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Biexcitons in semiconductor quantum wires

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We report on spectrally resolved four-wave mixing experiments on $In_xGa_{1-x}As/GaAs$ quantum wires for a wide range of lateral sizes. Due to the polarization dependence of the four-wave mixing signal, beats in the decay of the signal and an additional emission line in the four-wave mixing spectrum can be clearly attributed to biexcitons. We find that the biexciton binding energy depends on both the vertical and lateral dimensions of the wires. For quantum wires with a large vertical confinement we observe an enhancement of the binding energy of about 40% as compared to a two-dimensional reference sample whereas the biexciton binding energy is found to be wire width independent in wires with shallow vertical confinement. [S0163-1829(98)52328-4]

Biexcitonic features in low-dimensional semiconductor structures have been investigated experimentally and theoretically in a number of works in recent years.[1] In two-dimensional (2D) systems, biexcitons first have been observed in 1982 by Miller *et al.*[2] Since then their existence has been confirmed by photoluminescence studies[3] and, more recently, in nonlinear spectroscopy, e.g., in four-wave mixing (FWM) experiments.[4–7]

The FWM technique is well suited to study biexcitons. Previous studies on 2D structures have shown characteristic beats between excitonic and biexcitonic states in the time-integrated FWM signal.[5,6] The heavy-hole (hh) as well as the light-hole (lh) biexciton have been observed in spectrally resolved (SR) FWM experiments.[4,7] Excitonic and biexcitonic contributions to the FWM signal can be separated by a proper choice of polarizations of the exciting beams.[8,9]

In 2D structures the biexciton binding energy was found to be greatly enhanced compared to bulk semiconductors. In $GaAs/Al_xGa_{1-x}As$ quantum wells (QW's) biexciton binding energies as high as 3.5 meV have been reported[10] that have to be compared to a value of 0.13 meV observed in bulk GaAs.[11] This enhancement has been attributed to confinement effects, but lately the importance of polariton effects has also been pointed out.[12] Recently, Birkedal *et al.* systematically investigated the QW width dependence of the biexciton binding energy and found that the ratio of the biexciton and exciton binding energies is independent of the well width as long as the width of the QW is smaller than the exciton and biexciton diameters.[7]

In zero-dimensional (0D) quantum dot structures biexcitons have been reported in a number of material systems.[13–15] The binding energy was found to be enhanced by more than an order of magnitude over the corresponding bulk values and increased with decreasing dot diameter in agreement with theoretical predictions.

To the best of our knowledge, biexcitons in one-dimensional (1D) structures have not been observed experimentally to this point. However, the existence of biexcitons in 1D quantum wire structures has been addressed in a few theoretical works. In an early study biexciton binding energies were calculated variationally for cylindrical $GaAs/Al_xGa_{1-x}As$ quantum wires (QWR's).[16] More recently, Madarasz and co-workers also used variational calculations to determine biexciton binding energies in rectangular $GaAs/Al_xGa_{1-x}As$ QWR's.[17] It has also been suggested that due to strong polariton effects bound biexciton states should not exist at all in ideal 1D structures.[12] However, these effects are expected to play a minor role in real QWR's due to exciton localization.

In this Rapid Communication we present the results of polarization dependent two-beam FWM experiments that show clear evidence for the existence of biexcitons in free-standing $In_xGa_{1-x}As/GaAs$ quantum wires with lateral sizes between 24 nm and 85 nm. In previous studies it has been shown that the quasi-1D confinement changes the excitonic properties in this type of QWR's. For lateral sizes comparable to the excitonic diameter an increase of the hh exciton binding energy (E_b^X) was observed.[18] It was also found that the lateral confinement strongly enhances the exciton-exciton scattering in these structures.[19] Here we show that the presence of biexcitons causes pronounced beats in the decay of the FWM signal for collinearly polarized incident fields and that the hh biexciton can be clearly resolved in SR-FWM when the incident fields have perpendicular polarizations. We find that the binding energy of the hh biexciton (E_b^{biX}) in the QWR's does not only depend on the lateral size but also on the vertical confinement. In QWR's with a small vertical confinement potential the biexciton binding energy does not vary significantly with the lateral size of the QWR's. However, for larger vertical confinement we observe an increase of E_b^{biX} with decreasing wire width.

