Picosecond time evolution of free electron-hole pairs into excitons in GaAs quantum wells

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We measure picosecond time resolved luminescence spectra in GaAs quantum wells using frequency upconversion luminescence spectroscopy. A careful line-shape analysis of the spectra is performed to separate the free exciton and free carrier related luminescence. From the time evolution of the free carrier luminescence, we deduce the characteristic time constant (τ_f) for the bimolecular process of exciton formation by free electron-hole pairs. For an estimated initial carrier density of 4×10^{10} cm^{-2}, τ_f is found to be 50 ps. [S0163-1829(96)08031-9]

I. INTRODUCTION

The dynamics of exciton formation in GaAs quantum wells (QWs) has been a subject of considerable interest in recent years.[1–4] Since the excitons formed by the electrons and holes near their band edges are expected to have a large wave vector ($\vec{K}$), they do not couple to photons.[1] The excitons have to relax to sufficiently small K values at low temperatures before they can undergo radiative decay. Thus, determination of the exciton formation time from the time evolution of the exciton photoluminescence (PL) is generally not possible. A direct measurement of the exciton formation dynamics, however, can be made for those material systems for which the exciton-LO phonon coupling leads to excitonic transitions from large $\vec{K}$ vectors to the photonlike polariton branch via emission of one or more numbers of LO phonons. If the time evolution of the luminescence due to such LO phonon assisted Stokes sidebands can be measured, it can provide direct information on the free exciton formation and exciton energy relaxation dynamics. These sidebands can be easily seen in materials like CdS and CdSe. The exciton formation time in CdSe was recently deduced to be about 7–10 ps using the time evolution of the luminescence due to 2LO phonon Stokes side band of the free exciton.[5]

Since such sidebands are not very prominent in GaAs or GaAs QWs, the exciton formation time in GaAs QWs has been deduced indirectly by various ways. Damen *et al.*[1] observed that the homogeneous linewidth Γ_L of the exciton PL initially decays rapidly in less than 20 ps for an excitation density n_0 of 2×10^{10} cm^{-2}. A time constant of <20 ps for the decay of the e-h pair density due to exciton formation was then deduced on the basis of the expected linear dependence of Γ_L on the carrier density.[6] Blom *et al.*[2] studied very narrow QWs in which the time for exciton relaxation from large $\vec{K}$ to $\vec{K}\approx0$ states was expected to be small. The exciton formation time then was believed to be approximately given by the exciton luminescence rise time, measured to be about 25–40 ps for $n_0=5\times10^{10}$ cm^{-2}. Deveaud *et al.*[3] deduced an exciton formation time of the order of 200 ps for $n_0\sim10^{11}$ cm^{-2} by relating it to the time of survival of the high energy exponential tail of the time resolved exciton luminescence. Recently, Robart *et al.*[4] argued that the rapid initial decay of the exciton homogeneous linewidth, observed by them to take place in less than 10 ps for $n_0=7\times10^{10}$ cm^{-2}, in fact is related to the fast approach towards thermodynamical equilibrium between the free carriers and the excitons. It was suggested that the above time of about 10 ps should be taken as the free exciton formation time, although the free carrier luminescence was found to survive for a few hundred psecs. On the theoretical side, Thilagam and Singh[7] calculated the transition rate for a free e-h pair at the band edge to an excitonic state by acoustic phonon emission via deformation potential coupling. They obtained a time constant of a few 100s of psecs for this exciton formation process, the exact value of the time constant depending upon the QW width, taken to be in the range of 2.5–20 nm.

Since many aspects of the exciton formation dynamics in GaAs QWs are still not fully clarified, it should be of interest to study the time resolved PL in GaAs QWs in more detail. A detailed modeling of the PL spectral line shapes to isolate the exciton and free carrier related PL energy distributions as a function of time has not been reported so far. In this paper, we report our measurements of picosecond time resolved PL spectra in high quality GaAs QWs using the frequency upconversion (UC) technique. To separate the exciton and free carrier related luminescence spectra, we carry out a line-shape analysis of the spectra, corrected for the instrument spectral response. Relating the time evolution of the energy integrated intensity of the PL due to free e-h pairs to the time dependence of the free carrier density, we deduce the time constant τ_f, which determines the effective rate of bimolecular formation of excitons from free e-h pairs. For an

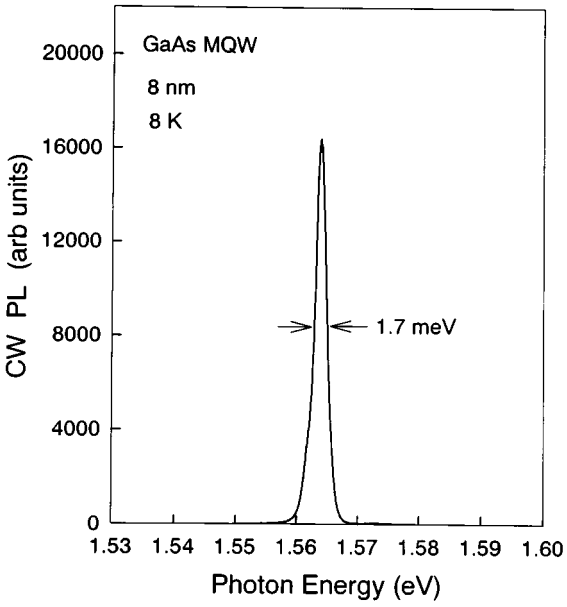

FIG. 1. The CW PL spectra at 8 K.

