Excitonic signatures in the photoluminescence and terahertz absorption of a GaAs/$Al_xGa_{1-x}As$ multiple quantum well

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Measurements of the THz absorption and the time-resolved photoluminescence have been performed on the same GaAs quantum well sample. The strength of the absorption at the internal 1*s*-2*p* exciton transition frequency is used as a measure of the density of excitons in the sample. When the interband pump laser is resonant with the 1*s* exciton frequency, induced absorption at the 1*s*-2*p* frequency is clearly seen. If the same density of carriers is created pumping in the continuum, no significant 1*s*-2*p* absorption is seen in a time window of 450 ps. Complementary time-resolved photoluminescence experiments, detecting the emission at the exciton energy under the same pump conditions, show the PL intensity in resonant and nonresonant cases to be similar. The counter-intuitive existence of luminescence at the exciton energy simultaneously with the absence of the 1*s*-2*p* absorption is consistent with the recent theoretical predictions of Kira *et al.*, Phys. Rev. Lett. **81**, 3263 (1998).

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Excitons, i.e., hydrogenlike bound states of electrons and holes, play a central role in the band-edge optical properties of semiconductors. This is especially so in quantum well systems where the confinement to two dimensions increases the exciton binding energy, and indeed in some materials the 1*s* binding energy can exceed k_bT at room temperature. The experimental measurement of exciton dynamics however is often indirect and the photoluminescence (PL) at the exciton frequency is taken to indicate the presence of excitons with center of mass momenta within the light cone. One example of this is the determination of the formation time of excitons from a free carrier plasma.[1–8]

Recently, the intuitive notion that a peak in the PL spectrum at the exciton frequency indicates a population of bound excitons in the light cone has been called into question. Kira *et al.*[9] studied a microscopic model of a plasma of *unbound* electron-hole pairs, which included Coulomb correlations but not the possibility of formation of incoherent excitons. They found that within this model a sharp peak in the PL spectrum developed as the carriers relaxed to the bottom of their respective bands. Support for this view was obtained by Oestreich *et al.*[10] who traced the electron-hole exchange energy in photoexcited quantum wells as a function of magnetic field. They observed a gradual change from excitons to a free electron-hole plasma as the excitation power is increased from 4 mW to 20 mW but saw at all powers the PL emission at the magnetoexciton line.

As time-resolved photoluminescence (TRPL) is a very widely used technique it is essential to understand the relationship of an electron-hole gas to its emitted spectrum and hence the inferences which can be confidently drawn from the photoluminescence. In a recent paper Kaindl et al[11] used the measured terahertz absorption spectrum to determine the formation time of excitons following nonresonant injection of a density of 10^{10} cm^{-2}. They found that the 1*s*-2*p* absorption peak is fully developed after 1 ns and has a linewidth of around 2 meV. Another recent study by Chatterjee[12] examined deviations from the Kubo-Martin-Schwinger relation in both PL spectra and microscopic calculations to deduce the influence on the PL of both bound and unbound electron-hole contributions.

In this paper we present both TRPL and terahertz absorption results, and find that indeed PL at the exciton energy can be produced without the simultaneous coexistance of a 1*s*-2*p* absorption, as predicted by Kira.[9] First we perform both resonant and nonresonant TRPL to measure the onset of PL at the exciton energy. Second, under essentially the same excitation conditions, we directly detect the presence of excitons around $\mathbf{K}=0$ by measuring the 1*s*-2*p* absorption transition using a far infrared free electron laser. From the time dependence of these two signals we can identify whether or not there is a correlation between the PL signal and the presence of an excitonic population around $\mathbf{K}=0$.

The sample is a GaAs/AlGaAs multiple quantum well with 120 wells of 6.5 nm width. The barrier width is 8 nm. The GaAs substrate was chemically etched to enable transmission measurements which show clear heavy and light hole exciton absorption peaks at 1.594 eV and 1.615 eV, respectively (Fig. 1). All experiments reported in this paper were performed in a continuous flow helium cryostat at 4 K.

