Coherent generation and interference of excitons and biexcitons in GaAs/$Al_xGa_{1-x}As$ quantum wells

K.-H. Pantke, D. Oberhauser,* V. G. Lyssenko,† and J. M. Hvam
Fysisk Institut, Odense Universitet, Campusvej 55, DK-5230 Odense M, Denmark

G. Weimann
Walter Schottky Institut, D-8046 Garching, Germany
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We report measurements of two-photon transitions to the biexciton state and exciton-biexciton transitions (M band) in GaAs/$Al_xGa_{1-x}As$ multiple quantum wells by spectrally resolving the self-diffraction in a four-wave-mixing experiment. Furthermore, nonlinear quantum beats between a coherently prepared population of excitons and biexcitons are observed. The analysis yields a binding energy of 1.8 meV for the biexciton in 116-Å quantum wells.

In quasi-two-dimensional quantum wells, theoretical calculations predict a significant enhancement of the binding energy of biexcitons even relative to the free-exciton binding energy.[1,2] A considerable effort has therefore been invested in the search for the biexciton contributions to the linear and nonlinear optical properties of GaAs/$Al_xGa_{1-x}As$ multiple quantum wells (MQW's).[3-8]

One of the means of identification has been the radiative recombination of biexcitons, leading to an emission band, often called the M band in bulk II-VI semiconductors. This band is redshifted by the biexciton binding energy relative to the lowest free-exciton resonance, which is the heavy-hole (hh) exciton in GaAs. There are, however, competing luminescence processes in the same spectral range, such as luminescence from bound excitons, excitons localized at interface islands, or excitons from different well widths, that make positive identification difficult. Therefore, firm evidence for biexcitons in MQW's is most likely to come from nonlinear optical spectroscopy in the region below the hh resonance,[3] and indeed there has been reported a contribution of biexcitons to the nonlinear four-wave-mixing (FWM) signal in GaAs/$Al_xGa_{1-x}As$ MQW's, albeit with poor resolution.[9] Several groups have reported observations of quantum beats in the FWM signal from the interference of (i) heavy-hole excitons and light-hole excitons,[10-12] (ii) free and bound excitons,[13] and (iii) excitons in different confinements.[14]

In the present work, we report clear and well-resolved evidence for the existence of biexcitons in GaAs/$Al_xGa_{1-x}As$ MQW's also from nonlinear four-wave-mixing spectroscopy. A nonlinear signal is emitted as a result of coherent exciton-biexciton transitions (M band), as well as a result of two-photon transitions (TPT) to and from the biexciton state. Furthermore, from a coherently prepared population of excitons and biexcitons, nonlinear quantum beats are observed in the time-integrated four-wave-mixing signal, when recorded as a function of the time delay between the interfering input pulses. From the beat period, and from the luminescence and the FWM spectra, the biexciton binding energy is determined.

In a coherent time-resolved four-wave-mixing experiment, two ultrashort mutually coherent light pulses are incident on the sample with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$. If the delay τ between the input pulses is shorter than the dephasing time of the resonant polarization in the sample, a self-diffracted nonlinear signal can be detected in, e.g., the direction $2\mathbf{k}_2-\mathbf{k}_1$. We record the time-integrated signal as a function of τ, which we define to be positive when pulse number one arrives before pulse number two. The dominant contribution will be for positive delay when photons from the beam $\mathbf{k}_2$ are diffracted in a polarization grating with scattering vector $\mathbf{k}_2-\mathbf{k}_1$, setup by the two interfering input pulses. For negative delay, however, there is also a possible contribution from the diffraction of the polarization from pulse number two in the above polarization grating.[15] This contribution is enhanced by exciton interaction[9] and can even become dominant in the case of biexciton formation.[16] In this case, there is a strong nongrating contribution that can be described as resonant two-photon absorption (from beam number two) to the biexciton state followed coherently by emission, in the direction $2\mathbf{k}_2-\mathbf{k}_1$, stimulated by pulse number one.[16] Thus, a significant nonlinear signal for negative delay is an indication of biexciton formation. The nonlinear four-wave-mixing signal involving biexcitons should be resonant at half the biexciton energy, corresponding to direct two-photon transitions to the biexciton state, as well as in the M band, corresponding to exciton-biexciton transitions.

