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Control of fine-structure splitting and biexciton binding in $In_xGa_{1-x}As$ quantum dots by annealing

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The distribution of the fine-structure splitting $\hbar\delta_1$ and of the biexciton binding energy $\hbar\delta_B$ are measured in a series of annealed InAs quantum dots. We find a decrease of $\hbar\delta_1$ from 96 μeV to 6 μeV with increasing annealing temperature, indicating a symmetrizing of the in-plane confinement potential. The biexciton binding energy shows only a weak dependence on the confinement energy, which we attribute to a compensation between decreasing confinement and decreasing separation of electron and hole.

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In semiconductor quantum dots (QD's), the energetically lowest lying exciton states have the longest coherence times as compared to higher states, and are therefore of interest for application as sources of entangled photons,[1,2] in quantum cryptography[3] and quantum information processing.[4] The coherence time in $In_xGa_{1-x}As$ QD's can be several hundred picoseconds, close to the population lifetime limit.[5–7] Neglecting the exchange interaction, the lowest exciton level in $In_xGa_{1-x}As$ QD's is fourfold spin degenerate, with two optically active states. By short-range exchange interaction, the degeneracy between the bright and the dark exciton states is lifted, with the dark state several hundred μeV below the bright one.[8] The degeneracy between the two bright states is lifted by the long-range exchange interaction if the QD shape does not have a cylindrical in-plane symmetry. The magnitude of the splitting of these states (fine-structure splitting) and the energy renormalization of the two-exciton state (biexciton binding energy) relative to twice the single exciton energy are important parameters to design photon cascades for single-photon sources,[2,9,10] and quantum algorithms which involve the two-exciton state.[11]

We report here the measurement of fine-structure splitting and biexciton binding energy in $In_xGa_{1-x}As$ QD's, and the control of these properties by annealing. The investigated samples were grown by molecular beam epitaxy on a semi-insulating GaAs(100) substrate. The self-assembled QD's were prepared in the following way: Deposition of a nominal coverage of 2.1 monolayers InAs at a substrate temperature of 515 °C resulted in InAs islands with a density of $(2-3)\times10^{10}\,cm^{-2}$. The islands were overgrown with 8 nm GaAs at a reduced substrate temperature of 505 °C. Ten QD layers, spaced by 100 nm GaAs, were embedded in AlAs/GaAs short-period superlattices. After the growth, the QD's were exposed to a rapid thermal annealing of 30 s duration at temperatures ranging from 800 °C to 960 °C. The thermally activated In diffusion influences mainly the In profile in growth direction, which is the smallest dimension of the rather flat quantum dots. The resulting reduction in the vertical confinement leads also to an increased in-plane extension of the excitonic wave function.[12] In this way, the QD ground-state exciton transition energy at low temperatures was tuned from 1.05 eV to 1.4 eV as can be seen in the low-temperature photoluminescence spectra shown in Fig. 1.[13] The confinement energy of the QD exciton ground state to the wetting layer was reduced in this series from 332 to 69 meV. In order to avoid multiple reflections in the time-resolved experiments, the sample surfaces were antireflection coated.

The coherent dynamics of the exciton polarization was measured by transient four-wave mixing (FWM). Two laser pulses of 100 fs duration resonant to the QD ground-state transition were sent in the directions $\mathbf{k}_1$ and $\mathbf{k}_2$ close to normal incidence onto the planar samples with a relative delay time τ, positive for pulse $\mathbf{k}_1$ leading. The FWM signal was selected directionally at $2\mathbf{k}_2-\mathbf{k}_1$, and was additionally discriminated by a frequency selection scheme,[14] detecting the