The TRPL measurements used a microscope based instrument[13] with two passively *Q*-switched picosecond AlGaAs lasers providing for resonant or nonresonant excitation. The laser beam was focussed on the sample to a roughly

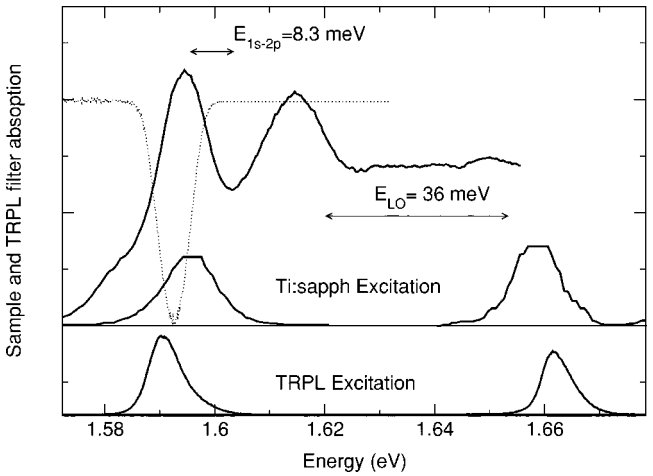

FIG. 1. Linear absorption spectrum of the sample (upper solid curve). Also shown are the spectra of the interband pump pulses. The dotted line depicts the spectrum of the bandpass filter used in the TRPL.

circular spot of 14 μm diameter, the pulse duration was $\approx$15 ps. The pulse spectra are shown in Fig. 1. The detector was a developmental, actively quenched single photon avalanche diode (SPAD).[14] The setup uses the time-correlated single photon counting technique, and the TRPL overall instrument response [full-width at half-maximum (FWHM) $\approx$100 ps] is shown in Fig. 2. Photon energy discrimination of the nonresonant PL was provided by a combination of interference filters which gave a narrow passband at the exciton PL energy of 1.593 eV (see Fig. 1). Care was taken to minimize the reflected signal of the pump laser by using oblique incidence and a knife-edge as a beam-block. A polarizing beam splitter in front of the detector further reducing the back scatter from the pump. Using measurements of the pump spectrum and the optical density, the pump fluence was adjusted to give a carrier density of $\approx 2\times 10^9$ cm^{-2} for both resonant and nonresonant pumping.

The TRPL results are shown in Fig. 2. For the resonant case there is some breakthrough of the pump laser but after

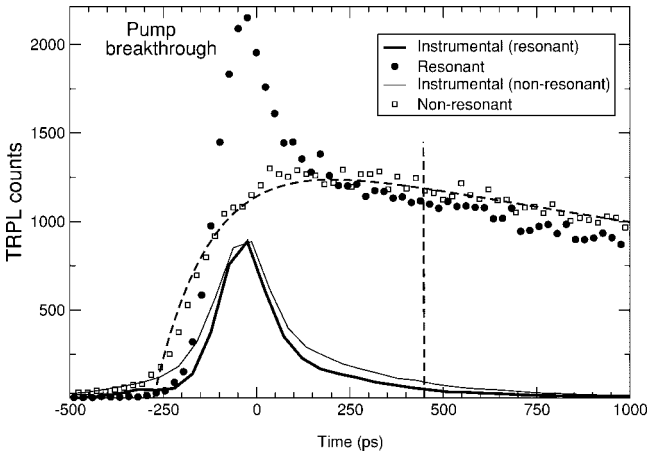

FIG. 2. TRPL counts at the exciton frequency as a function of time and the instrumental response profiles. The dashed line is a biexponential least squared fit as described in the text.

$\approx$100 ps both resonant and nonresonant decays are essentially equal. The area under the resonant spike contributes a negligible 6% of the total PL counts. We have fitted the nonresonant TRPL time profile with the sum of two exponential contributions, a rise of 160 ps for the buildup of the necessary conditions for PL at the exciton frequency and a 3 ns decay for the emission process itself. Measurements were also done at a range of fluences from 0.5 to 2 times the value for the data presented here. The risetime of the TRPL was found to be unchanged in this power range.

