Biexciton creation and recombination in a GaAs quantum well

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The conditions required for the generation of biexcitons in quantum wells are discussed, and a model line shape for biexciton recombination is fitted to observed biexciton photoluminescence spectra. It is shown that the biexciton density at a given optical injection rate is much enhanced by resonant generation at either the light-hole or the heavy-hole exciton. Unlike the case of silicon, the biexciton density is found not to vary as the square of the exciton density and this is attributed in part to the short lifetime of the excitons and biexcitons.

I. INTRODUCTION

In three-dimensional semiconductors such as CuCl and Si it has been shown that excitons may interact to produce excitonic molecules (biexcitons) under appropriate circumstances.[1] In bulk silicon the excitons and biexcitons thermalize much faster than they recombine, and as a result the equilibrium between the exciton and the molecule takes on the classical Arrhenius form: the particles behave like a classical gas.[2] In bulk GaAs the calculated energy of binding for excitons in a biexciton is rather small, about 0.13 meV,[3] and the radiative lifetime is much shorter than in Si; as a result biexciton effects are not seen in steady-state conditions. In order to observe biexcitons in GaAs it has been necessary to confine the excitons in two dimensions in quantum wells, which leads to a somewhat increased interaction.[4] The resulting binding energy of about 1 meV makes it likely that biexcitons will be stable at temperatures below about 10 K. In order to observe directly the recombination of biexcitons it is necessary for samples to have a low impurity concentration and for the exciton linewidth to be less than the biexciton binding energy. These conditions have been satisfied in several experiments on quantum wells, in which high levels of optical pumping led to the generation of a luminescence transition on the low-energy side of the exciton line.[4–6] The much greater recombination rate in the direct-band-gap GaAs quantum well leads to equilibrium conditions different from those found for silicon. We show in this paper that the classical Arrhenius equilibrium does not apply exactly in the quantum wells, that the formation of the the molecular state is substantially enhanced by the use of resonant injection of cold excitons, and thus in previous studies the formation of the biexciton has been impeded by the need for the initial optically injected excitation to lose substantial amounts of energy before reaching the cold heavy-hole exciton. The paper begins with a short discussion of the expected symmetry of the biexciton and discusses a cw line shape based on quasithermal equilibrium within the biexciton population.

II. CREATION AND RECOMBINATION OF BIEXCITONS

The reduction in symmetry of GaAs in going from three dimensions to the structure of a quantum well leaves the appropriate point group as D_{2d}, or D_{4h} if the underlying lack of inversion symmetry is neglected.[7] In the corresponding double group for D_{2d} both the conduction band and heavy-hole band carry the Γ_6 representation, so the lowest-energy biexciton (with totally symmetric envelope function) will belong to[8]

$$\{\Gamma_6 \otimes \Gamma_6\} \otimes \{\Gamma_6 \otimes \Gamma_6\} \otimes \Gamma_1 = \Gamma_1 ,$$

and the lowest-energy exciton belongs to

$$\{\Gamma_6 \otimes \Gamma_6\} \otimes \Gamma_1 = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_5 .$$

For one-photon transitions the dipole operator for E vectors in the plane of the quantum well carries Γ_5, and the two-photon operator[7] carries $\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_4$. This means that the Γ_1 biexciton state is accessible from the ground state via three routes: by two-photon absorption, by excitation of a Γ_5 exciton which then absorbs a second photon, or by first generating two Γ_5 excitons which subsequently condense to the biexciton by emission of acoustic phonons. Thus in the case of excitation at a photon energy $(2E_x - E_b)/2$ it is expected that, for sufficiently high values of optical power density, direct injection of biexcitons by two-photon absorption should occur, followed by two-step recombination via the exciton, giving rise to a population of excitons as well. For nonresonant injection, and for low-injection levels, the two-step processes will dominate. In the present experiments there is no evidence for the two-photon absorption process, since there is no emission at E_x when the energy of exciting photons is tuned to $(2E_x - E_b)/2$. The rest of the discussion therefore focuses on the system of excitons which may recombine to the ground state, or either condense in pairs or absorb extra photons to reach the biexciton state.