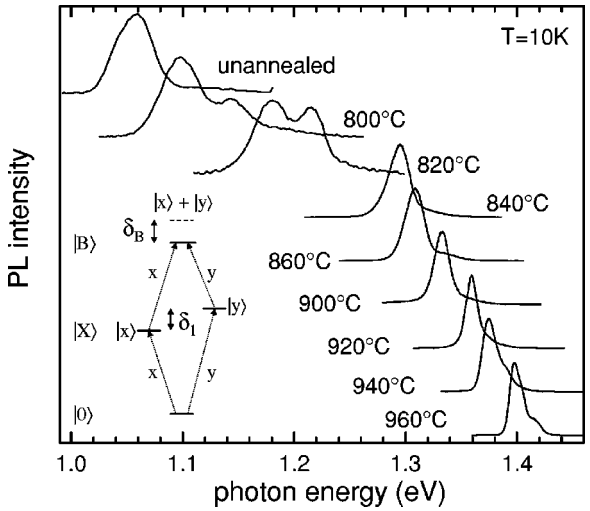

FIG. 1. Nonresonantly excited PL spectra of the investigated QD samples at low temperature (10 K). The nominal annealing temperature is given for each spectrum. Spectra are vertically displaced for clarity. A sketch of the exciton levels and transitions in the QD relevant for FWM resonant to the exciton ground state is also given, showing the QD ground state $|0\rangle$, the single exciton states $|x\rangle$, $|y\rangle$ split by δ_1, and the biexciton state $|B\rangle$ bound by the δ_B.

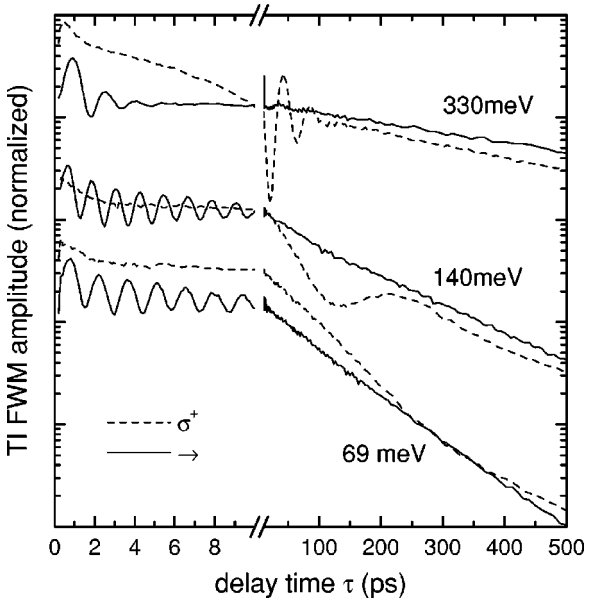

FIG. 2. Time-integrated FWM amplitude versus delay time τ at $T=5$ K for cocircular (dashed lines, σ^+) and colinear (solid lines, $\rightarrow$) excitation and detection polarization. Data for three different annealing temperatures (none, 860 °C, 960 °C) with the indicated confinement energies are shown.

time-resolved FWM field amplitude. In this way we detected FWM intensities down to 15 orders of magnitude below the intensity of the transmitted beams. The excitation intensities were adjusted to the third-order regime of the nonlinear response, and were in the order of 1 μJ/cm^2 per pulse. The samples were held at $T=5$ K in a helium cold-finger cryostat.

The FWM signal of the inhomogeneously broadened QD ensemble is a photon echo in real time,[5] with a time duration determined by the inhomogeneous broadening of the resonantly excited transitions, and thus similar to the exciting pulse duration. The dynamics of the microscopic polarization is probed in the delay-time dependent, time-integrated photon-echo amplitude, which is shown in Fig. 2 for different excitation polarization configurations as indicated. In the vicinity of zero delay, nonresonant FWM of the GaAs substrate is dominating the signal, so that the resonant FWM of the QD ground state is observable only for $\tau > 0.3$ ps. This transition consists of two opposite circularly polarized parts, whose degeneracy is lifted by the breaking of the cylindrical symmetry of the QD shape, resulting in two orthogonal linearly polarized transitions (see sketch in Fig. 1). The splitting energy of the two states $\hbar\delta_1$ is typically in the 100 μeV range.[8,15,16] In the FWM, transitions to the two-exciton states (biexciton) are also active. The biexciton is, like the QD ground state, a spin-singlet state, but with valence- and conduction-band states fully occupied. Therefore, each of the fine-structure exciton states has a polarized transition to the biexciton state. The energy of the biexciton is lower than the sum of the two-exciton energies, by the biexciton binding energy $\hbar\delta_B$ of several meV. By controlling the excitation polarization, we can thus select the transitions that contribute to the FWM.

