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Double-resonance spectroscopy of InAs/GaAs self-assembled quantum dots

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We present far-/near-infrared double resonance measurements of self-assembled InAs/GaAs quantum dots. The far-infrared resonance is unambiguously associated with a bound-bound intraband transition in the neutral dots. The results show that the interband photoluminescence (PL) lines originate from conduction levels with successively increasing in-plane quantum numbers. We determine the confinement energies for both electrons and holes in the same dots. Furthermore, we show that the inhomogeneous broadening of the PL cannot be attributed solely to size and composition fluctuation.

Crystal growth and lithographic techniques now allow the fabrication of semiconductor microstructures such as quantum box or dot systems.[1] The study of these dots is motivated in part by interest in confinement of charges on very small length scales and interactions between them. They also have potential advantages for optoelectronic emitters, quantum computation etc., due to the singular density of states of individual dots. Some of these advantages have yet to be fully realized due to the lack of complete understanding of the nature of the excited excitonic states and the way charges relax down the ladder of quantized levels. Furthermore, dot ensembles can show considerable inhomogeneity, and even the best photoluminescence (PL) linewidths are typically 15 to 20 meV.

There have been many measurements of intraband spectroscopy in semiconductor quantum dots[2–8] as a means to probe the excited states, but we describe here an inter/intraband double resonance investigation of quantum dots. The interest of this technique is that unlike far-infrared (FIR) absorption or even photoinduced FIR absorption it has allowed us to make an unequivocal assignment of the resonant electronic bound-bound intraband absorption simultaneously with the interband excitonic transition in neutral dots (i.e., giving the electron and hole splittings within the same dots, and without the need for *n*-type and *p*-type samples). These transitions may be strongly dependent on charge due to the Coulomb energy,[8] and it is important to study the transitions in neutral systems since these are of primary technological interest. The technique has allowed us to investigate the relative importance of the causes of the inhomogeneous broadening.

The samples used were InAs/GaAs self-assembled quantum dots grown at a low rate,[9] which are capped with GaAs. The low temperature PL from these dots under high laser power shows a series of very well resolved lines [Fig. 1(a)]. For sample A the lowest energy transition, E1-H1, is at 1046 meV, and higher peaks are observed at 1114 meV, 1181 meV, which are assigned to transitions involving higher bound states (E2-H2 and E3-H3) in the dots. The peaks are spaced roughly 68 meV apart and exhibit a full width at half maximum of about 23 meV. Sample B has lowest PL peaks at 1239 and 1278 meV, i.e., separated by 39 meV, and full width 28 meV (data not shown). The PL from the confining layer[9] and the GaAs matrix are at 1.43 and 1.5 eV, respectively. Atomic force micrographs of an uncapped sample grown under the same conditions indicate that the dots are of in-plane diameter $L_{xy} \sim 50$ nm and height $L_z \sim 7$ nm, with a density of about $1.7 \times 10^{10}\,\mathrm{cm}^{-2}$. Cross-section scanning transmission electron micrographs of the capped dots show that they are of similar size but lens shaped (with the axis perpendicular to the plane of the substrate) rather than pyramidal.

Our double resonance technique is far-infrared modulated photoluminescence (FIR-MPL) (Ref. 10) analogous to optically detected cyclotron resonance (ODCR).[11–13] The sample was mounted on the cold finger of a liquid helium flow cryostat, with ZnSe or polypropylene windows. The interband excitation was with $0.4\,\mathrm{Wcm}^{-2}$ from a c.w. He:Ne laser, incident on the top surface of the sample. The PL was collected and focussed into a 0.5 m grating monochromator, and detected by a liquid nitrogen cooled Ge *p-i-n* diode. The FIR from the Rijnhuizen free-electron laser, which is continuously tunable from 5 μm to 250 μm, was incident normal to the substrate side of the sample, and induced a change in the PL intensity. The FIR light comes in macropulses, 5 μs long and separated by 200 ms, and each macropulse consists of a train of micropulses about 1 ps in duration, separated by 1 ns. The detector rise time is fast enough to resolve the modulation effect of the train as a whole (but not of the individual micropulses) which was boxcar averaged. The PL and the