We have investigated two sets of $In_xGa_{1-x}As/GaAs$ QWR samples. The first set of quantum wires (sample A) was fabricated from a multiple quantum well structure consisting of 20 quantum wells. The quantum wells had an In content of $x=0.135$ and a width of 3 nm and they were separated by 60 nm wide GaAs barriers. The second set (sample B) was based on a 5 nm wide single quantum well with an In content of $x=0.115$ embedded between 50 nm wide GaAs barriers. The vertical confinement in this set of samples is about 25 meV larger than in sample A due to the larger quantum well width. A detailed description of the fabrication of the wires has been given elsewhere.[18] The width of the quantum wires was obtained from high-resolution scanning electron micrographs. For comparison, each set of

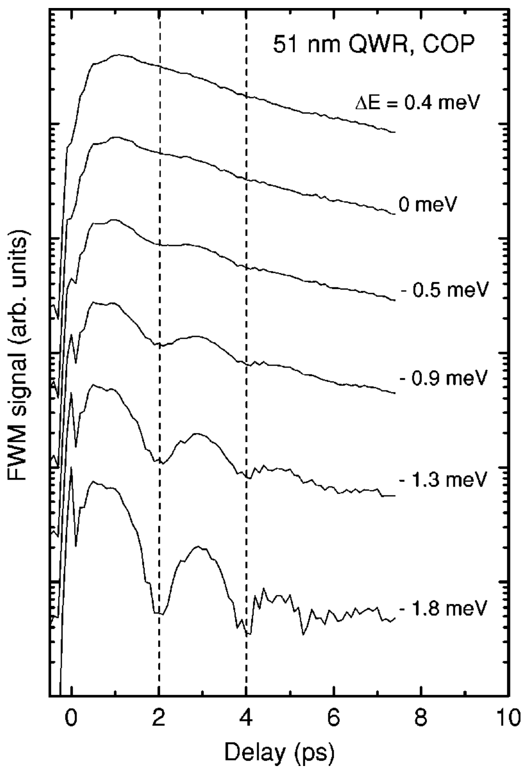

FIG. 1. FWM signal from a 51 nm wide, 3 nm high $In_{0.135}Ga_{0.865}As/GaAs$ quantum wire as a function of delay time for various detunings and collinearly polarized incident fields. $\Delta E = 0$ corresponds to the center of the hh exciton absorption line. For clarity the curves are shifted with respect to each other. The vertical lines indicate the minima in the oscillations.

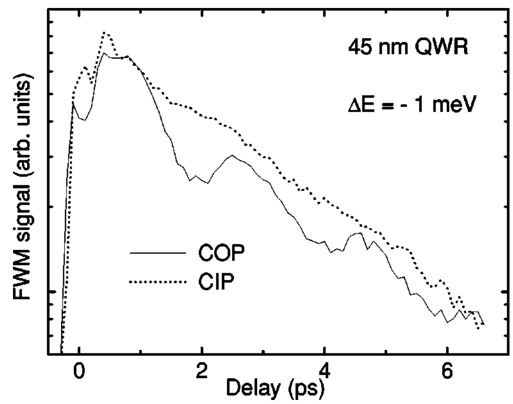

FIG. 2. FWM signal from a 45 nm wide, 3 nm high QWR as a function of delay time for a detuning of $\Delta E = -1$ meV for collinearly polarized (full line) and cocircularly polarized (dotted line) fields.

samples also contained a 2D reference sample. For the experiments the samples were held in a temperature controlled He gasflow cryostat at a temperature of 5 K.

The experiments were performed using spectrally resolved, degenerate FWM in the two pulse self-diffracting transmission geometry. In this configuration two pulses of equal intensity with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ are focused onto the same spot on the sample with a variable delay τ and the FWM signal is detected in the direction ($2\mathbf{k}_2$-$\mathbf{k}_1$) as a function of photon energy E and delay τ. The linear polarization of the exciting beams could be altered by inserting a $\lambda/2$ plate and cocircular polarization was achieved by inserting a $\lambda/4$ plate in the path of the two collinearly polarized beams. As an excitation source we used a fs Ti:Sapphire laser, pumped by an Ar ion laser. The laser pulses had a length of 75 fs and a spectral width of 30 meV (FWHM). The photon energy of the exciting light was tuned well below the hh exciton absorption maximum to avoid the excitation of higher states. The carrier density is estimated to be lower than 1×10^{10} cm^{-2} in the 2D reference sample. The FWM signal was spectrally resolved by a 25 cm monochromator and detected by a liquid nitrogen cooled Si charge coupled devices camera giving a resolution of 0.1 meV.

