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Biexcitonic binding energies in the transition regime from three- to two-dimensional semiconductors

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We study the dependence of the binding energies of excitonic molecules on the confinement in semiconductor quantum wells. A set of symmetrically strained (GaIn)As/Ga(PAs) quantum wells with different well depths and equal well widths is investigated with transient degenerate four-wave mixing. The ratio of biexcitonic to excitonic binding energy increases with stronger confinement. This experimental result is discussed in detail in the framework of recent theoretical predictions and experimental results. [S0163-1829(97)51440-8]

The optical properties of direct-gap semiconductors at the fundamental absorption edge are strongly dominated by Coulomb interaction between carriers. The most important consequence is the formation of bound electron-hole pairs, i.e., excitons, which dominate the optical properties at low to moderate excitation densities and at low temperatures. At higher densities, carrier-carrier correlations of higher order have to be taken into account. In analogy to the binding of hydrogen atoms to molecules, excitons form excitonic molecules, so-called biexcitons. A variety of groups have investigated the influence of dimensionality on biexcitons experimentally[1–3] as well as theoretically.[3–6] However, the dependence of biexcitonic binding energies on dimension is still controversially discussed. While the ratio of biexcitonic (E_{BX}) to excitonic (E_X) binding energies, E_{BX}/E_X, in the transition from three- (3D) to two-dimensional (2D) semiconductors is found to be rather independent of confinement in Ref. 3, it is expected to depend on the dimension in Refs. 4, 5, and 6. These discrepancies are due to the fact that the theoretical description of quasi-2D biexcitons only becomes possible on the basis of several simplifying approximations for this four-body problem of two electrons and two holes. The Schrödinger equation is solved either by means of variational methods,[4,5,7] Monte Carlo simulations,[6] or analytically with further simplifications.[3,8] The dimension of the electronic system in the respective semiconductor is treated either in the ideal 2D and 3D limits,[4,5,7] with a fractional dimension approach,[3,8] or by considering potential wells for electrons and holes.[4,6] However, the different theoretical approaches lead to different predictions for the dependence of the biexciton binding energy on confinement. Therefore, in this communication, we report a systematic experimental investigation of the dependence of biexcitonic binding energies on confinement.

Variation of the confinement, i.e., the transition from 3D to 2D semiconductors, can be approached either by reducing the width of a quantum well (QW) or by increasing its depth. Variation of QW width, e.g., has the disadvantage that the carrier wave functions penetrate deeper into the barriers with decreasing well width. Therefore, confinement is not continously increased for decreasing well width, but is even reduced again for very thin QW's. In the limit of zero well width, bulk properties (of the barrier material) again dominate.[9] In contrast, increasing the well *depth* leads to stronger confinement and *reduced* penetration of wave functions into the barriers.

Accordingly, we investigate the transition regime from quasi-3D to quasi-2D in strain compensated (GaIn)As/Ga(PAs) QW's where the indium content in the wells and the phosphorus content in the barriers are adjusted so that the well depth is varied without changing the well width. The samples are grown by metal organic vapor phase epitaxy (MOVPE) and consist of 50 periods of a (GaIn)As/GaAs/Ga(PAs)/GaAs layer sequence grown on an (AlGa)As/GaAs buffer layer. The QW widths are about 8 nm. Individual layer thicknesses, indium and phosporous contents, are determined by high-resolution x-ray diffraction (HR XRD) in combination with dynamical XRD simulations. Details of the sample structure, the growth process, and the determination of the sample parameters are given in Ref. 10.

We performed quantum beat spectroscopy on the basis of transient degenerate four-wave mixing (DFWM) experiments in order to evaluate the biexcitonic binding energies. This is the most accurate method for the determination of the relevant binding energies. It was shown that even in undoped QW's charged excitons, so called trions, accidentally may be interpreted as biexcitons in cw photoluminescence experiments.[11] Additionally, biexcitonic transitions in linear spectroscopy are often obscured by inhomogeneous broadening due to the small molecular formation energies. Line shape analysis is then the only, though rather indirect way to determine the biexciton binding energy.[12,13] Quantum beat spectroscopy has the great advantage of being particularly sensitive to small energy differences while being insensitive to inhomogeneous broadening of the respective transitions.[14–16] Consequently, degenerate four-wave mixing (DFWM) turns out to be a versatile tool for studying the contributions of biexcitons to the higher-order optical nonlinearities at the fundamental band gap.[14,15,17]

