Resonant Femtosecond Emission from Quantum Well Excitons: The Role of Rayleigh Scattering and Luminescence

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(Received 9 December 1996)

We study the ultrafast properties of secondary radiation of semiconductor quantum wells under resonant excitation. We show that the exciton density dependence allows one to identify the origin of secondary radiation. At high exciton densities, the emission is due to incoherent luminescence with a rise time determined by exciton-exciton scattering. For low densities, when the distance between excitons is much larger than their diameter, the temporal shape is independent of density and rises *quadratically*, in excellent agreement with recent theories for resonant Rayleigh scattering. [S0031-9007(97)02590-8]

PACS numbers: 78.35.+c, 71.35.–y, 78.47.+p, 78.66.–w

Since the early work of Wannier and Hopfield it has been widely accepted that excitons are the fundamental excitations of a direct semiconductor which interact with light under conservation of momentum [1,2]. In quasi-two-dimensional systems such as quantum wells (QWs), due to the broken translational symmetry, excitons with in-plane momenta $\mathbf{K}_{\parallel}$ smaller than the wave vector of light couple to a continuum of photon modes [3], which results in a picosecond decay of the excitonic luminescence [4].

A fundamental issue is to understand the formation, i.e., the temporal rise, of secondary radiation (SR) in directions other than those of the reflected and transmitted laser beam. SR includes disorder-related Rayleigh scattering [5,6] which is coherent with the excitation and incoherent luminescence from excitons which have experienced energy or phase relaxation [7]. First femtosecond experiments under resonant excitation have revealed a finite rise time of SR [8] which shortens for high exciton densities when exciton-exciton (X-X) and exciton-free carrier scattering are important. As interface disorder has been neglected, excitons were assumed to be plane wave states, and the emission has been attributed solely to luminescence. In this approximation, the rise time is a consequence of momentum and energy conservation, which require that excitons have to change momentum before they can emit in directions different from the excitation beam.

It is well known, however, that QW interfaces have a finite roughness, which shows up in steady-state spectra as an inhomogeneous broadening of the excitonic transitions [9]. Recent theories which account properly for interface disorder have pointed out that resonant Rayleigh scattering (RRS) from QW excitons does not rise within the excitation pulse but exhibits, like luminescence (PL), a finite rise time [10,11]. It has been predicted, however, that the initial Rayleigh signal increases quadratically in time [10,11], unlike luminescence which rises linearly. Furthermore, as RRS is related to static disorder, its temporal shape does not depend on the exciton density. Both properties of RRS have not yet been observed. The different temporal evolution could then be used to differentiate between PL and RRS. The main difficulty is that the exciton density has to be sufficiently low so that the excitonic interference only evolves due to the inhomogeneous broadening and is not perturbed by inelastic dephasing processes (X-X scattering) which would lead to luminescence.

In this Letter, we investigate thoroughly the effect of exciton density on the femtosecond SR under resonant excitation for the first time. Thanks to improved detection techniques we can change the exciton density by 3 orders of magnitude, down to a few 10^8 cm^{-2}. This enables us to see that the origin of the emission changes gradually as the exciton density is lowered: luminescence of rapidly dephased excitons at high densities and Rayleigh scattering due to interface disorder at lowest densities. At the lowest exciton densities we indeed observe a quadratic rise of the secondary emission and a temporal shape which is density independent. The temporal features in the low-density regime are well explained by a classical model of RRS in a quantum well with interface roughness [10].

Femtosecond time resolution of resonantly excited SR is achieved by frequency up-conversion in a two-color experiment using the 1.5 μm output of a synchronously pumped parametric oscillator as the gating beam. The temporal and spectral resolution are 150 fs and 12 meV, respectively. We used a liquid nitrogen cooled charge-coupled device (CCD) for detecting the sum frequency signal, providing high sensitivity and low background signal [12]. We have studied a variety of high quality GaAs multiple QWs with well thicknesses between 100 and 220 Å, and 70 Å barriers of $Al_{0.4}Ga_{0.6}As$ or AlAs.

