RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 43, NUMBER 3 15 JANUARY 1991-II

Biexcitonic contribution to the degenerate-four-wave-mixing signal from a GaAs/$Al_xGa_{1-x}As$ quantum well

B. F. Feuerbacher, J. Kuhl, and K. Ploog
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-7000 Stuttgart 80, Federal Republic of Germany
(Received 4 October 1990)

We report experiments on degenerate-four-wave mixing in a high quality GaAs/$Al_{0.3}Ga_{0.7}As$ quantum well using the time-resolved self-diffraction technique. Frequency-dependent measurements around the heavy-hole exciton transition reveal a strong biexcitonic nonlinearity.

Time-resolved degenerate-four-wave mixing (DFWM) has proven to be a powerful tool to study the relaxation dynamics of excitons in GaAs/$Al_xGa_{1-x}As$ quantum wells (QW). In the last few years, the dephasing time T_2, the lifetime τ, and the orientational relaxation time T_1 of excitons have been determined with DFWM.[1] Recently, quantum beats of excitons in QW have been demonstrated with this technique.[2,3]

In most experiments, a special configuration of DFWM, the self-diffraction technique, has been used. With this technique, the phase relaxation of a system can be investigated. We apply this method to study the phase relaxation of the heavy-hole (hh) exciton in a GaAs/$Al_{0.3}$-$Ga_{0.7}As$ single QW. Two short laser pulses are tuned to the exciton resonance and focused on the sample. Due to interference between the two laser pulses and absorption of the laser light, an excitonic grating is generated in the sample. Each of the two laser pulses is subsequently diffracted by this grating, pulse 1 into the direction $2\mathbf{k}_1-\mathbf{k}_2$ and pulse 2 into the direction $2\mathbf{k}_2-\mathbf{k}_1$, where $\mathbf{k}_1$ and $\mathbf{k}_2$ denote the wave vectors of the incoming laser pulses. When pulse 2 is delayed with respect to pulse 1, the polarization coherence in the sample that has been induced by pulse 1 is reduced at the time when pulse 2 arrives on the sample due to phase-breaking processes. Therefore the grating amplitude and the self-diffracted intensity decay with increasing delay between the two pulses. For a homogeneously broadened transition, the diffracted intensity decays exponentially with $T_2/2$ for increasing delays, and for inhomogeneously broadened transitions the exponential decay time is $T_2/4$. Recently, the third-order density-matrix theory of Yajima and Taira[4] which describes the self-diffraction experiment has been extended to the case of quantum beats and an additional contribution to the measured signal for negative time delays.[2] This additional contribution has first been mentioned by Göbel *et al.*[5] and attributed to anharmonic exciton-exciton interaction. We have recently pointed out that there could be yet another process contributing to the DFWM signal from a GaAs/$Al_xGa_{1-x}As$ QW for negative delays:[6] the large nonlinearity of the biexciton transition, which has been thoroughly studied in II-VI compounds.[7] The existence of this biexciton nonlinearity in GaAs/$Al_xGa_{1-x}As$ QW has recently been predicted,[8] but to the best of our knowledge no experimental evidence for it has been reported up to now, possibly because of the small biexciton binding energy (compared to the II-VI compounds) of less than 1 meV,[9,10] which is in the range of the inhomogeneous line broadening of the samples investigated so far and less than the spectral width of the laser pulses normally used. In our experiments, we use spectrally narrow laser pulses [0.9 meV full width at half maximum (FWHM)] and a QW sample with a modified layer sequence resulting in an extremely narrow hh exciton line with no line splitting caused by monolayer fluctuations. We are therefore able to demonstrate the biexciton nonlinearity of a GaAs/$Al_xGa_{1-x}As$ QW in the self-diffraction experiment.

There are three ways to build up a third-order nonlinear signal into the direction $2\mathbf{k}_2-\mathbf{k}_1$ using the wave vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ of the two incoming laser pulses. The first process is the grating process described above, where we start with the first pulse (giving us the wave vector $-\mathbf{k}_1$) and then the desired signal is obtained by double interaction of the polarization in the sample with the electric field of the second pulse. We denote this process as $(-\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_2)$, thus indicating the order of the interactions between light and matter.