We performed experiments on samples grown by molecular-beam epitaxy on a [100]-orientated GaAs substrate which was removed by selective chemical etching. The MQW's consist of 20 periods of GaAs layers (116 Å) with $Al_{0.3}Ga_{0.7}As$ barriers (150 Å). The linear absorption shows a narrow ($\approx$1 meV) hh peak at 1.54315 eV (Fig. 1, dashed curve) indicating the high quality of the MQW's. The hh luminescence, after band-to-band excitation with a power of 10 kW/cm^2 (Fig. 1, solid curve), is Stokes shifted by about 0.5 meV relative to the absorption peak. A simple division by the transmission spectrum suggests that the observed shift is mainly due to

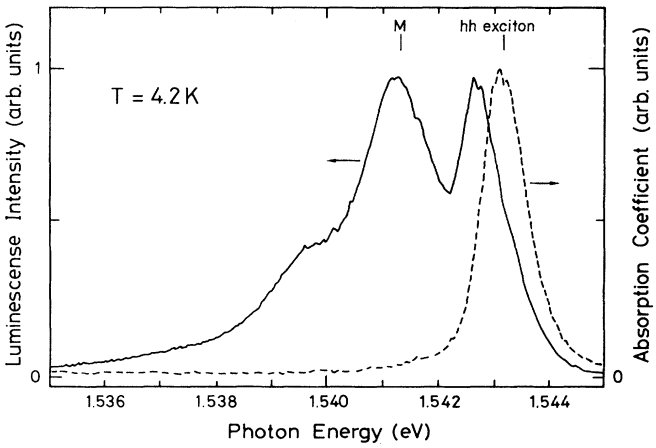

FIG. 1. Luminescence spectrum at an excitation power of 10 kW/cm^2 (solid curve) and absorption spectrum measured with a halogen lamp (dashed curve).

reabsorption of the luminescence. In the low-energy wing of the hh emission, a pronounced peak which grows superlinearly with excitation power,[7,8] and a small shoulder can be detected at 1.5412 and 1.5396 eV, respectively. We attribute the main contribution to this nonlinear luminescence to biexciton recombination, as corroborated by the FWM experiments.

The laser source is a mode-locked argon-ion laser which pumps synchronously a tunable dye laser (Styryl 8) with a repetition rate of 82 MHz. Although the pulse duration is about 7 ps, the time resolution in the coherent FWM is only limited by the coherence time of the laser pulse. Tuning the spectral width of the laser to 8 meV, we obtained a coherence time of ≤ 200 fs. The laser pulses are split into two beams which are focused with a spot size of about 50 μm on the sample, which is immersed in liquid helium cooled to 2 K. After spatial filtering, the emitted nonlinear signal is dispersed in a spectrometer and is monitored, time integrated, but spectrally resolved, by an optical multichannel analyzer system as a function of the variable time delay τ between the incoming pulses (correlation trace).

Our broad-spectrum laser system cannot resolve any fine structure in the region of the hh resonance. However, by dispersing the diffracted beam of the FWM process, strong resonance enhancements of the signal, representing the third-order susceptibility $\chi^{(3)}$, are expected near the exciton resonance ω_x. Two new resonances appear, one resulting from two-photon transitions to the biexciton resonance at ω_m, and the other from induced exciton-biexciton transitions (M band); see Fig. 2. Including population effects of the exciton and biexciton states, the fully resonant terms near the exciton resonance give rise to the third-order susceptibility $\chi^{(3)}$,[17]

$$\chi^{(3)} \sim \frac{\mu_{gx}^2 \mu_{xm}^2}{(\omega-\omega_x)(2\omega-\omega_m)} \left[\frac{1}{\omega-\omega_x} - \frac{1}{\omega+\omega_x-\omega_m} \right], \quad (1)$$

where μ_{gx} and μ_{xm} are the dipole-matrix elements for the ground-state–exciton and exciton-to-biexciton transitions, respectively (Fig. 2).