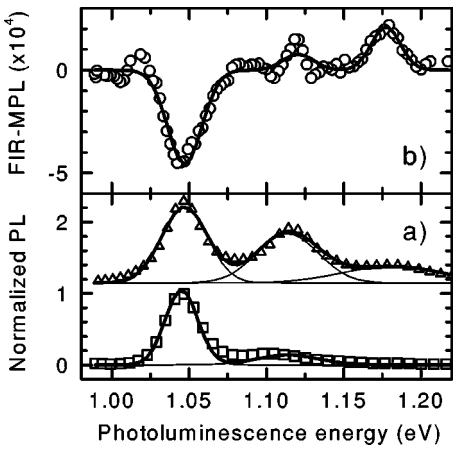

FIG. 1. (a) Squares: PL spectrum taken simultaneously with the FIR-MPL data of (b), normalized to the peak of the ground-state signal. Triangles: PL spectrum for five times larger intensity showing the clearly resolved higher frequency transitions (offset for clarity). Also shown are fits to the low intensity data using two Gaussian lines (giving a width of the ground state of 23 ± 1 meV, solid line). (b) The FIR-MPL spectrum at a FIR photon energy of 65 meV, on the same scale as (a) (i.e., showing the change in PL as a fraction of the peak PL signal). The circles are the experimental data and the solid curve is a fit with three Gaussian lines, the lowest having a width of 22 ± 1 meV. All data are for sample A. The decrease of the PL for the first transition and the increase for higher transitions is associated with the transfer of population from the ground to higher states.

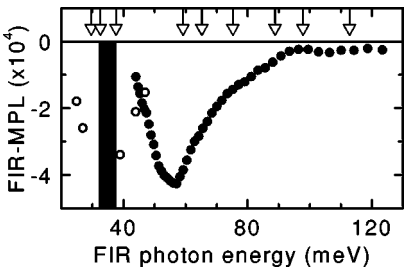

FIG. 2. FIR-modulated PL as a function of the FIR frequency at a fixed PL energy [same units as Fig. 1(a)]. Filled symbols: sample A at PL energy = 1043 meV. The FWHM$=21\pm1$ meV. Open symbols: sample B at PL energy of 1239 meV. The signal is negative, i.e., a PL decrease, at a visible pump laser power corresponding to about 0.2 e-h pair per dot. The arrows mark the one-, two- and three-phonon energies described in the text, and the filled area marks the GaAs restrahlen band.

change in the PL due to the FIR (i.e., the FIR-MPL) were collected simultaneously to ensure the correspondence of features in each by monitoring both the dc and ac outputs of the detector. Spectra were obtained by scanning either the monochromator at fixed FIR frequency or scanning the FIR frequency at a fixed PL frequency. The FIR beam was unfocussed in order to avoid heating the sample, and the intensity was estimated to be $\sim10^{16}$ photons/micropulse/cm^2, i.e., of the order of 10^6 photons per dot/micropulse.

Figure 1(b) shows the FIR-MPL for sample A at a FIR photon energy of 65 meV (a value chosen to be close to the separation between the PL lines). Figure 1(a) shows the (low pump intensity) PL collected simultaneously with the data of Fig. 1(b). From the intensity dependence of the PL we estimate that under the conditions for Fig. 1(b) the ground-state emission was about one tenth saturated, with only a small population in the higher states. The average number of electron-hole pairs per dot was therefore about 0.2 (because the ground state is doubly degenerate with spin). However, the MPL experiment only detects those dots with excitons, i.e., with at least one electron and one hole. The FIR-MPL shows a negative feature at the same photon energy as the lowest PL peak, i.e., there is a reduction in the population of the ground state by the FIR. There is a small increase in the first excited-state population, and a larger increase in the second excited state. The effect is resonant with FIR energy, at 55 meV for sample A. There is no detectable difference in the shape (only amplitude) of the spectrum at different fixed FIR energies, but the effect disappears when detuned sufficiently, as shown in Fig. 2 (where the PL photon energy is kept fixed). We believe that the only explanation for these results is that the FIR is resonantly exciting electrons from the conduction band ground state into higher bound states. Figure 2 also seems to show a weak transition at 110 meV, which may be due to intersublevel transitions from the ground to the second excited state. The resonance for sample B occurred inside the restrahlen band of the GaAs, but we estimate it to be centered about 34 meV.

A full understanding of the strength and width of the features of Fig. 1(b) requires knowledge of the precise photon absorption probabilities from E1 to E2 and from E2 to E3 etc. This in turn depends on which dots have which absorptions exactly in resonance with the FIR laser. The ladder is not perfectly harmonic, and electrons may only be excited up the ladder so far, in our case up to E3 (giving a strong positive MPL associated with E3). The population of E2 is increased by excitation in from E1, but some electrons are lost to E3 (giving a less strong MPL). The shape and width of the features is also likely to be influenced by this interplay.

