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Optically induced charging effects in self-assembled GaSb/GaAs quantum dots

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We report photoluminescence (PL) measurements on self-assembled GaSb/GaAs quantum dots. As the laser excitation is increased from very low levels, the PL shows a strong red shift, and then a blue shift, such that it presents a U-shaped curve. Raising the temperature causes a large ($<$100 meV) blue shift of the PL, and shifts the minimum of the PL energy versus laser excitation curve to higher laser powers. Applying a magnetic field at lasers powers $\ll 1$ W cm^{-2} red shifts the PL energy. We explain these effects by population or depopulation of dots that are filled in the dark with holes supplied by carbon acceptors.

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Nanometer-sized self-assembled quantum dots (QDs)[1] exhibit strong charge confinement effects, earning them the name "artificial atoms."[2] Manifestations of the atomiclike character of QDs include ultrasharp lines observed in photoluminescence (PL)[3] or in absorption experiments,[4] and the filling of shell-like levels as the result of optical pumping.[5] The majority of studies on such effects are conducted on type-I InAs/GaAs QDs, in which both electron and hole are confined. Thus, shell filling by optical pumping, for example, is observed for both types of charge carriers. A possibly richer source of physical phenomena are type-II QDs in which the confining band structure spatially separates the electron and hole. One such system is GaSb QDs in GaAs, in which the holes are strongly localized, and the electrons are free, making it a suitable candidate for room-temperature single-carrier (hole) memory devices. A well known, even characteristic, feature of this system is the increase of the QD PL energy with increasing laser excitation, as observed by a number of groups.[6–9] This effect has been attributed to the combination of occupation of excited states,[7,8] i.e., shell filling, and capacitive Coulomb charging.[8]

Here, we present the results of experiments in which the incident laser power density, P, is varied over seven orders of magnitude. Remarkably, in addition to the usual blue shift which is seen when the laser power is increased above about 1 W cm^{-2}, we observe a similar blue shift as the laser power is *reduced* below this level, such that the PL peak energy versus laser power presents a U-shaped curve. The PL energy also strongly increases with increasing temperature, and the shape and minimum position of the U is found to be temperature dependent. Furthermore, when a magnetic field is applied in the very low excitation regime, we observe a *decrease* in the PL energy. These anomalous effects are explained by Coulomb discharging and recharging of GaSb dots by holes that are supplied in the dark by carbon acceptors. Indeed, we argue that everything we observe, even the PL signal itself, originates entirely from the d-like shell of the dots: the s- and p-like shells remain fully occupied and so play no role.

The samples were grown by low-pressure metalorganic chemical-vapor deposition (MOCVD) on a GaAs (001) substrate using triethylgallium and triethylantimony for the GaSb QDs, and trimethylgallium, temethylaluminium, and AsH_3 for the buffer and cap layers. Sample A consists of nominally 3 monolayers (ML) of GaSb 30 nm from the upper interface of a 130 nm GaAs matrix, surrounded by $Al_{0.3}Ga_{0.7}As$ barriers, while in samples B and C about 4.5 and 5 ML, respectively, of GaSb are 20 nm from the surface in a 120 nm GaAs buffer, i.e., there is a lower but no upper $Al_{0.3}Ga_{0.7}As$ barrier. Further details about the growth of similar samples is given in Ref. 10, but here we note that the MOCVD growth leads to the introduction of significant levels of carbon impurities into the sample. PL experiments were carried out in a He bath cryostat or in a variable temperature insert placed in the bore of a 12 T superconducting magnet.[11] The samples were excited by an Ar^+ laser at 514.5 nm, or by a solid-state laser at 532 nm, via an optical fiber. In both cases, the laser excitation is at a similar energy and well above the GaAs band gap, thus the two laser sources can be considered equivalent. The laser excitation power density was varied from 6.6×10^{-5} to 50 W cm^{-2}, though the main emphasis of our work is on the results at low laser powers (<1 W cm^{-2}). The PL was collected by a bundle of six optical fibers surrounding the excitation fiber, and dispersed in a 0.3 m spectrometer. Photon integration was performed with a multichannel InGaAs diode array. Integration times varied between 1 ms and several minutes, depending on the laser power. In our experiments a very large ensemble of dots are probed, thus the average behavior is observed.

