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Anti-Stokes photoluminescence of InP self-assembled quantum dots in the presence of electric current

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An intense anti-Stokes photoluminescence was observed in a structure with InP quantum dots (QD's) in the presence of both a direct electric current and optical pumping below the lowest electron-hole transition in quantum dots. The discovered phenomenon provides clear evidence of deep energy levels in the vicinity of the QD's. A simple model was proposed which allowed us to estimate the energies of the deep states and the lower limit of the product of the electron and hole relaxation rates from the QD's to the deep states. [S0163-1829(99)51744-X]

Observation of the anti-Stokes photoluminescence (ASPL) usually attracts particular attention of researchers due to its enigmatic origin. Along with two-photon excitation several other mechanisms such as two-step excitation[1–6] and cooperative processes[7,8] have been proposed. In semiconductor heterostructures, the ASPL can be excited by the Auger processes.[9,10] In structures with quantum dots (QD's), however, the ASPL has not been observed so far.

The epitaxial growth in the Stranski-Krastanov mode allows one to obtain arrays of self-assembled QD's with nearly perfect crystal structure. Nevertheless, the existence of deep states localized near QD's is considered by a number of authors[11–14] because of their possible important role in nonradiative relaxation processes. In Refs. 11–13, the existence of deep states was used to explain fast relaxation of hot carriers in QD's. In Ref. 14, the built-in electric field was explained by carrier trapping by the deep states in the vicinity of a QD. However, until now there has been no direct experimental evidence of the existence of these states.

In this paper, we report an observation of the ASPL in InP QD's in the presence of electric current flowing through the sample. This phenomenon can be explained only by assuming the existence of deep states. We studied the dependence of the ASPL intensity on the wavelength, optical pump power, and magnitude of the electric current. We propose a physical model that allows us to determine the energy position of the deep levels and the relaxation time of electrons and holes from the QD's to these levels. The fast relaxation time (<10 ns) indicates that the deep states are positioned sufficiently close to the QD. This effect opens up a new opportunity in the study of deep states.

The heterostructure studied was grown by the gas-source molecular beam epitaxy on a n^+ GaAs substrate. After growing a thick GaAs buffer layer and a 100 nm $\mathrm{Ga_{0.5}In_{0.5}P}$ barrier layer, the QD's were formed by the deposition of four monolayers of InP. Then the structure was covered with a top 100 nm $\mathrm{Ga_{0.5}In_{0.5}P}$ layer. The areal density of the QD's is about 10^{10} cm^{-2}. The average base diameter is ≈ 40 nm and the height is ≈ 50 nm. A detailed optical and transmission electron microscopy characterization presented elsewhere[14–16] indicates a high quality of the sample.

The sample was provided with a semitransparent gold Schottky contact on the top surface and with an ohmic contact on the back surface. Both the applied bias and the electric current flowing through the sample were controlled during the experiments. We stabilized the electric current to compensate for a small photocurrent appearing in the illuminated sample. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded under a continuous wave (cw) Ti:sapphire laser excitation. A 1 m-double monochromator and a photon counting system were used to detect the signal. All the measurements were done at 5 K.

With no bias, the sample showed a bright PL band of the InP QD's peaked at 1700 meV with a half width of ≈ 50 meV upon excitation above the PL band in the absorption region of the QD's or of the $\mathrm{Ga_{0.5}In_{0.5}P}$ barrier [Fig. 1(a)]. Upon excitation within the PL band of the QD's, the PL is observed only in the Stokes part of the spectrum [Fig. 1(b)]. No PL is observed upon excitation below the PL band of the QD's [Fig. 1(c)].

When a negative bias is applied to the samples surface, the PL intensity decreases. This effect has been thoroughly studied in another paper,[16] where it has been shown that the decrease in the PL quantum yield q is caused by tunneling of the holes from the QD's.