The samples were kept at a temperature of 8 K and excited by 100 fs pulses from a Kerr-lens-modelocked Ti:sapphire laser, energetically tuned slightly below the respective 1s heavy-hole (hh)–exciton resonance. The experiments were performed in the standard two-pulse DFWM geometry. The two pulses with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$, respectively, hit the samples with a time delay of τ between them. The DFWM signal in direction $2\mathbf{k}_2-\mathbf{k}_1$ was detected either by a slow photodiode or, spectrally resolved, by an optical multi-

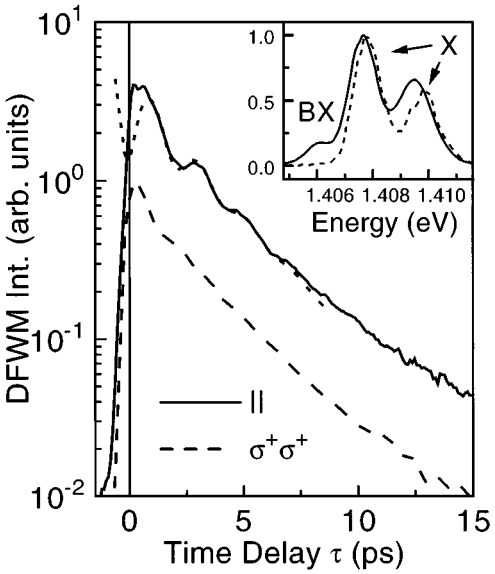

FIG. 1. Time-integrated DFWM transients for linear (solid line) and circular (dashed line) copolarized excitation. A damped cosine function visualizes the beat minimum at $\tau=0$ (dotted line). The inset shows the respective normalized spectra of the diffracted signals for $\tau=2$ ps.

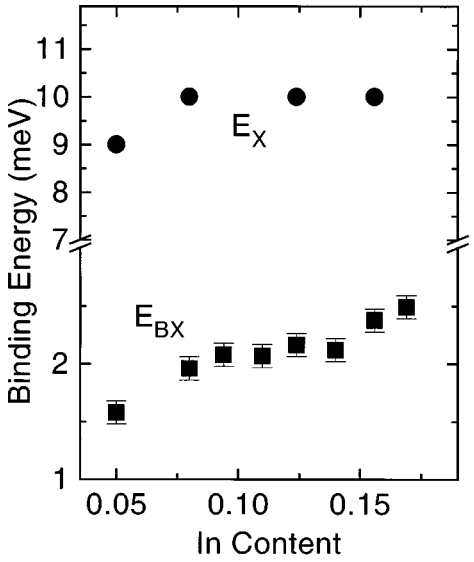

FIG. 2. Experimentally determined binding energies of excitons (circles, Ref. 25) and biexcitons (squares) versus indium content. Note the different scales. The absolute accuracy of E_X is 1.5 meV (Ref. 25).

channel analyzer at the exit of a spectrometer with a resolution of about 1 meV. We performed our polarization-dependent measurements either with circularly polarized laser beams of the same handedness or with linearly polarized laser beams with parallel or perpendicular polarization using $\lambda/4$ and/or $\lambda/2$ retardation plates, respectively. The excited carrier densities in all the measurements were about 10^{10} cm^{-2}.

Figure 1 compares typical transients of a DFWM experiment on a sample with $x_{\mathrm{In}}=0.11$ for linearly copolarized (solid line) and circularly copolarized (dashed line) excitations, respectively. A pronounced periodical beating is seen for the linear polarization. From the distance of maxima and minima we obtain a beat period of 2.0 ± 0.1 ps, corresponding to an energetic splitting of 2.07 ± 0.1 meV.

First, we discard the possibility of the occurrence of quantum beats: Beating between excitonic transitions in growth islands differing by about one monolayer is excluded by a calculation of exciton energies in wells with thicknesses differing by single monolayers. In all samples, the measured energy splitting is larger than the calculated energy difference of excitonic transitions in two wells differing by one monolayer. But in all samples, with the exception of the $x_{\mathrm{In}}=0.05$ sample, the experimental values are smaller than calculated for wells differing by two monolayers. Additionally, the calculated energy splittings depend more on indium content in comparison with the energies corresponding to the beating frequencies.