 0031-9007/97/78(11)/2228(4)$10.00

These samples show narrow PL linewidths and very small Stokes shift (0.6 and 0.1 meV, respectively, for the 180 Å sample), as measured by PL excitation (PLE). The spectral width of the exciting fs pulses is 18 meV. The laser spectrum is centered 6–8 meV below the heavy-hole (hh) resonance to minimize generation of free carriers, but it excites the heavy- and light-hole 1*s*-exciton states simultaneously in most samples. The exciton densities are estimated assuming 10% max absorption per well for a hh exciton and taking into account the finite spectral width of the exciton line. All measurements were performed at $T = 10$ K. We used circularly polarized light (no creation of biexcitons), and excitation and detection were copolarized for all spectra shown here.

Figure 1 shows the time-resolved emission of GaAs MQWs with different widths. All transients exhibit three distinct features on a 40 ps range (inset Fig. 1). The peak at zero delay stems from laser light scattered at the sample surface and demonstrates the temporal resolution. The long, nearly exponential decay is observed in all samples with a slightly sample dependent decay time (16–25 ps). These decay times are very similar to those observed in resonant excitation experiments with ps time resolution and are related to the radiative decay of hh excitons [4]. The dominant signal, observed within the first 10 ps, is accessible here only thanks to the fs time resolution. It is more than 95% circularly copolarized with the exciting laser and would therefore not be distinguished from laser scatter in ps experiments. Pronounced oscillations are observed (Figs. 1 and 2) which are identified as quantum beats between the heavy- and light-hole exciton 1*s* states, as also reported in [8]. The beat frequency ν_{HL} corresponds exactly to the exciton splitting Δ_{HL} observed in PLE spectra (130 Å QW: $\nu_{\mathrm{HL}} = (490\,\mathrm{fs})^{-1}$ and $\Delta_{\mathrm{HL}} = 8.3$ meV). The visibility decay (damping of the relative beat amplitude) provides valuable information about the coherence between both exciton states.

We will concentrate now on the effect of exciton density n_X on the temporal shape of the emission [Fig. 2(a)]. At high densities ($n_X \geq 2 \times 10^9$ cm^{-2}) we observe a decrease of the rise time of the SR when the exciton density is increased, which is in agreement with [8]. The temporal shape can be approximated by the following double-exponential function with rise and decay times τ_R and τ_D, respectively, and a beating part with a visibility decay time τ_{HL}, and amplitude a,

$$I_{\mathrm{PL}}(t) \propto \frac{e^{-t/\tau_D}}{\tau_D - \tau_R}\,(1 + a\,\cos\nu_{\mathrm{HL}} t e^{-t/\tau_{\mathrm{HL}}})\,. \quad (1)$$

The temporal shape is found to be strongly dependent on the exciton density. First, the rise and decay times, which are almost equal at any density, shorten when n_X is increased [3.2 to 2.2 ps for the densities indicated in Fig. 2(a)]. Second, the beat visibility decay time τ_{HL} reduces to 5 ps for the highest densities ($n_X \geq 5 \times 10^{10}$ cm^{-2}) indicating a loss of coherence between the heavy- and light-hole excitons.

Important information is also provided by the time-resolved reflectivity [Fig. 2(b)] which shows an increasing decay time when the exciton density is decreased. The reduction of the decay time of the reflectivity demonstrates that homogeneous broadening dominates the exciton response for $n_X \geq 5 \times 10^9$ cm^{-2}. When the emission in scattered directions is detected time integrated, allowing for a better spectral resolution, we observe actually a line broadening for an initial density of $n_X \geq 2 \times 10^{10}$ cm^{-2}