Under positive bias, the PL quantum yield also decreases due to the hole tunneling. However, as the bias increases over $+0.7$ V, a new phenomenon appears. The PL intensity of the InP QD's starts growing, as is shown in the inset of

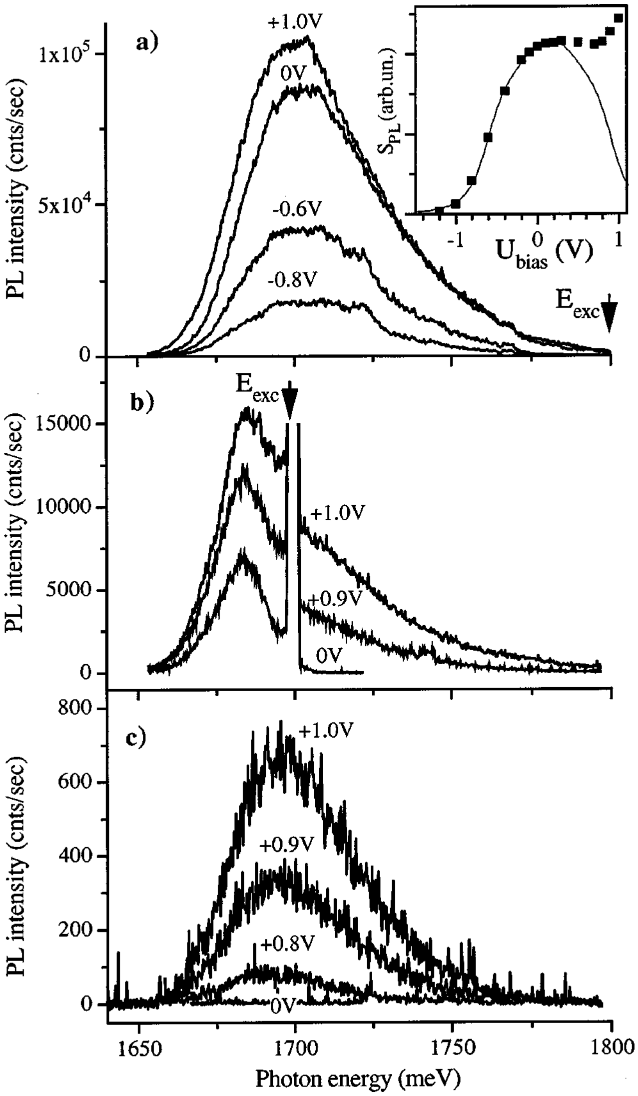

FIG. 1. PL spectra of the InP QD's under the excitation above the PL band (a), at the maximum of the PL band (b), and below the PL band (c) under different applied bias indicated near each spectrum. Excitation photon energies are $E_{exc}=1800$ meV for (a), 1700 meV for (b), and 1350 meV for (c). Inset: The integral PL intensity versus U_{bias} (solid squares). The solid curve shows the dependence of the quantum yield q on U_{bias}.

Fig. 1(a). Moreover, upon excitation at the maximum of or even below the PL band, the PL arises in the anti-Stokes region [Figs. 1(b) and 1(c)]. The effect is fairly strong: for the bias $U_{bias}=+1$ V, the total PL intensity in the anti-Stokes region exceeds the total PL intensity in the absence of the bias [see Fig. 1(b)]. Upon excitation below the PL band, $E_{exc}<1650$ meV, the PL spectrum of the QD's observed in the electric field resembles that under high photon energy excitation, $E_{exc}>1800$ meV [compare Figs. 1(a) and 1(c)]. In this case, the PL band shape does not depend on E_{exc} and U_{bias}.

Simultaneously with the appearance of the ASPL, the electric current flowing through the sample abruptly increases. It reaches 1 mA/mm^2 at $U_{bias}=1$ V. In the absence of the optical pumping, the current does not induce any luminescence of the QD's.