In order to get a signal for negative delays, we must reverse the time axis of the experiment, i.e., delay pulse 1 with respect to pulse 2. In the following, we will always use the term "negative delay" for the case when pulse 2 arrives on the sample before pulse 1. The polarization created in the sample by pulse 2 then interferes with pulse 1 and again produces a grating. In the third-order density-matrix theory of Yajima and Taira,[4] this leads to a small contribution to the signal for negative delays when the delay is smaller or comparable to the laser-pulse width, because then the rest of pulse 2 can be diffracted by the grating which was just built up together with pulse 1. However, if the negative delay is larger than the laser-pulse width, the grating is still produced but pulse 2 cannot be diffracted any more. We denote this process by $(+\mathbf{k}_2-\mathbf{k}_1+\mathbf{k}_2)$.

Recently, it has been pointed out that anharmonic exciton-exciton interaction also results in a process $(+\mathbf{k}_2-\mathbf{k}_1+\mathbf{k}_2)$ giving an additional contribution to the self-diffracted signal even for negative delays considerably larger than the laser-pulse width.[11] In an $In_xGa_{1-x}As$/$In_yAl_{1-y}As$ multiple QW for laser intensities exceeding 10 MW/cm^2, even a fifth-order process contributing to the signal for negative delays has been identified; it also is

ascribed to nonlinear exciton-exciton interaction.[12] A grating is still produced for negative delays larger than the laser pulse width, but there is no electric field of pulse 2 that can be diffracted by this grating. However, nonlinear exciton-exciton interaction can give rise to a signal in the direction of $2\mathbf{k}_2-\mathbf{k}_1$, as a part of the coherent rest of the *excitonic polarization* from pulse 2 can be diffracted by the grating. This is in contrast to the contributions to the signal discussed above, where always the *electric field* of one of the laser pulses is diffracted. For nonlinear exciton-exciton interactions, the coherence of the polarization induced in the material by pulse 2 is necessary for two steps of the third-order process (grating generation *and* diffraction of the polarization). For homogeneously broadened transitions the self-diffracted intensity thus decays exponentially with $T_2/4$ for increasing negative delays, whereas for positive delays the dephasing curve remains unchanged.[11]

There is yet another nonlinear third-order process generating a signal in the direction $2\mathbf{k}_2-\mathbf{k}_1$ for negative-time delays[13] that has been demonstrated for several II-VI compounds.[13-17] This process is due to two-photon absorption which leads to the generation of biexcitons. The biexciton contribution to the nonlinear self-diffracted signal for negative delays can be explained in two steps. In the first step, two photons of pulse 2 create a biexciton which then, in a second step, interacts coherently with pulse 1 and gives a signal in the direction $2\mathbf{k}_2-\mathbf{k}_1$. We abbreviate this process with $(+\mathbf{k}_2+\mathbf{k}_2-\mathbf{k}_1)$. The nonlinearity of the biexciton transition due to the so-called "biexciton giant two-photon absorption"[18] has been demonstrated to be very strong. We show in this paper that it is also present in a $GaAs/Al_xGa_{1-x}As$ QW.

Our sample is a 27-nm-wide single $GaAs/Al_{0.3}Ga_{0.7}As$ QW grown by molecular-beam epitaxy with three monolayers of AlAs inserted between the QW and the barriers to smooth the interface. Figure 1 shows the cw photoluminescence (PL) spectrum for an excitation intensity of 5 W/cm^2. There is no Stokes shift between the PL and the photoluminescence excitation (PLE) spectrum (not shown here). The light-hole exciton and hh exciton transitions occur at 1.5242 and 1.5215 eV, respectively. The spectral width of the hh exciton line (FWHM) is 0.195 meV (taken from high-resolution spectra). There is no splitting of the exciton lines caused by monolayer fluctuations. The growth conditions and a comprehensive characterization of the sample are given elsewhere.[19] On the low-energy side of the PL spectrum, some impurity-bound features can be seen.