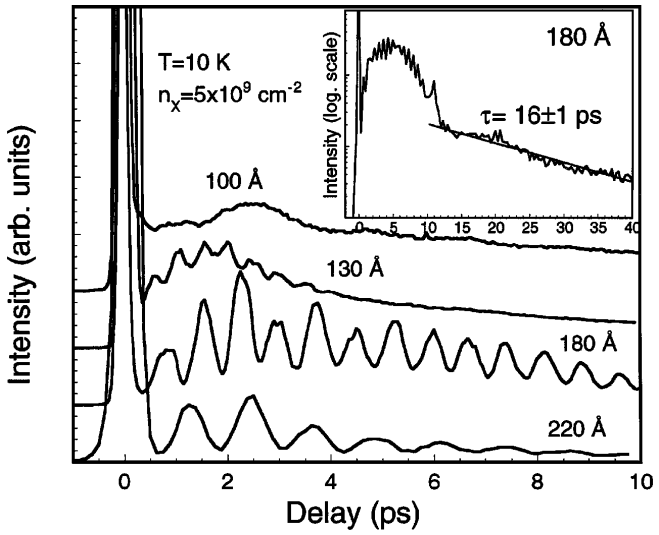

FIG. 1. Time-resolved emission at 10 K for different well widths measured with excitation and detection circularly copolarized. The period of the quantum beats decreases with increasing heavy-light-hole exciton splitting for smaller well widths. Inset: Time-resolved emission from a 180 Å MQW showing the excitonic radiative decay at long times.

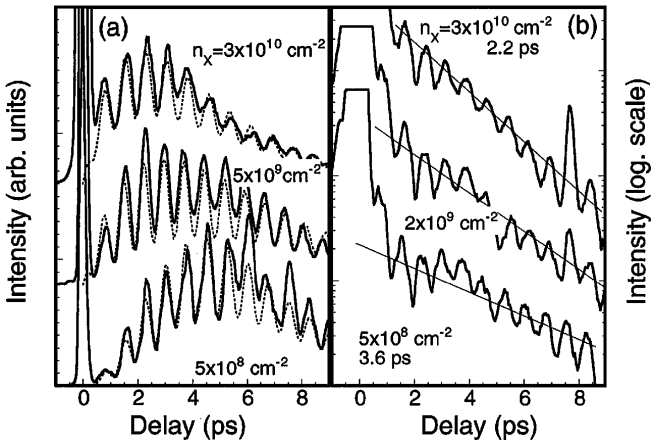

FIG. 2. (a) Effect of exciton density on the time-resolved emission of the 180 Å quantum well. The maximum of the emission is shifted to longer times when the exciton density is lowered. The experimental data (thick lines) are compared with the theory discussed in the text (dotted line). (b) Time-resolved reflectivity showing a reduction of the decay time for increasing exciton density.

[13]. We can therefore conclude that the emission at $\mathbf{K}_\parallel \neq \mathbf{K}_\parallel^{\mathbf{0}}$ stems from "dephased" excitons and is attributed to luminescence in agreement with [8]. The decay and rise times are then interpreted as scattering times out and into the in-plane $\mathbf{K}_\parallel$ states from which the emission is collected. In particular, the decay time of reflectivity (excitons leaving $\mathbf{K}_\parallel^{\mathbf{0}}$) and the rise time of luminescence (scattering into $\mathbf{K}_\parallel \neq \mathbf{K}_\parallel^{\mathbf{0}}$) must be equal in this picture, as we do observe. The luminescence decay time is presumably given by scattering to larger momenta $K_\parallel$ which are out of the detection cone or nonradiative. Note the linear rise of the signal [Figs. 2(a) and 3(a)].