It is also necessary to point out that if a particular dot has an electron in E1 and a hole in H1, then an excitation from E1 to E2 will not produce by itself an increase in E2-H2 luminescence (and E2-H1 is forbidden). However, charges may spend long periods of time in excited states due to several effects including Pauli blocking and random dot filling[14] (although this is less likely to apply in our low-density regime), or the phonon bottleneck.[15]

The MPL effect was suppressed below our signal/noise level when the FIR beam was moved to 60° to the normal, significantly reducing the component of the electric field in the growth plane. This shows that the higher states involved in the PL have differing in-plane quantum numbers. Transitions involving bound states with differing out-of-plane quantum numbers, states in the wetting layer, free states, holes or phonons would not have the same FIR polarization selection rule as that observed. Furthermore, it is the PL of the dots that is being modulated resonantly, and there is no effect on the PL of the GaAs matrix.

Several authors [e.g., Ref. 16] have reported that in conventional photoluminescence excitation measurement peaks in the absorption occur at multiples of the LO phonon energy above the detection energy. The phonon energy for the dominant 3D confined InAs phonon is at 32.6 meV, with small contributions possible from the InAs wetting layer and bulk GaAs at 29.6 and 37.6 meV, respectively.[16] Our resonance

lies between the one- and two-phonon energies, and no sign of three-phonon (Fig. 2) peaks was observed. In any case such an effect would have neither the polarization selection rule observed, nor the possibility of phonon emission (at 4 K) to enhance the PL of the excited states as described above, and we therefore conclude that the MPL signal does not arise from the absorption of phonons.

For sample A, the resonant FIR photon energy of Fig. 2 (E2-E1 = 55 ± 2 meV) is slightly lower than the separation between the two lowest PL lines [(E2-H2) − (E1-H1) = 68 ± 1 meV]. The errors were estimated from the least-squares fitting. This indicates that the separation between the hole states is H2-H1 = 13 ± 2 meV. Furthermore this proves our earlier assumption about the selection rule for the interband transition, namely that E2-H1 is not allowed, as the PL line separation in this case, (E2-H1)-(E1-H1), would give the same as the FIR resonance energy, E2-E1. The uncertainty in the measurement of sample B is larger and makes quantification difficult.

In the absence of other broadening mechanisms (which is *not* the case as we shall see) our measurement would be able to distinguish between inhomogeneity in the dot spatial size and in the dot potential depth (i.e., composition), by analyzing spectral holes burnt in the PL by the FIR. We describe the energy levels for a dot ensemble assuming a top-hat potential and a disclike spatial shape, since this is a common approximation, although the end result is not dependent on this assumption. The energy separation of the lowest in-plane levels varies like $1/L_{xy}^2$.[17] The level separation is independent of the potential depth and L_z, because in the absence of an energy dependent effective mass, only levels near the top of the dot potential are sensitive to band offset. This means that choice of FIR frequency selects a particular lateral dot size, and a spectral hole should be burnt (if weakly) into the PL, manifesting itself as a sharp MPL feature. In fact the widths of both Figs. 1(b) and 2 are within 2 meV of the PL width Fig. 1(a).

We illustrate the above for sample A with a double resonance tuning diagram, Fig. 3, for dot ensembles with various broadening mechanisms. The figure shows a contour plot of the number density of dots with a given FIR resonance frequency and given PL resonance frequency, and this density corresponds to the strength of the FIR-MPL signal. The double resonance (FIR-MPL) spectrum at fixed FIR energy is obtained by taking a cross-section horizontally across Fig. 3, and the MPL at fixed PL energy is obtained by cross-secting vertically. The PL linewidth is given by the integrating over FIR frequency, i.e., the total width projected onto the abscissa, and is 23 meV in each case. Fig. 3(a) shows an ensemble with inhomogeneity dominated by a Gaussian distribution for L_{xy}, which affects both the FIR and PL energies in a correlated way—larger dots have red shifted FIR and PL, i.e., giving rise to a diagonal stripe distribution. Figure 3(b) shows potential depth (or L_z) fluctuation, which affects only the PL energy—dots with higher composition or larger L_z have red shifted PL but unaffected FIR frequency, i.e., giving rise to a horizontal stripe distribution. Figure 3(c) shows equal amounts of both together (by equal we mean equal broadening of the PL when either is switched off).

