Resonant Generation of Biexcitons in a GaAs Quantum Well

D. J. Lovering,[a] R. T. Phillips,[a] and G. J. Denton[a]
Department of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, Great Britain

G. W. Smith
DRA, Royal Signals and Radar Establishment, St. Andrews Road, Malvern WR14 3PS, Great Britain
(Received 1 July 1991)

Generation of cold excitons in GaAs quantum wells is shown to lead to enhanced condensation to the biexciton state under cw illumination. Resonant two-photon absorption to the biexciton state in the same structure is found to account for a quantum beating phenomenon involving the biexciton and exciton states in a more complex three-level system than hitherto investigated.

PACS numbers: 71.35.+z, 42.50.Md, 78.47.+p, 78.55.Cr

Excitons in three-dimensional materials have been known for some time to be an important paradigm for the interacting boson system, where a precursor to Bose-Einstein condensation is the formation of excitonic molecules, or biexcitons [1]. Only recently has it become clear that biexcitons also play an important role in the nonlinear optical response of GaAs quantum-well structures [2]. So far, however, there has been no systematic study of the behavior of biexcitons in GaAs under the conditions of resonant excitation which are implicit in the investigation of the excitonic resonances in the third- and higher-order optical nonlinearities which mediate four-wave mixing. In order to observe biexcitonic effects in GaAs it is necessary to work with quantum wells, since in two dimensions the binding energy of the excitonic molecule is increased over the bulk value by nearly an order of magnitude, to ~ 1 meV. For material of appropriate high quality the free exciton linewidth may be reduced to 0.5 meV thus permitting the spectral resolution of the biexciton [3–6]. This narrow, largely homogeneous, linewidth also ensures that the dephasing time for the excitonic system is of the order of picoseconds, so coherent transient effects may be resolved in the time domain if light pulses of duration ≈ 1 ps interact with the excitons. Recent work has indicated that biexcitons play an important role in such coherent interactions, but there has been no clear corroboration by combined time- and frequency-domain measurements. In this Letter we report optical processes dominated by biexcitons generated in both two-photon and single-photon transitions in a single GaAs quantum well, and show that the biexcitons are involved in coherent processes over a range of biexciton densities.

The simplest model of an exciton in GaAs treats it as a two-level quantum system. The excitons interact little at very low densities, but as the density is increased, pairs of excitons may bind weakly together to form excitonic molecules. These biexcitons add an extra level to the two-level scheme, at an energy $2E_x - E_b$, where E_x is the exciton energy and E_b the binding energy of the molecule. Three-level systems recently investigated by quantum-beating spectroscopy using self-diffraction include light- and heavy-hole excitons [7], exciton transitions split by spatial variations in well thickness [8], and free and bound excitons [9]. For each of these systems the optical emission process ends with the crystal in its ground state. In the case of the system of excitons and biexcitons, the biexciton state may be reached by two-photon absorption from the ground state—a process expected at high excitation levels—or by successive one-photon absorption with the exciton level as a real intermediate state. Emission from the biexciton level at $2E_x - E_b$ is to the exciton level at E_x; this transition therefore gives a peak in the photoluminescence (PL) spectrum at $E_x - E_b$. The same polarization selection rule applies to both the exciton $\rightarrow$ ground state and the biexciton $\rightarrow$ exciton transitions, which may therefore interact.

We have studied a sample, grown in (100) orientation by molecular-beam epitaxy, consisting of three undoped GaAs quantum wells of widths 204, 102, and 51 Å between $Al_{0.33}Ga_{0.67}As$ barriers 150 Å thick. The structure was capped by 600 Å of GaAs, and grown over a ten-period (28 Å)/(28 Å) superlattice of GaAs/AlAs on top of a 5000-Å etch-stop layer of $Al_{0.6}Ga_{0.4}As$. Samples for self-diffraction experiments were made by selective etching such that windows were opened in thinned substrates, leaving about 250-μm-diam regions of self-supporting epilayer.

For the 102-Å well on which this Letter will concentrate, the samples show sharp exciton lines in low-temperature photoluminescence, of FWHM in the region of 0.6 meV, with some slight spatial dependence. The free-standing epilayers exhibited slight buckling which led to small shifts of the PL transition energies, but no appreciable broadening of the line. For both unprocessed and free-standing materials the sample may be excited so that the exciton shows a distinct second peak on the low-energy side, which may be attributable to either bound excitons or excitonic molecules. To establish that the latter is the correct explanation of this peak we have measured the dependence of the intensity of the peak on the optical injection level I, and find a variation as $I^{1.4}$ for