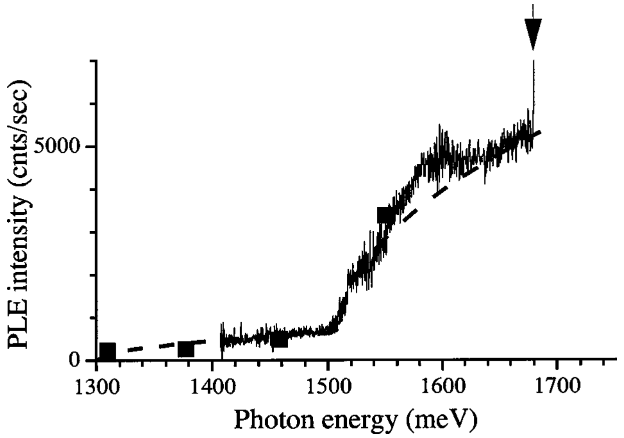

FIG. 2. The PLE spectra of the InP QD's at electric current $I=1$ mA/mm^2 (a solid curve). Solid squares are the PLE signal detected with high accuracy in selected spectral points. The vertical arrow shows the spectral position of the photodetector. The dashed curve is a fit by the expression $I_{PL}=I_1\sqrt{E-E_{d1}}+I_2\sqrt{E-E_{d2}}$ with $E_{d1}=1300$ meV and $E_{d2}=1508$ meV.

Figure 2 shows the PLE spectrum of the ASPL when the signal was detected at the maximum of the PL band, $E_{PL}=1700$ meV, and excitation was *below* this spectral point. One can easily see that the ASPL is clearly observed under excitation in the whole spectral region studied.

We studied the dependence of the total intensity of the ASPL, S_{ASPL}, on the electric current density, I, flowing though the sample. To exclude the effect of the decrease of the PL quantum yield, q [see inset in Fig. 1(a)], on our subsequent analysis, we normalized the PL intensities S_{ASPL} by the q. The value S_{ASPL}/q is linearly dependent on I in the whole range of the electric current densities upon excitation in different spectral points of the PL band. The total intensity of the ASPL varies linearly also with the optical pump power within the studied range of $P_{exc}=0.1-1$ kW/cm^2 under a fixed electric current of $I=1$ mA/mm^2.

For photoexcitation within the PL band of the QD's in the presence of the electric current, the PL spectrum consists of two components as shown in Fig. 3. The anti-Stokes component of PL is well approximated by the spectrum obtained under the excitation below the PL band. Total intensity of this approximating spectrum (dashed line in Fig. 3) normalized to the quantum yield varies linearly with the current density I (inset in Fig. 3).

Based on the experimental data presented above we propose the following model of the physical processes causing the ASPL. The electric current provides electrons, some of which are trapped by the lowest quantum-confined level of the QD's. Optical excitation generates holes, some of which are also trapped by the QD's. Radiative recombination of the electrons and holes produces the ASPL of the QD's.

The origin of the electric current through the sample is fairly clear. The electrons are pulled out from the doped substrate n^+ GaAs by the positive bias. These electrons travel to the surface of the sample through the layer of QD's. When the applied bias exceeds $+0.7$ V, they get over the Schottky barrier formed by the gold electrode on the surface of the sample.

The nature of optical transitions that produce the holes is not so evident. Since the ASPL is observed under the exci-

