Photoluminescence up-conversion in InAs/GaAs self-assembled quantum dots

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We report up-converted photoluminescence in a structure with InAs quantum dots embedded in GaAs. An efficient emission from the GaAs barrier is observed with resonant excitation of both the dots and the wetting layer. The intensity of the up-converted luminescence is found to increase superlinearly with the excitation density. The results suggest that the observed effect is due to a two-step two-photon absorption process involving quantum dot states. © *2000 American Institute of Physics.* [S0003-6951(00)02232-4]

Photoluminescence (PL) up-conversion in semiconductor heterojunctions (HJs) and quantum wells (QWs), i.e., the observation of an emission at energies higher than that of the excitation energy, has attracted much attention in the last few years.[1–8] Up-conversion is a well-known phenomenon in nonlinear optics, but processes like second-harmonic generation and two-photon absorption (TPA) occur primary at high excitation intensities ($\geqslant$kW/cm^2) and are usually quite inefficient in continuous-wave (cw) experiments.[9] On the other hand, a highly efficient PL up-conversion at extremely low excitation intensity (0.1–10 W/cm^2) has been observed in semiconductor heterostructures.[1–8] In these experiments, the carriers photoexcited in the narrow gap material are redistributed into the wide gap material where they undergo recombination and give rise to an up-converted PL (UPL). For the mechanisms that up convert the carriers, Auger process[1–3] and two-step, two-photon absorption (TS-TPA) have been suggested.[4–8] In the Auger process, the energy released by the electron-hole recombination is transferred to another electron or hole. The excited carriers are ejected into the barrier and after relaxation to the band edges they recombine radiatively to give UPL. The presence of a heteroboundary lifts the **k**-conservation requirement in the direction perpendicular to the interface and allows Auger recombination without a thermal threshold. On the other hand, the TS-TPA must be distinguished from the purely TPA in nonlinear optics, because the intermediate state is real and relaxation of the excitation to lower-lying real states may occur before the second photon is absorbed. The up-converted band-to-band luminescence has also been previously observed in bulk semiconductors.[10,11] The effect has been explained by a TS-TPA process involving a deep energy level as an intermediate state. Recently, PL up-conversion has been reported for InP/GaInP self-assembled quantum dots (QDs)[12] and InP and CdSe colloidal QDs.[13] In Ref. 12, QD emission in the presence of electrical current flowing through the sample has been observed with an optical excitation below the ground state. The electrical current provides electrons, some of which are trapped into the QDs, while the holes are optically excited via deep energy levels localized close to the QDs. In the case of colloidal QDs, the PL up-conversion has been explained by a microscopic mechanism that involves the surface states near the valence band and conduction band edges.[13]

Here we report on PL up-conversion in InAs/GaAs self-assembled QDs. We find an efficient PL from the GaAs barrier when the excitation energy is scanned within the absorption band of the InAs dots. The excitation spectrum and the density dependence of the UPL are studied and the mechanism for this emission is proposed.

The self-assembled InAs QD structures studied were fabricated by molecular beam epitaxy (MBE) on (100) GaAs substrate.[14] At the initial stage of the growth 40 periods of GaAs/AlAs (2 nm/2 nm) short period smoothing superlattice was grown at the substrate temperature of 630 °C, followed by the deposition of a 200-nm-thick GaAs buffer layer at $T_g = 580\,^\circ$C with substrate rotation. The dots were formed by depositing 1.7 monolayers of InAs at $T_g = 530\,^\circ$C. A growth interruption of 30 s was used to narrow down the size distribution. Then the dots were covered at 530 °C with a thin GaAs cap of a thickness 1 nm, followed by a second 30 s growth interruption. Atomic force microscopy (AFM) after such a growth procedure, revealed well defined islands of lateral dimension $\approx$60 nm and height $\approx$1.5 nm. A final 50-nm-thick GaAs capping layer was grown at a temperature of 580 °C to further protect the QDs layer. The PL and PL excitation (PLE) measurements were done at low temperature ($T = 2$ K) using a cw Ti-sapphire laser. The luminescence was dispersed by an 0.85 m double monochromator (SPEX 1404) and detected with a cooled InGaAsP/InP photomultiplier tube (Hamamatsu R5509-42) using a conventional lock-in techniques. The detection system provided a spectral resolution of 0.2 nm.

Figure 1(a) shows the PL spectrum of the sample with an excitation energy above the GaAs band gap ($E_{\rm exc} = 1.63$ eV). The excitation intensity is $I_{\rm exc} = 80$ W/cm^2. The spectrum involves both the QD emission and the emission of the GaAs barrier. A weak PL from the InAs wetting layer (WL) is also observed at $E_{\rm WL} = 1.423$ eV. The QD emission can be deconvoluted into three Gaussians with a full width at half maximum (FWHM) of 23–26 meV and peak energies

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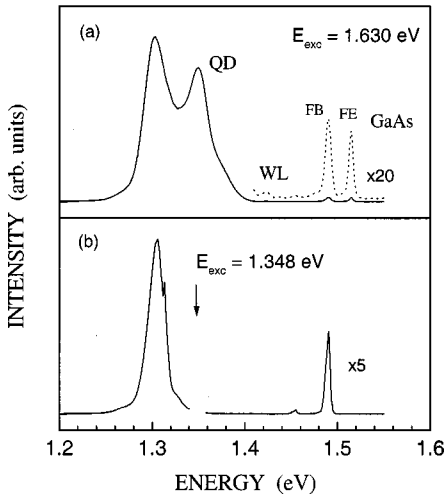

FIG. 1. Photoluminescence spectra of the sample excited above the GaAs band gap (a) and resonantly with the first excited state of QDs (b). The excitation intensity is $I_{exc}=80\ \mathrm{W/cm^2}$.