The inset to Fig. 1 shows a 10 K spectrum for sample A taken at relatively high laser power (15 W cm^{-2}). The details of the spectra vary depending on the sample and the laser power, but always comprise three elements. At low energy

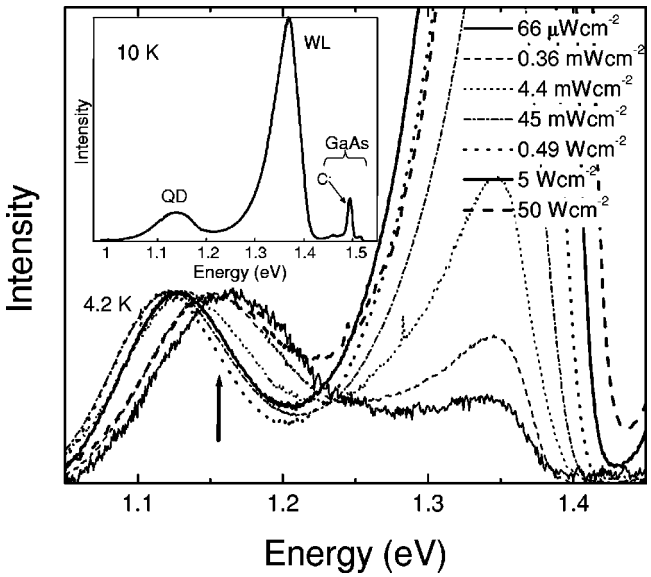

FIG. 1. Dependence of the QD PL of sample A on incident laser power density P at 4.2 K. With increasing P the QD PL red shifts and then blue shifts. The peak position at $P=50$ W cm^{-2}, indicated by the arrow, is the same as with $P=3.6\times10^{-4}$ W cm^{-2}, while for $P=0.045$ and 0.49 W cm^{-2} the PL energy reaches a minimum. The inset shows a complete PL spectrum of sample A at 10 K. The spectral features going from low to high energy are assigned to the QDs, the wetting layer (WL), and the GaAs matrix. The peak labeled C^- at 1.49 ev is attributed to recombination between free electrons and holes bound to carbon acceptors.

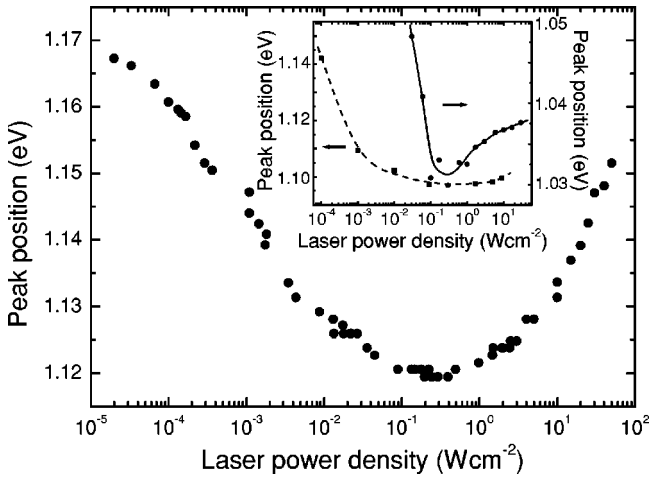

FIG. 2. QD PL peak energy of sample A as a function of laser power at 4.2 K. The upper inset shows the equivalent data for samples B (circles, 10 K) and C (squares, 4.2 K). The lines are guides to the eye.

