Giant Excitonic Resonance in Time-Resolved Four-Wave Mixing in Quantum Wells

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We report a strong (300:1) excitonic resonance in time-resolved (100 fs) four-wave mixing in GaAs quantum wells as a function of the incident photon energy and show that it results from the large difference in the dephasing rates of excitons and free carriers. We conclude that excitons dominate even when they make up only a small fraction of the excited states. These results, in conjunction with new results on exciton-phonon scattering, provide new insights into previous studies performed with spectrally broad ultrashort pulses.

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Interactions among excitons, free carriers, and phonons in quantum wells and bulk semiconductors have been intensely studied over the last decade using many techniques, among them the powerful methods of transient coherent spectroscopy. In the simplest of these coherent techniques [time-resolved two-pulse self-diffracted four-wave mixing (FWM)], two laser pulses propagating along $\mathbf{k}_1$ and $\mathbf{k}_2$ interfere in a sample to generate a transient polarization grating which diffracts photons into the background-free direction $2\mathbf{k}_2-\mathbf{k}_1$. Using this technique, the dephasing of excitons was first studied several years ago [1], and a number of elegant studies on excitons have been reported during the last two years. These include the observations of quantum beats of excitons [2–5], coherent interactions of excitons resulting in unexpected FWM signals [6], time-resolved photon echoes [7,8], and oscillatory FWM signals arising from coherent oscillations of an electronic wave packet in a double-well potential [9].

Free-carrier states can be thought of as being inhomogeneously broadened in momentum space, so that the FWM signal results primarily from photon echoes. By contrast, free-induction decay is observed in the case of selectively excited excitons in high-quality samples. In both cases, however, the time evolution still yields the dephasing rates. Pioneering coherent transient experiments in bulk GaAs [10] and GaAs quantum wells [11], with excitation pulses <10 fs, determined decay times ranging from 3.5 to 50 fs. These times were attributed to carrier-carrier scattering and information about the screening was deduced from their density dependence. Both these subjects are of considerable current interest in semiconductor physics. Despite the wealth of information obtained from these studies, some fundamental aspects of the physics remain uncertain. The extremely broad spectrum of an ultrashort pulse encompasses many different exciton and free-carrier transitions. Their relative contributions to the coherent transients play a crucial role in the interpretation of the results, but have not yet been investigated. Similarly, the role of phonons in the dephasing process, and its influence on the interpretation of the data, remains poorly understood because of the limited range of lattice temperature in most of the earlier studies.

In this Letter, we present FWM studies of the various scattering mechanisms in a GaAs/AlGaAs multiple-quantum-well (MQW) structure with 100-fs time resolution over a wide range of photon energies, temperatures, and excitation densities. Our most interesting findings are as follows: (1) The FWM signal shows a strong (300:1) resonance at the $n=1$ exciton. We conclude that the excitonic contribution to the FWM signal dominates even if only a small fraction of the excited states are excitons. (2) We present a theoretical calculation that explains the observed resonance and shows that it is primarily caused by the large ratio of exciton to free-carrier dephasing. (3) We show that both optic and acoustic phonons make an important contribution and must be considered before estimating exciton-carrier or carrier-carrier scattering rates. (4) After accounting for the phonon contributions, the dephasing rate depends linearly on the excitation density over a wide range of excitation densities and lattice temperatures, showing that screening is not an important factor, at least up to a density of 4×10^{10} cm^{-2}, the highest density investigated at 10 K.

The sample investigated was a 65-period 100/100-Å GaAs/AlGaAs MQW ($x=0.3$) grown on a n-doped [100] GaAs substrate. The substrate was removed to allow transmission experiments. A passively mode-locked Ti-sapphire laser with 100-fs pulses (20 meV bandwidth) and tunable between 780 and 860 nm was used for the FWM experiments [11]. Data were obtained by varying the temperature (10–300 K), excitation density (from 2×10^{8} to 4×10^{10} cm^{-2}), and photon energy. The average density was estimated by measuring the total power absorbed by the sample and the profile of the focal spot.

