-valley related state (either in the QDs or in the GaAs matrix) occurs above 1.7 eV. This will be discussed in detail below. At 7.4 GPa the overall QD luminescence is almost completely quenched, the intensity dropped by a factor of 30 and a set of peaks, labelled D emerges, which is attributed to defects created by pressure induced dislocations. The remaining signal from the QDs is centered at about 1.55 eV and slowly shifts to lower energies with increasing pressure.

The pressure dependence of all observed peaks is summarized in Fig. 1b. The solid black lines depict the pressure dependence of the direct \(\Gamma\)–\(\Gamma\) and indirect \(X\)–\(\Gamma\) band gap of bulk GaAs taken from Ref. [9].

© 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim www.pss-b.com
All QD ground state transitions shift to higher energies with increasing pressure, slightly diverging, i.e. the peak separation increases with pressure. At 1.1 GPa the PL from the ninth subensemble of dots appears. The WL peak closely follows the band gap of GaAs, separated by 20 meV. At about 4 GPa the WL line is quenched abruptly, the fingerprint of the $\Gamma\text{--}X$ crossover. This is followed by the successive quenching of the higher energy QD lines, when the pressure is further increased. At some pressure steps it is possible to observe that while loosing its intensity due to the occurrence of the crossover, the highest energy peak departs from the rising trend of the direct transition to follow that of a $X\text{--}\Gamma$ indirect one. Nevertheless, the weak signal is masked by that of its next lower-energy neighbor, such that it is not possible to further trace its pressure dependence. The peaks denoted $R$ are attributed to the indirect transition in $k$-space between the $X$ conduction band and the valence band of GaAs in the nearest vicinity of the QD. Both bands are split due to the increasing tensile biaxial strain near the quantum dot, resulting in the effective band-gap being locally lowered with respect to that of bulk GaAs. The existence of a bound $X_z$ state at the interface between the quantum dot and the barrier material has also been demonstrated for very small InP QDs embedded in GaP, GaP being an indirect semiconductor at ambient pressure [10].
The quenching of the quantum dot confined states occurs, when they cross the nearby X_Z conduction band state of GaAs.

The pressure coefficient of the direct QD transitions are obtained by fitting the data points using a quadratic function \( E_i(p) = E_0 + aE + bE^2 \), where \( a \) and \( b \) are the linear and quadratic pressure coefficients, respectively. The pressure coefficients of all QD related transitions are summarized in Fig. 1c. The variation of the pressure coefficients with the emission energy is strikingly large. The values for the linear (quadratic) coefficient range from about 65 meV/GPa (~1 meV/GPa²) for the largest dots to 112 meV/GPa (~5 meV/GPa²) for the smallest ones. This spans the complete range of measured pressure coefficients for self-assembled InAs/GaAs quantum dots compiled and reported in Ref. [11]. Furthermore, the linear pressure coefficients measured here are mostly much smaller than those of bulk GaAs (117 meV/GPa) [9] and InAs (~100 meV/GPa) [12], whereas the sublinearity of the pressure dependence of the QD emission given by the \( b \) coefficient is comparable to that of the bulk semiconductors.

4 Strain model calculation

To understand the pressure dependence of the transition energies of the quantum dots strain simulations have been carried out. The strain simulations are based on an atomistic valence force field (VFF) after Keating [13] with corrections made by Williamson et al. [14] to account for the pressure dependence of the bulk modulus. The total elastic energy reads

\[
E_{\text{tot}} = \sum_i \sum_{j<i} \frac{3}{8} \left[ \alpha_{ij}^{(1)} \Delta d_{ij}^2 + \alpha_{ij}^{(2)} \Delta d_{ij} \right] + \sum_i \sum_{j<i} \frac{3\beta_{ij}}{8d_{ij}^2d_{k_j}^2} \left[ (R_i - R_j) \times (R_i - R_j) - \cos \theta_{ij} d_{ij}^2 d_{k_j}^2 \right],
\]

where \( \Delta d_{ij} = [(R_i - R_j)^2 - (d_{ij}^0)^2]^{1/2} \), \( R_i \) are the coordinates of the atoms, \( d_{ij} \) the unrelaxed bond length, \( \theta_{ij} = \arccos(-1/3) \) the ideal tetrahedral angle. The first and second term correspond to bond stretching and bending interactions, respectively, with force constants \( \alpha^{(1,2)} \) and \( \beta \) taken from Ref. [14]. Four different quantum dot sizes with 2, 4, 6 and 8 monolayers height have been considered and modelled according to information obtained from structural analysis of the real samples. The base length of the smallest dots amounts 13 nm. The overall simulation volume extends over 55 lattice constants of GaAs in each direction, containing more than 1.3 million atoms. After minimizing \( E_{\text{tot}} \), the local hydrostatic and shear strain is determined by looking at the distortion of an elementary tetrahedron. Histograms of the strain distribution exhibit clearly separable peaks of strain magnitude which correspond to the strain in the QD, in the WL and in the surrounding matrix. For further analysis we will assume a constant value equal to the