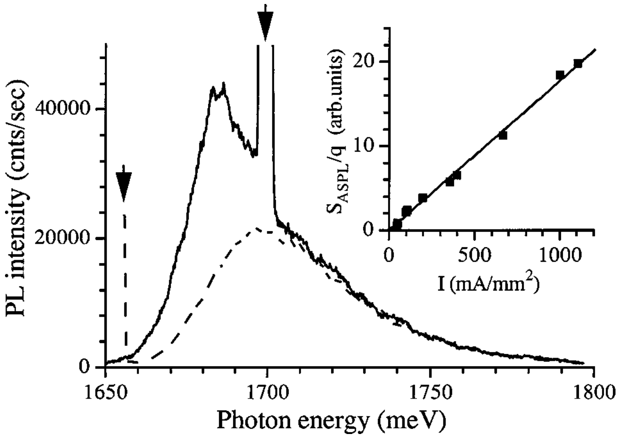

FIG. 3. The PL spectra of QD's under resonance excitation at $E_{exc}=1700$ meV (solid curve) and under the excitation below the PL band of QD's at $E_{exc}=1653$ meV (dashed curve) with electric current $I=1$ mA/cm^2. Inset: The integral intensity of the ASPL normalized to the quantum yield, S_{ASPL}/q, versus the electric current I under the resonant excitation at $E_{exc}=1700$ meV (solid squares), and fit by linear dependence (solid line).

tation in the transparent region of the sample, below the absorption edge of all layers of the heterostructure and of the substrate, we have to assume that the holes are generated due to optical transitions into the deep levels. The holes produced in the buffer GaAs layer or in the substrate cannot be trapped by the QD's because the electric field pulls out the holes into the substrate. For this reason, the deep states, responsible for the ASPL should be located in the QD layer or in the barrier $Ga_{0.5}In_{0.5}P$ layers.

The described model is schematically illustrated in Fig. 4. The processes shown in Fig. 4 can be described by the following rate equations for populations of electrons (n_e) and holes (n_h) in the QD:

$$\frac{dn_e}{dt}=P_e-(\gamma_e+\gamma_{PL}n_h)n_e, \tag{1}$$

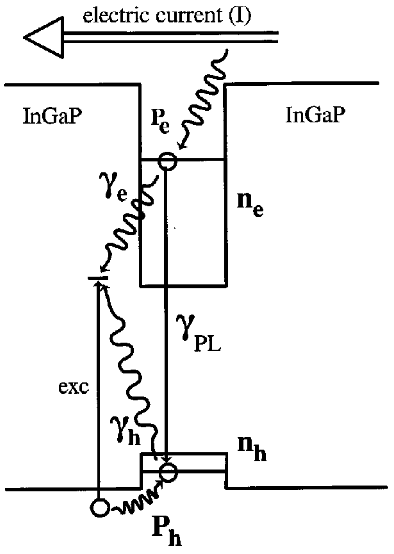

FIG. 4. A model of the processes involved in the observed phenomenon.

$$\frac{dn_h}{dt}=P_h-(\gamma_h+\gamma_{PL}n_e)n_h. \tag{2}$$

Here, γ_{PL} is the radiative decay rate in the QD, P_e and P_h are the electron and hole capture rates, and γ_e and γ_h are the relaxation rates of the electron and hole from the QD's to the defect level, respectively.

In steady state, the solution of Eqs. (1) yields the dependence of the PL intensity, $I_{PL}=\gamma_{PL}n_en_h$, on the optical pump power and electric current which is, in general, nonlinear. To explain the *observed linear dependence* of the ASPL, we have to assume that the relaxation rates of electrons and holes to the deep states, γ_e and γ_h, are sufficiently fast, i.e., they should meet the inequalities $\gamma_e>\gamma_{PL}n_h$ and $\gamma_h>\gamma_{PL}n_e$.

Taking into account these inequalities, we obtain an approximate solution for the PL intensity suitable for further analysis

$$I_{PL}=\frac{P_eP_h}{P_e+P_h+(\gamma_e\gamma_h)/\gamma_{PL}}. \tag{3}$$

From Eq. (3) it follows that the observed linear dependence of the PL intensity on the excitation rates P_e and P_h is explained under the condition,