We now consider the interband/intraband pump probe measurements. In contrast to the interband optical properties of semiconductors which are relatively well understood (see, e.g., Refs. 15–17 and references therein), the theory of photon-excited intraband transitions has been studied much less extensively. An equilibrium Green's function approach has been developed,[18] but at high densities the theory becomes intractable, and at low densities it reduces to a simple Fermi's golden rule result. More recently, results on the THz absorption of a sample in a photonic environment have been obtained using the equation of motion for four point excitonic correlations.[19,20] One can obtain useful information on the THz absorption spectra from a calculation, based on Fermi's golden rule for an ensemble of 1s excitons. We include transitions from a population of 1s excitons to all p states, both bound and continuum. Transitions to other states are forbidden by conservation of angular momentum. The required two-dimensional (2D) excitonic wave functions are well known,[15] and the THz absorption coefficient is then

$$\alpha_{\mathrm{THz}}(\omega) = \alpha_0(\omega)[\mathcal{S}_{\mathrm{B}}(\omega) + \Theta(\hbar\omega/E_{\mathrm{Ry}})\mathcal{S}_{\mathrm{C}}(\omega)],$$

$$\mathcal{S}_{\mathrm{B}}(\omega) = \frac{1}{8}\sum_{n=2}^{\infty}\left[\frac{(n-1)^{2n-5}(2n-1)^5}{n^{2n+3}} \times \delta\left(\frac{\hbar\omega}{E_{\mathrm{Ry}}} - 4 + \frac{1}{(n-(1/2))^2}\right)\right],$$

$$\mathcal{S}_{\mathrm{C}}(\omega) = 288\frac{\left|F\left(\frac{3}{2} + \frac{i}{\mathcal{K}(\omega)};4;3;\frac{1}{(1/2)-(i/\mathcal{K}(\omega))}\right)\right|^2}{(4+\mathcal{K}(\omega)^2)^3\left(1+\exp\left(-\frac{2\pi}{\mathcal{K}(\omega)}\right)\right)}.$$

Here, $\mathcal{S}_{\mathrm{B}}$ is due to transitions between the 1s and bound p states, $\mathcal{S}_{\mathrm{C}}$ is due to transitions to continuum states, $\alpha_0(\omega) = \pi^2 n_0 e^2 a_B^2 \omega/(8E_{\mathrm{Ry}} n_B c)$, n_0 is the exciton density, e the charge on an electron, a_B the exciton Bohr radius, E_{Ry} the exciton Rydberg and c the speed of light. $F(a,b;c;z)$ is the hypergeometric function, $\Theta(x)$ is the Heaviside step function and $\mathcal{K}(\omega) = \sqrt{(\hbar\omega/E_{\mathrm{Ry}}) - 4}$. We note that as in the interband case, the absorption due to transitions to exciton p states merges smoothly into the continuum at the band edge.

We show in Fig. 3 the results of our calculation for a variety of phenomenological broadenings. The energy scale has been adjusted from the pure two-dimensional value to account for the finite well width in the sample. There is a sharp resonance at the 1s-2p energy for FWHM broadenings below about 1 Rydberg (approximately 4.5 meV in GaAs).

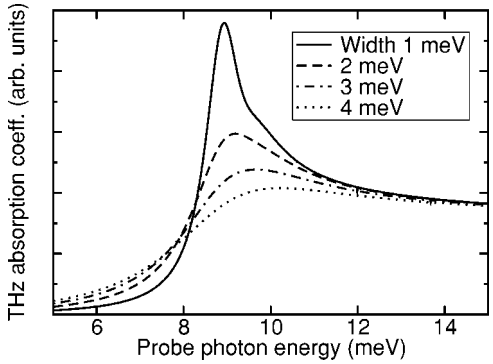

FIG. 3. Theoretical THz absorption spectrum of an ensemble of GaAs quantum well 1*s* excitons for a range of different broadenings. The linewidth quoted refers to the FWHM of a single absorption line.

We expect the inhomogeneous broadening of the 1*s*-2*p* peak due to well width fluctuations, etc., to be less than that of the exciton features in the interband spectrum, as such fluctuations alter the exciton binding energies less than the band gap. This is confirmed by broadband THz measurements in which a FWHM linewidth of around 2 meV was found for a similar system of 50 quantum well periods.[21] Thus we can reliably use the induced absorption at the 1*s*-2*p* transition energy as a signature of the presence of bound states in the electron hole plasma.

