Light-induced spectral diffusion in single self-assembled quantum dots

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Small ensembles of $In_{0.55}Al_{0.45}As$ self-assembled quantum dots have been studied at low temperatures using near-field scanning optical microscopy. We observe spectral diffusion in individual quantum dot luminescence lines. The phenomenon increases in magnitude with optical power density, but is not visible at low powers. We believe the spectral diffusion to be caused by long time-scale trapping and untrapping of charges created by photoionization or thermal ionization in the immediate vicinity of the quantum dots.

In material systems where the optical spectrum is dominated by emission from localized, zero dimensional (0D) states, spectral diffusion (SD) is a well-known phenomenon.[1–10] By definition, SD is the change over time of the shape of the optical spectrum of a system, seen, for example, as a gradual broadening of a hole burnt in the spectrum. Microscopically, it is caused either by a slow excitation transfer between different localized emitters, or by slow changes in the energetic positions of the emitters themselves. For the remainder of this paper, SD will refer to the latter of these mechanisms.

In self-assembled quantum dots (SAD's) (Refs. 11–14) the optical spectrum is dominated by luminescence from 0D states, and the emitters are embedded in a highly inhomogeneous matrix, making it likely that SD should occur in this system, in particular, in light of recent observations of SD in semiconductor nanocrystallites.[10] In this paper, we present what, to our knowledge, is the first direct observation of SD in SAD's. Our experiment is microscopic—allowing us to observe SD in individual quantum dots, as well as localizing the perturbation which causes the phenomenon.

The sample under study consists of an $In_{0.55}Al_{0.45}As$ quantum well containing the dots, embedded in $Al_{0.35}Ga_{0.65}As$, grown by molecular-beam epitaxy a GaAs substrate. It has previously been studied extensively,[15–19] and is known to have a dot density of ~ 200 dots/μm^2. The dots are 18–20 nm in diameter, and both measurements and calculations yield a ground state–to–first excited state splitting of ~ 35–40 meV.

In order to be able to observe emission from individual quantum dots, we use near-field scanning optical microscopy (NSOM) (Refs. 20 and 21) to restrict excitation to a small ensemble of quantum dots. Figure 1 shows a typical photoluminescence spectrum taken in the optical near field. The feature at 1995 meV is the $Al_xGa_{1-x}As$ barrier exciton, and the sharp emission lines at lower energies are the PL of single quantum dots.

All subsequent data presented in this paper were taken in the optical near field at 4.2 K, with the NSOM operating in illumination mode—using the tip to excite the sample — and conventional optics to collect the luminescence. During data taking, the tip was always kept at least 10 nm away from the surface of the sample. This was done since previous work[19] has shown that touching the sample with the tip will cause spectral shifts similar to what we expect for spectral diffu-

sion. The excitation energy was kept below the barrier exciton energy, so excitons were only created in the WL, which in this sample contains no 2D continuum, but is exclusively made up of localized states.[22] This limits the carrier diffusion length to < 200 nm (determined by direct measurement), reducing the number of dots contributing to the recorded spectrum.

Figure 2 shows PL spectra taken continuously at a single point in the sample as a function of time as the optical power is varied. The PL emission intensity is plotted in a gray scale, with each bright vertical trace corresponding to the emission from a single quantum dot. The power quoted is that measured at room temperature with the tip far from any surface. The actual power coupled into the sample is likely to be larger, since some of the electromagnetic modes around the tip that are evanescent in air will couple into propagating modes in the higher index sample.[23] The data sets plotted in Fig. 2 were acquired in the order (a)–(f) (bottom to top), with short interruptions of the light as the optical power was changed between scans. In the first two scans, at 1 μW and 2 μW nominal power, no spectral diffusion is seen. In scan (c) (4 μW), a discrete jump in a number of lines is observed after 4 min followed by a slow, continuous shift throughout the scan. In (d) and (e), the SD is quite striking, in particular between 34 and 58 min in scan (d) (shown by arrows). During that time the tip-to-sample distance was reduced from 20 nm to 10 nm, resulting in an increase in the local excitation density, mainly due to an increase in the coupling of light into the sample. In the last scan (top), the
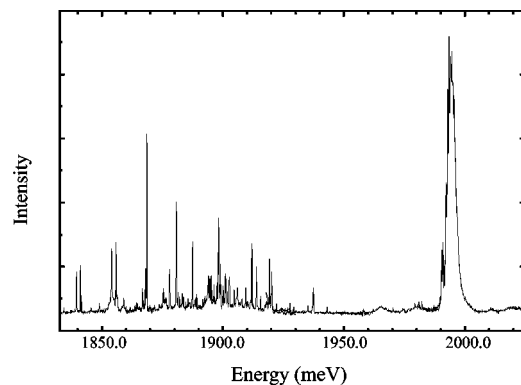