In Fig. 1 we show the FWM signal excited by collinearly polarized (COP) pulses from a 51 nm wide QWR of sample A as a function of the delay time at different detection energies. At the center of the hh exciton absorption line ($\Delta E = 0$) the signal decays mono-exponentially with a decay constant of 4 ps. On the low-energy side ($\Delta E < 0$), however, pronounced beats are observed with a period of 2 ps corresponding to an energy splitting of the involved transitions of 2.1 meV. These oscillations were observed for all QWR's of sample A as well as for the corresponding 2D reference and their frequency did not vary significantly with the lateral width of the wires. It should be noted that the beats start with a minimum at $\tau = 0$. This is in contrast to excitonic quantum beats such as hh-lh beats that start with a maximum for COP excitation.[20] However, a start of the oscillations with a minimum has been suggested to be typical of biexcitonic beats.[6]

To confirm that the observed oscillations are due to the presence of biexcitons we also performed FWM experiments with cocircular polarization (CIP) of the exciting pulses. In this configuration the creation of biexcitons is strongly suppressed by selection rules because the biexciton as a singlet state can only be created by an optical excitation containing both σ_+ and σ_- components.[9] In Fig. 2 we compare the decay of the FWM signal of a 45 nm wide QWR for collinear and cocircular excitation at a detuning of $\Delta E = -1$ meV. It is evident that no beats are observed for cocircular excitation, demonstrating that the oscillations are indeed of biexcitonic origin.

An example for the spectral shape of the FWM signal obtained from the QWR's of sample A is given in Fig. 3(a) for a 29 nm wide QWR. The spectra were taken at a delay of 1 ps. For collinear polarization the FWM spectrum peaks at the center of the absorption line. However, the line is asymmetric and shows a shoulder on the low-energy side of the spectrum. For CIP excitation, on the other hand, the spectrum of the FWM signal is almost symmetric around the center of the absorption line and it does not display any additional features. This supports the biexcitonic origin of the low-energy shoulder that is observed in the COP case.

We also performed spectrally resolved FWM with cross-polarized (CRP) exciting fields, i.e., the polarizations of the incident beams were linear but perpendicular to each other. In this configuration the FWM spectra of the QWR samples and the 2D reference consist of two distinct lines, as shown by the full line in Fig. 3(a). For CRP excitation the excitonic screening that was found to be the dominant contribution to the excitonic FWM signal vanishes and thus the FWM signal is dominated by biexcitonic contributions.[8] We therefore assign the low-energy peak in the CRP spectrum, that is cen-

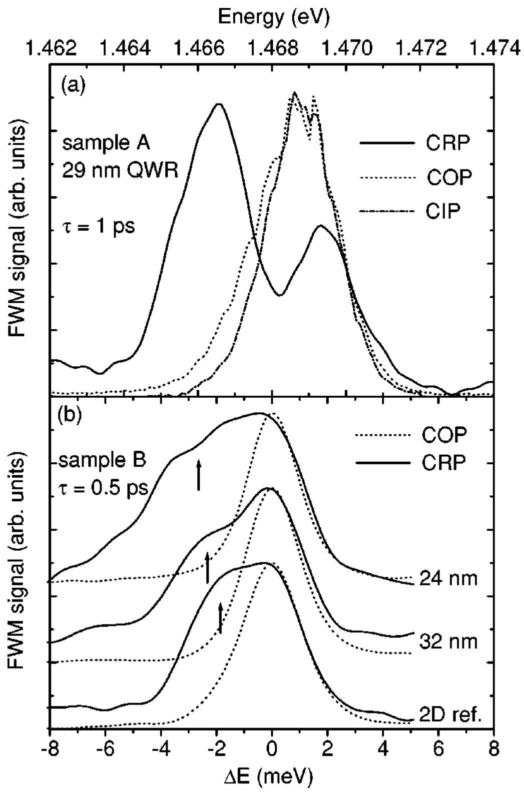

FIG. 3. Spectrally resolved FWM signals: (a) from a 29 nm wide, 3 nm high QWR at a delay of 1 ps for crosslinear (full line), collinear (dotted line), and cocircular (dash-dotted line) polarizations, (b) from 5 nm high QWR's with different lateral sizes and the corresponding 2D reference at a delay of 0.5 ps for crosslinear (full line) and collinear (dotted line) polarizations. In (b) the energy ΔE is taken with respect to the center of the exciton absorption line. The curves are shifted for clarity and the arrows indicate the spectral position of the biexciton.

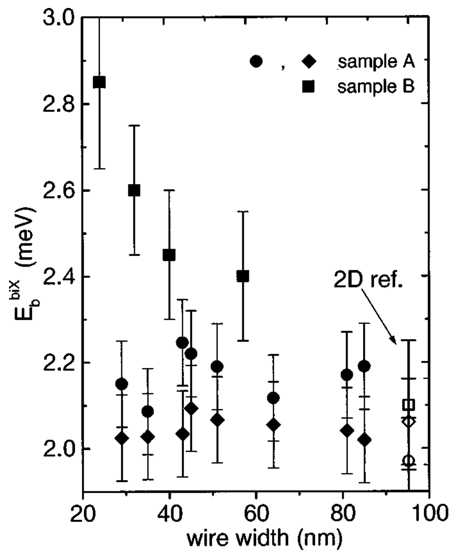

FIG. 4. Heavy-hole biexciton binding energy as a function of wire width. Dots and diamonds show the biexciton binding energy for sample A obtained from the spectra and the biexciton beats, respectively. Squares show the values for sample B. The open symbols correspond to the 2D reference samples.