Before analyzing the beat structures in Fig. 2, we note that the fast polarization decay during the first few picoseconds is due to dephasing of phonon-assisted transitions,[5,17,18] which are relevant since the strongly localized excitons in the QD's create a significant local lattice distortion. The strength of these transitions in the investigated series of $In_xGa_{1-x}As$ QD's is found to increase with the confinement energy and the lattice temperature.

For circularly polarized excitation at $t=0$, the excited exciton state is[19] $|\Psi(0)\rangle = |\sigma^+\rangle$, a coherent superposition of the linearly polarized states ($\sqrt{2}|\sigma^\pm\rangle = |x\rangle \pm i|y\rangle$). The exciton state is evolving in time due to the splitting energy $\hbar\delta_1$ and the average transition frequency ω_0:

$$e^{i\omega_0 t}|\Psi(t)\rangle = \frac{1}{\sqrt{2}}(e^{-i\delta_1 t/2}|x\rangle + ie^{+i\delta_1 t/2}|y\rangle)$$
$$= \cos(\delta_1 t/2)|\sigma^+\rangle + i\sin(\delta_1 t/2)|\sigma^-\rangle. \quad (1)$$

For small delay times ($\delta_1\tau \ll 1$), the exciton is in the $|\sigma^+\rangle$ state, and the second pulse, being cocircularly polarized to the first one, cannot excite the biexciton state due to the selection rules. Accordingly, no biexcitonic contribution to the FWM is present. For larger delay times, the exciton has an admixture of $|\sigma^-\rangle$, and biexcitonic FWM is created. However, the photon-echo formation of the biexcitonic contribution is compromised by the inhomogeneous broadening of δ_B,[20] which limits the biexcitonic photon echo to $\tau < 5-20$ ps in the investigated samples, always shorter than the time scale of the fine-structure beat. The FWM creating the photon echo is thus only due to the Pauli blocking nonlinearity of the $|0\rangle$-$|\sigma^+\rangle$ transition, giving rise to a circular polarized FWM amplitude $P^{(3)}$ proportional to the $|\sigma^+\rangle$ state amplitude at the arrival time $t=\tau$ of $\mathbf{k}_2$. This third-order polarization is also evolving with time as given by Eq. (1), and its circularly polarized amplitude is detected at the time of the photon echo $t=2\tau$, i.e., $P^{(3)} \propto \cos^2(\delta_1\tau/2) \propto 1 + \cos(\delta_1\tau)$.

The corresponding beats are observed in the FWM dynamics (see Fig. 2 top), with a period of about 50 ps. The strong damping versus delay time is due to an inhomogeneous distribution ρ of the fine-structure splitting δ_1 within the ensemble, so that the FWM amplitude of the ensemble can be shown to be $P^{(3)}(\tau) \propto 1 + \int d\delta_1 \rho(\delta_1)\cos(\delta_1\tau)$. Assuming that ρ is Gaussian with average $\overline{\delta_1}$ and variance σ_1, one finds $P^{(3)}(\tau) \propto 1 + \cos(\overline{\delta_1}\tau)\exp(-\sigma_1^2\tau^2/2)$. To extract from the experimental data only the fine-structure beat, we divide the FWM amplitude for circular polarization configuration (σ^+) with the one for linear polarization ($\rightarrow$), which does not exhibit the fine-structure dynamics.[21] An example is given in the right part of Fig. 3. The measured beat amplitude in the experimental data is actually lower than expected from the model [Eq. (2) with $p_T=0$]. A significant part of the QD's therefore does not show a fine-structure beat. We attribute this part to charged QD's, in which only a single circularly polarized transition exists, and no second exciton can be excited in the electronic ground state due to Pauli blocking.[8]