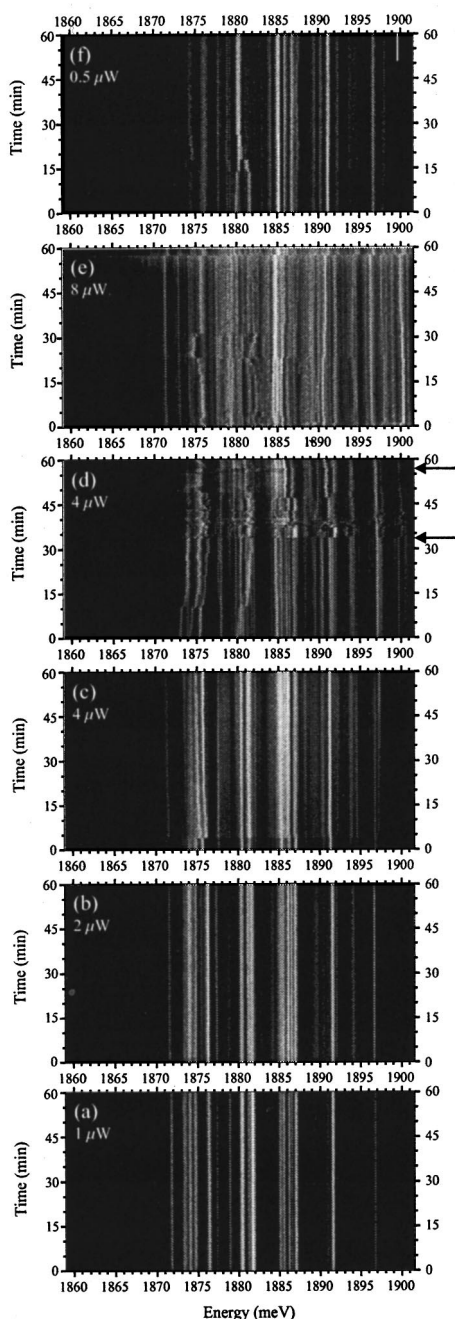FIG. 1. Photoluminescence spectrum from the SAD sample taken in the near field at $T = 4$ K.

FIG. 2. Spectral diffusion of individual dot emission lines. Each panel consists of 289 consecutive spectra taken with a stationary NSOM tip. The approximate optical power incident on the sample is indicated in the upper left corner. Tip-to-sample distance was ~ 20 nm throughout, except in (d) where it was reduced to ~ 10 nm.

FIG. 3. Luminescence intensity at 1889.68 meV as a function of position. The diameter of the near-field tip is about 150 nm. The image was created by interpolation of a set of 40×40 data points.

power was reduced to 0.5 μW, and the SD slowly reduces. In a subsequent scan at the same power no SD is observed.

From these scans and others like it, it is clear that the general trend is for the spectral diffusion to become progressively stronger at higher excitation power densities, although there seems to be no simple relation between the two. Also, once the optical power has reached such levels that SD occurs, the emission lines will keep diffusing for up to an hour after the optical power has been reduced to a level where SD is not normally seen. This latter observation rules out multi-
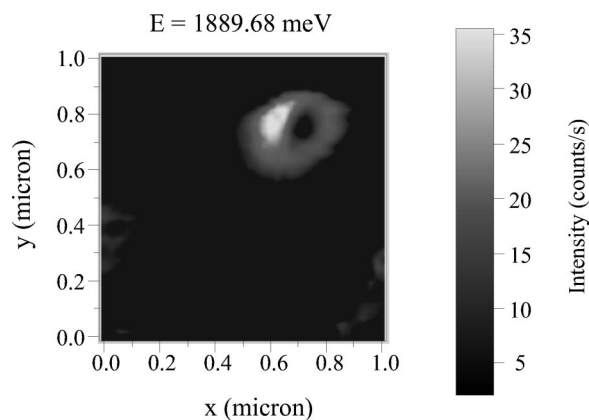
excitonic states as a possible cause, since they require high optical power to exist.

The photoluminescence intensity at a particular wavelength is plotted in Fig. 3 as a function of position as the NSOM tip is scanned across a 1×1 μm area of the sample. Due to the parallellism of the charge coupled device detector, 578 such images are generated simultaneously, each corresponding to a different emission wavelength. The ringlike shape in the image represents the spatial position of a single quantum dot. The dot appears to be a ring due to shadowing when the tip is positioned directly above the dot.[24] The asymmetry in the brightness is due to the off-axis position of the collection optics.

