Strain effects on individual quantum dots: Dependence of cap layer thickness

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We have studied the effects of strain on individual self-assembled quantum dots (QDs) exemplified by InP dots embedded in GaInP. The quantum dot sample was etched from the top and in this way the amount of capping material was reduced. In a sequence of etch cycles, the cap layer was thinned, and the photoluminescence from several individual QDs could be followed as a function of cap layer thickness. The evolution of the emission spectra clearly depended on the quantum dot size. We interpret this as arising from differences in the aspect ratio for quantum dots of different sizes. The influence of the capping layer, for different QD geometries, was modeled using deformation potential theory with the strain calculated using a full three-dimensional linear elasticity model. The results agree well with the experimental observations.

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The electronic structure of semiconductor quantum dots (QDs) is highly sensitive to variations in their local environment. This has been observed experimentally by modifying the properties of the surroundings by, for instance, varying the electric field[1–3] or reducing the presence of excess carriers.[1,4] Embedding of the QDs is vital in order to reduce emission quenching caused by surface states,[5] but it can also be a method to change the strain pattern around the dots, and thereby tuning their emission energies.[6–10] Consequently, QDs have been investigated in the presence of different cap layer materials such as, for example, the $In_xGa_{a-x}As/GaAs$ system.[11–13] There have, however, been few experiments in which the thickness of the capping layer has been varied.[7,8,12,14] We have previously presented such investigations for InP QDs overgrown with thin layers of GaInP, showing how the embedding matrix affects the optical properties both of QD ensembles[7] and of single dots.[8,15] Photoluminescence (PL)[7] and scanning tunneling luminescence[8,15] were used to investigate the optical properties, and scanning tunneling microscopy and transmission electron microscopy (TEM)[8] were used to determine the structure of the QDs and that of the overgrown material. We showed that the overgrowth occurs in three stages, and that the geometrical structure of the overgrown material profoundly influences the electronic states of the QDs. The growth mechanisms for thinly capped InP QDs are complex,[8] and we here present a simpler method to study epitaxial strain effects on the single dot level. This approach has the advantage that the evolution of a single QD can be followed for different strain situations.

The samples initially contained fully strained QDs, i.e., QDs having a cap layer thick enough to ensure that strain effects were saturated. The spectra of more than 10 QDs were characterized individually. The GaInP cap layer was then thinned by wet-etching and the evolution of the emission, for the QDs originally selected, was studied on a single-dot level as a function of cap layer thickness. We also present results from theoretical modeling of the bandgap energies for the InP QDs as a function of the cap layer thickness. The results agree well with the observed QD emission.

The samples were grown by metal-organic vapor-phase epitaxy at low pressure in the Stranski-Krastanow growth mode. A lattice-matched layer of $Ga_{0.51}In_{0.49}P$ was grown on a GaAs substrate. On top of this, 1.9 monolayers of InP were grown, and the dots were formed after a 12 s growth interrupt.[16] A final cap layer of 95 nm GaInP was then grown. It has previously been shown that the dots grow in a bimodal fashion, and that the slightly *n*-type GaInP plays a major role for size dependently charging the dots.[1] The sample thus provides QDs of a variety of sizes and characteristics for the measurements. A coordinate system was fabricated on the sample surface, using standard UV lithography, to enable subsequent measurements of the same QDs. The coordinate system and the fact that each QD has a characteristic PL spectrum made it straightforward to locate the selected dots repeatedly as the capping material was reduced.

A frequency-doubled neodymium-doped yttrium-aluminum-garnet (Nd:YAG) laser emitting at 532 nm was used as a continuous excitation source. The sample was mounted in a cold-finger cryostat and all measurements were performed at 8 K. The emission was collected using an objective lens with 0.4 numerical aperture, providing a spatial resolution of approximately 1.5 μm. The collected luminescence was sent to a CCD camera for imaging, or to a 0.46 m spectrometer with a LN_2-cooled CCD camera for spectroscopy. The spectral resolution of the setup was approximately 100 μeV. The samples were nonselectively wet-etched using ($HBr:H_2O_2:HCl:H_2O$) [2:1:5:100]. The etching rate was determined by atomic force microscopy (AFM) and TEM to be 0.6 ± 0.1 nm s^{-1}. In the case of AFM, the etching depth was obtained from the difference in height between etched and unetched (gold covered) areas of the surface. These measurements showed that the etching was homogeneous and that local strain around the QDs did not affect the etching rate measurably (see Fig. 1).