Figure 1 shows the FWM signal at zero time delay

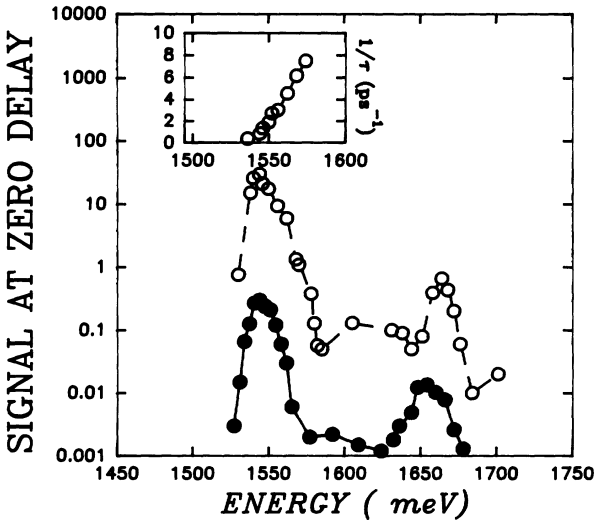

FIG. 1. The resonance profile of the FWM signal at zero time delay. The solid circles are taken at room temperature and the open circles represent data taken at 10 K; both at 2×10^{10} cm^{-2}. Inset: The decay rate vs excitation energy at 10 K, at 2×10^{9} cm^{-2}.

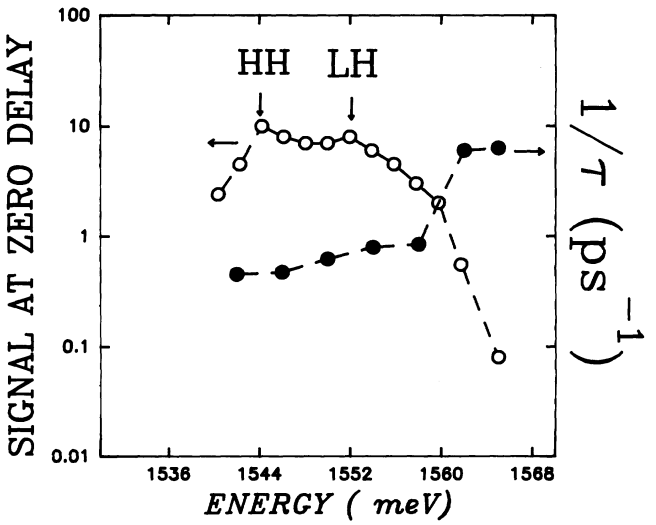

FIG. 2. The FWM signal at zero time delay and the decay rate vs excitation energy at 10 K, obtained with a laser pulse width of 500 fs (4-meV bandwidth).

versus incident photon energy at 300 K (solid circles) and 10 K (open circles). The 300-K curve is shifted on the energy axis so that the $n=1$ peaks overlap. The data clearly show a strong resonance at the $n=1$ exciton and another at the $n=2$ exciton. Heavy-hole and light-hole excitons are not resolved because the bandwidth of the laser exceeds the splitting between these excitons. Similar resonances are observed for other quantum wells and bulk GaAs. The decay rate ($1/\tau$) of the diffracted signal at 10 K (determined as discussed below), is plotted versus laser photon energy in the inset of Fig. 1, and shows a linear increase with excitation energy.

Figure 2 shows the FWM signal at zero time delay and the decay rate of the diffracted signal versus incident photon energy at 10 K. These data are obtained by limiting the laser bandwidth to 4 meV corresponding to 500-fs pulses. They show both heavy-hole and light-hole $n=1$ exciton resonances. The decay rate and the FWM signal remain nearly constant for excitation across the exciton resonances. Above the band-gap energy, there is an abrupt increase in the decay rate to a value limited by time resolution, and a coincident decrease in the FWM signal by about 2 orders of magnitude.

The inset of Fig. 3 shows a logarithmic plot of the diffracted signal at the $n=1$ exciton resonance versus time delay at 10 K (curve *a*) and 150 K (curve *b*). The decay rates, obtained from the exponential decay following the oscillations at early times (most likely due to heavy-light-hole exciton quantum beats [3,4]), show a strong temperature dependence. A plot of the decay rates $1/\tau$ versus excitation density (Fig. 3) shows essentially the same linear dependence on density at four different temperatures. By extrapolating the decay rates to the limit of zero density, we deduce the contribution of phonons to the dephasing. The results are shown in Fig. 4. The actual dephasing rates are related to the decay rate of the diffracted signal by $1/T_2=1/2\tau$ for a homogeneously broadened system, and $1/4\tau$ for an inhomogeneously broadened system.