It is important to realize that because of the serial nature of any scanned probe microscopy, each pixel in Fig. 3 represents a different time as well as a different spatial position. In fact, the time difference between consecutive horizontal lines is about 500 s, for a total scan time of ~ 6.5 h. Thus one expects, and we observe, spectral diffusion in spatial scans carried out at sufficiently high power. Figure 4 shows a typical example. Clearly, when the tip is scanned over the area immediately north of the dot, the PL line is redshifted ~ 0.4 meV and the center of emission switches from spectral slice (a) to slice (i). Integration over the entire spectral range of emission from the dot is displayed in (j), which illustrates that the SD is a pure shift, unaccompanied by any intensity change. A close examination of the area where the shift occurs (Fig. 5) shows that it is triggered by the presence of the tip—in the scan lines marked 1, 2, and 3 in Fig. 5, the shift occurs at about the same x position of the tip. Note also that for lines 2 and 3, the PL line remains shifted even as the tip is scanned away from the area.

One possible explanation is that the presence of the light-confining metal coating on the NSOM tip affects the optical properties of the dot, similar to what has been observed in single molecule NSOM spectroscopy.[25] However, since the shift remains in place for several minutes as the tip is moved away from the dot, this explanation can be excluded.

Therefore, the spectral shifts must be caused by the light from the near-field tip. The very long time scale of the shifts severely restricts the number of mechanisms that could accomplish this, and all but one can be excluded. The Overhauser effects occur on the right time scale, but does not
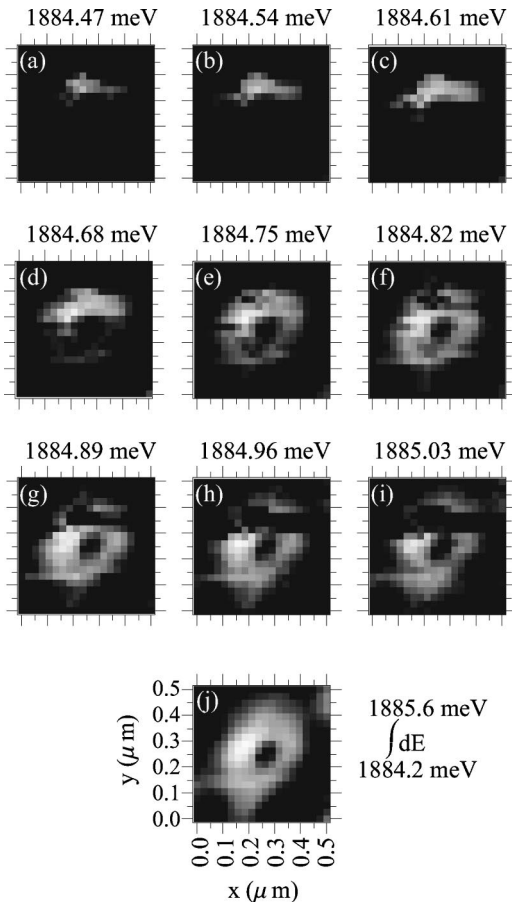
FIG. 4. Spatial plots of PL intensity from a single quantum dot in the near field in narrow wavelength slices (a)–(i), and integrated over the entire spectral range of the dot (j). Each panel plots the same 0.5×0.5 μm area as indicated in (j).

FIG. 5. Closeup of Fig. 4(h). The area framed by the white border is spectrally redshifted by 0.4 meV.

exist at 4 K and zero magnetic field. The incident light could raise the local temperature, but shifts due to this should be continuous and not discrete, and should disappear when the tip is removed from the vicinity. The local temperature gradient could be strong enough to create defects in the material, changing local strain, but such events should be irreversible and lead to reduced quantum efficiency. The only likely explanation is that the SD is caused by charges trapped near the dots, creating a Stark shift in the exciton binding energy. Free charges can be created in the undoped semiconductor through ionization of excitons, either by direct photoabsorption, thermal excitation, or some more complicated process such as auger recombination of biexcitons. This ionization creates free charges that subsequently can get trapped in the semiconductor matrix near a quantum dot, where Coulomb interaction with the 0D exciton causes a shift of the energy of the QD emission.