$1 < I < 100$ mW cm^{-2}. This is in good agreement with the data of Miller *et al.* [3], and the attribution of this transition to a biexciton is confirmed by the line shape. This is illustrated in Fig. 1, which shows photoluminescence spectra of the biexciton transition in the 102-Å quantum well at 1.4 K. The spectra show the dependence of the spectral shape on the injection level for the condition of resonant injection with the laser tuned to the light-hole (lh) exciton, corresponding to the peak in the photoluminescence excitation spectrum shown in the inset in the figure. The continuous line gives the line shape at very low injection intensity ~ 1 μW cm^{-2}. This has been normalized to the peak of the exciton transition for the higher injection level of ~ 70 mW cm^{-2} shown by the dots, in order to give the contribution of the biexciton. The theoretical fit to the data represents a simple model line shape for the biexciton transition, which assumes that the biexcitons have a Boltzmann distribution of energies for motion in the plane of the well, and a step-function density of states. When a biexciton emits a photon energy $E_x - E_b$ it leaves behind an exciton, and for the case in which the photon momentum may be neglected, the line shape $I(\hbar\omega)$ then becomes [10]

$$\int g(E_b)\Theta(E_x - E_b - \hbar\omega) \times \exp[-(E_x - E_b - \hbar\omega)/kT_{\text{eff}}]dE_b .$$

The integral over a Gaussian distribution $g(E_b)$ models broadening of the transition (we used a standard deviation of 0.3 meV); Θ is the Heaviside step function. This is a somewhat more convincing line shape than that used by Cingolani, Chen, and Ploog [6] since it does not give an artificial step function in the spectrum at $E_x - E_b$. The conditions of the cw experiment are such that thermal equilibrium is established, but the effective temperature of the excitonic system is raised above the lattice temperature by "recombination heating," since the emission of a photon by a biexciton leaves the exciton to carry away the recoil momentum. This accounts for the need to use the values of $T_{\text{eff}} \approx 10$ K. The important feature of these cw experiments is that in contrast to the previous work [6], we have used resonant excitation at the lh exciton. Using excitation by photons of higher energy also generates biexcitons, but at injection levels 2 to 3 orders of magnitude higher than we have used. The probability of biexciton formation therefore is massively enhanced when cold excitations are injected: In the case of Fig. 1, cold light-hole excitons have to emit a small amount of energy to reach the cold heavy-hole exciton state. We have found similar behavior at comparable injection density for direct resonant creation at the high-energy side of the heavy-hole (hh) exciton, with a slightly stronger intensity dependence.

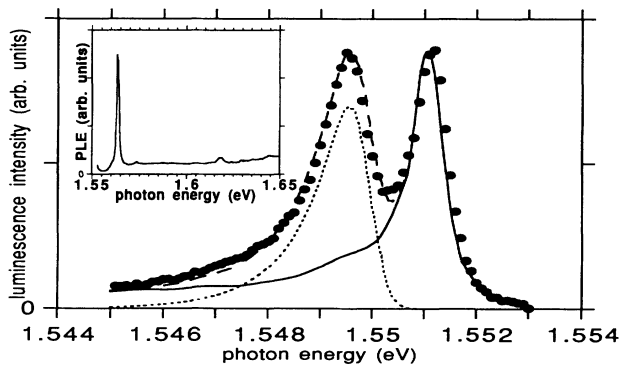

FIG. 1. Photoluminescence spectra obtained at 1.4 K on the 102-Å quantum well. The exciton spectrum obtained at ~ 1-μW cm^{-2} excitation density is shown by the continuous line. Data points correspond to ~ 70 mW cm^{-2}, and the dotted line is a fit to the biexciton line shape with $E_x = 1.551$ eV, $E_b = 1.1$ meV, and $T_{\text{eff}} = 10$ K. Inset: The photoluminescence excitation spectrum of the biexciton; the peak corresponds to the excitation energy used for the luminescence in the main figure.

Two factors ensure that the biexciton population consists essentially entirely of hh biexcitons: first the efficient relaxation of the lh excitons to hh, and second the strong dependence of the biexciton binding energy on the ratio of effective masses of the carriers, which favors hh biexciton binding [1]. The present cw experiments prove that under conditions of resonant injection, biexcitons are significant in GaAs quantum-well emission even at very low injection levels. Under cw conditions the method of excitation is by successive absorption of two photons, since we have found no evidence for emission at E_x when excitation is tuned to $E_x - E_b/2$, the expected energy for single-step two-photon absorption. The line shape of the emission spectrum is a direct result of the establishment of a thermal distribution of energies for center-of-mass motion among the biexciton population. In resonant injection by short pulses with photon momentum perpendicular to the quantum well, the injected (cold) excitons have no transverse momentum. The thermalized excitons and biexcitons which give the tail of the spectrum in Fig. 1 will not contribute to coherent optical interactions.