In the following, we prove the biexcitonic origin of the investigated beats. The polarization dependence of the DFWM directly indicates that the observed beating results from a polarization interference of excitonic and biexcitonic transitions: Bound biexcitonic complexes consist of two excitons with opposite spins and are therefore not observed when photons with the same circular polarization are used for excitation. Figure 1 shows that the beating is absent for the $\sigma^+\sigma^+$ excitation (dashed line). This change with polarization manifests itself in a consistent way in the spectrally resolved signal (inset of Fig. 1). The spectrum of the diffracted signal is dominated by the 1s hh exciton (X). The exciton resonance appears as a double peak structure (peaks at 1.408 and 1.410 eV), because of the strong reabsorption of the signal during its propagation through the thick sample.[18–22]

A third, less pronounced peak (BX), energetically 2 meV below the X line, appears for linear polarization and disappears for $\sigma^+\sigma^+$ excitation. Tuning the time delay τ between the two incident pulses reveals an intensity modulation of the BX peak and the low energetic X peak with the same period as observed in the beating of the spectrally integrated transients.[23] Biexcitonic beating in time-integrated DFWM in disordered semiconductor QW's was first reported by T. F. Albrecht and co-workers.[15,24] Consistent with their findings, our transients start at $\tau=0$ with a beat minimum for parallel linear polarization (Fig. 1) and with a maximum for perpendicular linear polarization (not shown). We can therefore clearly attribute the BX peak to a transition from the bound biexcitonic state to the one exciton state and the energy corresponding to the beat frequency to the biexcitonic binding energy E_{BX}.

Now, we discuss the dependence of the measured biexciton binding energies on confinement in the framework of various theoretical approaches. Figure 2 shows the experimentally determined binding energies E_{BX} (squares) as a function of indium content x_{In}. Starting with 1.6 meV for $x_{\mathrm{In}}=0.05$, E_{BX} increases almost linearly with x_{In} up to 2.5 meV for $x_{\mathrm{In}}=0.17$. For comparison, the excitonic binding energies E_X, as determined from magneto-optical studies by Volk and co-workers,[25] are also shown for some of the same samples in Fig. 2 (circles). The exciton binding energies increase slightly with increasing In content from 9 meV for

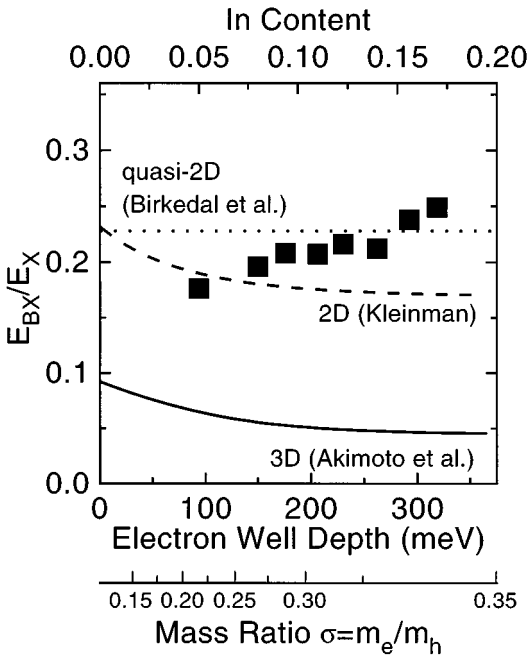

FIG. 3. Experimentally determined binding energy ratio E_{BX}/E_X (squares) as a function of indium content (top axis) and electron well depth (bottom axis). The absolute error bar is about ± 0.045 for all samples and is mainly due to the uncertainty in the determination of E_X. The additional bottom axis shows the changes in the mass ratio $\sigma = m_e/m_h$ with indium content. The lines represent theoretical dependences on σ for the ideal 3D (solid line, Ref. 7), ideal 2D (dashed line, Ref. 4), and quasi-2D (dotted line, Ref. 3) case.

$x_{\mathrm{In}} = 0.05$, to 10 meV (± 1.5 meV) for higher In concentrations.[26] The saturation of exciton binding energies for higher indium contents as seen in Fig. 2 is reproduced, e.g., by model calculations with the fractional dimension approach[27] using the respective properties of the samples, especially the well depths.[16]

The ratio E_{BX}/E_X is depicted in Fig. 3 as a function of the In content of the QW's (squares). The absolute accuracy of this ratio is limited by the precision of E_X given in Ref. 25 and amounts to about 0.045. In contrast, the accuracy of the qualitative behavior of E_X is much higher, since it is strongly supported by other experimental, as well as theoretical, results[16] and therefore we also achieve a high accuracy for the trend of E_{BX}/E_X in Fig. 3. Note that an increase is observed with increasing In concentration, i.e., with increasing well depth.