When an electric charge is placed in the vicinity of an exciton, the energy of the exciton is shifted by an amount $\Delta E = -\Delta E_{hh} - \Delta E_e + E_{pol}$, where ΔE_{hh} and ΔE_e are the energy losses of the electron and hole due to their displacement from the potential of the charge, and E_{pol} is the gain due to the polarization of the exciton. We have carried out a simple Hartree simulation, assuming a harmonic dot potential,[26] with a $\hbar \omega = 38$ meV, $m_e^* = 0.1 m_e$, $m_{hh} = 0.3 m_e$, and a dot diameter of 22 nm (this value gives the co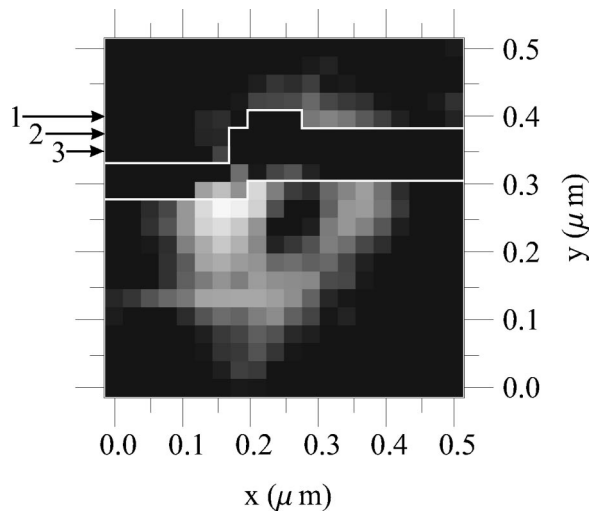rrect binding energy for the dot states). We find that if a charge is trapped within 5 nm of the dot boundary, an observable redshift of the luminescence line by as much as 0.5 meV will result. If the charge is brought closer to the dot, it will tunnel into the dot, creating the larger shift associated with a charged exciton. As is the case for the conventional quantum confined Stark effect, the effect is quadratic in the external field for small perturbation. It does, however, become linear for shifts larger than ~ 1 meV.

Quantitative comparison of the simulation with data such as that in Fig. 2 is difficult since since there is no way of knowing if a particular shift corresponds to adding or removing charge. In the spatial scans, however, we can assume the surroundings of a dot to be relatively unperturbed when the tip first comes within a diffusion length of the dot. We have measured the shifts in 30 individual dots, randomly chosen from our spatial scans subject to the condition that the emission energy of each dot be sufficiently different from its neighbors' that the luminescence can be unequivocally attributed to that dot. All 30 dots show a clear redshift, always smaller than 1.1 meV. Also, whenever discrete jumps can be identified, these are smaller than 0.5 meV. Thus the data are consistent with the simulation for charges trapped within a few nm of the dots.

The median edge-to-edge, nearest neighbor dot separation in this sample has been shown through Monte Carlo simulations to be 10 nm.[22] From our calculation, the interaction between a charge and an exciton located in two different dots separated by this distance would be 0.02 meV, where other sources of charge traps must be considered. It is known that the wetting layer in SAD systems is strongly disordered[27] providing plenty of shallow, localized states where charges can remain trapped on the very long time scale required by our observations. As mentioned above, this sample has such large disorder in the WL that no extended states are present[22] and we infer that the WL contains a particularly large number of potential trap states. For the case of charge trapped in the dots themselves, the exchange interaction should cause a discrete redshift of the charged (X^-) exciton by several meV. In over 30 scans, we have only found a single possible instance of this. This dearth of large shifts does not necesar-

ily mean that a QD is unlikely to trap a charge, although it is conceivable that free charges have difficulty penetrating the strain-induced potential surrounding the QD. It is possible, for example, that charges trapped in a dot are rapidly ejected due to auger-type recombination of the X^- state.[28]

In conclusion, we have observed spectral diffusion attributable to trapping of light-induced charge in a system of self-assembled quantum dots under high optical power density. The SD manifests itself as discrete redshifts of the ground state emission energy when a single charge is trapped near a particular dot, and as a continuous tuning of the emission line when larger numbers of charges are trapped at somewhat larger distances. Our results suggest that the presence of trapped charges in either the wetting layer or the dots themselves must be taken into account when attempting to understand the physics, even in a SAD system where no or very few traps are present, and spectral diffusion therefore does not occur. For example, it is known[29,30] that under high optical power, new emission lines are added to the optical spectrum. This effect is present in our data as well [compare panels (c)–(e) to panel (f) in Fig. 2] at power levels comparable to those where SD occurs. We therefore believe it is important to consider the possibility that some such lines, that in previous work has been assigned to neutral multiple exciton states, could in fact be due to charged or stark shifted excitonic states.

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