To probe the nonlinear response of cold biexcitons we measured the strength of the spatial parametric interaction between two 700-fs-long light pulses which were focused to overlapping spots on a free standing epilayer, held in helium gas at 4 K. The pulses were provided by a single hybrid mode-locked Styryl 9M dye laser and the beams converged at 9° with each forming a spot of diameter about 50 μm. The orthogonally linearly polarized incident pulses had wave vectors k_1 and k_2, and arrived at the sample at times t_1 and t_2, respectively. One pulse could be delayed by a variable amount, $\Delta t = t_2 - t_1$, with respect to the other. The interaction between these pulses generated outgoing light pulses along directions close to $2k_2 - k_1$ and $2k_1 - k_2$ and the intensity of such *self-diffraction* pulses carries information about the time evo-

lution of the sample's excitations between t_1 and t_2. For the data presented the laser was tuned to give maximum self-diffraction efficiency and its spectral content spanned both exciton and biexciton transitions. Our experiment measured the integrated energy of the self-diffraction pulses, the variation of which with Δt can be predicted from the density matrix by standard perturbation techniques [11]. In the delta-function limit this yields for the pulse emitted along $2k_n - k_m$ a zero signal for $t_n - t_m = \Delta t = 0$ with a step at $\Delta t = 0$ followed by an exponential decay with time constant $T_2/2$ for $\Delta t > 0$, where T_2 is the phase coherence time for the exciton ensemble; the signals measured for $2k_2 - k_1$ and $2k_1 - k_2$ are expected to correspond to one another under the reversal of sign of Δt.

The macroscopic polarization which results when the sample contains coherent dipole moments from two nearly degenerate transitions will contain a beating term with period $h/\Delta E$, where ΔE is the energy splitting between the transitions. This quantum-beating phenomenon is illustrated in Fig. 2, which shows the signals measured for both $2k_2 - k_1$ and $2k_1 - k_2$. The point at which these signals cross on the rising edge identifies $\Delta t = 0$, and the figure illustrates the spreading of the step response caused in part by the finite laser-pulse length. The beats must originate from two oscillators excited within the laser's spectral profile, one of which is the exciton. The cw PL results show no monolayer splitting nor bound exciton transitions; the beating oscillators are therefore the exciton and biexciton. Figure 3 shows the dependence of the self-diffraction signal on the intensity of excitation, from which it can be seen that the relative beat amplitude goes through a maximum as the power in the excitation beams is increased. This is consistent with the main contribution to the oscillating polarization being due to the exciton at low power, and transferring to the biexciton as the power is increased. The maximum beating corresponds to some relative degree of biexciton generation and is consistent with the exciton and biexciton systems possessing equal polarization strengths—the depth of the beating is limited by the fact that our laser pulses are a significant fraction of the beat period. At low power levels beating is seen on the decaying signal; at higher levels the beating disappears, T_2 shortens, and the "rising" edge broadens. This behavior at high power is a signature of biexciton-related processes and has been investigated previously in systems with conjectured biexcitonic behavior, and is here explicitly shown for this biexcitonic system. Exciton-exciton interaction effects at high injection levels have been investigated theoretically [12] and experimentally [13], and may also contribute to modification of the temporal profile.

The quantum beating shown in Fig. 2 represents a more complex phenomenon than that for the simple double oscillator. In the present case we believe that the first stage of the excitation of the biexciton is through a two-photon transition, followed by subsequent interactions with the fields at resonance on the biexciton → exciton transition. This leaves the system with one exciton for every final emitted photon. The exciton transition, on the other hand, is resonantly excited in the normal way, and the final emission of a photon from the oscillating polarization leaves the system in the ground state. The beat period τ should be related to the splitting between the oscillators, $\delta\omega$, by $\delta\omega\,\tau = 2\pi$, or $\hbar\delta\omega(\text{meV}) = 4.14/\tau(\text{ps})$. Here it is important to take as the splitting the value of $E_b = \hbar\delta\omega$ deduced from the fit shown in Fig. 1 (i.e., 1.1 ± 0.1 meV), which, because of the cold injection relevant to the self-diffraction case, is less than the peak splitting in the spectral data (1.6 meV). In Fig. 2 a clearly resolved beat is visible at 3.7 ps from the peak of the signal which agrees well with the energy splitting, given the uncertainty in the fitting of the biexciton binding energy. However, Fig. 2 also shows resolved beats occurring with periods shorter by a factor 2 ± 0.1, and in Fig. 3 these half-period beats are dominant; they are not