(1.14 eV in this case) there is a broad peak due to recombination from the GaSb QDs, the dominant peak at 1.37 eV is from a thin GaSb wetting layer (WL), while the group of peaks around 1.5 eV are from the GaAs matrix.[8,9] For the remainder of this paper we will concentrate on the PL from the QDs, the power dependence of which is shown for sample A in Fig. 1, for $P=6.6\times10^{-5}$ to 50 W cm^{-2}. At very low laser powers, the WL PL has almost disappeared from the spectrum, whereas at high laser powers it dominates (see also inset to Fig. 1). More interesting, however, is the behavior of the QD PL energy, which decreases as the laser power is increased, reaches a minimum at around 0.05–0.5 W cm^{-2}, and then increases again. In fact, apart from the contribution from the WL, the spectra taken at 3.6×10^{-4} and 50 W cm^{-2} are essentially indistinguishable.

This remarkable behavior can be seen more clearly in Fig. 2, where we plot the position of the QD PL as a function of P. The equivalent data for samples B and C are shown in the inset. The exact shape of the power dependence seems to vary from sample to sample, but the general behavior is the same. As P is increased from very low values, the PL energy shows a strong decrease, reaches a minimum, and then increases again. We stress that the increase at relatively high laser powers has been widely reported,[6–9] but the decrease that precedes this is totally unexpected.

Figure 3(a) shows the temperature (T) dependence of this effect for sample A, again for a range of laser powers. For all laser powers the QD PL shows a blue shift with increasing temperature of the order of tens of meV. It should be noted that at 70 K, k_BT, where k_B is the Boltzmann constant, is only about 6 meV, and that semiconductor band gaps decrease rather than increase with increasing temperature. Indeed, at temperatures above 80 K, the PL energy decreases again, consistent a band-gap reduction (not shown). It can

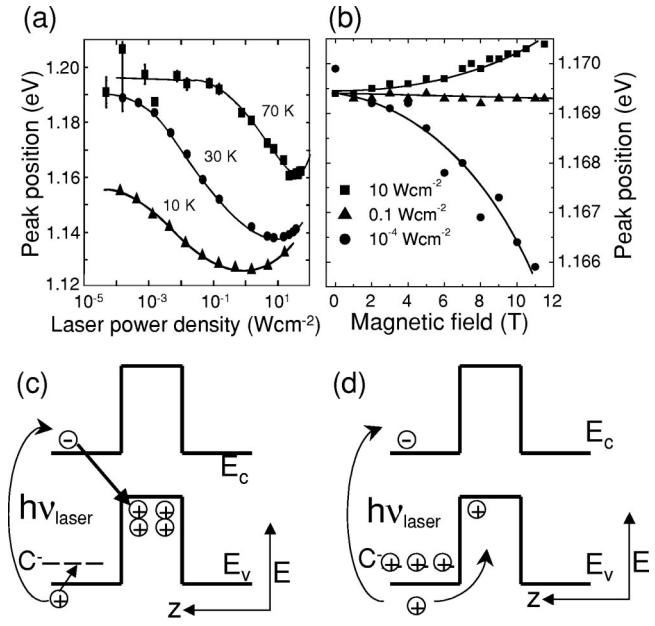

FIG. 3. QD PL peak energy for sample A for different laser power densities as a function of (a) temperature and (b) magnetic field. In (b) the 0.1 and 10^{-4} W cm^{-2} data have been shifted vertically for clarity. The lines are a guide to the eye. (c) and (d) schematically show the mechanisms for depopulation and repopulation of the dots with holes. At low power (c) photoexcited holes are captured by unoccupied carbon acceptors, C^-, while photoexcited electrons recombine with the holes in the dots, reducing the hole population and causing a red shift in the PL. At high laser powers (d) all the carbon acceptors are occupied, so photoexcited holes are rapidly captured by the QD, causing a blue shift in the PL.

also be seen from Fig. 3 that as the temperature is increased the minimum of the curve moves to higher laser power, and that at 70 K the PL energy seems to saturate at low powers to a value which is slightly below 1.2 eV.