Figures 2 and 3 show three series of single QD luminescence spectra where the QD emission is shifted towards lower energies as the cap layer thickness is reduced (upper to lower curves). The QD from which Fig. 2 is derived is small, and the emission spectrum shows narrow lines with full-widths at half-maximum (FWHM) of around 100 μeV, which is the resolution limit of our setup.[17] In contrast, the fully developed dots have emission spectra with a group of broader emission lines, each 1–2 meV FWHM, spread over

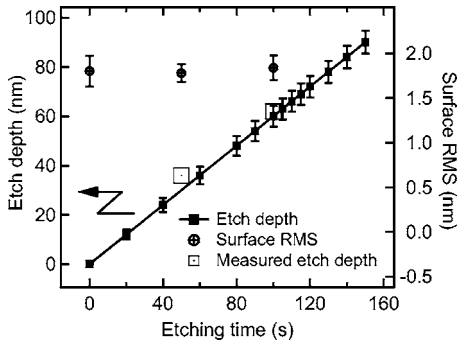

FIG. 1. Estimated etch depth (solid squares), measured average surface root-mean square (RMS) roughness (circles), and etch depth measured by TEM (open squares) as a function of etching time. The surface roughness was measured by AFM over 10×10 μm^2 areas at several different locations on the surface for each sample.

a larger energy range even at very low excitation power[18] (see Fig. 3). It has previously been shown that the difference in spectral behavior is the result of a size-dependent electron accumulation. The fully developed InP QDs are large enough to be heavily charged (15–20 excess electrons) by the slightly *n*-type GaInP host material.[1] The different emission lines originate from electrons in each of the populated states recombining with a single hole. However, the smallest QDs in the sample are neutral, since confinement effects push the electron ground state above the Fermi level.[17]

Figures 2(a) and 2(b) show the evolution of the emission spectrum as a function of the cap layer thickness. Several peaks are present around 1.77 eV when the QD is fully capped. A small dot like this is affected by few-particle effects as soon as the excitation power becomes sufficiently high. Figure 2(c) shows the power-dependent PL of this QD at 26 nm cap thickness. A single emission line is observed at low excitation power, attributed to a single exciton, just above 1.766 eV. Additional lines show up at higher excitation power, located at lower energies than the first emission line. A detailed analysis of the origin of the various emission lines requires more elaborate measurements than here reported.[19]

Figure 2(b) shows the QD emission at different cap thicknesses, shifted in energy in order to facilitate comparison of the spectra. All the spectra in the figure share the characteristic peaks, although the intensities vary slightly between the spectra. This is not surprising, since the number of carriers that are captured by the QD, and thus the electron population, is sensitive to the excitation volume and to the number of nonradiative decay channels induced as the local environment of the QD is changed. The total redshift of the QD emission in this capping range was 32 meV. Additionally, the widths of the emission lines increased as the thickness of the cap layer decreased. The FWHM of peaks from this QD covered by a thickness greater than 30 nm was approximately 130 μeV. This increased to 265 μeV for a cap thickness of 20 nm. It increased further to 1 meV for a cap thickness of 15 nm [bottom spectrum in Fig. 2(b)]. We believe that the line-broadening, for low cap thicknesses, is a near-surface effect as will be discussed below.[14,20,21]

Figure 3 shows spectra from two fully developed QDs. These spectra exhibit the same general change in the emission as the small QD of Fig. 2: the spectrum shifts to lower emission energies with decreased cap thickness. The QDs have PL spectra dominated by several broad emission peaks, distributed around 1.66 and 1.62 eV, respectively, in the fully strained case [top traces in Figs. 3(a) and 3(b)]. The spectral differences between these QDs can be attributed to differences in size and shape, leading to a different electronic structure.[22] The spectra undergo redshifts of 33 and 53 meV in Figs. 3(a) and 3(b), respectively, as the cap thickness decreases from 95 to 20 nm. Notably, for the fully developed QDs, background emission from the GaAs substrate partially overlaps the QD emission when the cap layer thickness is less than 30 nm. This made it necessary to correct for the background, and this was achieved by recording a spectrum from the substrate close to the QD and subtracting this signal from the QD spectrum. Figure 3 makes it clear that it is the electronic states at the highest energies that are affected the most. The intensity distribution for the QD in Fig. 3(a), for example, shifts towards lower energies as the highest states depopulate at lower cap layer thicknesses. Similarly, the intensity of the highest state in the QD spectra in Fig. 3(b) gradually decreases as the cap is removed, and is not present in the spectrum for cap thicknesses below 30 nm.