In three-dimensional systems the line shape of the biexciton emission has a characteristic tail to low energies, which has been modeled in the lowest order of approximation by considering a thermal distribution of biexciton energies.[1] Following the same reasoning in the two-dimensional case, the energy before recombination is $2E_x - E_b + \hbar^2k^2/4m$ where m is the exciton effective mass. For the case in which k is greater than the photon momentum, after recombination the total energy is $\hbar\omega + E_x + \hbar^2k^2/2m$, which gives the photon energy as $\hbar\omega = E_x - E_b - \hbar^2k^2/4m$. For a Boltzmann distribution of kinetic energies this leads to a model line shape

$$I(\hbar\omega) \propto \exp[-(\hbar^2k^2/4m)/kT]$$
$$\propto \exp[-(E_x - E_b - \hbar\omega)/kT] \quad \text{for } \hbar\omega < E_x - E_b$$

with a sharp cutoff at $\hbar\omega = E_x - E_b$ corresponding to the limit of zero center-of-mass kinetic energy. It is near this limit that the model should be least successful owing to neglect of the photon momentum. In order to introduce realistic line broadening this spectrum should be integrated over all the possible contributing values of E_x or equivalently for this purpose, of E_b, in which case the line shape becomes

$$\int g(E_b)\Theta(E_x - E_b - \hbar\omega) \times \exp[-(E_x - E_b - \hbar\omega)/kT_{\text{eff}}]dE_b \ ,$$

where $g(E_b)$ is used to model the broadening, and Θ is the Heaviside unit-step function corresponding to the cutoff at zero kinetic energy. This line shape does not suffer from the artificial cutoff at $\hbar\omega = E_x - E_b$ which an alternative form of broadening produces.[6] The temperature T_{eff} is expected to be greater than the lattice temperature even for a system of excitons and biexcitons in equilibrium as a classical gas. This is due to the randomization of the momentum left behind in the center-of-mass motion of the exciton when a biexciton recombines. In the present experiments the absorbed photon momentum has been in the growth direction, and taken up as Δk_z associated with the breaking of translational invariance in that direction. Emission from the biexcitons does give a nonzero expectation for k^2 in the exciton population simply because the emission is not channeled only along z. This mechanism therefore leads to "recombination heating" of the exciton population, and therefore of the biexciton population also.

Determination of the dependence of exciton- and biexciton-emission intensity on the generation rate of excitons was an important aspect of the characterization of the previously studied biexciton systems, in particular silicon. The assumptions made in describing the equilibrium between the exciton and biexciton were those of simple chemical equilibrium, with a generation term affecting only the exciton population. This model therefore relates to the case in which all biexcitons arise from the collision of two excitons, and is valid mainly because thermal equilibrium between the two populations is only slightly perturbed by the finite lifetime of the species involved. In this case the exciton density n_{ex} varies with the generation rate g as $[(1+g/g_0)^{1/2} - 1]$, where g_0 is a characteristic generation rate.[2] This leads to a sublinear variation of the exciton intensity with injection intensity, but the biexciton recombination rate always tracks the exciton rate as n_{ex}^2. For the case of the GaAs quantum well the simple analysis is no longer valid, and a much more complex set of rate equations describes the system. One particular problem is that the recombination time in this direct-band-gap material is much shorter than in silicon, and consequently the assumption that the population of excitons and that of biexcitons are always in thermal equilibrium is not likely to be valid. If this is the case it may be expected that the quadratic relationship between exciton and biexciton signals will no longer occur. Specifically, since the radiative lifetime of biexcitons is less than that of excitons, it is to be expected that the biexciton density will probably vary less strongly than quadratically as the exciton density is increased. Just as for the case in which n_{ex} varies with generation rate as $[(1+g/g_0)^{1/2} - 1]$ the value of the exponent found in an attempt to fit a simple power law to the relationship between recombination signal and generation rate will depend upon the generation rate used.

III. EXPERIMENTAL STUDIES

In order to satisfy the requirements of low impurity concentration and narrow linewidth, a very-high-quality quantum well is required. Since our specimen was required to be grown over an etch-stop layer for other purposes, the growth specification given in Table I was adopted. The effect of the superlattice was to reduce interface roughness, and the quality of the resulting material is reflected in the linewidth of the $n=1$ electron–heavy-hole (hh) recombination at 1.6 K illustrated in Fig. 1. Typical full width at half maximum for the luminescence peak is 0.7 meV. Comparison of the position of the peak of the photoluminescence (PL) shown in the insets to Fig. 1 and that of the photoluminescence excitation (PLE) gives a maximum value for any Stokes shift of 0.2 meV, which confirms that the recombination is free-excitonlike. The PLE in Fig. 1 was measured with the detection centered on the biexciton luminescence at 1.5495 eV. The PL spectra in the insets show the dramatic change in the nature of the spectra obtained on

TABLE I. Growth specifications.