However, for smaller exciton densities ($n_X \leq 1 \times 10^9$ cm^{-2}) a new effect is observed: The transient is nearly independent on n_X [Fig. 3(a)] and rises quadratically in time. The quadratic rise is more obvious in Fig. 3(a) where we have plotted the data without hh-lh exciton beats. The smoothed curves are obtained by Fourier transforming the raw data (after removing the $t = 0$ peak), filtering the beat frequency component, smoothing in the frequency domain, and transforming back into the time domain. The change from a linear to a quadratic rise opens a new regime of exciton scattering which requires a completely different description. Note also that $n_X \leq 1 \times 10^9$ cm^{-2} corresponds to a distance between excitons of roughly 300 nm, an order of magnitude larger than the Bohr diameter, so that *X*-*X* scattering is no longer important. Interaction of excitons with interface roughness is now the relevant process, as acoustic phonon scattering can be neglected for the low temperatures used. Regarding the heavy-hole/light-hole exciton beats, the visibility decay time is increased to $\tau_{\mathrm{HL}} = 25 \pm 5$ ps at the lowest densities. We will show that this rather long value is also explained by disorder effects and not any longer by excitonic dephasing.

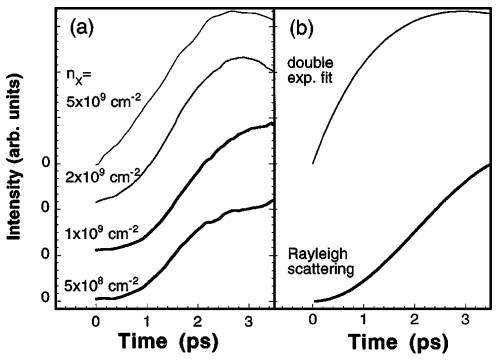

FIG. 3. (a) Rise behavior of the secondary radiation for different exciton densities. For clarity, the hh-lh exciton beats are removed and the curves are shifted vertically (note respective zeros). The rise changes from linear to quadratic in time when the exciton density is $n_X \leq 1 \times 10^9$ cm^{-2}. (b) Comparison of the temporal rise of RRS [Eq. (2)] relevant for the lowest exciton densities and the double-exponential function with $a = 0$ [Eq. (1)] used for the fit of the high-density data.

An intuitive explanation for the origin of the density-independent rise time is given as follows. Because of localization, excitonic eigenstates are linear combinations of in-plane momenta $\mathbf{K}_\parallel$. The incident plane wave, representing the pulsed excitation, is now imprinted in the QW by a superposition of the spatially distributed and weakly localized excitons. Initially, the excitonic eigenstates interfere such that light is emitted only in the reflected and transmitted directions. The excitonic superposition subsequently evolves with time according to the different exciton frequencies (inhomogeneous broadening). After a time, which is determined by the inverse of the inhomogeneous linewidth, excitonic interference leads to an increase of the emission into scattered directions, before the signal decays again. This is the picture of RRS under excitation of the whole inhomogeneous linewidth [11].

Another interesting observation is that the temporal behavior of the secondary emission is independent of the external observation angle, explored within our detection cone which corresponds to a light cone of $\pm 5°$ inside the sample. This finding is also consistent with Rayleigh scattering if we assume that the exciton localization length ζ does not exceed the wavelength λ/n and is of the order of 100 nm [6,10]. The small Stokes shift and the short PL decay time are consistent with a long ζ. Weak localization is indeed expected for a 180 Å QW [14]. In this respect, the present study is quite different from previous work on transient RRS [6] performed on samples with much stronger localization effects.

We will show in the following that our observations for the *lowest densities* are explained in a classical description of Rayleigh scattering based on interface roughness [10]. Assuming an excitonic center-of-mass potential $V(\mathbf{R})$ which reflects the local well width variations, with spatial correlation $\langle V(\mathbf{R})V(\mathbf{R}')\rangle = \hbar^2 g_{\mathbf{R}-\mathbf{R}'}$, the final expression for the scattered intensity reads

$$I_{\mathrm{RS}}(t) \propto \Theta(t)\mu^4 \exp(-t^2\sigma^2) \int d^2\mathbf{R}[\exp(g_{\mathbf{R}}t^2) - 1], \tag{2}$$