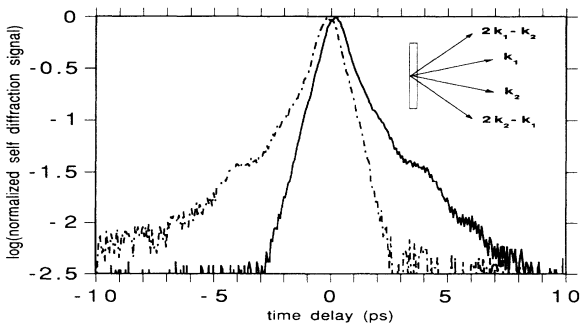

FIG. 2. Self-diffraction signals as a function of delay between exciting pulses, for the directions shown in the inset, for the 102-Å quantum well, with a pronounced quantum beat at 3.7 ps from the peak for each beam. Half-period features are also visible.

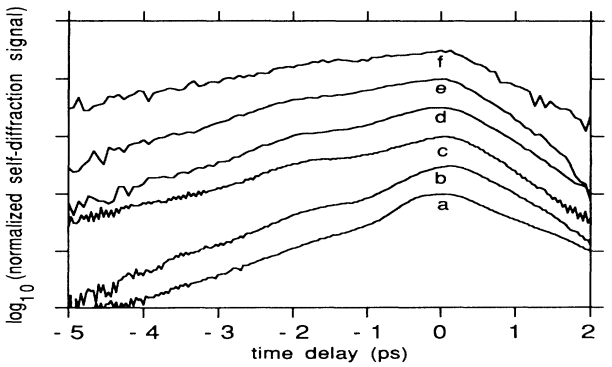

FIG. 3. The logarithm of normalized self-diffraction signals (plotted with constant arbitrary offsets for clarity) for six different power levels in the exciting beams. Suppression of the beating occurs at both high and lower powers. Powers were (a) 2.6 mW, (b) 0.94 mW, (c) 0.24 mW, (d) 0.17 mW, (e) 0.096 mW, and (f) 0.040 mW cw.

at present fully understood but may be related to higher-order anharmonic behavior involving the biexciton. We note that beat components with period shorter than expected appear in some earlier data, obtained from a quantum well showing some evidence for biexcitonic features in the spectral dependence of the self-diffraction efficiency [2,14].

In conclusion, we have observed very large enhancement of the generation of biexcitons in GaAs quantum wells when the exciton population is resonantly excited, and have shown that in the same sample quantum beat signals originating from the exciton-biexciton system are obtained in time-resolved self-diffraction. We attribute the halving of the beat time period to the anharmonic nature of the two-photon resonance which generates the biexciton, and show that at high levels of injection this system produces an effective time reversal in the evolution of the beat signal.

We have enjoyed helpful discussions with Maurice Skolnick, Izo Abram, and Rama Raj. This work was supported by SERC and ESPRIT BRA 3043. We acknowledge the expert assistance of Robert King and John Codd.

[a]Present address: University of Cambridge, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, Great Britain.

[1] E. Hanamura and H. Haug, Phys. Rep. **33**, 209 (1977).
[2] B. F. Feuerbacher, J. Kuhl, and K. Ploog, Phys. Rev. B **43**, 2439 (1991); R. Raj, I. Abram, and J. A. Levenson, Superlattices Microstruct. (to be published).
[3] R. C. Miller, D. A. Kleinman, A. C. Gossard, and O. Munteanu, Phys. Rev. B **25**, 6545 (1982).
[4] D. A. Kleinman, Phys. Rev. B **28**, 871 (1983).
[5] S. Charbonneau, T. Steiner, M. L. W. Thewalt, E. M. Koteles, J. Y. Chi, and B. Elman, Phys. Rev. B **38**, 3583 (1988).
[6] R. Cingolani, Y. Chen, and K. Ploog, Phys. Rev. B **38**, 13478 (1988).
[7] K. Leo, T. C. Damen, J. Shah, E. O. Göbel, and K. Köhler, Appl. Phys. Lett. **57**, 19 (1990).
[8] 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).
[9] K. Leo, T. C. Damen, J. Shah, and K. Köhler, Phys. Rev. B **42**, 11359 (1990).
[10] R. T. Phillips, D. J. Lovering, G. J. Denton, and G. W. Smith, Phys. Rev. B (to be published).
[11] T. Yajima and Y. Taira, J. Phys. Soc. Jpn. **47**, 1620 (1979).
[12] C. Stafford, S. Schmitt-Rink, and W. Schaefer, Phys. Rev. B **41**, 10000 (1990).
[13] 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).
[14] B. F. Feuerbacher, J. Kuhl, R. Eccleston, and K. Ploog, Solid State Commun. **74**, 1279 (1990).