tered 2.1 meV below the excitonic peak in the CIP spectrum, to the biexciton. The energy separation of 2.1 meV agrees very well with the frequency of the biexciton beats. For wires in this set the second emission line in the CRP spectrum (at $E \approx 1.469$ eV) peaks at a higher energy than the emission in the CIP configuration and is therefore likely not due to excitonic contributions. Previously it has been assigned to unbound two-exciton states.[21]

Figure 3(b) shows the FWM spectra of different QWR's of sample B and the corresponding 2D reference for crosslinear and collinear polarizations at a delay of 500 fs. The COP spectra are again dominated by the excitonic contribution, resulting in an almost symmetrical line shape. In the CRP spectra a pronounced shoulder can be observed on the low-energy side of the exciton line. The energy separation of this shoulder from the exciton line increases significantly when the lateral size of the QWR's is reduced. However, excitonic and biexcitonic contributions cannot be resolved as separate peaks due to a smaller relative intensity of the biexcitonic contribution.[22]

Using a line-shape analysis we obtained the biexciton binding energy in the different wire structures from the energy difference between the low-energy peak of the CRP spectrum (due to biexcitons) and the peak of the CIP spectrum (due to excitons). For sample A we also calculated the biexciton binding energy from the period of the biexciton beats in the decay of the FWM signal. For this sample both methods give values for the biexciton binding energy of $E_b^{biX} \approx 2.1$ meV, independent of the wire width.[23] For sample B, on the other hand, we find that the biexciton binding energy increases from ~ 2.1 meV for the 2D reference sample to ~ 2.9 meV for a 24 nm wide QWR sample. The results for E_b^{biX} for the different structures are summarized in Fig. 4.[24]

The biexciton binding energy is determined by the complicated balance of attractive and repulsive interactions between the carriers forming the exciton complex. Both the electron-electron and the hole-hole interactions as well as the electron-hole interactions are enhanced by confinement. In case of strong confinement the attractive interactions dominate resulting in a net increase of the biexciton binding energy. This increase is observed in Fig. 4 for the wires of sample B that are fabricated from a quantum well with a comparatively deep quantum well confinement.

In order to explain the wire width independence of the biexciton binding energy in sample A we propose the following model: The wires of sample A are fabricated from quantum wells in which the electronic states are only weakly confined. In this case the penetration of the carrier wave functions into the surrounding barriers has to be taken into account. For the present 3 nm wide $In_{0.135}Ga_{0.865}As/GaAs$ quantum well we find that the hole wave function is still well confined, while the electron wave function already significantly penetrates into the GaAs barriers. This leads to a mismatch of the electron and hole wave functions in the Coulomb interaction matrix elements. Therefore the repulsive interaction matrix elements in the biexciton increase more strongly with decreasing wire width than the attractive ones. In conjunction with the rearrangement of the carriers in the biexciton this may lead to the observed almost constant binding energy.

In conclusion, we have used spectrally resolved fs four-wave mixing to study two sets of $In_xGa_{1-x}As$/GaAs quantum wires with different lateral and vertical sizes. In the decay of the FWM signal produced by collinearly polarized incident fields we observed strong beats. For perpendicularly polarized incident fields an additional feature in the spectrum of the FWM signal could be resolved below the heavy-hole exciton signal. Both effects were interpreted as biexcitonic contributions to the FWM signal. For samples with a large vertical confinement the biexciton binding energy increases from ∼2.1 meV for the 2D reference sample to up to ∼2.9 meV in the narrowest quantum wires. However, the biexciton binding energy in QWR's fabricated from a very narrow quantum well does not show a significant wire width dependence. These results show the strong influence of the quantum wire confinement on the biexciton binding energy.

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[22] All samples in this set showed a very rapid decay of the FWM signal with a decay time shorter than 2 ps. Therefore, no oscillations in the decay trace, which are expected to have a comparable period, could be resolved.
[23] Generally the values of E_b^{biX} for the QWR's determined from the spectra are seen to be slightly (by about 0.1 meV) higher than the values from the beat period. However, this difference that is due to a disorder-renormalization of the beat period has been predicted theoretically (Ref. 21).
[24] The values reported here for the biexciton binding energies in QWR's are significantly smaller than those calculated in Ref. 17 for rectangular QWR's. However, it is difficult to compare our results directly to the available calculations because all theoretical investigations of biexcitons in QWR's used infinite barriers in their calculations. Furthermore, the calculations of Madarasz *et al.* are based on the GaAs/$Al_xGa_{1-x}As$ material system and they emphasize wire widths that are small compared to the ones used in this study.