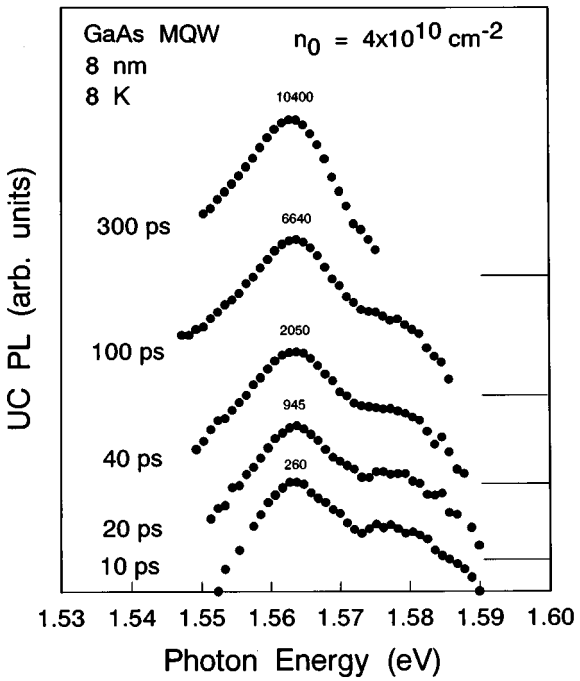

FIG. 2. The measured UC PL spectra at 10, 20, 40, 100, and 300 ps are shown for an excitation density n_0 of 4×10^{10} cm^{-2}. The horizontal lines represents a count of 1 per sec, whereas the maximum absolute number of counts per sec have been indicated for each delay.

excited carrier density of 4×10^{10} cm^{-2}, τ_f is found to be 50 ps. The change in the rise time of the free carrier luminescence for the initial excitation above and below the $Al_{0.3}Ga_{0.7}As$ barriers is found to be less than 10 ps in our samples.

II. EXPERIMENTAL RESULTS

Our experiments are performed using a pulsed Nd-YAG (where YAG denotes yttrium aluminum garnet) pumped dye laser, using either Rhodamine-6G dye (at 612 nm) or DCM dye (at 665 nm). The pulse width, as given by an autocorrelator, is about 2 ps. The sample, maintained at 8 K in a cryostat, consists of high quality GaAs QWs, 8 nm wide and 20 in number. The QWs are separated by $Al_{0.3}Ga_{0.7}As$ barriers, 15 nm wide. The carrier density excited in a single QW per pulse at 612 nm is estimated to be about 4×10^{10} cm^{-2} for an average excitation intensity of 1 mW. The time resolved PL spectra are measured using frequency upconversion (UC) in a standard photon counting setup. The continuous wave (CW) PL spectrum obtained at 8 K using a HeNe laser excitation with an intensity of 300 μW (Fig. 1) shows the free exciton peak at 1.564 eV with a narrow linewidth of about 1.7 meV, indicating the high quality of the samples. Insignificant Stokes shift in the PL excitation spectrum was reported previously for these QWs.[8] A semilogarithmic plot of the spectrum (not shown) reveals a small peak (400 times smaller in height than the exciton peak) at $\hbar\omega=1.573$ eV and is presumably due to free carriers, from the known heavy hole exciton binding energy of about 9 meV for 8 nm QWs.[9] A small asymmetry on the lower energy side of the main exciton peak may be due to excitons localized at the interfaces. At the temperature of these measurements (8 K), the light-hole exciton expected at 1.579 eV cannot be seen.