In Fig. 3(a) sharp MPL spectra would be expected for both directions, in case (b) a sharp MPL at fixed PL energy would be expected, and in case (c) both MPL spectra would be expected to be about half the width of the PL. Only for a distribution as in Fig. 3(d) would equal widths for all three spectra be expected, as shown experimentally in Figs. 1 and 2. It is clear from the fact that the widths of the PL and both MPL spectra are equal, that cases (a)–(c) *do not apply*. In fact the maximum possible width for Fig. 2 in this model is 70% of the PL width,[8] or 16 meV. The experimental resolution (limited by the FIR laser spectral width) was about 1 meV. Although the calculations of Fig. 3 were made using a one-band, top-hat potential model, use of other, more sophisticated Hamiltonians or other forms for the potential profiles (e.g., for a parabolic potential the FIR energy varies as $1/L_{xy}$) would not change the qualitative conclusion [namely that a distribution as Fig. 3(d) may not be achieved]. It is not known whether the fluctuation in depth and size are correlated in our dots, e.g., spatially smaller dots may have deeper potential if the total indium content is fixed, but this would tend to narrow the distribution on the tuning diagram (Fig. 3) towards a stripe, rather than rounding it. The distribution of Fig. 3(d) may only arise for a mechanism or mechanisms which affect the FIR and PL resonance frequencies in uncorrelated or orthogonal ways, and we must postulate processes which might do this. (It may also occur for homogeneous broadening of the PL, e.g., by phonon or Auger scattering, but PL measurements of individual dots have shown very narrow lines by comparison with the entire ensemble, e.g.,

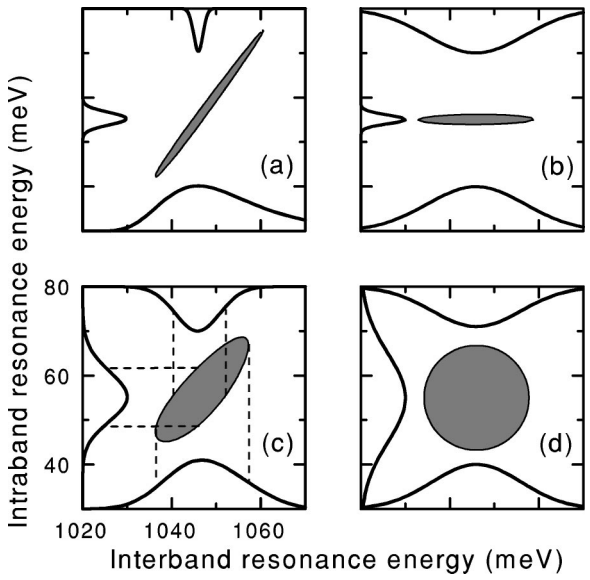

FIG. 3. Double resonance tuning diagram for dots of sample A of different sizes and depths etc. The axes are level separations E2-E1 versus E1-H1, and correspond to the FIR and PL resonant frequencies, respectively. The gray contour shows where the density of dots with a particular combination of FIR and PL energies is 50% of its peak. (a) L_{xy} fluctuation dominating, (b) compositional/L_z fluctuation dominating, (c) equal amounts of both together. (d) The distribution required to explain the data of Figs. 1 and 2. In all cases the normalized PL spectrum (FWHM 23 meV) is shown against the bottom axis. The FIR-MPL spectrum at fixed FIR frequency of 55 meV is shown against the top axis. Finally, the FIR-MPL spectrum at fixed PL frequency of 1046 meV is shown against the left axis. The widths of all three of these spectra are only equal for a distribution as in (d). The dashed lines of (c) are guides to the eye, and mark the FWHM of each type of spectrum.

Ref. 18, and we discount this possibility.)

The remaining random variables are the charge (and state occupancy) in each dot, the separation between dots, and indium fluctuations within the dots. The charge in each dot is determined by the excitation power, and the excitonic binding energy differs between X, XX, X^-, and X^+ etc. The spread of photon energies which may be generated by a recombination may thus vary, with a range from about 3–4 meV[8,19–21] for singly charged excitons. This mechanism is therefore unlikely to be solely responsible for the double resonance linewidths. A small separation between dots can cause e-h pairs to couple with adjacent dots via the wavefunction overlap or via the Coulomb interaction (if there is charge or a dipole in those dots), and the strength of such coupling depends on the separation.[8,17,22–26] Our dot density corresponds to a mean center-to-center dot separation which is quite large, about 85 nm and as dipole-dipole interactions fall off as $1/r^3$, it seems unlikely that in our weakly-excited and neutral system that such coupling is strong either. However, when these mechanisms are convoluted with several other stochastic mechanisms (size, depth, interdot coupling) a distribution more like Fig. 3(d) may result.

In summary, we have measured the intersublevel absorption in self-assembled quantum dots, and shown that higher energy PL lines arise from the in-plane confinement. We make a quantitative determination of the separation between both lowest electronic states and corresponding hole states (E2-E1 = 55 meV, H2-H1 = 13 meV) in a single experiment. Lastly, the measurements of the inhomogeneity of our very narrow linewidth sample show that mechanisms other than spatial size or potential depth fluctuations must also contribute to the broadening of the PL spectra.

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