where μ^2 is the exciton oscillator strength. The evaluation of the integral leads to the quadratic rise of the signal, in clear contrast to the linear rise of the biexponential function which fits the high-density data [Figs. 3 and 2(a)]. The actual rise and decay of the signal is entirely given by the variance $\sigma^2 = g_{\mathbf{R}=\mathbf{0}}$. For a Gaussian correlation $g_{\mathbf{R}} = \sigma^2 \exp(-R^2/2\xi)$, the signal has a maximum at $t_{\max} \approx 1.2/\sigma$. The variance is related to the inhomogeneous absorption linewidth $\delta = \sqrt{8 \ln 2}\,\hbar\,\sigma$. If light-hole excitons are included in Eq. (2), the beating term and its visibility decay is related to the nonvanishing cross correlation function $g_{\mathbf{R}}^{\mathrm{HL}}$ defined in [10]. In particular, if the center of mass potentials $V(\mathbf{R})$ of hh and lh excitons were perfectly correlated the beats would not be damped at all ($\tau_{\mathrm{HL}} \rightarrow \infty$).

The comparison with the low-density spectra is performed including the light-hole 1*s* exciton [10], and the result is displayed in Fig. 2(a) as the lowest dashed curve. The beating amplitude is well reproduced taking into account the respective oscillator strengths and the amount of hh and lh excitons excited. The value of σ used to fit the temporal shape is only about half as large as the inhomogeneous linewidth observed in PLE. The discrepancy is probably related to the fact that PLE is not identical to absorption (relaxation processes, photon reabsorption). Nevertheless, comparing the QWs with different thicknesses, a larger PLE linewidth always leads to a shorter rise of the secondary emission.

Even though we can entirely explain the main features found at the lowest densities with the model of resonant Rayleigh scattering, we still need to show that luminescence is unimportant on these short time scales. This issue has been discussed quite controversially, in particular from a theoretical point of view [6,7,10]. However, we have enough experimental information to show that inelastic dephasing (leading to luminescence) is inefficient for the lowest densities at early times. First, the time-resolved reflectivity shows that homogeneous broadening due to *X*-*X* scattering is indeed strongly reduced at $n_X = 5 \times 10^8$ cm^{-2}. Second, four-wave-mixing experiments on free excitons in high-quality GaAs QWs at low temperatures and exciton densities below 10^9 cm^{-2} have revealed phase relaxation times of $T_2 = 2$-3 ps [15]. As T_2 is mainly determined by *X*-*X* scattering (even at low densities), these processes start to be dominant only at times later than T_2. As a consequence, we can attribute the rising part of the secondary emission mainly to RRS [7]. PL will appear in the secondary radiation at later times. Finally, an additional way to identify RRS would be to probe the phase relation of the emission with respect to the exciting pulse by a more complex interferometric experiment.

In conclusion, we have shown that resonant Rayleigh scattering and luminescence can be differentiated by their different dependence on the exciton density. In the high-density case, rapid excitonic dephasing leads to luminescence characterized by a density-dependent rise behavior. In contrast, in the low-density regime the temporal shape of the secondary emission is density independent, and the rise is quadratic in time. The transition between both regimes occurs when the inter-excitonic distance is roughly ten times the Bohr diameter. All temporal features observed in the low-density regime are in perfect agreement with our theory describing RRS. The rising edge of the secondary emission is dominated by RRS at low exciton densities.

The authors acknowledge helpful discussions with M.-A. Dupertuis, V. Savona, P. E. Selbmann, R. Stanley, and J. Shah. We are grateful to A. Regreny for the sample growth. The work is supported by the Fonds National Suisse pour la Recherche (Contract No. 2100-040345.94), by EEC/OFES (CHRX. CT93-0133/OFES 93-0332), and by the Swiss Priority Program Optics (Contract No. 322).

Note added.—It has been shown recently that resonant Rayleigh scattering and luminescence can also be clearly distinguished in a time-resolved experiment which uses two pulses with interferometrically controlled delay for excitation and time-integrated detection [16].

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