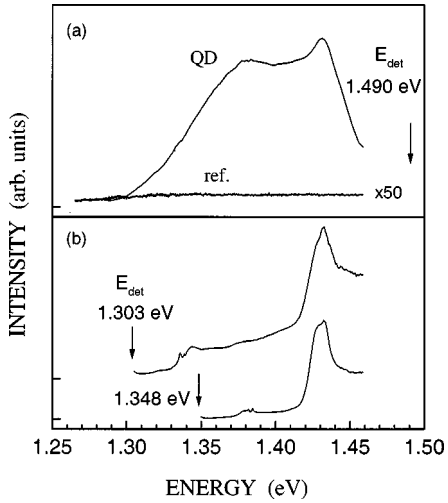

FIG. 2. (a) Up-converted PLE spectra of the QD sample (top spectrum) and the reference sample without QDs (bottom spectrum). (b) PLE spectra of the QDs detected at the ground state and the first excited state, respectively. The second spectrum is shifted for clarity.

centered at 1.303, 1.348, and 1.385 eV. The peak at $E_0=1.303\,\mathrm{eV}$ originates from the ground-state emission, while the peaks at $E_1=1.348\,\mathrm{eV}$ and $E_2=1.385\,\mathrm{eV}$ correspond to the electron-hole recombination at the first and the second excited states of QDs, respectively. The excited-state nature of the high energy peaks is unambiguously confirmed by magneto-PL measurements where a splitting between the states with different angular momentum has been observed.[15] The GaAs peaks at 1.515 and 1.490 eV are attributed to free-exciton (FE) and conduction-band-to-acceptor (FB) recombination, respectively. The small feature at 1.453 eV can be assigned as a LO-phonon replica of the FB peak. The fact that the QD emission dominates over the GaAs PL implies an efficient capture of the photoexcited carriers by the WL and afterward by QDs. However, the luminescence of QDs can be observed even at excitation below the WL emission peak. The PL spectrum at $E_{exc}=1.348\,\mathrm{eV}$ is shown in Fig. 1(b). The same excitation intensity as above band gap excitation is used. Now, the carriers are generated directly into the first excited state of QDs and after relaxation recombine from the ground state. This resonant excitation selects only the dots of an appropriate size; namely, the dots with an excited state energy that matches the excitation energy. As a result, the QD emission intensity decreases more than one order of magnitude in comparison with the above band gap excitation and the width of PL peak is reduced to 18 meV. The sharp line at 33.8 meV below laser excitation is due to the Raman mode of a bulk GaAs phonon. More interestingly, the PL from the barrier can also be detected although the excitation energy is well below the GaAs band gap. The right part of the spectrum in Fig. 1(b) clearly reveals the FB peak at 1.49 eV and its phonon replica, implying an up conversion of the exciting photon energy. We note that a RG850 long-pass filter was used after the laser to prevent the directly excitation of GaAs with the short-wavelength luminescence of the Ti:sapphire laser. The spectrally integrated intensity of the UPL is about 2% of the total PL output. On the other hand, the ratio of the intensities of the FB emission excited below and above the band gap is of the order of 0.2, indicating a high efficiency of the up-conversion process.

The UPL is observed at different excitation energies in the spectral range of the QDs emission. To clarify the physical origin of the up-conversion process, we study the dependence of the UPL on the excitation energy. The emission at 1.490 eV is monitored while varying the laser energy below the GaAs band gap. This ''up-converted'' PL excitation (UPLE) spectrum is shown in Fig. 2(a). For a comparison, the ''normal'' PL excitation (PLE) spectra detected at the ground state ($E_0=1.303\,\mathrm{eV}$) and the first excited state ($E_1=1.348\,\mathrm{eV}$) of QDs is presented in Fig. 2(b). The UPLE spectrum shows that the UPL signal has disappeared if the laser is tuned below QD emission. The low-energy tail of the spectrum in Fig. 2(a) represents quite well the energy distribution of the first excited state of the QD ensemble. Therefore, the up-conversion process must be generated by the formation of electron-hole pairs in the excited states of QDs or in the WL. Indeed, the UPLE spectrum exhibits the same features as the normal PLE spectra in Fig. 2(b). There is an enhancement of the UPLE at excitation energies of 1.385 and 1.43 eV which correspond to the absorption into the second excited state of QDs and the WL. The absorption peak at the first excited state of the QDs, however, is not resolved in the UPLE spectrum. This can be explained by the fact that when exciting between 1.348 and 1.385 eV dots of different sizes contribute to the UPL signal: the large dots are excited in their second excited state and the small dots are excited in their first excited state. In the PLE measurements, the dots are selected by both the excitation energy and the detection energy. For completeness, we checked on the possibility that the UPL is due to an excitation process in the GaAs barrier itself. The UPLE spectrum of a reference sample with the QDs and the wetting layer etched away, measured at same experimental conditions is shown in Fig. 2(a). In fact, the UPL is also detected in the reference sample, but its intensity is more than two orders lower and no clear structure in the spectral region of the QD emission is observed.