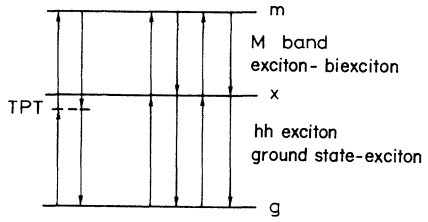

FIG. 2. Level diagram for the exciton-biexciton three-level system. To the left are sketched the direct two-photon transitions to the biexciton state, which can give a nongrating contribution to the FWM signal for negative delay. To the right are sketched the two grating contributions, which can give rise to beats in a coherently prepared mixture of excitons (x) and biexcitons (m).

In order to detect the contribution of the biexciton to two-photon absorption and subsequent stimulated emission for negative time delay τ, we tuned the laser in the region of the heavy-hole resonance and recorded the self-diffracted FWM spectrum for different delays τ. The dominant peak in Fig. 3 is due to the hh transition (see Fig. 2, lower right). The signal is redshifted with respect to the absorption peak due to linear absorption just as for the hh luminescence peak in Fig. 1. All the spectra in Fig. 3 are normalized to the maximum intensity near the hh resonance that is strongly peaked around $\tau=0$. For

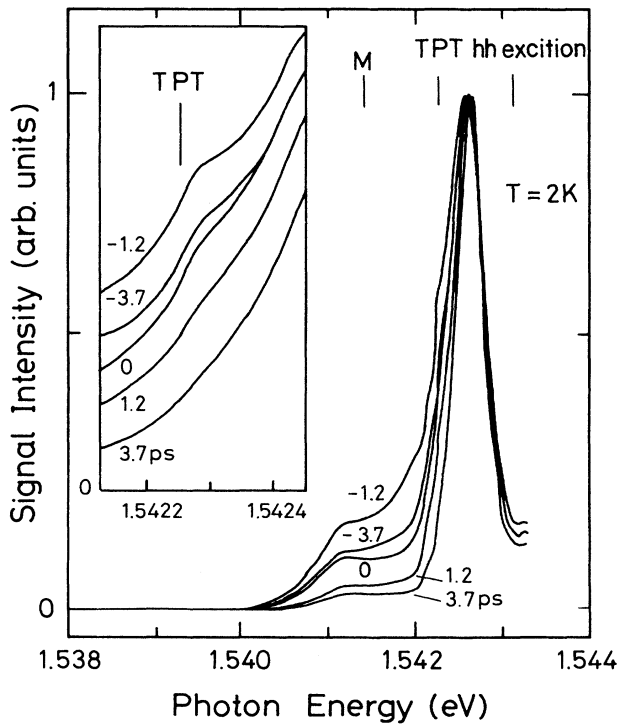

FIG. 3. Intensity of the self-diffracted signal for different time delays τ. All spectra are normalized to the maximum intensity.

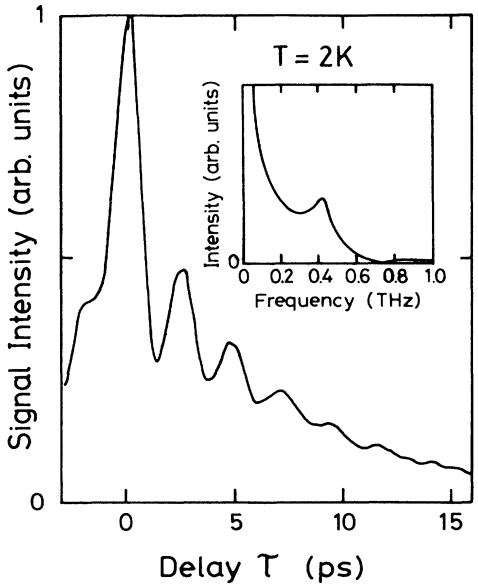

FIG. 4. Decay of the self-diffracted signal in the spectral region of the M band as function of the time delay τ. The inset shows the Fourier transform of the decay curve.