Figure 2 shows typical UC PL spectra, obtained at a delay of 10, 20, 40, 100, and 300 ps with an initial carrier density of 4×10^{10} cm^{-2} for excitation above the $Al_{0.3}Ga_{0.7}As$ barriers (excitation wavelength=612 nm). Since the light hole exciton is resonant with the heavy hole subband in 8 nm QWs, the light hole exciton is not expected to be seen in the PL spectra of Fig. 2 due to its rapid transfer to the heavy hole subband.[10] It is interesting to note in Fig. 2 that at small delays (e.g., 10 and 20 ps), a small dip is seen approximately at about 1.573 eV, the $n=1$ subband edge (E_1), separating the excitonic and free carrier PL. The free carrier PL is peaked slightly on the higher energy side of E_1 (by about 2 meV), presumably as a result of the carrier temperature and broadening. At longer delays, a shoulder with a high energy tail is seen. A clear change of slope is seen in the UC PL spectra near the band edge, showing the contribution to the total PL of the free carrier recombination, above the subband edge, and the exciton recombination, below the subband edge. As the delay increases beyond 250 ps, the free carrier related luminescence becomes vanishingly small. At 300 ps, the free carrier contribution to the PL can be seen to be quite small in Fig. 2. This rapid decrease of the free carrier luminescence can be studied in further detail by carrying out a theoretical analysis of the data to isolate the free carrier and exciton related PL at different delays.

III. THEORETICAL ANALYSIS

In order to obtain the free carrier contribution to the total PL, the exciton contribution can be separated by performing a line shape fit to the exciton PL. The spectra recorded in the experiments in fact are convolutions over the actual line shapes and the system spectral response. In order to obtain the actual PL spectra, the measured line shape has to be deconvoluted with the instrument response function (R), where R is well approximated by a Gaussian of width Γ_R.[11]

Equivalently, an appropriate model for the actual exciton line shape can be convoluted with an experimentally determined response function and the result can be compared with the measured spectra. The difference between the two can then be used to obtain the actual PL spectra due to free e-h pair recombination using a similar procedure.

For a predominantly inhomogeneous broadening, the (actual) exciton line shape is usually given as a Gaussian:[12] $G(E)=(1/\sqrt{2\pi}\Gamma_G)\exp(-(E_0-E)^2/2\Gamma_G^2)$, where Γ_G, which is $(2\sqrt{2\ln 2})^{-1}$ times the Gaussian full width at half maximum (FWHM), represents inhomogeneous broadening and is referred to here as the Gaussian width and E_0 is the peak position of the exciton PL. On the other hand, a Lorentzian form $L(E)=(2/\pi\Gamma_L)[1+4(E_0-E)^2/\Gamma_L^2]^{-1}$ is used in the literature for a homogeneously broadened exciton line, with Γ_L, the Lorentzian FWHM, representing the homogeneous linewidth. For the general case, the exciton line shape is usually described in the literature[12] to be a convolution of the Gaussian and Lorentzian (G∗L). In our analysis described below, it is understood that a convolution of such line shapes with R is implied whenever the measured data are compared with a theoretical calculation.

We first consider a Gaussian-Lorentzian convolution line shape for the exciton PL. In order to extract the homogeneous and inhomogeneous linewidths, we employ the following procedure: At long delays, it is expected that the free carrier density vanishes and the excitons cool towards small $\vec{K}$. The contribution of the homogeneous linewidth to the total linewidth then will be small, being determined mainly by exciton collisions with carriers and phonons. The largest delay used in our experiments is 1 ns. The exciton peak, as measured in our UC PL spectra at a delay of 1 ns, is therefore fitted using a Gaussian-Lorentzian convolution line shape, keeping the Gaussian linewidth as large and the Lorentzian linewidth as small as needed for getting a satisfactory fit to the data. (A somewhat similar procedure was used by Robart *et al.*[4] to calculate the homogeneous FWHM of the exciton peak.) For smaller delays, the Gaussian width is now kept approximately constant, close to its value at 1 ns, and the Lorentzian width is adjusted so as to get a good fit to the main exciton peak.

The Gaussian-Lorentzian convolution line shape, however, has a long tail which extends well into the free carrier region, thus reducing the apparent free carrier contribution to the total PL. A purely Lorentzian line shape for the exciton PL also has the same difficulty. In the past, an artificial cutoff has been used sometimes to remove this extension.[13] As an alternative, a Gaussian line shape for fitting the exciton PL peak may be considered. This has a high and low energy tail decaying faster than the Gaussian-Lorentzian convolution or pure Lorentzian line shape. Since a theory giving a more satisfactory description of the exciton line shape remains to be developed, we deduce the free carrier related PL intensity for a Gaussian-Lorentzian convolution as well as for a pure Gaussian line shape, as both can fit the main exciton peak reasonably well. It turns out, as shown presently, that the rise and decay time constants for energy integrated free carrier PL do not appear to depend upon the choice of the fit functions used.

Using the above procedure to separate the exciton luminescence from the measured spectra, the (actual) PL due to free e-h pairs can be obtained. In order to obtain the area under the free carrier related PL spectra, we may fit a smooth curve to the data in terms of the well known free carrier PL line shape for band to band recombination in 2D systems, including the Gaussian broadening of the density of states and the Sommerfield factor, which is introduced because of the modification in the density of states due to Coulomb interaction between the electrons and the holes.[14]

IV. COMPARISON WITH EXPERIMENTS

The procedure outlined in Sec. III with the exciton line shape given by G∗L allows us to determine the actual values of Γ_G and Γ_L. The instrument response function is found to have a Gaussian width (Γ_R) of 1.7 meV. We obtain the exciton inhomogeneous linewidth (Γ_G) to be 1.1 meV. The homogeneous linewidth $\Gamma_L(t)$ is found to peak to 2.6 meV at about 30 ps, and then to decrease, first rapidly to 1.0 meV at about 200 ps and then slowly to ≈0.3 meV at 1 ns.