Fig. 2 Hydrostatic strain in the wetting layer and a 6 monolayer thick quantum dot as a function of pressure. For comparison the bulk strain pressure dependence of InAs is displayed, obtained by evaluating the Murnaghan equation of state.
average strain in the QD, WL and the matrix. Figure 2 shows the pressure dependence of the averaged hydrostatic strain in the wetting layer and in a quantum dot of 6 monolayers height. For comparison the Murnaghan equation of state for bulk InAs is evaluated and displayed. We deduce that at ambient pressure the strain inside the quantum dot is comparable to bulk InAs under an external pressure of about 5 GPa and that with increasing pressure the strain increases at a rate much lower than that in the bulk. This is the result of the different compressibility and lattice constants of InAs and GaAs. As InAs has a higher compressibility than GaAs, it is forced to take roughly the GaAs lattice positions. Upon external pressure the InAs bonds along the interface will shrink by the same amount as those of GaAs, but for InAs the same absolute bond length compression corresponds to a lower strain than for GaAs. The slope of the strain-pressure dependence translates to a band-gap pressure coefficient (PC) of 63 meV/GPa, using an InAs deformation potential from literature, compared to a bulk PC of about 100 meV/GPa [12]. This is in fact the primary origin of the considerable low band-gap pressure coefficients of quantum dots reported so far by many groups. However, the band-gap pressure coefficients obtained by the strain analysis have only a small dependence on the quantum dot size and thus cannot explain the large variation of the PCs. We note that the shear strain, which is responsible for the splitting of the degenerate valence band at \( k = 0 \), is taken to be constant since its pressure dependence is two orders of magnitude smaller than the hydrostatic one.

5 Discussion

The strong variation of pressure coefficients obtained in the experiment can easily be explained by considering the effects of quantum confinement within a simple envelope function approximation picture. As the base length of the quantum dots is large compared to their height and their shape is rectangular we will consider the quantum dot potential as a one-dimensional square well. It is commonly assumed that the valence band offset is independent of pressure. Thus, taking into account the reduced band-gap PC for embedded InAs, the conduction band offset will rise at a rate of 40 meV/GPa, which is the difference of the pressure coefficients of the GaAs matrix and the embedded InAs dot. States which are close to the bottom of potential well, i.e. the ground states in the larger dots are hardly affected by the rising confinement potential and will follow the InAs band edge as the pressure rises. However the ground state energy of the smaller dots will rise at a rate comparable to that of the GaAs band edge. In other words electronic states with wave functions which extend to a large part in the GaAs matrix, will adopt the band-gap pressure dependence of GaAs, whereas states whose wave functions are almost completely confined to the InAs region will rise upon pressure with the reduced rate of embedded InAs. In fact the experimental data of the smallest dots reveals a pressure coefficient (112 meV/GPa) very close to that of bulk GaAs (117 meV/GPa [9]). The electronic states have been calculated within the envelope function approximation, taking into account the energy dependence of the electron mass [15] for different quan-

Fig. 3 Comparison of calculated pressure coefficients with those obtained from the experiment.
tum dot heights as a function of pressure. The resulting pressure coefficients are shown in Fig. 3 together with those obtained from the experiment. Note that the emission energy is underestimated as the confinement energy of the holes has been neglected and the potential is only one-dimensional. Considering the simplicity of the model the results are in good qualitative agreement with the experiment.

In conclusion, we have measured the pressure dependence of the ground-state transition energies of self-assembled quantum dots up to 8 GPa. Depending on the quantum dot size, the pressure coefficients range from 65 meV/GPa for the largest dots to 112 meV/GPa for the smallest ones. Pressure dependent strain simulations based on an atomistic valence-force field yield that the pressure coefficient of the InAs band-gap is strongly reduced when InAs is embedded in a GaAs matrix. The large variation of the pressure coefficients can be explained by taking into account confinement effects within the envelope function approximation, which yields PCs which are in good agreement with the experimental findings.

Acknowledgement  This work was partly founded by SFB 296 of DFG.

References