Our results imply the existence of an effective mechanism that kicks out the carriers from the QDs into the barrier.

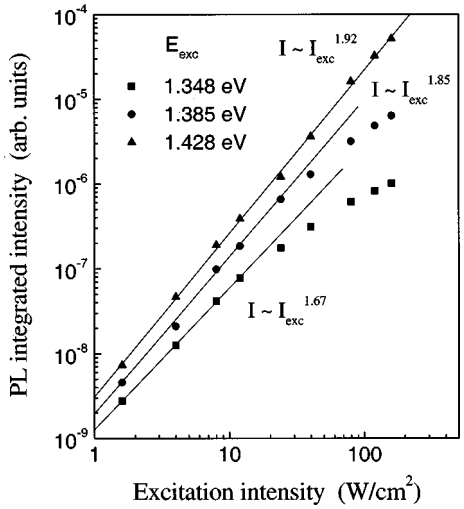

FIG. 3. Excitation intensity dependence of the spectrally integrated UPL at three excitation photon energies. The lines show the linear regression in the double-logarithmic plot. The slope of each dependence is also indicated.

Since the measurements are performed at low temperature ($T=2$ K), the thermal excitation of the carriers can be ruled out. Furthermore, the low excitation intensity used ($I_{ex}<200$ W/cm^2) makes the contribution of direct TPA negligible. As a more plausible explanation of the UPL, we consider the TS-TPA mechanism. The up-conversion process starts with the creation of electron-hole pairs in the excited states of the QDs. In the next step, the electron-hole pairs relax to form excitons in the ground state. These excitons have a very limited spatial extension due to the strong confinement in QDs and can survive long enough to be excited by another photon. The second absorption process creates electron-hole pairs with an energy higher than the GaAs band gap, which can reach the lowest barrier states before the relaxation process into QDs occurs. Then the carriers are trapped again in the QDs or recombine radiatively in the barrier giving rise to the UPL. A similar excitonic up-conversion process has been observed in CdTe/CdMgTe QWs.[4] At higher excitation energies the excited states of QDs can also participate as an initial state for the second excitation process. This consistently explains the enhancement of the UPL when exciting at the second excited state of QDs and at the WL. The larger number of the available intermediate states should increase the probability for the TS-TPA.

Within the above model, the number of up-converted electron-hole pairs is proportional to the population of the intermediate states and to the number of photons responsible for the second excitation process. Assuming that the population of the QD states increases linearly with the excitation intensity, a quadratic intensity dependence of the UPL should be expected. Figure 3 shows the excitation intensity dependence of the spectrally integrated UPL at 1.49 eV. The double logarithmic plot indicates a linear regression with a slope close to 2 at low excitation intensities. When the excitation energy is within the QD excited states, a decrease of the slope at higher intensities is observed. This is probably due to the saturation in the population of the intermediate states for the TS-TPA process. The QD states can be occupied by a limited number of electron-hole pairs, i.e., two for the ground state and six for the first excited states. Therefore, increasing the excitation intensity a situation can be reached where all low lying states of QDs selected by the resonant excitation are populated. It is seen from Fig. 3 that there is no change in the slope if the excitation is resonant with the WL. In this case, all dots in the ensemble are excited and the saturation cannot occur at the intensities used in our experiment.

It is worth noting that with above band gap excitation, the FE and FB GaAs peaks exhibit an almost linear intensity dependence. The slopes are found to be 1.1 and 0.85, respectively. Furthermore, the FE emission quenches at excitation intensities below 10 W/cm^2. In the up-conversion process, the corresponding excitation levels are even lower because a limited number of carriers are excited into the barrier. This is the reason that the FB peak is only observed in UPL spectrum.

The Auger recombination in QDs can also be considered as a possible mechanism for the up-conversion. In this case, however, the UPL should exhibit a cubic dependence on the excitation intensity, because both the electron-electron-hole (eeh) and the hole-hole-electron (hhe) processes are required to excite one electron-hole pair into the barrier. The observed quadratic dependence can be explained if the Auger process is of an excitonic origin, i.e., one electron-hole pair recombines while a second one is excited into the barrier, but the saturation behavior on Fig. 3 is still difficult to understand. Hence, we conclude that the Auger process is not a dominant up-conversion mechanism in the samples studied here.

In summary, we report on PL up-conversion in a heterostructure with InAs QDs embedded into GaAs. An intense PL of the GaAs barrier was observed upon a resonant excitation of QDs. The experimental results suggest that the UPL is due to a two-step, two-photon absorption process involving the QD states.

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