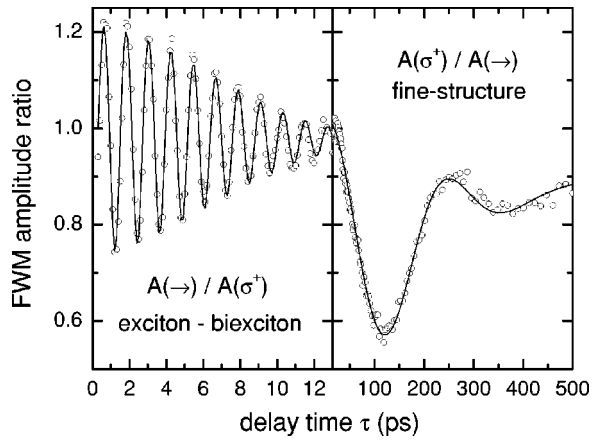

FIG. 3. Fit of the exciton-biexciton beats (left) and of the fine-structure beats (right), exemplified for the 860 °C sample of 140 meV confinement energy. The experimental ratio between the time-integrated FWM amplitudes for the polarization with and without beats is fitted with the expected dependence for a given distribution of biexciton binding energy or fine-structure splitting energy in the ensemble (see text).

With the probability p_T that a QD is occupied by a charge, the FWM dynamics is then described by

$$P^{(3)}(\tau) \propto 1 + (1 - p_T)\cos(\overline{\delta_1}\tau)\exp(-\sigma_1^2\tau^2/2). \qquad (2)$$

Fitting this formula to the experimental data, we find the average fine-structure splitting and its relative full width at half maximum ($\sqrt{8\ln 2}\sigma_1/\delta_1$) for each sample [see Fig. 4(a)]. The measured splitting decreases from 96 μeV for the sample without annealing, down to 6 μeV for the highest annealing temperature. The strong reduction of $\hbar\delta_1$ with annealing indicates that the In diffusion leads to a symmetrizing of the in-plane exciton confinement potential. We also find an increase of p_T with increasing annealing temperature from 0.2 to 0.8.[22]

Using a linearly polarized excitation along the [110] direction, no fine-structure related beats are observed. This shows that only one of the fine-structure split states is excited, and thus that in the investigated samples the $|x\rangle$, $|y\rangle$ states are aligned along the [110] and [1$\bar{1}$0] directions. On the other hand, the biexciton can be excited, since the $|x\rangle$-$|B\rangle$ transition has the same linear polarization as the $|0\rangle$-$|x\rangle$ transition. Therefore, the FWM consists of two components, one polarization of the $|0\rangle$-$|x\rangle$ transition at frequency $\omega_0 - \delta_1/2$, and the one of the $|x\rangle$-$|B\rangle$ transition at frequency $\omega_0 + \delta_1/2 - \delta_B$. These two polarizations are created out of phase by the pulse $\mathbf{k}_2$.[23] The FWM is measured in the photon echo, i.e., a time τ later, at which the superposition of the two polarizations can be shown to be $\propto 2 - \exp[i(\delta_1 + \delta_B)\tau]$. Here we assumed that the oscillator strength of the $|X\rangle$-$|B\rangle$ transition is equal to the one of the $|0\rangle$-$|X\rangle$ transition. We account for a Gaussian distribution ρ of the beat frequency $\delta_1 + \delta_B$ with mean value $\overline{\delta_B}$ and variance σ_B, as well as for the charged exciton probability p_T, and we find