Our results show that the magnitude of the redshift is mainly determined by the size of QDs. Furthermore, it is clear that the shifts observed here are significantly larger than the shifts reported due to changed electric fields in the vicinity of the dots.[1,2,23] Apart from the energy shifts and the reduced intensity of the higher lying states, remarkably little happens with the spectrum as the cap layer is thinned. It is probable that our spectral resolution is insufficient to reveal more subtle effects, e.g., changes of the line splitting. The spectrum from the neutral QD in Fig. 2 thus remains more or

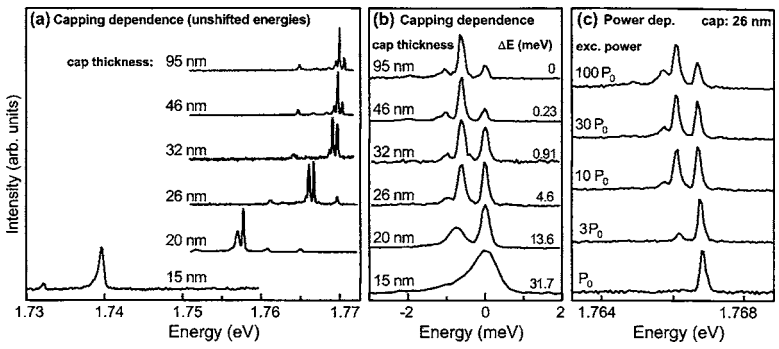

FIG. 2. Photoluminescence spectra of a single small InP QD for varying cap layer thicknesses. (a) The effect of cap layer thickness on the emission. The spectra have been normalized and offset for clarity. (b) The same data as in (a) but shifted in energy to facilitate comparison between the different cap layer thicknesses. (c) The evolution of the photon-emission for the dot as a function of excitation power (P_0=0.1 W cm^{-2}), at a cap layer thickness of 26 nm.

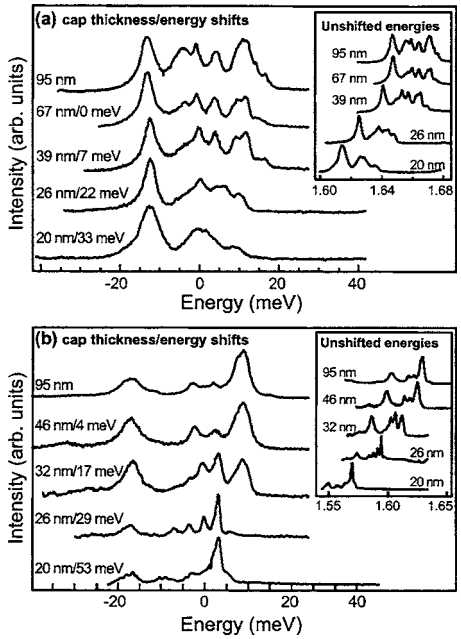

FIG. 3. Photoluminescence spectra of fully developed InP QDs for varying cap layer thicknesses. The spectra have been normalized and offset for clarity, and shifted in energy to facilitate comparisons. (a) Quantum dot emitting around 1.66 eV. (b) Larger quantum dot emitting around 1.62 eV. The insets show the unshifted (measured) spectra.

less the same when the cap thickness is changed, except for the line broadening at thin capping layers. The spectra from larger dots change more dramatically as the cap becomes thinner. The relative intensities of the peaks are modified as soon as the cap thickness is below 40 nm. Nevertheless, the same emission lines having constant splitting are present in the spectra at all cap thicknesses, as can be seen in Fig. 3. It has previously been reported that the energy separation of the electronic states decreases with increasing cap thickness.[8] However, the effect rapidly saturates and is solely visible for cap thicknesses under 20 nm, a region beyond reach of this study.

We have calculated the bandgap energy of the QDs for different thicknesses of the cap layer, in order to model the QD strain evolution. We used a fully three-dimensional calculation and calculated the strain field using a linear continuum elasticity model.[22] No confinement was included in the model. The energies of the band edges were found, using the deformation potential theory, which included the mixing of eight bands. The QDs were modeled as truncated pyramids situated below a flat GaInP overlayer. We assumed that differently sized dots have the same base width but different aspect ratios. This assumption is supported by AFM and TEM investigations of similar samples[24–26] and is also consistent with a kinetic growth model describing the growth transition from small to large InP QDs with increase of supplied dot material.[27] The model shows that dot growth is due to nucleation of material where the strain is most relaxed (close to the top of the island), whereas the areas around the island base perimeter cannot accept any more material. Thus, the growth continues without increasing the base area of the QD and only steepens the side facets. Note that the geometry used for the calculations, see insets in Fig. 4, is a slight simplification of the reported multifaceted structure of InP QDs.[17,24,25] Previously, detailed calculations on the band-structure of capped large[22] as well as small[17] InP QDs have been presented.