Figure 3(a) shows, as an illustration, a fit to the excitonic part of the UC PL spectra at 50 ps, obtained using the Gaussian-Lorentzian convolution, for an initial excitation density n_0 of 4×10^{10} cm^{-2}. The homogeneous linewidth Γ_L is 2.5 meV. The fit indicates that there may be a small contribution from the localized excitons on the lower energy side of the exciton peak. The inset in Fig. 3(a) is the enlarged view of the high energy tail side of the exciton peak, showing in detail the measured data points (filled circles), the fit to the exciton peak (dash dotted curve), and the free carrier part (open circles) obtained as the difference of the two. Similar fits are also obtained for measurements performed at other delays. The contribution of the localized excitons to the measured PL spectra, not included in the fit to the delocalized exciton line shape above, can be similarly obtained. Having separated the three contributions to the total PL, we can now obtain the time evolution of the total luminescence due to free carriers, excitons, and the localized excitons by calculating the time evolution of their respective energy integrated PL intensities.

The free carrier PL line shape fit is also shown in Fig. 3(a) (dashed curve), along with the sum of the exciton and free carrier contribution (continuous curve). The fit is seen to match the experimental data quite well on the higher energy side. The homogeneous exciton PL linewidth at 50 ps was found to be 2.5 meV. Carrier temperature of 40 K and density of state broadening of 2.2 meV was used for the free carrier PL fit in Fig. 3 for a delay of 50 ps. We should mention here that if one is interested only in the area under the free carrier PL spectra as a function of delay, the values of the parameters used in these fits are not of any consequence at this stage so long as the curves fit the data points well.

Figure 3(b) shows the Gaussian fit to the exciton PL at 50 ps ($\Gamma_G=2.2$ meV) along with the fit for the free carrier PL on the higher energy side. For the free carrier PL fit in Fig. 3(b) the Gaussian broadening of density of states is 2.2 meV, whereas all other parameters are the same as in the case of the Gaussian-Lorentzian convolution fit. As has been pointed out earlier, the difference between the total PL and the exciton PL on the lower energy side is presumably caused by the localized excitons. This can be fitted to a Gaussian in order