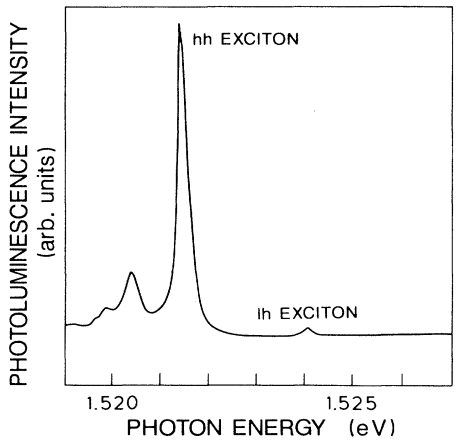

FIG. 1. cw photoluminescence spectrum from the 27-nm $GaAs/Al_{0.3}Ga_{0.7}As$ quantum well for an excitation intensity of 5 W/cm^2.

Figure 2 depicts the spectral response of the self-diffracted DFWM intensity for an excitation intensity of 5 kW/cm^2 at zero delay, which gives a measure for the third-order nonlinearity. The duration of the laser pulses is 2.7 ps and the spectral width is 0.9 meV (FWHM) which gives a considerably improved spectral resolution of the self-diffraction experiment compared to the femtosecond pulses widely used.

The hh biexciton binding energy in a 27-nm-wide $GaAs/Al_{0.3}Ga_{0.7}As$ QW is 0.7 meV.[9,10] Therefore the biexciton contribution to the DFWM signal is expected to occur at 0.35 meV (half of the biexciton binding energy) below the hh exciton transition, and indeed there is a shoulder at this spectral position in Fig. 2. The shoulder does not disappear when the excitation intensity is reduced by an order of magnitude. We can therefore exclude fifth or even higher-order processes as the origin of this spectral feature. This model has been used to explain the temporal and intensity-dependent behavior of an $In_xGa_{1-x}As/In_yAl_{1-y}As$ multiple QW at excitation intensities above 10 MW/cm^2,[12] which is 3 orders of magnitude higher than in our experiment. If the shoulder found in Fig. 2 is caused by the biexciton transition, then the dephasing curves for negative delays are expected to change drastically when the laser is tuned to the biexciton resonance, as on the biexciton transition the $(+\mathbf{k}_2+\mathbf{k}_2-\mathbf{k}_1)$

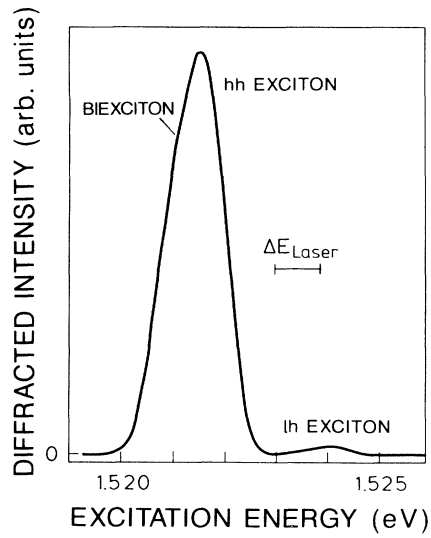

FIG. 2. Spectral response of the self-diffracted intensity at zero delay. At 0.35 meV below the hh exciton resonance, there is a shoulder in the signal which is ascribed to the biexcitonic nonlinearity. The inset shows the spectral FWHM of the laser pulses.

process should generate an additional contribution to the DFWM signal for negative delays.

In Fig. 3 we show the dephasing curves for four different settings of the laser photon energy. In Fig. 3(a), the laser is tuned to the high-energy side of the spectral response given in Fig. 2, and the resulting dephasing curve is as expected from the Yajima and Taira theory[4] without additional signal for negative delays. However, as the laser spectrum partly covers the shoulder in the spectral response in Fig. 2 [Figs. 3(b) and 3(c)], there arises a signal for negative delays. This signal increases and finally dominates the dephasing curve in Fig. 3(d), when the laser is tuned to the low-energy side of the spectral response of the self-diffracted intensity. We interpret our results as follows: (i) At 1.5215 eV, the hh exciton transition which is found in the PL and PLE measurements gives rise to the usual strong self-diffracted signal. When we tune the laser to the high-energy shoulder of the hh exciton nonlinear response [Fig. 3(a)], the temporal behavior of the self-diffracted intensity (dephasing curve) can be fitted by the two-level theory of Yajima and Taira,[4] and we find $T_2=6$ ps for the hh exciton. (ii) At about 1.5211 eV, which is 0.4 meV below the hh exciton transition, the biexcitonic nonlinearity generates another self-diffracted signal. The time axis of the biexcitonic nonlinear signal is reversed in comparison to the hh exciton nonlinear signal,[13] as is clearly demonstrated in Fig. 3(d). We can rule out exciton-exciton interaction as the origin of this signal, because for negative delays it decays with approximately the same time constant as the signal for positive delays in Fig. 3(a). However, for the case of exciton-exciton interaction, the decay for negative delays is found to be twice as fast as for positive delays.[11] By tuning the laser across the nonlinear response curve of Fig. 2, we can continuously vary the biexcitonic contribution to the DFWM signal from the hh exciton, as demonstrated in Fig. 3(a)–3(d).