Finally, the low-temperature magnetic field dependence of the QD PL for sample A is shown in Fig. 3(b) for three different laser power densities. At high laser power (10 W cm^{-2}) the PL energy increases with increasing magnetic field.[9] For $P=0.1$ W cm^{-2}, i.e., just below the minimum in the zero-field peak position, the PL energy appears to be independent of magnetic field, at least up to 12 T. The behavior at even lower laser power (10^{-4} W cm^{-2}) is astonishing: the PL energy *decreases* as the field increases, dropping by about 4 meV over the whole field range.

We now turn to the explanation of our data. It is believed that the blue shift of the PL energy in the "high" laser power regime is the result of occupation of the dots with photoexcited holes, giving rise to Coulomb charging and the occupation of excited states.[7–9] From the symmetry in the PL energy versus P curve, it is reasonable to suppose that the dots are also being occupied with holes as the laser power is decreased towards very low levels. The question is then, where do these holes come from? A crucial clue to answering this is given by a close examination of the contribution of the GaAs matrix to the spectrum[12] shown in the inset to Fig. 1. The dominant peak is found to be at ~1.495 eV, and can be assigned to the recombination of free electrons in the GaAs with holes bound to acceptors.[13] The band to band recombination, which is at about 1.52 eV, is somewhat weaker (see also Fig. 1 in Ref. 9). Trimethylgallium, which is used to grow the GaAs matrix, is well known to be a source of carbon acceptors in MOCVD growth,[13,14] as is trimethylaluminum used for the $Al_xGa_{1-x}As$ barriers.[15] For our samples, the doping profile is quite complex due to the different growth temperatures for the GaSb dots plus ~10 nm of the GaAs covering them (~500 °C), and for the remaining epitaxial layers (~600 °C). This 10 nm layer just above the QDs is expected to be p doped (~10^{17} cm^{-3}), and so will supply about 10 holes per dot [there are ~10^{10} dots cm^{-2} (Ref. 10)]. The $Al_xGa_{1-x}As$ barriers will be similarly or more highly doped, and since they are 100 nm thick, can supply an order of magnitude more holes to the dots.

The following description of the laser power dependence of the PL now unfolds. At very low or zero laser power, the QDs are filled with holes from the carbon acceptors. Since the dots can hold up to 15 holes,[16] it is likely that the carbon acceptors in the GaAs matrix just above the dots are totally unoccupied. When laser light is incident on the sample, photogenerated holes are captured by the numerous unoccupied acceptors, while the electrons are strongly attracted to the dots by the large number of holes confined therein. Recombination occurs, reducing the hole occupation. However, even at low temperatures, the high acceptor concentration above the dots allows hopping conduction, and the holes eventually find a depleted dot to occupy. If this takes much longer than the time for the photoexcited electrons to recombine with the holes in the dots, the average dot occupancy is reduced, and there is a red shift of the PL [Fig. 3(c)]. This effect is (above band-gap) optically induced density depletion, and has been studied in detail for two-dimensional systems.[17] As the laser power increases, the acceptors start to refill, and at sufficiently high laser power they become completely occupied, so that photoexcited holes are very rapidly captured by the dots, and the usual picture of dot filling via photoexcited carriers holds [Fig. 3(d)].

With this model we can also explain the temperature and magnetic-field dependence of the QD PL. As the temperature is raised, hole mobility in the GaAs matrix is enhanced, increasing the rate at which holes return to the dot, and so reducing the optical depletion. The magnetic field has two important effects on the PL energy. The first is the usual diamagnetic increase in the confined energy levels in the dots. This is the only effect in the high power regime, when the acceptors are occupied [Fig. 3(b) and Ref. 9]. However, in the low power regime, when the density depletion mechanism is active, the magnetic field also suppresses the hopping conduction, thereby reducing the rate at which holes refill the dots. The strange decrease in PL energy for the lowest power data in Fig. 3(b) is thus an enhancement of the density depletion of the holes from the dots, which reduces the charging energy. This decrease in energy competes with, and overcomes, the increase in PL energy from the usual diamagnetic shift.