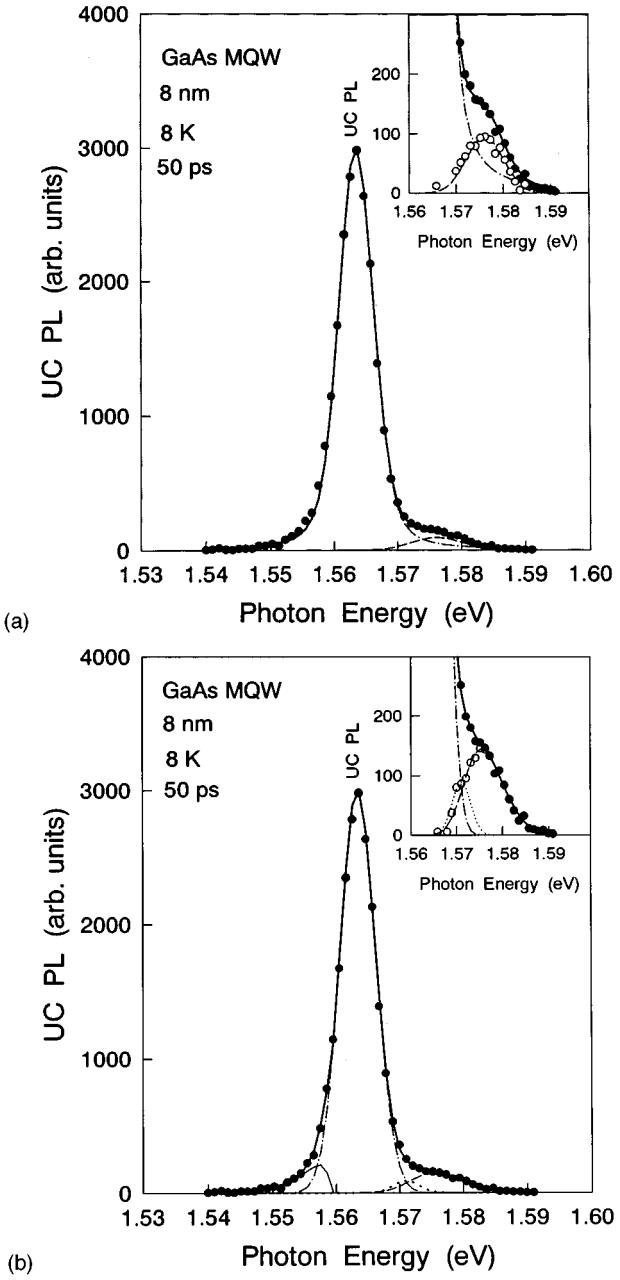

FIG. 3. The UC PL spectrum with $n_0=4\times10^{10}$ cm^{-2} at 50 ps is shown, along with the calculated line shapes for the excitons and the free carrier PL. Two different line shapes have been considered for free exciton PL: (a) Gaussian-Lorentzian convolution and (b) a Gaussian. Both figures show the experimental data points (filled circles), $n=1$ free exciton (dashed dotted curve) and the fit to the free carrier PL (dashed curve). For a Gaussian line shape for exciton PL, contributions from the $n=2$ excitons (dotted curve) and localized excitons (continuous curve on the low energy side) are also shown. The solid line corresponds to the sum of the exciton and free carrier PL in (a) and to the sum of the free exciton ($n=1$ and 2), free carrier, and localized exciton PL in (b). The inset shows the enlarged view of the free carrier region of the curve. The free carrier contribution is shown as open circles.

to extract the localized exciton contribution. The sum of the calculated exciton and free carrier PL has a small dip occurring at an energy where the $n=2$ state of the exciton is expected. Taking a Gaussian line shape ($\Gamma_G=2.0$ meV) for

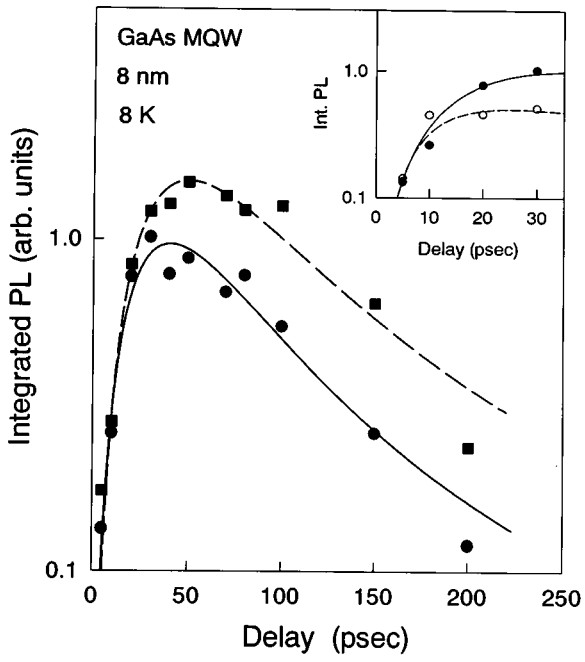

FIG. 4. Energy integrated free carrier PL is shown as a function of delay for $n_0=4\times10^{10}$ cm^{-2} with a Gaussian-Lorentzian convolution (filled circles) and a Gaussian line shape (filled squares) for exciton PL. Also shown are the fits obtained using Eq. (1). The inset shows the integrated free carrier PL for excitation above (filled circles) and below (open circles) the $Al_{0.3}Ga_{0.7}As$ barrier with a Gaussian-Lorentzian convolution line shape for exciton PL.

$n=2$ exciton, the sum of the free exciton ($n=1$ and 2), free carrier, and the localized exciton PL matches very well with the measured spectra, as shown in Fig. 3(b). [Such a fit including the higher excited states of the exciton was earlier shown to be satisfactory for the CW PL measured in the temperature range of 2–50 K in bulk GaAs (Ref. 15)]. The overall fits are as good as in the case of the Gaussian-Lorentzian convolution fit, shown in Fig. 3(a). The inset of Fig. 3(b) shows the enlarged view of the high energy tail side of the exciton peak, showing the measured data points (filled circles), and the fits to the $n=1$ (dash dotted curve) and $n=2$ (dotted curve) exciton peak and the free carrier part (dashed curve) obtained as the difference between the sum of the fits for $n=1$ and 2 and the localized exciton PL and the total PL (open circles). Also shown is the sum total of the different contributions to the total PL (continuous curve).

Figure 4 shows the temporal evolution of the energy integrated PL for free carriers (i.e., the area under the ''actual'' free carrier PL curve) for $n_0=4\times10^{10}$ cm^{-2}, obtained as above for the Gaussian-Lorentzian convolution (filled circles) and the Gaussian (filled squares) fits to the exciton peak. As expected, the integrated free carrier PL is smaller for an assumed Gaussian line shape for the exciton PL as compared to a Gaussian-Lorentzian convolution line shape. It may be noted, however, that the rise and decay rates for the free carrier PL do not seem to depend upon the choice of the line shape, as is evident from the very similar time evolutions for the two cases in Fig. 4. In the following section, we discuss how this may be related to the effective exciton formation time.