The two-color pump-probe absorption measurements were performed at the Dutch Free Electron Laser Facility (FELIX) with a 100 fs, 75 MHz Ti:sapphire laser as the tunable excitation source and the free electron laser as the far-infrared (FIR) probe. The Ti:sapphire laser was electronically synchronized to the free electron laser.[22] FELIX operates with macropulses of typically 4 μs width at a repetition rate of 5 Hz. The macropulse consists of a train of micropulses, each with duration 15 ps, and with a pulse separation of 40 ns. The repetition rates of the probe and pump pulses are in the ratio 1:3 but every probe pulse overlaps in time with a pump pulse. To reduce the effect of probe pulse fluctuations an identical reference was taken from the probe beam with a beam splitter, delayed by 20 ns and recombined colinearly with the probe. The reference pulse passes through the same part of the sample but arrives 6.7 ns later than the previous pump pulse (by which time the PL from the sample has almost completely decayed, see Fig. 2). By reversing the bias of the probe detector at 50 MHz the time-averaged output of the detector was thus balanced to zero unless the pump pulse causes a change in the transmission of the probe pulse relative to its reference copy.[23]

The pump beam and the probe/reference beam were focussed on the sample with a $f=7.25$ cm parabolic mirror resulting in spot sizes of 800 μm and 900 μm, respectively. An 800 μm aperture was placed close to the sample to ensure full overlap of the pump and probe beams at the sample. The probe and reference pulse fluences at the sample were estimated to be 3 $\mu J\,\mathrm{cm}^{-2}$ each. The sample was cooled in a continuous flow helium cryostat and the whole experiment including the cryostat was set in a box purged with nitrogen,

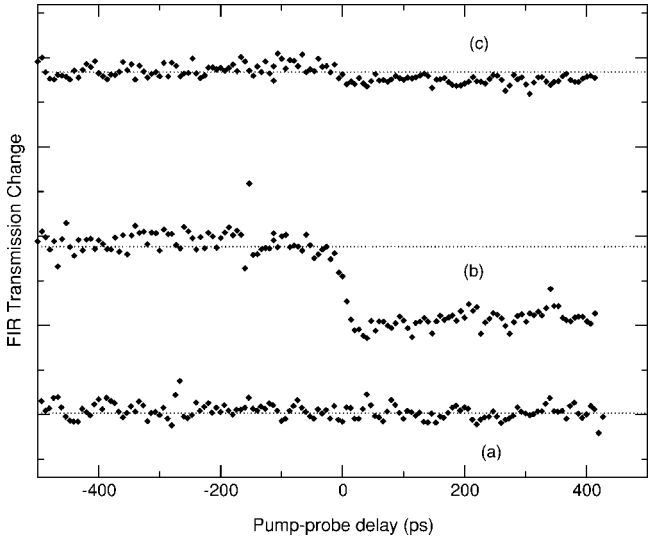

FIG. 4. Transmission change of the FIR probe pulse as a function of pump-probe delay. The pump is tuned at (a) 1.560 eV (below resonance), (b) 1.596 eV (on resonance), (c) 1.658 eV (above resonance). The traces have been offset vertically for clarity.

as there is strong water absorption at these wavelengths. The spectral width of the pump pulses was 10 meV.

It is important, in order to meaningfully compare the TRPL and the pump-probe results, that the number of photoexcited electron-hole pairs be the same in both experiments. In such short pulse experiments the carrier density is determined by the fluence and thus the laser power at the sample was adjusted to have the same fluence in both the pump-probe and TRPL experiments thereby generating the aforementioned pair density of $\approx 2\times 10^9\ \mathrm{cm}^{-2}$.

