Excited states of individual quantum dots studied by photoluminescence spectroscopy

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The photoluminescence from individual InP quantum dots embedded in a matrix of GaInP has been studied. In addition to the ground state emission that consists of several peaks, we observe excited states of the dot. These states are observed either via state filling or with photoluminescence excitation spectroscopy. We observe a fast relaxation to the set of states with lowest energy but no relaxation between these states. © 1996 American Institute of Physics. [S0003-6951(96)01630-0]

One of the advantages of studies of individual objects is that the linewidths become much more narrow, due to the absence of inhomogeneous broadening. There has recently been strong progress in the growth of semiconductor dots using the Stranski–Krastanow growth mechanism. These dots have good optical properties and have sharp line emission spectra. However, due to a high density of dots it has proved difficult to determine whether individual sharp lines originate in different dots or if they are excited states of a single dot. In this letter we will report on photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopy from individual InP dots, in a matrix of Ga0.5In0.5P. We have measured more than fifty individual dots. Differences between samples are sometimes seen. The results presented in this letter are typical of most of the dots in one particular sample, having a low density of dots. All the results in this letter have been obtained on the same dot, with the exception of those presented in Fig. 1. We will show that the emission spectra of individual dots are similar to each other, despite their complicated spectra, and we will present the excited states of individual dots.

The Ga0.5In0.5P/InP dot structures were grown by metal-organic vapor phase epitaxy on a GaAs substrate. Under the growth conditions used, a bimodal distribution of dots is obtained. On the one hand, there is a large population of fully developed dots, having a well-defined shape. The base area is 45 × 60 nm² with the elongation in the [110] direction and the height is typically between 12 and 18 nm. The density of the fully developed dots is higher if a growth interrupt is used on the upper interface. On the other hand, a large number of partially formed dots are also obtained under these growth conditions. These partially formed dots have very different emission energies, and also a different emission linewidth compared with the fully developed and coherent dots that are investigated in this letter. The samples investigated here were specifically designed (using no growth interrupt) to have a low density of fully formed dots (10⁹ cm²), a concentration which was confirmed by cathodoluminescence. The emission energy of the individual quantum dots investigated in this sample is the same as observed, using broad-area PL, in high-density samples that have been destructively characterized by transmission electron microscopy (TEM). We thus expect the shape of the quantum dots in this sample to be quite similar to quantum dots grown with growth interrupt. A gold metal film was evaporated on the surface in which a large number of holes with sizes between 0.5 and 1 μm were made using electron beam lithography, metallization, and lift-off. The emission from the holes was excited by an Ar laser or by a Ti:Sapphire laser and collected by a microscope, dispersed by a high resolution (0.02 meV) monochromator, and subsequently detected with a GaAs photomultiplier. For the time-resolved measurements, a pulsed laser diode (emitting at 653 nm) was used for excitation and the luminescence was dispersed by a low resolution (0.4 meV) monochromator and detected by a streak camera. The measurement temperature was 6 K.

Figure 1 shows an image of the gold mask with the holes and examples of representative spectra from some of the holes. The holes are squares with a side length of 0.7 μm that would give an average of 0.5 dots/hole. Previous investigations, which averaged the photoluminescence over many dots, have found that the emission from the dots seems to consist of two peaks. In the majority of the holes, shown in Fig. 1, we also find two main peaks although a close inspec-

FIG. 1. An image of the gold mask using optical microscopy and representative spectra taken at low power (about 0.5 W/cm²) from some of the holes.
tion usually reveals the presence of weaker peaks in addition to the two main peaks. One hypothesis in Ref. 5 was that the two peaks were due to fluctuations in the dot heights that now are excluded since they also appear in single dots. This is also confirmed by PLE spectroscopy, described below. In some holes we see no emission and in some holes we see more than two main peaks. The emission spectra from different dots are usually quite similar with respect to energy spacing between the peaks, although the intensity ratio of the peaks varies. Some of the dots have virtually identical emission spectra, with only a small shift in energy. Emission spectra from holes with higher emission energies have a larger separation between the main peaks. We, thus, interpret the energy shift as being due to different sizes of the dots rather than different strain situations.

Figure 2 shows the emission spectrum of one hole in detail, using an excitation power density of \(0.5 \text{ W/cm}^2\). There are peaks with energies of 1.622 eV (denoted A), 1.644 eV (denoted B), and 1.665 eV (denoted C). The latter two peaks (B and C) are what above was called the main peaks. In addition there are weak peaks, e.g., at 1.675 eV. The spectra from the quantum dots are very stable, and repeated thermal cycling between 5 and 300 K does not change the spectra. The linewidths are around 2 meV, which is larger than \(kT\) (0.4 meV) at the measurement temperature (5 K). This linewidth is considerably larger than that for InAs dots in GaAs (0.1 meV) (Ref. 3) and also for partially formed InP dots in GaInP (0.04 meV), also observed in these samples.\(^7\) The linewidth is independent of excitation energy and of excitation power density (at low excitation power density), which leads us to conclude that this is the intrinsic linewidth of this dot. The lifetime of the emission is around 0.7 ns, see below, which would give a life-time broadening of about 1 \(\mu\)eV. We do not know the reason for this large linewidth, but one possibility is phonon coupling. We will call the states seen in emission at low excitation power density, the ground manifold of states.