negative delays, we observe, on the low-energy side of the hh resonance, a small shoulder (TPT) at 1.542 25 eV and a broader band (M band) at lower energies around 1.5413 eV. The shoulder at 1.542 25 eV is, by its reproducibility, well separated from the noise level (see inset in Fig. 3) and we assign it to resonant enhancement of the FWM signal due to TPT's directly to the biexciton state, as sketched on the left-hand side of Fig. 2. From that we estimate a binding energy of 1.8 meV for the biexciton. The broader band for negative delays corresponds, then, to the resonant enhancement due to exciton-biexciton transitions (see Fig. 2, upper right) and coincides with the M band observed in luminescence. The shoulder at 1.5396 eV, which is also observed in luminescence, could be due to bound excitons or possibly to biexciton-biexciton collisions,[6] but since we do not observe it in the nonlinear spectra, we will not consider it further in the present context.

The correlation trace of the self-diffracted signal, detected in the spectral region of the M band, reveals pronounced oscillations with a period of 2.3 ps for positive delay as *well as for negative delay*, as shown in Fig. 4. These oscillations are strongest when detecting in the M band, and we interpret them as quantum beats between exciton and biexciton transitions in the FWM process. The modulations of the correlation trace are clearly revealed as a single oscillation by the Fourier transform shown in the inset of Fig. 4, and the corresponding energy separation $\Delta E = 1.8$ meV agrees well with the biexciton binding energy as determined above. Thus, the two FWM processes that are beating are the upper and lower transitions, which are sketched on the right-hand side of Fig. 2 and are explained in the following. Since our laser covers a spectral range of several meV just below the hh resonance, there is an enhanced coherent formation of biexcitons by TPT, either directly or via the hh resonance. Therefore, a coherent mixture of excitons and biexcitons is created, which leaves two possible routes for the FWM processes, namely, through ground-state–to–exciton transitions or through exciton-to-biexciton transitions. Since excitons and biexcitons are created mutually coherent and stay coherent with the field within the dephasing time, the two possible routes for FWM give rise to quantum beat as observed. The fact that we also observe beats for negative delay supports the idea that biexcitons are involved.

The biexciton binding energy of 1.8 meV, determined here, is somewhat larger than that theoretically calculated[2] and from that estimated from previous experiments.[1,5] However, we feel that the present simultaneous and consistent determination from luminescence spectra, FWM spectra (for negative delay), and nonlinear quantum beat spectroscopy is very convincing.

Since the completion of this work, a publication has appeared showing quantum beats in FWM of GaAs quantum wells.[18] These quantum-beat data are, in fact, very similar to those presented here. However, the authors infer a much smaller biexciton binding energy (1.1 meV) by neglecting the fastest-oscillating components, which they call half-period beats and relate to some unexplained anharmonic effects. From our data, which show a nice singly peaked Fourier transform of the observed quantum beats (see inset in Fig. 4), such an interpretation is not at all justified.

In conclusion, the presence of biexcitons in GaAs quantum wells is confirmed by the emission of a nonlinear signal in the exciton-biexciton resonance (M band), and in the spectral region of the two-photon transition to the biexciton state. We report quantum interference in a coherently prepared exciton-biexciton system in a nonlinear four-wave-mixing experiment. From our measurements, we can conclude that in thin GaAs quantum wells of good quality, i.e., with a small inhomogeneous broadening of the exciton peaks, the biexciton binding energy is 1.8 ± 0.1 MeV This is an important result because there is increasing evidence that exciton interaction and biexciton formation plays a significant role in the (nonlinear) optical properties of GaAs quantum wells. At the same time there are conflicting reports by various authors of biexciton binding energies ranging from about 1 meV (Refs. 1 and 18) to almost 3 meV (Ref. 19) in different samples.

