Direct measure of the exciton formation in quantum wells from time resolved interband luminescence

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We present the results of a detailed time resolved luminescence study carried out on a very high quality InGaAs quantum well sample where the contributions at the energy of the exciton and at the band edge can be clearly separated. We perform this experiment with a spectral resolution and a sensitivity of the set-up allowing to keep the observation of these two separate contributions over a broad range of times and densities. This allows us to directly evidence the exciton formation time, which depends on the density as expected from theory. We also evidence the dominant contribution of a minority of excitons to the luminescence signal, and the absence of thermodynamical equilibrium at low densities.

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Excitons in quantum wells form quite an appealing quasiparticle showing a large range of optical properties that have proven at the same time technologically useful, and physically interesting [1]. A large part of this interest is linked with the appearance of excitonic resonances in absorption up to room temperature. It is also well known, since the seminal work of Weisbuch et al [2], that free excitons appear to dominate the luminescence response of semiconductor quantum wells at low temperatures. Part of the origin of this effect lies in the breakdown of the translational symmetry which brings a very efficient recombination channel to free excitons in quantum wells [3, 4].

Interestingly, in the low density regime, time resolved luminescence (TR-PL) in quantum wells is observed to be always dominated by light coming at the exciton energy, even under non resonant excitation. The observations of this dominant contribution are so numerous that only a very partial list of references may be given here [5, 6, 7, 8, 9] (in order to be specific, we only consider here the case of quantum wells grown on GaAs substrates). A double question has then been debated for more than 10 years in the literature: first how do free electron hole pairs bind into excitons and second does indeed the luminescence at very short time proceed from bound excitons. A brief survey of the literature allows to find that experimentalists have reported formation times ranging from less than 10 ps up to about 1 ns [7, 8, 9, 10] and theoretical values range from 100 ps [11, 12, 13] to over 20 ns [14]. Clearly, the origin of this spreading in the reported values lies in the poor sensitivity of the experiments used in general to probe the exciton formation process, except for the case of the recent terahertz absorption experiments [10]. On the theoretical side, binding of an electron hole pair into an exciton requires, at low temperatures, the emission of an acoustic phonon, which brings long formation time due to the small coupling of acoustic phonons to excitons.

The long formation time of excitons, together with the observation of luminescence at the exciton energy at the shortest times [7, 15] led Kira et al [16] to introduce the idea that a free electron hole plasma, properly including Coulomb correlation effects, should give rise to luminescence at the exciton energy, without any exciton population. Although this proposed interpretation is currently largely questioned (see for example Hannewald and Glutsch et al [17]), the dominance of the excitonic transition at the shortest time has not received a sensible explanation yet.

In the present work, we use a properly designed sample with a particularly high quality, together with a luminescence set-up with improved sensitivity, to study the exciton formation and to give clues on the origin of luminescence in quantum wells. We will show that the formation times of excitons depend on the excitation density as expected from theory. We will also evidence how a very small population of excitons has a large enough recombination rate to dominate the luminescence spectrum, even at the shortest times accessible in the present experiment.

We have selected a particular sample, because of its unequalled quality. It consists of a single $In_x Ga_{1-x} As$ 80 Å quantum well (QW), with a low indium content of about x = 5% grown by molecular-beam epitaxy. This QW is embedded in the middle of a GaAs layer of total mean thickness λ (where mean λ corresponds to the wavelength of the excitonic resonance in the QW), which was grown over a 10 period distributed Bragg reflector (DBR). This DBR allows to measure the absorption of the sample in the reflection configuration without any sample preparation. It also increases the optical coupling of the QW, but do not disturb the shape of the observed luminescence spectrum, because the resonance mode has a spectral width of about 40 nm. Such a DBR changes slightly the radiative properties of free carriers, but does not affect their relaxation properties which we are studying here. The spectrum was recorded with a CCD camera in cw and with a streak camera in the timeresolved experiment (resolution of 3 ps, photon-counting mode). The temporal resolution of the whole setup is limited to about 20–30 ps, because of the spectral resolu-



FIG. 1: Cw absorption (calculated as 1 - Reflectivity; bold line, left axis) and the TR-PL integrated over 1300 ps of the sample (logarithmic scale, right, for luminescence). The structure at 1.4823 eV corresponds to the 1s heavy-hole exciton, at 1.4888 eV to the plasma transition and at 1.4988 to the light-hole exciton (vertical lines). The low energy exponential tail of the excitonic transition originates from the trion transition at 1.4807 eV (discussed in [18]).

tion of 0.1 meV. The excitation energy we use was $\hbar\omega = 1.5174 \text{ eV}$ with the power within the ranges 1.0–300 μ W (photon density $N_{\nu} = 9 \times 10^8 \text{--}3 \times 10^{11} \text{ photons/cm}^2 \text{ per pulse}$; 85 μ m spot). More details about the sample and experimental setup can be found in [18].