Figure 1 clearly demonstrates that there is a giant FWM resonance at the exciton. The signal level out of resonance is about 300 times smaller than that on reso-

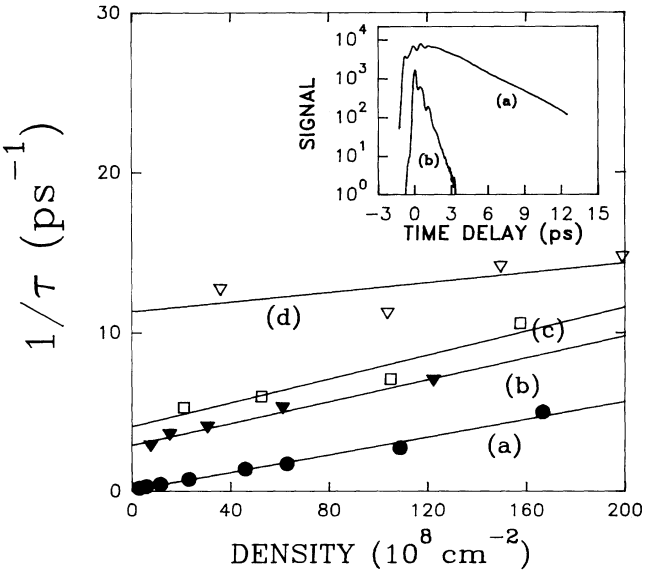

FIG. 3. The decay rate vs excitation density at 10 K (curve *a*), 150 K (curve *b*), 225 K (curve *c*), and 300 K (curve *d*). Inset: FWM signal at the $n=1$ exciton resonance vs time delay at 10 K (curve *a*) and 150 K (curve *b*). The exciton density is approximately 2×10^{9} cm^{-2}.

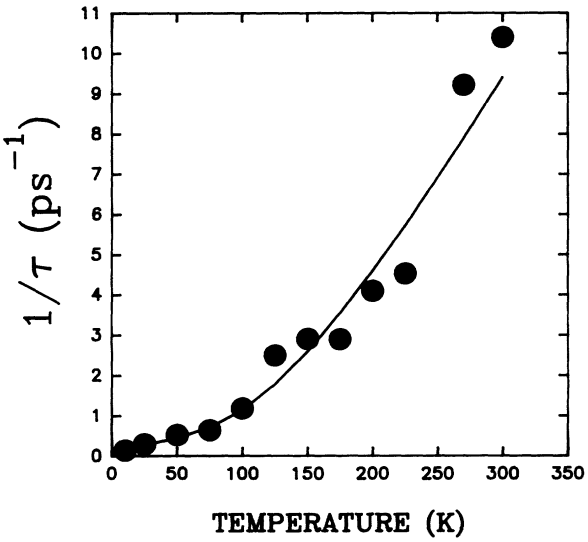

FIG. 4. The decay rate at the $n=1$ exciton resonance in the zero-density limit vs temperature. The solid line is a least-squares fit with $A=0.11$ ps^{-1}, $B=0.007$ ps^{-1}K^{-1}, and $C=21$ ps^{-1} (see text).

nance, at both 10 and 300 K. The observed resonance is much stronger than the square of the absorption coefficients (about 4 in cw absorption, but 1 for 20 meV bandwidth). In order to understand these results, we have calculated the strength of the FWM signal under various conditions, using the microscopic many-body theory of FWM in semiconductors described earlier [6]. For excitation with 70-fs pulses at the exciton resonance, and one binding energy above the band gap, we find the following results: (1) If the dephasing of the free-carrier states is taken to be the same as that of excitons (800 fs), then the diffracted signals at zero time delay for excitons and continuum are about the same (for spectrally narrow pulses a ratio of about 4 is obtained, as discussed above). (2) If, however, we assume that the free-carrier dephasing is 80 fs compared to 800 fs for excitons, then the calculated signal is 300 times stronger at the exciton than one binding energy above the band gap. While these numbers depend on the precise values of the parameters, it is clear that the difference in the dephasing rates is the primary cause of the observed resonance.