V. DISCUSSION

A. Exciton formation time

Having obtained the time evolution of the free carrier related luminescence, we now need to use this to deduce the exciton formation time. One way to do this is to relate the time dependent energy integrated free carrier PL to the time evolution and decay of the free carrier density. For this, we may note that the area under the free carrier related PL spectra, such as the one in the insets of Figs. 3(a) and 3(b), can in fact be related to the free carrier density. The time dependent carrier density thus deduced can then be compared with a theory based on the reasonable assumption that the free carrier density decays mainly by forming excitons in good quality QWs.

The free carrier PL line shape fit to the data [as in Figs. 3(a) and 3(b)] has been obtained in Sec. III by appropriately selecting the carrier density and temperature at each delay. This gives us the experimentally determined time dependent free carrier density. Alternatively, we may note that if a Boltzmann energy distribution is assumed for a $2D$ free e-h assembly, the energy integrated PL can be shown to be proportional to $n_c^2(t)/T_c(t)$, where $n_c(t)$ is the free carrier density near E_1. T_c is the effective carrier temperature at time t, determined from the PL fit to the free carrier contribution to the total PL. (T_c is found to decrease rapidly to about 40 K in about 20 ps, beyond which the cooling is slow, with T_c reaching 25 K after about 150 ps).

To obtain a simple estimate of the exciton formation time, we make the reasonable assumption that the density of free e-h pairs decays in good quality QWs mainly due to exciton formation. (That the density decay due to carrier diffusion may not be important in our case may be verified by estimating the spread in the carrier density distribution due to lateral diffusion.[16] For this, we solve the time dependent carrier diffusion differential equation in cylindrical coordinates for an initial Gaussian radial density distribution.[17] With a low density ambipolar diffusion coefficient of 200 cm^2/sec in GaAs QWs,[18] an initial Gaussian FWHM of 60 μm, as in our case, increases only by about 0.4 μm in 200 ps due to carrier diffusion,[19] making the carrier density decay, associated with carrier diffusion, insignificant in these experiments.) The time evolution of free carrier density $n_c(t)$ therefore may be taken to be determined mainly by the exciton formation process and given as a solution to

$$\frac{dn_c}{dt} = g(t) - Cn_c^2, \tag{1}$$

where $g(t)$ is the rate of carrier density buildup near the $n=1$ subband edge and C gives the effective coefficient for the bimolecular process of exciton formation. As a simplification, $g(t)$ may be written as $n_0 \exp(-t/\tau_0)/\tau_0$, where τ_0 represents the rise time for free carrier density in the QWs near E_1. We now compare in Fig. 4 the time evolution of the integrated free carrier PL with n_c^2/T_c, where n_c is given by Eq. (1).

The above procedure allows us to estimate the coefficient C for exciton formation by free e-h pairs to be 5×10^{-13} $cm^2\ ps^{-1}$. By defining the effective time constant τ_f for free e-h pair density decay due to exciton formation as $1/Cn_0$, we find that τ_f is 50 ps for $n_0=4\times10^{10}$ cm^{-2}. We have also performed time resolved luminescence measurements for a larger initial excitation density of 2×10^{11} cm^{-2}. As with $n_0=4\times10^{10}$ cm^{-2}, the UC PL for $n_0=2\times10^{11}$ cm^{-2} shows a shoulder with a high energy tail on the higher energy side of the exciton peak. However, unlike the low density case, this structure is found to exist for delays as high as 500 ps. A simple theoretical analysis of the UC PL in this case, as described in Sec. III (but not including the high density effects such as exciton screening, change in the Sommerfield enhancement factor, etc.), leads to τ_f of about 250 ps in this case. This seems to suggest that the higher the excited carrier density is, the slower is the decay of the free carriers into excitons, contrary to the expectation that $\tau_f(=1/Cn_0)$ decreases as n_0 increases. Presumably, as the excited carrier density is increased, effects like band gap renormalization, screening, and slower carrier cooling can make the decay of the free e-h pair density slower. Such considerations may help in explaining the wide range of values obtained in previous experiments in determining the exciton formation time.[1–4] The rise time τ_0 does not seem to depend on n_0 (within experimental uncertainty) and is about 25 ps. As seen in Fig. 4, the theoretical fits based on Eq. (1) show good agreement with experiments.[20]