A couple of remarks concerning the theoretical model have to be made: We locate the band edges of the conduction and valence bands independently. The resulting band gap is not necessarily the same thing as the minimum band gap at a given position in the QD. To facilitate a comparison with the experimental data 100 meV was added as a constant to compensate for this effect. In this way, the calculated energy values for the larger dots agree well with the measured values. Furthermore, confinement is rather large for the small dots. In this case, an additional constant confinement energy of 60 meV was added to the calculated energies to enable a comparison with the experimental values.[30] The value of 60 meV is in agreement with values previously obtained for these QDs.[17]

Figure 4 shows the experimental results from six QDs and the curves calculated from the model. The calculated curves agree well with the experimental results. It is clear that the shifts are smallest for dots with the smallest aspect ratio. This is expected, since a "dot" with a zero aspect ratio is a quantum well, for which the emission spectrum does not shift with decreasing cap thickness. Dots with a large aspect ratio will relax and become unstrained as soon as the dot is uncovered, and thus the shifts for such dots are large. For each of the QD categories of Fig. 4, the spectral evolution of several additional dots were followed. However, some dots quench in luminescence rather quickly.[31] It is interesting to note that it was not possible to follow any of the fully developed QDs to a cap layer thickness below 20 nm. We believe that it is primarily due the interaction between the QDs and the surface. At these cap layer thicknesses (given from the base of the QDs) the distance from the top of the dot to the sample surface is very small (less than 10 nm), making the confining barrier minimal. Previously, a similar intensity behavior of the photoluminescence, as the distance to the sur-

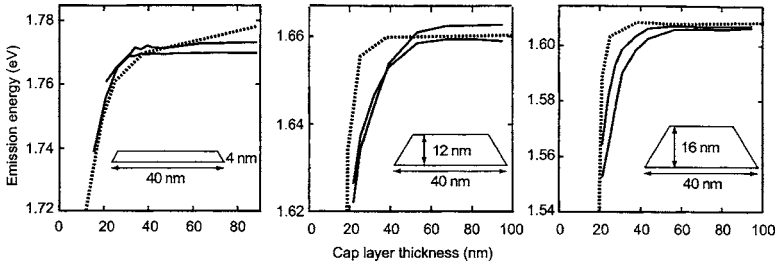

FIG. 4. The results of the theoretical calculations for dots with three different heights (aspect ratios). The solid lines show the experimental data and the dotted lines are the calculated energies. The insets show the geometry of the QDs and the aspect ratios used for the modeling.

face is decreased, has been observed for QD ensembles[28] as well as on the single QD level[14] for the InAs/GaAs system. Also in these measurements almost no QD emission could be detected as the surface-to-dot distance was reduced to less that 10 nm. The close proximity of a surface also influences the linewidth of the QD emission. Notably, surface states have been shown to modify the emission characteristics in a complicated manner, for both bulk material and low-dimensional structures.[5,20] However, it is clear that the surface states can provide a continuum of additional energy states in the band gap. Charges trapped by the surface states might then randomly alter the electric field in the vicinity of the dot, which leads to broadening of the measured QD emission lines. The physical mechanism for this broadening is dependent on the time scale of the trapping.[14]

An interesting observation for the fully developed QDs, as shown in Fig. 3, is that the emission from the highest lying electronic states are most drastically changed as the cap layer thickness is reduced. We have earlier shown that the multitude of lines in the emission spectra originates from charges accumulated in the dot.[1] By tuning the quasi-Fermi level (using Schottky diodes and varying electric fields) the excess carriers in the QD could be reduced. It was observed that the emission peaks then disappeared one by one, starting from the high energy side. We believe that the surface states are causing a related effect here. The exact mechanism is not known, but we speculate that nearby surface states lead to local variations in the quasi-Fermi level and thereby altered level population. This process can then effectively lead to a reduction of electrons in the dot and hence a reduction in intensity of the high energy emission peaks as the cap layer is reduced. As a final remark we note that surface states in close vicinity to the dots can act as local charge traps involved in QD blinking.[29] This subject is outside the scope of this work and we only note that we did observe an overall increase of QDs blinking in the sample after several etch cycles. However, we did not see any blinking behavior on the time scale of minutes to tens of minutes for the dots investigated in this work. In general only about 1 out of 100 QDs do blink in our samples.

In conclusion, we have studied the effect of strain on the photoluminescence of single InP/GaInP QDs of different sizes. We show that the size and the aspect ratio of a QD has a large effect on the strain-induced energy shifts. The maximum strain-induced shifts for small QDs (having small aspect ratios) were about 14 meV, while the strain shifts for larger QDs (with larger aspect ratios) reached 60 meV, when the thickness was reduced from 95 to 20 nm. The strain-induced shifts, for different QD geometries, was modeled using strain-dependent deformation potential theory and the results agree well with the experimental observations.

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[30] As determined by more elaborate calculations (Ref. 17), the used height value of 4 nm for the smaller dots nicely reproduces the observed emission energies in the experiment.
[31] This may be due to a very large spectral shift, which made it impossible to relocate the QD when imaging the sample after etching.