These results show that the correct way to view ultrashort-pulse FWM is to consider the time domain, where *the transition with the longest dephasing time eventually dominates, even if it is only weakly excited initially. Thus, the signal comes from excitons even when the laser excites many more free carriers than excitons.*

The nearly constant dephasing rate and FWM signal below the band gap, and the abrupt, coincident changes in these as the photon energy exceeds the band gap (Fig. 2), both give strong support to this interpretation. It is also reinforced by the other experimental observations reported here, such as the linear variation of the dephasing rate with excitation density (Fig. 3), and photon energy (inset of Fig. 1), which result from the dephasing of excitons by free carriers created by the high-energy part of the laser pulse. For a laser tuned far below the exciton resonance, the dephasing is determined by exciton-exciton scattering. Analysis of these results shows that the exciton-free-carrier interaction is 10 times stronger than the exciton-exciton interaction, in good agreement with the earlier work [1]. The $n=2$ resonance is weaker than that at the $n=1$ exciton because it is hybridized with the continuum states of the first subband. On the basis of these observations and discussion, we conclude that *for excitation centered either at the exciton energy or in the continuum, we measure the dephasing rate of excitons and not that of free carriers, as long as the exciting spectrum overlaps the excitonic region.*

The measured dephasing rates versus temperature provide an ideal means of determining the exciton-phonon scattering rates without other effects (such as inhomogeneous broadening and influence of other spectral features) which influenced earlier measurements of this important quantity. The zero-density decay rate shows a very strong temperature dependence (Fig. 4), varying from 0.1 to 10 ps^{-1} between 10 and 300 K. The linearity at low temperature plus the sharper increase at higher temperature suggest contributions from both acoustic and optic phonons. We fitted the temperature dependence using a phenomenological model, assuming for the decay rate $1/\tau = A + BT + Cn(T)$, where T is the lattice temperature, $n(T)$ is the thermal optic-phonon population, BT represents the acoustic phonon contributions, $Cn(T)$ represents the optic phonon contributions, and A denotes the rate at $T=0$. The best fit to the data is shown by the solid line in Fig. 4 (for parameters given in the caption). We deduce from this fit that at room temperature the dephasing rate ($1/T_2 = 1/2\tau$) is (950 fs)$^{-1}$ for acoustic phonons and (300 fs)$^{-1}$ for optic phonons. The latter value is in excellent agreement with the exciton ionization time at room temperature determined by the pump-probe method [12]. Our measurements show that acoustic-phonon contributions are also important, contrary to some earlier assumptions. The values we determine for $1/T_2$ are in good agreement with the scattering rates (750 fs)$^{-1}$ and (260 fs)$^{-1}$ calculated by Lee, Koteles, and Vassell [13] for scattering of heavy-hole excitons by acoustic and optic phonons, respectively.

These results have strong implications for the interpretation of the results obtained with 10-fs pulses [11] that excite an extremely broad region. Our results show that even if the exciting pulse creates a large number of free carriers and only a small number of excitons, the signal originating from excitons is likely to dominate because of the resonance discussed above. In this case, the measured decay is likely to correspond to the dephasing of excitons and not that of free carriers. Furthermore, phonon contributions as determined by us must be subtracted from

the measured rates before drawing any conclusions about the density dependence. Therefore, the earlier conclusions about the screening of carrier-carrier scattering in quasi-2D systems must be reexamined.

A possible approach for determining free-carrier dephasing times is to consider the FWM resonance profile (Fig. 1). If one could calculate the dependence of the free-carrier dephasing rate on the energy of the carriers and include this information in the calculation of the FWM signal as discussed above, then one could calculate the resonance profile. Comparison with experimental resonance data would then provide useful information about carrier dephasing rates in semiconductors. Our observation that the resonance at 300 K is as strong as that at 10 K implies that both the exciton and free-carrier dephasing times decrease with increasing temperature.

In conclusion, our four-wave-mixing measurements over a wide range of photon energy, temperature, and density have provided answers to previously unaddressed questions of fundamental importance. We observe a giant excitonic resonance and show that it results primarily from the large ratio of the dephasing times of excitons and free carriers. We conclude that excitons dominate the FWM signal even when they make up only a small fraction of the excited states. Our measurements at various temperatures and densities show that exciton dephasing varies linearly with the density of excitation as a result of exciton–free-carrier scattering. They furthermore enable us to determine exciton-phonon interaction and show the importance of both acoustic and optic phonons in exciton dephasing. These results lead to a reinterpretation of the earlier results obtained with spectrally broad 10-fs pulses. Finally, the resonance profile may provide a means of determining the carrier dephasing rates.

The sample for which detailed results are presented here is the same used by Knox *et al.* [12]. We thank W. H. Knox for the loan of this sample and for helpful discussions, J. E. Henry for the processing, K. W. Goossen for general help with sample processing, and D. A. B. Miller for discussions.

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