The question as to whether the above measurement of τ_f gives the true, elementary rate of transition from an initial free e-h pair state to an exciton in our GaAs QWs needs to be examined here. Immediately after photoexcitation of carriers with excess kinetic energy, the carriers undergo different processes overlapping on the time scale, such as capture into QWs from barrier regions, thermalization among themselves via carrier-carrier interactions, intervalley scattering, cooling due to LO phonon emission, exciton formation, etc. Depending upon the relative strengths of LO phonon couplings to free carriers and excitons, the hot carriers may approach the energy band edges first before forming excitons, or they may form hot excitons, resonant with free e-h pair energy band. These hot excitons may then relax to lower energies by LO phonon emission. In GaAs QWs, the former process is expected to occur with greater probability. The excitons formed by the e-h pairs near the band edge may attain thermalization among themselves via exciton-exciton collisions within a few psecs, if the exciton density is sufficiently large ($>10^9$ cm^{-2}). Whether excitons attain thermodynamic equilibrium also with free carriers via free carrier-exciton collisions is not immediately clear. Previously, Shah[21] found that the hot carrier and exciton temperatures in CdSe were not the same. On the other hand, Robart *et al.*[4] find that the similar time dependence observed for the exciton homogeneous linewidth and the carrier temperature in GaAs QWs is consistent with the assumption of thermodynamic equilibrium for the free carrier and the exciton assembly. This would then imply that the number of e-h pairs forming excitons per unit time is equal to the number of excitons ionizing per unit time at any time, the time dependence of the corresponding populations arising mainly due to cooling by phonon emission. The assumption of a 2D mass action law in the exciton formation and exciton thermal ionization[22] under steady state conditions was used in the past in analyzing CW PL experiments.[23] However, in view of the long times (100s of psecs) expected for acoustic phonon assisted exciton formation,[7] and the small phonon den-

sity at low lattice temperatures, it seems unlikely that acoustic phonons can achieve thermodynamic quasiequilibrium among the excitons and free e-h pairs in the transient case on a psec time scale. In that case, carrier-exciton collisions may play a greater role in the exciton formation and ionization processes than the slow acoustic phonon interactions. While the validity of a 2D mass action law in the exciton formation and ionization processes on a psec time scale remains to be fully investigated, it is possible that C, as determined here, is influenced, to a certain extent, by the exciton ionization process. Thus, C may be regarded only as an effective coefficient for exciton formation, giving a lower bound for the ''true'' rate of the bimolecular process.

The above results raise the question: what is the main mechanism of exciton formation by free e-h pairs which leads to a formation time of a few 10s of psecs? A calculation based on acoustic phonon emission via deformation potential interaction[7] led to a time constant of 100s of psecs. Emission of LO phonons with energy of 36.5 meV and an exciton binding energy of a few meVs in GaAs QWs does not seem to play a role in the exciton formation near the $n=1$ subband edge. It is possible, however, that exciton formation via LO phonon emission occurs when the carriers are hot in the early stages of carrier relaxation after their excitation. As the carriers cool, the effective rate of exciton formation and carrier density decay may slow down. Whether exciton (X) formation can occur also due to carrier-carrier scattering [of the type $e+h+c \rightarrow X+c'$, with carrier $c(c')$ accounting for energy-momentum conservation] is not clear at present. A calculation of exciton formation rates via the above mechanisms for different (time dependent) electron and hole energy distributions has not been performed so far. It should be interesting to investigate this question further theoretically.

B. QW capture time

In Eq. (1), τ_0 represents the rise time for the density of carriers near the $n=1$ subband edge, giving the luminescence spectra such as that shown in Fig. 3(a) and 3(b). To investigate the contribution to τ_0 caused by the delay in the carrier transition from the barrier to QW states, we obtain the time evolution of the free carrier related total PL in the QWs for initial carrier excitation energy both above and below the band edge of the $Al_{0.3}Ga_{0.7}As$ barriers (15 nm wide). For this, excitation at 612 nm using Rhodamine-6G and at 665 nm using DCM dye was used. The inset of Fig. 4 shows the energy integrated free carrier PL for $n_0=4\times10^{10}$ cm^{-2} for the two different excitation wavelengths for the initial delays of a few 10s of psecs. A comparison of the two curves shows that the contribution to the rise time due to capture of carriers in the $Al_{0.3}Ga_{0.7}As$ barriers is less than 10 ps in our samples. We may mention here that earlier such studies[24] have often relied on the difference between the rise time of the exciton luminescence obtained under conditions of excitation above and below barrier energy gap, rather than directly using a detailed analysis of the free carrier PL, as performed here.

VI. CONCLUSION

In summary, we study the picosecond time resolved UC PL spectra in GaAs MQWs. The free carrier contribution to the total PL is isolated using a detailed line-shape analysis of the exciton PL. For $n_0=4\times10^{10}$ cm^{-2}, the effective time constant for exciton formation is found to be 50 ps. A theoretical understanding of the mechanism of exciton formation from free e-h pairs giving a time constant of a few 10s of psecs, however, is still not available. The difference in the rise time of the free carrier PL for the initial excitation above and below the $Al_{0.3}Ga_{0.7}As$ barriers is found to be less than 10 ps in our samples.