Al content	Material	Nominal thickness	
	GaAs	600 Å	
33%	Al-Ga-As	150 Å	
	GaAs	204 Å	
33%	Al-Ga-As	150 Å	
	GaAs	102 Å	
33%	Al-Ga-As	150 Å	
	GaAs	51 Å	
33%	Al-Ga-As	150 Å	repeated 10 times
	GaAs	28 Å	repeated 10 times
33%	Al-Ga-As	28 Å	repeated 10 times
	GaAs	28 Å	repeated 10 times
60%	Al-Ga-As	5000 Å	etch stop
	GaAs	1 μm	
substrate			

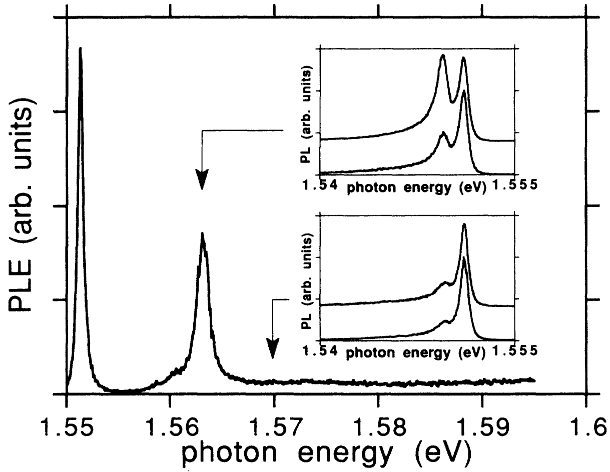

FIG. 1. The photoluminescence excitation spectrum of the biexciton recombination at 1.5495 eV, measured at 1.6 K. The large peak is associated with cold heavy-hole exciton injection, the smaller with light-hole exciton generation. The insets give luminescence spectra for light-hole-resonant and nonresonant excitation; details are given in the text.

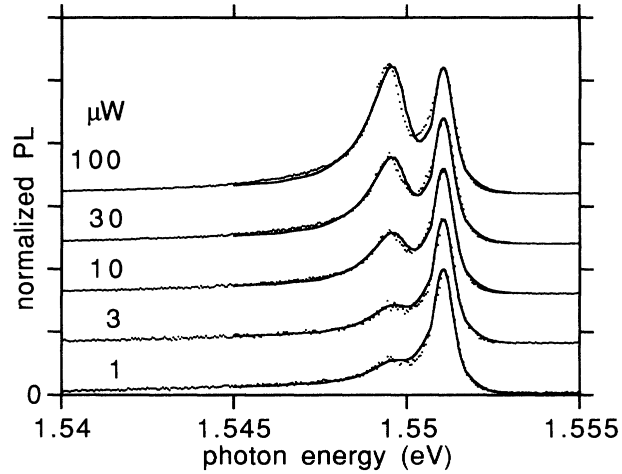

FIG. 2. The development of the biexciton emission at different excitation levels is shown in the form of spectra normalized to the exciton peak (dots). The continuous curves are derived from the model discussed in the text and each curve is calculated by varying only the intensity of the biexciton contribution.

and off resonant injection of (lh) light-hole excitons. The upper inset gives the spectra in the hh exciton and biexciton region corresponding to laser excitation at the peak of the PLE curve corresponding to light-hole exciton generation. The total power densities for the spectra were approximately 0.1 $\mathrm{W\,cm^{-2}}$ for the upper and 0.01 $\mathrm{W\,cm^{-2}}$ for the lower trace. The lower inset corresponds to excitation at a photon energy of 1.57 eV, at which the excitation efficiency is about 8% of that for lh injection. The two traces correspond to 1 (upper) and 0.1 $\mathrm{W\,cm^{-2}}$ (lower), and consequently relate to approximately the same total generation rate in the quantum well. The enhancement of the condensation of the system to the biexciton state in the case of injection of cold light-hole excitons is very clear. Similar spectra for the biexciton line are found for excitation of cold heavy-hole excitons.