The constant peak position seen for a range of laser powers at 70 K in Fig. 3(a) implies that at this temperature the holes reach the dots as fast as they are removed, and that a recombination energy of ~1.195 eV in this sample corresponds to dots that are completely filled. From capacitance measurements it has been found that similar dots can be filled with 15 holes, and that the Coulomb charging energy, ΔE_c, and level quantization energy, ΔE_q, are 13 and 40 meV, respectively.[16] A dot occupation of 15 holes will completely fill the s and p atomic-shell-like levels, and partially fill the d-like shell with seven holes. With this information we can deduce how many holes remain in the dot when the PL energy is at its lowest value. Removing holes only from the d-like shell will reduce the PL energy by 91 meV to 1.104 eV, which is indeed comparable with the lowest PL energies we have observed. It should be noted that remounting the sample for different experimental runs can give a mimimum PL energy that is $\leqslant$10 meV lower than this, a discrepancy that we attribute to variations in dot size across the sample. Since optically induced density depletion requires that the recombination time be faster than the time it takes for the dot to capture a (photo-excited) hole, the emptying of the d-like shell may represent an intrinsic limit to the depletion. Indeed, a simple rate equation model shows that, even with the effects of inhomogeneous broadening of the PL included, removing just one hole from the p-like shell will cause a relatively abrupt reduction in the PL energy of $\Delta E_q=40$ meV, which is incongruous with the rather smooth decrease of the PL energy with laser power. We therefore reach the conclusion that all the effects we observe, including the PL itself, are restricted to the holes in the d-like shell. The holes in the s- and p-like shells play no active role. There are several possible mechanisms which could produce such behavior. We can expect that the hole wave function for the p-like state has a much lower penetration into the GaAs than the d-like state, a correspondingly lower overlap with

the electrons, and therefore a longer recombination time. Perhaps more likely, is that as the dot discharges reducing the Coulomb interaction between the recombining electron and the confined holes,[9] the wave function overlap, and hence the recombination rate, is reduced to the point where the density depletion saturates. Both of these mechanisms would produce a broad minimimum in the PL energy as a function of laser power, such as is seen for sample C, since the high-power blue shift only occurs when the carbon acceptors become full. The carbon acceptors may also become fully reoccupied before the *d*-like shell is emptied: approximately seven acceptors per dot is within the uncertainty of the estimate in the carbon impurity concentration. In this scenario, a more rapid onset of QD reoccupation after saturation of the depletion would be expected.

Finally, we remark that our explanation is entirely consistent with our earlier measurements of the QD exciton binding energy, E_b, which increased from 3.7 meV at $P = 0.5\ \mathrm{W\,cm^{-2}}$ (close to the minimum QD occupation) to 8.5 meV at $30\ \mathrm{W\,cm^{-2}}$.[9] In a hydrogenlike model $E_b \propto (Ze)^4$, where Z is the number of holes in the dot and e is the electron charge, so the change in E_b implies an increase in the number of holes of about 25%. If we take an occupation of eight holes at the PL minimum, we would expect there to be two extra holes for the higher power data.[18] An increase in the zero-field PL energy between the two P values of 28 meV was observed, and this indeed corresponds to $\sim 2\Delta E_c$.

In summary, we have studied GaSb/GaAs self-assembled quantum dots as a function of laser power, temperature, and magnetic field. In the absence of light the dots are filled with holes from carbon acceptors. Increasing the laser power from very low levels causes an optical depopulation of the dots resulting in a strong red shift of the photoluminescence. This effect is enhanced by magnetic field, suppressed by raising the temperature, and limited to depopulation in the *d*-like shell. Further increases in laser power neutralizes the acceptors and refills the dots with holes, causing a blue shift in the photoluminescence.

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