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[1] T. C. Damen, J. Shah, D. Y. Oberli, D. S. Chemla, J. E. Cunningham, and J. M. Kuo, Phys. Rev. B **42**, 7434 (1990); T. C. Damen, J. Shah, D. Y. Oberli, D. S. Chemla, J. E. Cunningham, and J. M. Kuo, J. Lumin. **45**, 181 (1990).

[2] P. W. M. Blom, P. J. van Hall, C. Smit, J. P. Cuypers, and J. H. Wolter, Phys. Rev. Lett. **71**, 3878 (1993).

[3] B. Deveaud, B. Sermage, and D. S. Katzer, J. Phys IV (Paris) Colloq. **3**, C5-11 (1993).

[4] D. Robart, X. Marie, B. Baylac, T. Amand, M. Brousseau, G. Bacquet, G. Debart, R. Planel, and J. M. Gerard, Solid State Commun. **95**, 287 (1995).

[5] S. S. Prabhu, A. S. Vengurlekar, and J. Shah, Phys. Rev. B **53**, 10 465 (1996).

[6] A. Honold, L. Schultheis, J. Kuhl, and C. W. Tu, Phys. Rev. B **40**, 6442 (1989).

[7] A. Thilagam and J. Singh, J. Lumin. **55**, 11 (1993).

[8] A. Vinnattieri, J. Shah, T. C. Damen, D. S. Kim, L. N. Pfeiffer, M. Z. Maialle, and L. J. Sham, Phys. Rev. B **50**, 10 868 (1994).

[9] R. Cingolani and K. Ploog, Adv. Phys. **40**, 535 (1991); C. Weisbuch, *Semiconductors and Semimetals* (Academic Press, San Diego, 1987), Vol. 24.

[10] R. Eccleston, R. Strobel, W. W. Rühle, J. Kuhl, B. F. Feuerbacher, and K. Ploog, Phys. Rev. B **44**, 1395 (1991).

[11] J. F. Zieglar and J. E. E. Bagia, J. Appl. Phys **42**, 2031 (1971).

[12] Y. Chen, G. P. Kothiyal, J. Singh, and P. K. Bhattacharya, Superlatt. Microstruct. **3**, 657 (1987); J. Christen, and D. Bimberg, Phys. Rev. B **42**, 7213 (1990).

[13] M. Capizzi, S. Modesti, A. Frova, J. L. Staehli, M. Guzzi, and R. A. Logan, Phys. Rev. B **29**, 2028 (1984).

[14] G. Bastard, *Wave Mechanics Applied to Semiconductor Heterostructures* (Halsted Press, New York, 1988).

[15] E. Grilli, M. Guzzi, R. Zamboni, and L. Pavesi, Phys. Rev. B **45**, 1638 (1992).

[16] The excited hot carriers cool rapidly by emitting LO phonons in a few psecs. For an average hot carrier velocity of 5×10^7 cm^{-3}, the carriers initially move ballistically only by 0.5 μm in 1 ps.

[17] J. Crank, The Mathematics of Diffusion (Clarendon Press, Oxford, 1956); H. B. Bebb and E. W. Williams, in *Semiconductors and Semimetals* (Academic Press, New York, 1972), Vol. 8.

[18] This may be estimated using the e-h mobilities at a carrier tem-

perature of 45 K, using the data given in, for example, C. Weisbuch, *Semiconductors and Semimetals* (Ref. 9).

[19] The corresponding increase is 3.3 μm for a 5 μm spot. The diffusion effect on the carrier density thus can be important for a sharply focused laser spot on the sample, smaller than the diffusion length, as pointed out by E. Okuno, T. Hori, N. Sawaki, I. Akasaki, and R. Höpfel, Jpn. J. Appl. Phys. **31**, L148 (1992). It may also be important when the diffusion coefficient is enhanced due to very high density excitations [N. J. Frigo, H. Mahn, and D. J. Erskine, IEEE J. Quantum Electron **QE-18**, 192 (1982)], and also in vertical direction in bulk crystals, and in CW experiments, as shown by Capizzi *et al.* (Ref. 13).

[20] Alternatively, we may describe the free carrier dynamics in terms of a double exponential behavior for the time dependence of n_c, defining a rise time τ_0 and a decay time τ_1, as is often done. This leads to $\tau_1=90$ ps for $n_0=4\times10^{10}$ cm^{-2}, whereas τ_1 increases to about 425 ps for $n_0=2\times10^{11}$ cm^{-2}.

[21] J. Shah, Phys. Rev. B **9**, 562 (1974).

[22] D. S. Chemla, Helv. Phys. Acta **56**, 607 (1983).

[23] M. Colloci, M. Gurioli, and A. Vinattieri, J. Appl. Phys. **68**, 6 (1990).

[24] P. W. M. Blom, R. F. Mols, J. E. M. Haverkort, M. R. Leys, and J. H. Wolter, Superlatt. Microstruct. **7**, 319 (1990).