Figure 2 shows the evolution of the exciton and biexciton spectra as the power of the excitation at the light-hole exciton is increased. For the excitation conditions used here 100 μW corresponds to 0.1 $\mathrm{W\,cm^{-2}}$. The dots are experimental data and the solid line is a combination of the model line shape for the biexciton proposed above, and a smoothed exciton line shape obtained at very low injection level. All the spectra are normalized, so the fit of the model to the exciton just reflects the constancy of the exciton line shape as the density is increased. The biexciton line shape was calculated by adjusting the parameters to give a satisfactory representation at one injection level, and this shape was then scaled to model all the other data. The parameters used were $E_x = 1551.1$ meV, $E_b = 1.1$ meV, $T_{\mathrm{eff}} = 10$ K, $\sigma_b = 0.3$ meV for Gaussian broadening. Good modeling of the observed line shape is possible over a wide range of excitation levels, and both the effective temperature and the binding energy are in excellent agreement with the expectation for the behavior of a biexciton. There is no evidence, within the limits imposed by the simple model adopted, of any systematic evolution of the biexciton line shape as the biexciton signal increases; we consequently consider the model adequate over the relevant density range. The dependence of the biexciton intensity on the exciton intensity for these data gives approximately $I_{\mathrm{biex}} \propto I_{\mathrm{ex}}^{1.6}$, which is also in accord with the reduction in the exponent from 2 expected to accompany a short radiative lifetime for the species involved. The fact that the biexciton intensity rises more steeply than the exciton intensity is illustrated in Fig. 3, where the exciton-PL intensity is plotted as a function of injection power at the lh exciton, and the biexciton intensity is plotted on the same scale of total power, but with excitation at the hh exciton. Downward curvature of both traces occurs as intensity increases, just as is expected from the classical approximation for long-lived exci-

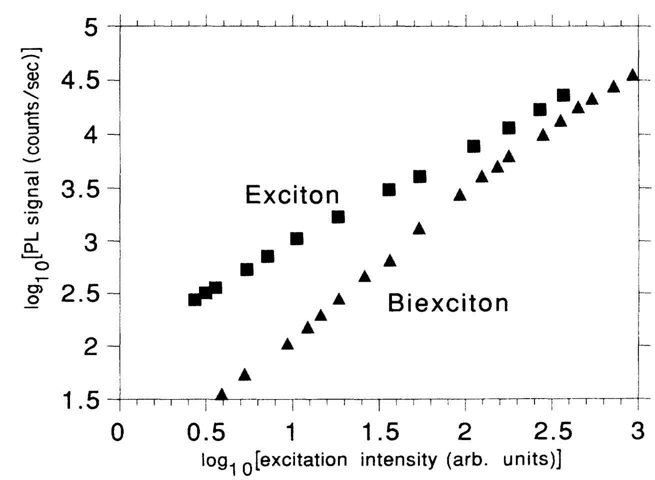

FIG. 3. The variation of exciton and biexciton luminescence intensity with optical power density is shown, corresponding to injection at the lh exciton (for the hh exciton PL) and injection at the hh exciton (for the biexciton PL).

tons. The reduction in slope of the biexciton-intensity dependence at low power levels arises because the measurement was made at one emission energy only, corresponding to the peak of either the exciton or biexciton, and consequently the background contribution from the low-energy tail of the exciton is included in the biexciton signal.

IV. DISCUSSION AND CONCLUSIONS

The occurrence of biexcitons in GaAs quantum wells has been inferred previously from photoluminescence at very high excitation levels. Under such conditions the photoexcited carriers have to lose substantial amounts of energy by phonon emission to form excitons, or, for excitons formed with very high center-of-mass kinetic energy, they must lose this energy to the lattice before biexciton formation is likely to be significant. This is simply a consequence of the weak binding of the biexcitons, which can be broken up in an energetic collision. It is to be expected that the generation of essentially cold excitons favors biexciton formation, and this has been confirmed in the present experiments which show biexcitonic features in recombination at injection densities several orders of magnitude lower than in some previous studies using hot carrier excitation. Resonant generation of cold lh excitons leads to a substantial biexciton population, whereas nonresonant generation with just 7 meV excess energy is much less effective at allowing biexciton formation. This may be associated with the presence of excess translational energy in the case of nonresonant generation, but it is still not clear by what mechanism the cold lh exciton relaxes to form cold hh excitons.

The significance of these observations is that in the case of resonant excitation of the exciton in a GaAs quantum well biexcitonic effects may be very strong for "high" levels of excitation, particularly in pulsed experiments. In this context high excitation may correspond to very small laser powers. Indeed, in many low-temperature experiments, condensation effects in the exciton population in GaAs quantum wells may dominate the optical properties.

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[8]Here the $\{\otimes\}$ indicates the antisymmetric Kronecker product, to ensure antisymmetry of the biexciton under exchange of identical particles. The notation for the irreducible representations is that of G. K. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-two Point Groups* (MIT, Cambridge, MA, 1963).