Similar observations of quantum interference from a coherently prepared population of excitons and biexcitons are predicted for other semiconductors.

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*Permanent address: Universität Kaiserslautern, Fachbereich Physik, Erwin-Schrödingerstr., D-6750 Kaiserslautern, Germany.

†Permanent address: Institute of Microelectronics Technology and Superpure Materials, Chernogolovka, Moscow District 142432, Russia.

[1]R. C. Miller, D. A. Kleinmann, A. C. Gossard, and O. Munteanu, Phys. Rev. B **25**, 6545 (1982).

[2]D. A. Kleinman, Phys. Rev. B **28**, 871 (1983).

[3]L. Banyai, I. Galbraith, and H. Haug, Phys. Rev. B **38**, 3931 (1988).

[4]R. Cingolani, Y. Chen, and K. Ploog, Phys. Rev. B **38**, 13 478 (1988).

[5]S. Charbonneau, T. Steiner, M. L. W. Thewalt, E. S. Koteles, J. Y. Chi, and B. Elman, Phys. Rev. B **38**, 3583 (1988).

[6]R. Cingolani, K. Ploog, G. Peter, R. Hahn, E. O. Göbel, C. Moro, and A. Cingolani, Phys. Rev. B **41**, 3272 (1990).

[7]D. Oberhauser, K.-H. Pantke, W. Langbein, V.G. Lyssenko, H. Kalt, J. M. Hvam, G. Weiman, and C. Klingshirn, Phys. Status Solidi B **173**, 53 (1992).

[8]R. T. Phillips, D. J. Lovering, G. J. Denton, and G. W. Smith, Phys. Rev. B **45**, 4308 (1992).

[9]B. F. Feuerbacher, J. Kuhl, and K. Ploog, Phys. Rev. B **43**, 2439 (1991).

[10]K. Leo, T. C. Damen, J. Shah, E. O. Göbel, and K. Köhler, Appl. Phys. Lett. **57**, 19 (1990).

[11]B. F. Feuerbacher, J. Kuhl, R. Eccleston, and K. Ploog, Solid State Commun. **74**, 1279 (1990).

[12]D. Oberhauser, K.-H. Pantke, J. M. Hvam, K.-H. Schlaad, G. Weimann, and C. Klingshirn, *Proceedings of the International Conference on Laser '91, San Diego, 1991* (STS, San Diego, 1992), p. 368.

[13]K. Leo, T. C. Damen, J. Shah, and K. Köhler, Phys. Rev. B **42**, 11 359 (1990).

[14]E. O. Göbel, K. Leo, T. C. Damen, J. Shah, S. Schmitt-Rink, W. Schäfer, J. F. Müller, and K. Köhler, Phys. Rev. Lett. **64**, 1801 (1990).

[15]K. Leo, M. Wegener, J. Shah, D. S. Chemla, E. O. Göbel, T. C. Damen, S. Schmitt-Rink, and W. Schäfer, Phys. Rev. Lett. **65**, 1340 (1990).

[16]C. Dörnfeld and J. M. Hvam, IEEE J. Quantum Electron. **QE-25**, 904 (1989).

[17]I. Abram, A. Maruani, and S. Schmitt-Rink, J. Phys. C **17**, 5163 (1988).

[18]R. T. Phillips, D. J. Lovering, G. J. Denton, and G. W. Smith, Phys. Rev. Lett. **68**, 1880 (1992).

[19]S. Bar-Ad and I. Bar-Joseph, Phys. Rev. Lett. **68**, 349 (1992).