The high quality of the sample is evidenced through optical measurements. We do not observe any Stokes shift between the absorption and luminescence at $E_{\rm G}$ and E_{1s} (Fig. 1). Moreover the observed lifetime of the QW reaches 3.7 ns in the low density limit at 10K, which indicates the very low density of non-radiative recombination centers. The linewidth of the exciton is less than 1.0 meV and mainly given by the homogeneous broadening as the lorentzian lineshape shows. The luminescence from free carriers appears exactly at the position of the band gap, which is known from the measurement of the absorption of the sample at the same position (Fig. 1). The free carrier luminescence shows the expected high energy exponential tail, corresponding to the Boltzmann distribution of the carriers, with a temperature given by the temperature of the lattice for temperatures above 25 K [18].

The main interest of the sample is that the transitions at above gap energies can be resolved at all times and densities. Typical time-resolved luminescence traces are shown in Fig. 2 for the spectral and temporal domain. The sufficient dynamical range allows us to measure the free carrier temperature directly from the spectrum for all times after 100 ps delay. Although it is possible to fit the exponential decay to the slope of the plasma transition for t < 100 ps (these results are also shown in Fig. 3) we think that these results might not correspond to the real temperature. Likewise due to the finite linewidth of the free carrier transition there is the finite minimal temperature which we can determine. This reduces the time interval in which we can attribute the temperature precisely to about 100–1300 ps.



FIG. 2: Spectral a) and temporal b) traces of the TR-PL. $N_{\nu} = 2 \times 10^{10} \text{ photons/cm}^2$. a) the temperatures of the carriers are estimated 180 ps and 1150 ps after the excitation. b) the temporal dependence of the maxima of the excitonic and plasma transition. The small peak seen at t = 0 for plasma transition is caused by the diffused light of the laser pulse.

The thermalization of hot carriers can be modeled by computing the average energy-loss rate per electron-hole pair $\langle dE/dt \rangle \propto \langle dT/dt \rangle$ and deducing the variations of their temperature from:

$$T(t) = T_0 - \int_0^t \langle \frac{dT}{dt} \rangle dt \tag{1}$$

where T_0 is the carrier temperature at t = 0. Knowing the theoretical curve $\langle dE/dt \rangle$ for a Boltzman distribution in the case of bulk GaAs [19, 20] one can easily calculate the cooling curve by numerical integration with the only parameter T_0 . However in the case of QWs an ad hoc additional factor $\alpha > 1$ is added $\langle dE/dt \rangle_{\text{exper}} = \langle dE/dt \rangle_{\text{theor}} / \alpha$ by which the measured energy-loss rate is reduced compared to the theoretical value [19, 20, 21]. Here we obtain a good fit for $\alpha = 2.9$, see the bold line in Fig. 3.

Very importantly, the shape of the luminescence signal above the gap is the same within the two main theoretical descriptions (excitons plus free carriers [6, 22], or Coulomb correlated free carriers [16]). In both cases, we expect a Boltzmann like luminescence line provided electrons and holes are thermalized, which is the case for times longer than 100 ps. As will be shown below the luminescence of free carriers above the band edge provides a direct measure of the relative variations of the population of free electrons and holes. Indeed, in both models, the intensity at each energy is simply proportional to the product of the associated distribution functions f_e and f_h . Then, in the case of the low density regime we are



FIG. 3: Temperature of the carriers deduced from the exponential slope of the luminescence above gap $(N_{\nu} = 2 \times 10^{10} \text{ cm}^{-2})$. The full line corresponds to the theoretical cooling curve.

studying, the integrated intensity of the free carrier luminescence is proportional to the concentration of the electrons n and holes p via the bimolecular recombination rate B [23].

$$I_{\text{plasma}} \sim Bnp = Bn^2 \tag{2}$$

as we have n = p. The parameter B at low temperatures in QW is simply inversely proportional to the temperature T of the carriers [24]:

$$B = \frac{8\pi e^2 n_r}{m_0^2 c^3 (m_c + m_v)} \langle |P_{cv}|^2 \rangle \frac{E_g}{k_B T}$$
(3)

where n_r is the refractive index, c is the light velocity, m_0 is the free-electron mass, m_c and m_v are the reduced masses of the electron and holes, $\langle |P_{cv}|^2 \rangle$ is the squared momentum matrix element between electron and hole in each subband averaged over directions and polarizations of photons and over spins of electron end holes, E_g is the energy gap in QW [24]. Eq. 2 and 3 lead to

$$n \propto \sqrt{I_{\text{plasma}}T}$$
 (4)

Thus knowing the time evolution of both quantities – the free carriers luminescence intensity $I_{\text{plasma}}(t)$ and their temperature T(t) (Eq. 1) – we can deduce in a very simple and direct way the temporal evolution of the photoexcited free carrier density. This evolution is plotted in Fig. 4 (symbols) and is obtained from the results shown in Fig. 2 and 3 [26].