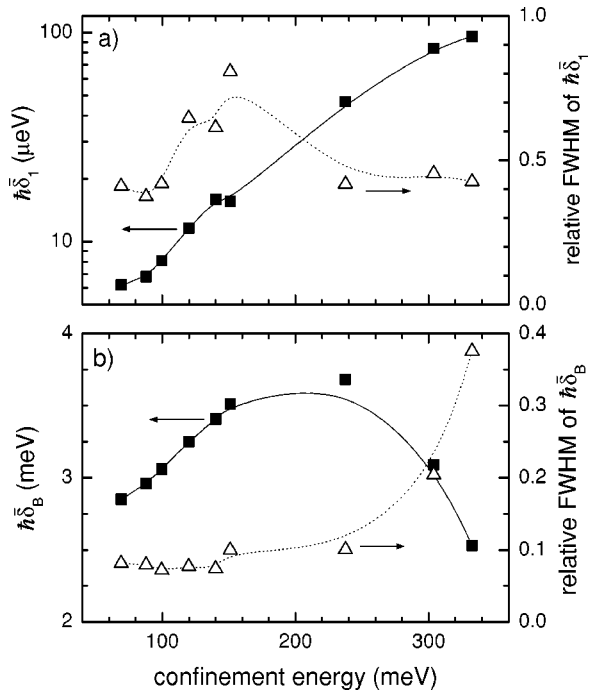

FIG. 4. Dependence on the annealing temperature expressed by the confinement energy of: (a) average fine-structure splitting (solid squares) and its distribution width (open triangles), (b): average biexciton binding energy (solid squares) and its distribution width (open triangles).

$$P^{(3)}(\tau) \propto \left| p_T + (1 - p_T)\left[2 + \exp\left(i\overline{\delta_B}\tau - \frac{\sigma_B^2\tau^2}{2} \right) \right] \right|. \qquad (3)$$

As in the case of the fine-structure related beats, but inverted, we divide the FWM signal for linear by the one for circular excitation to isolate the influence of the biexciton FWM. Then we fit the data with Eq. (3) (see left side of Fig. 3). The average biexciton binding energy $\hbar\overline{\delta_B}$ and its relative full width at half maximum ($\sqrt{8\ln 2}\sigma_B/\delta_B$) inferred from the fit are given in Fig. 4(b) for all investigated samples.[24] In the initial stage of the annealing ($E_c > 200$ meV), $\hbar\overline{\delta_B}$ is increasing with annealing temperature, and its inhomogeneous distribution is narrowing. For larger annealing temperatures, the inhomogeneous distribution stays constant at about 10%, suggesting that the In distribution in growth direction has reached a diffusion limited Gaussian shape. For such In distribution, the electron and hole wave functions are inversion symmetric, minimizing the Coulomb repulsion. In this regime of stable shape, $\hbar\overline{\delta_B}$ is decreasing with decreasing confinement energy, as it is expected from a theory assuming equal wave functions of electron and hole.[25] Conversely, the observed increase of $\overline{\delta_B}$ with decreasing confinement in the initial stage of the annealing is explained via the shape change of the electron-hole confinement in growth direction as follows. The In distribution of the as-grown QD's is asymmetric due to the directionality of the growth process. The consequent electron-hole charge separation[26] results in a repulsive exciton-exciton interaction, which diminishes the biexciton binding energy.[27,28] With annealing, the In distri-

bution tends to the Gaussian shape, reducing the repulsive interaction and thus increasing the biexciton binding energy.

In summary, we have measured the fine-structure splitting and the biexciton binding energy and their respective inhomogeneous distributions in a series of annealed InAs QD's. A strong reduction of the fine-structure splitting from around 100 μeV to below 10 μeV is found, showing the possibility to control this property by annealing. The biexciton binding energy, instead, is little affected by the annealing, varying between 2.5 and 3.7 meV. However, the annealing leads to a strong reduction of the inhomogeneous distribution of the biexciton binding energy, which is attributed to the symmetrization of the carrier confinement in the growth direction.

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