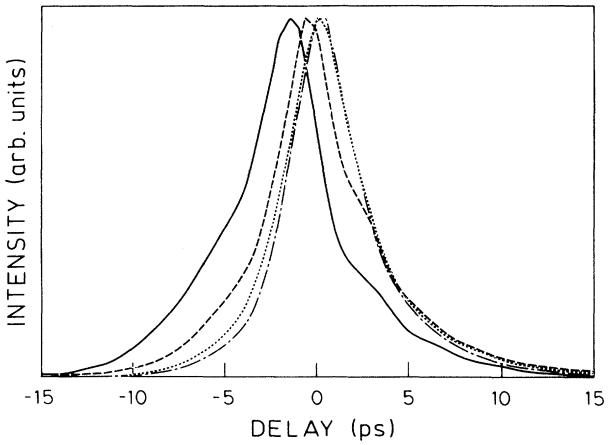

FIG. 3. Self-diffracted intensity vs delay for four different laser photon energies. (a): dash-dotted line, 1.5220 eV; (b): dotted line, 1.5216 eV; (c): dashed line, 1.5212 eV; (d): solid line, 1.5206 eV.

To conclude, in various II-VI semiconductors, a strong third-order nonlinearity on the biexciton transition is well established, which gives rise to a DFWM signal in the self-diffraction geometry for negative delays. We demonstrate the existence of this biexcitonic nonlinearity in a $GaAs/Al_{0.3}Ga_{0.7}As$ quantum well.

We gratefully acknowledge fruitful discussions with R. Cingolani and H. Kalt.

[1] J. Kuhl, A. Honold, L. Schultheis, and C. W. Tu, in *Advances in Solid State Physics,* edited by U. Rössler (Vieweg, Braunschweig, 1989), Vol. 29. p. 157.

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

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

[4] T. Yajima and Y. Taira, J. Phys. Soc. Jpn. **47**, 1620 (1979).

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

[6] B. F. Feuerbacher, J. Kuhl, R. Eccleston, and K. Ploog (unpublished).

[7] R. Lévy, B. Hönerlage, and J. B. Grun, in *Optical Nonlinearities and Instabilities in Semiconductors,* edited by H. Haug (Academic, Boston, 1988).

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

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

[10] D. C. Reynolds, K. K. Bajaj, C. E. Stutz, R. L. Jones, W. M. Theis, P. W. Yu, and K. R. Evans, Phys. Rev. B **40**, 3340 (1989).

[11] C. Stafford, S. Schmitt-Rink, and W. Schäfer, Phys. Rev. B **41**, 10000 (1990).

[12] 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).

[13] C. Dörnfeld and J. H. Hvam, IEEE J. Quantum Electron. **25**, 904 (1989).

[14] I. Abram, J. Opt. Soc. Am. B **2**, 1204 (1985).

[15] H. Kalt, V. G. Lyssenko, R. Renner, and C. Klingshirn, J. Opt. Soc. Am. B **2**, 1188 (1985).

[16] A. Maruani and D. S. Chemla, Phys. Rev. B **23**, 841 (1982).

[17] M. S. Brodin, V. N. Kadan, and M. G. Matsko, Fiz. Tverd. Tela (Leningrad) **31**, 216 (1989) [Sov. Phys. Solid State **31**, 1037 (1989)].

[18] E. Hanamura, Solid State Commun. **12**, 951 (1973).

[19] K. Ploog, A. Fischer, L. Tapfer, and B. F. Feuerbacher (unpublished).