In Fig. 2 is also shown PLE spectra of the quantum dot where the detection energies are on the three peaks. The PLE spectra of peaks B and C, in particular, are quite similar, showing that they share the same excited states. The PLE spectrum of peak A has less pronounced peaks but is otherwise quite similar to the other PLE spectra. The PLE experiment along with the similarity of the emission spectra from different quantum dots, proves that we observe the emission from a single quantum dot.\(^8\) In the PLE spectra, it is notable that the observed peaks ride on a continuous background. The linewidth of the peaks seen in PLE are similar to those seen in emission, although the linewidth seen in PLE seems to depend on the detection energy, being more narrow for detection on higher energy peaks (such as peak C). The PLE shows that the relaxation is efficient also at low carrier density. Therefore, we cannot attribute this efficient relaxation to scattering induced by the injected carriers.

Theoretical calculations based on a six band envelope function approximation (including strain) give a level splitting of about 1 meV due to nonrelaxing electrons in the valence band and about 10 meV in the conduction band.\(^1\) We attribute the main peaks as being due to electrons in different conduction band states. However, holes localized in different strain-induced potential minima outside the pyramid can also cause some of the peaks.

Figure 3 shows the effect of different excitation power density on the emission. With increasing excitation power density, we see a broadening of the peaks and new peaks appear at higher energies. At the highest excitation power, the peaks have broadened to such an extent that the emission appears continuous within our spectral resolution. In Fig. 3 we also display a PLE spectrum (from peak B), and it can be seen that there is a good agreement between the peaks seen in PLE and the peaks seen in emission. The appearance of the new peaks at higher energies is due to state filling,\(^8\) where the lowest energy states become filled with excitons and subsequent excitons in the quantum dot must occupy higher energy states, due to the Pauli exclusion principle. Excitons are usually considered to be bosons, meaning that the wave function is symmetric under exchange of the exci-
tons as a whole. A given electron belongs, in this case, to a given exciton. However, in quantum dots, the excitons are in the same spatial position and it is meaningless to consider a given particle as being part of a specified exciton, and Fermi–Dirac statistics follow. An important conclusion from the comparison of the PLE and the state-filling experiment is that the excited states seen in state filling are due to single exciton states. It is not the case that the presence of several excitons in the dot causes a new multie exciton ground state at a higher energy. The perturbation of the single-exciton states by the presence of several excitons in the dot is seen as a broadening of the peaks (within our spectral resolution) rather than as the appearance of new peaks.

The integrated intensity of each of the major peaks, such as A, B, and C, increase at the same (nearly linear) rate with excitation power density, if there is no state filling. This does not support the interpretation that any of these peaks is a multie exciton peak. Some of the minor peaks, though, behave differently and may be due to multie exciton states such as biexcitons.

There does not seem to be any communication between the peaks belonging to the ground manifold, e.g., the PLE of peaks A and B do not show any contribution from peak C. Further support is given by time-dependent studies, see Fig. 4, in which is shown the time dependence of peaks A, B, and C, in addition to the time dependence of peak D, which is clearly seen only under state-filling conditions. The excitation energy corresponds to direct excitation in the dot. The time constant is about 0.7 ns for peak A, and 0.6 ns for peaks B and C. However, the time constant for peak D is 0.45 ns, which is significantly faster. This is consistent with a fast relaxation of peak D to the ground manifold of states, if these states are not occupied. At low excitation power, peak D is very weak, about twenty times weaker than peak C. Assuming that the recombination rate of peak D is similar to that of peak C, we obtain a relaxation time to the ground manifold of about 35 ps. The time dependence of peak B has initially a plateau, which is not seen for peak C. We interpret this as a feeding of peak B from peak D, which is consistent with the PLE spectra in which peak D is strongest when detecting on peak B. The energy separation between peak D and peak B is about 40 meV (i.e., close to the LO phonon energy). A consistent feature in our investigations of about fifty dots in different samples is that the energy range over which the ground manifold emission is seen is always less than 50 meV. This is in agreement with a phonon-assisted relaxation, but in contrast to InAs dots inbetween barriers of GaAs, the PLE spectra are not dominated by phonon-assisted relaxation in these dots. Studies of single quantum dots formed by interface fluctuations in the GaAs/AlGaAs system show, in contrast to these quantum dots, only one emission line for resonant excitation.

In summary, we have studied the optical properties of individual quantum dots. We observe complicated spectra displaying discrete states, which are very similar from quantum dot to quantum dot. The relaxation from high energy states to the ground manifold is very fast but the relaxation between the lowest energy states on the contrary is much slower, compared with the recombination rate.

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References

10. In studies of holes in which we suspect that two dots contribute to the emission, it is in fact possible to separate the emission from the (two) dots using selective excitation.