This trend, i.e., an increasing E_{BX}/E_X with increasing confinement has been predicted, e.g., by Zhang and co-workers,[6] but is in disagreement with the simple model suggested by Birkedal and co-workers.[28]

Before continuing the discussion, it has to be pointed out that increasing carrier confinement leads to changes in the carrier effective masses: The degeneracy of the heavy-hole and light-hole (lh) valence bands in bulk semiconductors, e.g., is removed by different quantization energies in semiconductor QW's. The resulting in-plane dispersions are strongly nonparabolic. Moreover, in strained heterostructures the strain strongly modifies the hh-lh splitting. Therefore it is necessary to pay attention to these indirect effects of confinement for a careful comparison of biexcitonic energies with theoretical models.

The effective masses of electrons m_e and holes m_h were determined experimentally for some of our samples in Ref. 25. The electron mass was found to be constant, resulting from the cancellation of two effects: The changes of the (GaIn)As conduction band mass at the band edge with increasing In content is compensated by the increasing influence of the nonparabolicity of the conduction band due to increasing confinement energy. The heavy-hole mass decreases with increasing In content due to larger hh-lh splitting, reducing the hh-lh subband mixing. The hh-lh splitting is caused by strain as well as by confinement.[25] The interpolated dependence of the mass ratio σ on the In concentration is used for the additional horizontal axis at the bottom of Fig. 3 so that the predicted σ dependence of E_{BX}/E_X for the ideal 3D case[7] (solid line) and the ideal 2D case[4] (dashed line) can be included in Fig. 3.

We now compare our results with other experimental results and theoretical predictions. A first theoretical estimate of the effect of confinement including the σ dependence was given by Kleinman (dashed curve in Fig. 3). Our values of E_{BX}/E_X are larger than this theoretical prediction, but the trend that E_{BX}/E_X should increase from 3D (see solid line, according to Ref. 7) to 2D is in agreement with our observations. Obviously, the 2D limit given by Kleinman underestimates the effect of confinement on the biexcitonic binding energy as already pointed out by Birkedal and co-workers.[3] These authors introduce an idealized model that predicts independence of E_{BX}/E_X on confinement. Experimentally, they find a weak dependence of E_{BX}/E_X on confinement: with decreasing well width (i.e., increasing the confinement) first a slight increase of E_{BX}/E_X occurs which is consistent with our observations.[29] But for the smallest well width a small decrease is observed which might be due to the fact that in this approach the well width is altered to vary the confinement. Consequently, for small well widths enhanced penetration of the carrier wave functions into the barriers has to be considered. This explanation is supported by theoretical calculations of Zhang and co-workers, who considered the full effective-mass biexcitonic Hamiltonian with realistic potential wells for electrons and holes of varying width.[6] However, though predicting the right qualitative trends, the Monte Carlo simulations by Zhang and coworkers provide biexciton binding energies which are much higher than the values observed in experiments. They expect the binding energy of a biexciton consisting of two hh excitons in a $GaAs/Al_{0.3}Ga_{0.7}As$ QW to increase from 2.7 meV at 270 Å well width up to about 7.7 meV at 40 Å and then to decrease with well width to, e.g., 2.9 meV at 5 Å. This has to be compared with a maximum value of about 2.3 meV observed experimentally in an 80-Å-thick $GaAs/Al_{0.3}Ga_{0.7}As$ QW in Ref. 3.

In summary, we have studied the binding energy of excitonic molecules in the transition from three- to two-dimensional semiconductor structures by performing quantum beat spectroscopy on (GaIn)As/Ga(PAs) QW's with varying depths but constant well widths. We found the biexcitonic binding energy to increase considerably with stronger confinement. More specifically, our results clearly demon-

strate that the biexcitonic binding energy increases more rapidly than the excitonic binding energy when confinement is enhanced. This is in contrast to predictions given by recent idealized models. Accordingly, a satisfying agreement with experiments can only be expected from improved theoretical approaches to the problem of excitonic molecules in semiconductor nanostructures.

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[18] A similar conclusion was drawn in Ref. 19. In our case it is supported by several experimental findings: First, the linear absorption spectrum exhibits one single 1s hh excitonic peak which coincides with the spectral position *between* the two high energetic peaks in Fig. 1 (1.409 eV). Second, although for $\sigma^+\sigma^+$ excitation the DFWM spectrum clearly shows the two X peaks, we observe no beating in the time-integrated transients. Therefore, excitons from different growth islands or excitons bound to impurities are ruled out, since they have been shown to result in beatings (Refs. 20 and 21). Third, the two peaks show the same dependences on polarization of the laser fields, pulse intensities, and sample temperature. Finally, it has been shown earlier that propagation effects in thick samples may strongly modify the DFWM power spectrum of excitonic transitions (Ref. 22).

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[28] The fractional dimension approach used in Refs. 3 and 8 does not distinguish between changes in QW width or QW depth. It thus should be applicable to our case as well.

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