$$P_e+P_h\ll(\gamma_e\gamma_h)/\gamma_{PL}. \tag{4}$$

We can determine an upper limit of the product $\gamma_e\gamma_h$ taking into account that the electronic and optical excitation rates are definitely faster than the PL rate, that is $(P_e+P_h)>2I_{PL}$. We have estimated the quantity I_{PL}, *the number of photons* emitted by one quantum dot per second, by measuring the absolute value of the signal and the sensitivity of the setup. Under the excitation conditions of the PL whose spectrum is shown in Fig. 3 the observed PL rate gives $I_{PL}\approx 5\times 10^5$ s^{-1}. Taking into account this value, the observed PL decay rate,[16] $\gamma_{PL}\approx 2\times 10^9$ s^{-1}, and the inequality (4), we have $\gamma_e\gamma_h>10^{16}$ s^{-2}. Thus, at least one of the nonradiative relaxation rates, γ_e or γ_h, should exceed 10^8 s^{-1}, i.e., the relaxation time should be shorter than 10 ns.

We can also estimate the energy position of the deep levels by using the spectral dependence shown in Fig. 2. We assume that the presence of two characteristic regions in the anti-Stokes part of the PLE spectrum is related to transitions from the $Ga_{0.5}In_{0.5}P$ valence band to two groups of deep levels located, relative to the valence-band top, at 1508 meV and below 1300 meV, respectively. Since the wave function of deep states is strongly localized, the spectral dependence of absorption is determined mainly by the square root of energy dependence of the density of states in the valence band. Therefore we fitted the PLE spectrum by square-root dependences. As is seen from Fig. 2, the fit agrees with the spectrum.

The nature of the deep states needs to be studied separately, but we would like to make a few comments. It is unlikely that these states are localized inside the QD's. Otherwise we should expect a small PL quantum yield of the QD due to the small energy separation of about 200 meV between the deep level and electronic level in the QD. On the other hand, the fast relaxation rate of γ_e or γ_h can be explained only if the deep states are close to the QD's.

The deep states could be InP/$Ga_{0.5}In_{0.5}P$ interface states[17] or intrinsic defect states due to vacancies or interstitial atoms. These defects can be created in the barrier layer around the QD's due to the large mismatch between the lattice constants of the QD's and of the barriers leading to the strong strain in the heterostructure.[18–20] It is also possible that these states are created by impurities. Optical properties of the QD's are very sensitive to any deep levels around the QD's due to the penetration of the electron and hole wave functions into the barrier layer. This is why the phenomenon discovered in this study may be considered as a inherent property of heterostructures with self-assembled QD's.

The estimates presented above allow us to determine the electron capture rate by the single QD, P_e, which lies within the range $I_{PL} < P_e < P_{current}$, where $P_{current}$ is the number of electrons per QD per second supplied by electric current. For the data presented in Fig. 3, the experimental conditions correspond to $I_{PL} = 5 \times 10^5$ s^{-1} and $P_{current} = 7 \times 10^7$ s^{-1}. So we can conclude that not less than 1% of the electrons are captured by the QD's. Taking into account the QD's areal density in the studied sample, $\rho_{QD} = 10^{10}$ cm^{-2}, we conclude that the electron capture cross section $\sigma_e > 10^{-12}$ cm^2. It is noteworthy that the lower bound of this cross section is smaller than the QD base area by only an order of magnitude.

In conclusion, we have observed an intense ASPL in the heterostructure with InP self-assembled QD's in the presence of direct electric current and cw optical pumping with photon energy below the lowest electron-hole transition in the QD's. The discovered phenomenon provides a clear evidence of the deep states localized around the QD's. Optical transitions from the $Ga_{0.5}In_{0.5}P$ valence band to the deep states generate holes which are captured by the QD's. Then the holes recombine with electrons supplied by the electric current and produce the ASPL. The detailed study of this process allowed us to estimate the upper limit for the relaxation time (10 ns) of carriers from QD into the deep states. This estimation shows that the states are localized closely to the QD's. In the spectral range studied, we found two types of the deep states with energies 1508 meV and less than 1300 meV above the top of the valence band of the $Ga_{0.5}In_{0.5}P$ barrier layers. The discovered phenomenon opens up opportunities in studying these states.

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