We characterized the 1*s*-2*p* transition by measuring the transmission change of the FIR pulse as a function of the delay between pump and probe for various values of the interband pump photon energy. The probe wavelength of 150 μm (8.3 meV, 2.0 THz) was chosen at the center of the 1*s*-2*p* absorption line. As can be seen in Fig. 4 when pumping at 1.56 eV, well below the interband exciton peak, no change in transmission was seen. This null result is an important one as it confirms that residual coherent interactions do not give rise to a measurable signal. When pumping directly into the exciton resonance, curve (b), a strong induced absorption was seen immediately after the pump pulse. This reflects the creation of geminate excitons and their subsequent excitation by the FIR pulse from the 1*s* to the 2*p* state. This induced absorption was long-lived, showing little decay over the 500 ps window afforded by the FEL setup, consistent with the decay seen in the TRPL.

As shown in curve (c), with the pump energy tuned to 1.658 eV as in the TRPL experiment, the absorption change becomes very small with no delay in the onset of absorption within the accuracy of the experiment ($\approx$7 ps). Neither is there any measureable evolution of the induced absorption during our 450 ps measurement window. Tuning the interband pump between curves (b) and (c) in Fig. 4 resonantly excites a significant fraction of light hole excitons which complicates the interpretation and we do not address these measurements here.

We now discuss the conclusions we can draw from Figs. 2 and 4. The main observation lies in the discrepancy between the TRPL and the FIR transmission measurements well after the pump pulse. For the TRPL detected at the exciton energy, both resonant and nonresonant signals are essentially equal after $\approx$100 ps, whereas the induced absorption at the 1*s*-2*p* energy is at least eight times larger for resonant than for nonresonant pumping. Thus the PL at the exciton energy and FIR transmission at the 1*s*-2*p* energy cannot both be reliable signatures of the presence of 1*s* excitons within the light cone.

Previous TRPL measurements[1–5] suggested that after nonresonant excitation, hot excitons with a finite center of mass momentum are created in $\sim$20 ps by emission of an LO phonon. These dark excitons then slowly relax along the exciton dispersion via acoustic phonons to the $\mathbf{K}=0$ state from where PL emission occurs. In a simple picture such excitons would induce an FIR absorption regardless of their center of mass momentum and would hence contribute to the induced absorption signal seen in the nonresonant pumping measurement. A more detailed examination shows that the 1*s*-2*p* energy is itself dependent on the exciton center of mass momentum,[24] increasing by about 1 meV in our case. Given that, the FIR probe is no longer fully resonant with this transition, from our measurements we cannot make any firm conclusions about the formation or otherwise of such hot excitons. However we note that hotexcitons, having a large center of mass momentum would in any case not contribute to the measured PL.

The residual absorption seen on curve (c) of Fig. 4 is about 13% of the signal in the resonant case. This could arise from the 1*s*-2*p* transitions of any nongeminate heavy-hole excitons formed from the plasma. These may be either within the light cone around $\mathbf{K}=0$ or, more likely, distributed over the exciton dispersion. By comparison with the resonant signal the total population of such excitons would be around 10% of the injected population. However, were this to be the case, we would expect the PL intensity to be accordingly reduced by a factor of at least 10 compared to the resonant case which is not what is observed. We conclude from this that the PL we are detecting at the exciton energy in the nonresonant pumping case arises from the majority of the injected population and not from a small fraction thereof.

Our observations are consistent with the proposal of Kira *et al.*[9] that uncorrelated plasma terms provide a source for PL at the exciton energy.

Further support comes from the 160 ps risetime of the TRPL in the nonresonant case. No such rise is seen in the nonresonant, induced absorption signal which appears promptly with the pump pulse. Thus this TRPL rise, which is often interpreted as the formation time of excitons in not accompanied by a concomitant rise in the FIR induced absorption at the 1*s*-2*p* energy.

The residual prompt absorption seen on curve (c) of Fig. 4 may have other contributions which are difficult to separate. One contribution will come from Drude-type free carrier contributions[11] and a second from 1*s*-2*p* transitions of light hole excitons which have been populated from the tail of the pump spectrum via LO-phonon emission.

In conclusion we have provided experimental evidence in support of the remarkable prediction of Kira *et al.*, that PL at the exciton energy may be observed *without* the existence of an excitonic population at $\mathbf{K}=0$.

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