This temporal evolution is governed by four factors: the electron-hole radiative recombination rate B, the non-radiative decay time τ_{nr} and the formation and ionization of the excitons – via the bimolecular formation coefficient C. We get two rate equations for the population of free carriers n and of excitons X:

$$\frac{d n}{d t} = -\gamma C n^2 + \gamma C N_{\rm eq}^2 - \frac{n}{\tau_{\rm nr}} - B n^2 \qquad (5a)$$

$$\frac{dX}{dt} = \gamma C n^2 - \gamma C N_{\rm eq}^2 - \frac{X}{\tau_{\rm D}}$$
(5b)



FIG. 4: Concentration of free carriers as a functon of time. The experimental data calculated according Eq. 4 for three different absorbed photon densities are shown together with the time decay fitting curves (solid lines, Eq. 5). The corresponding $N_{\rm eq}$ calculated with Eq. 6 are shown as a dotted lines. The number of absorbed photons is given per pulse per cm². The vertical line is set for the time of 100 ps.

where C is the rate calculated by Piermarocchi et al [13]. It depends upon both carrier and lattice temperature through the interaction with optical and acoustic phonons. γ is a multiplication factor by which the measured formation rate in our InGaAs QW is changed compared to the theoretical value obtained for GaAs. $N_{\rm eq}(n, X, T)$ is the equilibrium carrier concentration given by the Saha equation (for $n = p = N_{\rm eq}$) [25]:

$$\frac{N_{\rm eq}^2}{X} = K(T) = \frac{\mu_X k_B T}{2\pi\hbar^2} \exp(\frac{-E_b}{k_B T}) \tag{6}$$

where μ_X is the reduced mass of the exciton and E_b is the exciton binding energy. The therm CN_{eq}^2 , in the case of cw excitation, leads to thermodynamical equilibrium between the population of the excitons and carriers at the given temperature. In time-resolved experiments this term drives the system towards equilibrium.

Having a sample of unprecedented quality with lifetimes in excess of 3 ns, we can safely neglect the nonradiative processes $\tau_{\rm nr}$. The radiative decay of the electron-hole plasma is governed by the bimolecular processes. The initial concentration is given by the absorbed photon density which can be estimated from the excitation photon density N_{ν} and the value of the absorption coefficient (i.e. Fig. 1). In our case the InGaAs QW absorbs about 30 % of incoming photons. Using the value of B measured and computed by Matsutsue et al $B = 10^{-3}$ cm²/s [24] we get typical radiative decay times of the order of 20 ns for the temperatures and densities of our experiment [25]. Thus the dominant term in Eq. 5a comes from the formation of excitons.

In Fig. 4 the results of our model calculations are

shown as solid lines. We used the values of the initial carrier concentration estimated from the number of absorbed photons as above. The time dependence of the temperature was taken from the experiment (Fig. 3). We took a constant value for the thermalized exciton decay time $\tau_{\rm D} = 500$ ps (this only weakly affects the fit). The only fitting parameter was $\gamma = 5$.

Although very simple, this model includes most important ingredients of what should be a full theory, and includes the results of the model by Piermarocchi [12, 13]. Very importantly, increasing the carrier density results in a faster formation of excitons, because it leads to an increased probability of binding one electron and one hole through interaction with an acoustic phonon. This model also includes an initial drop of the carrier concentration by the rapid formation of excitons through emission of LO phonon by the initially hot carriers [13]. This process implies that, after non-resonant excitation, a population of excitons of a few percent may be formed within the first ps.

The parameters governing exciton formation are the equilibrium density, depending on the temperature and density according to the Saha equation and shown as dotted lines in Fig.4, and the formation rate γCn . The observed exponential decay of the free carrier density with slopes from 500 ps to 1050 ps only correspond directly to the exciton formation at the lowest density, for the largest densities, the equilibrium is reached within our temporal resolution, and the decay of the free carrier population follows the changes imposed by the Saha equation. The formation rate 1 ns after the excitation that fits best our results is $1/60 \text{ ps}^{-1}$ for the highest density, in very good agreement with the recent time-resolved terahertz absorption measurements [10].

It should be emphasized again that we do not assume thermodynamical equilibrium between free carriers and excitons to obtain this result. In fact for the lower excitation densities the process of the exciton formation is so slow compared to the radiative decay of excitons, that the system is never in thermodynamical equilibrium! What we demonstrate here is that, even for delays of the order of 200 ps, the population of excitons is less than 10% of the total population at low densities. However, a simple estimation of the rate of photon emission through excitonic radiative emission shows that this rate is roughly two orders of magnitude larger than the rate of radiative recombination of free carriers, in good agreement with our experimental observations. Therefore the excitonic transition dominates the luminescence spectrum. We cannot be conclusive yet about the relative importance of free carriers and excitons for times shorter than 100 ps, and further experiments with an improved sensitivity will have to be performed to answer this point.

In summary, we have described here the results of the time-resolved photoluminescence study of a very high quality InGaAs quantum well sample. It has been possible to perform this experiment with a spectral resolution and a sensitivity allowing to keep track of the separate excitonic and free carrier contribution over the whole time and density range. Thus we have measured directly the temperature of the carriers and are able to deduce the formation time of excitons. This time is measured over two orders of magnitude in density, it changes from 30 ps for densities of 10^{10} cm⁻² to 1000 ps for densities of 3×10^8 cm⁻². We show that, even a very small population of excitons may dominate the emission spectrum, at least for delays longer than 100 ps.

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