RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 41, NUMBER 5 15 FEBRUARY 1990-I

Biexciton-biexciton and exciton-electron scattering in GaAs quantum wells

R. Cingolani and K. Ploog
Max-Planck-Institut für Festkörperforschung, D-7000 Stuttgart 80, Federal Republic of Germany

G. Peter, R. Hahn, and E. O. Göbel
Fachbereich Physik, Phillips-Universität, D-3550 Marburg, Federal Republic of Germany

C. Moro and A. Cingolani
Dipartimento di Fisica, Universitá di Bari, I-70126, Bari, Italy
(Received 20 November 1989)

The dynamics of the interacting excitonic states in GaAs/$Al_xGa_{1-x}As$ quantum wells has been investigated by spatially resolved and time-resolved luminescence spectroscopy. The combination of these techniques allows us to determine the radiative recombination processes generated by inelastic biexciton-biexciton and exciton-electron collisions under high-excitation density. Our experimental results demonstrate that the dynamics of the interacting excitonic states in quantum wells are comparable to those in bulk materials, i.e., the dimensionality of the semiconductor does not have a significant effect on the specific inelastic collision processes.

The intrinsic radiative recombination processes occurring in direct-gap semiconductors can be classified into three regimes according to the quasiparticle density generated in the crystal: (i) radiative recombination processes of free excitons in a dilute boson gas, (ii) radiative decay of excitons due to inelastic scattering processes in a dense interacting excitonic gas, and (iii) electron-hole plasma above the screening threshold for the exciton ionization. In the case of semiconductor quantum wells (QW's) most of the work on the distinct properties of confined excitons has been carried out in the limit of a dilute boson gas, in which excitons can be considered as noninteracting elementary excitations undergoing the modified crystal potential of the superlattice, or in the high-density limit, when state filling and screening govern the nonlinear optical response of the crystal.[1] Despite their enhanced binding energy and oscillator strength, in semiconductor quantum wells no evidence of interacting excitonic states has been reported apart from a kind of exciton-exciton interaction occurring through the exchange of real or virtual acoustic plasmons at high exciton density.[2]

In this paper we report the first observation of radiative decay of excitons and excitonic molecules (biexcitons) generated by inelastic collision processes in GaAs/$Al_xGa_{1-x}As$ multiple quantum wells (MQW's). The dynamics of the interacting excitonic states are studied by spatially resolved and time-resolved high-excitation-intensity luminescence. The combination of these two techniques allows us to study in detail the radiative recombination processes induced by biexciton-biexciton and exciton-electron scattering under high-excitation conditions. The experimental results provide clear evidence that the dynamics of the interacting excitonic states in quantum wells do not significantly differ from those in bulk materials.

The GaAs/$Al_xGa_{1-x}As$ MQW's were grown by molecular-beam epitaxy on (001) GaAs substrates. They consist of 25 periods of 10-nm GaAs wells sandwiched between 15-nm $Al_{0.36}Ga_{0.64}As$ barriers grown on a 1-μm-thick $Al_{0.36}Ga_{0.64}As$ barrier layer to prevent carrier losses in the underlying GaAs buffer layer. The optical characterization of the samples reveals sharp excitonic peaks with about 1.5-meV full width at half maximum at low temperature and about 1-meV Stokes shift between the photoluminescence and photoluminescence-excitation spectra. The spatially resolved and time-integrated luminescence measurements are carried out either with short pulses or with pulses having a time duration comparable to the exciton lifetime of the investigated MQW's. A high-frequency mode-locked Ar^+ laser with 80-ps pulse width serves as the excitation source. The detection system consists of a 0.5-m spectrometer combined with a streak camera with an optical multichannel for readout (allowing a time resolution of 20 ps in the time-resolved luminescence measurements). Longer laser pulses (5 ns) are achieved by using a N_2 pumped dye laser operating at 570 nm with 10-Hz repetition frequency. A 0.6-m monochromator equipped with a photomultiplier tube and a boxcar integrator is used for the integrated luminescence measurements. All measurements are performed at a sample temperature of 5 K with an adjusted power density of 0.5 $MW cm^{-2}$. In the spatially resolved experiments the luminescence is collected in a backward direction at different distances (d) from the center of the excited spot (the focus diameter is about 40 μm). A spatial resolution of about 20 μm has been obtained by scanning an enlarged image of the sample surface (magnified by a factor of 10) across the entrance slit of the monochromator by means of micrometric displacements of the collecting lens (the spatial resolution is therefore controlled directly by the slit width).

In Figs. 1(a) and 1(b) we compare the spatially resolved time-integrated photoluminescence (PL) spectra taken under picosecond excitation with those obtained under stationary conditions (ns pulses). In both cases pro-

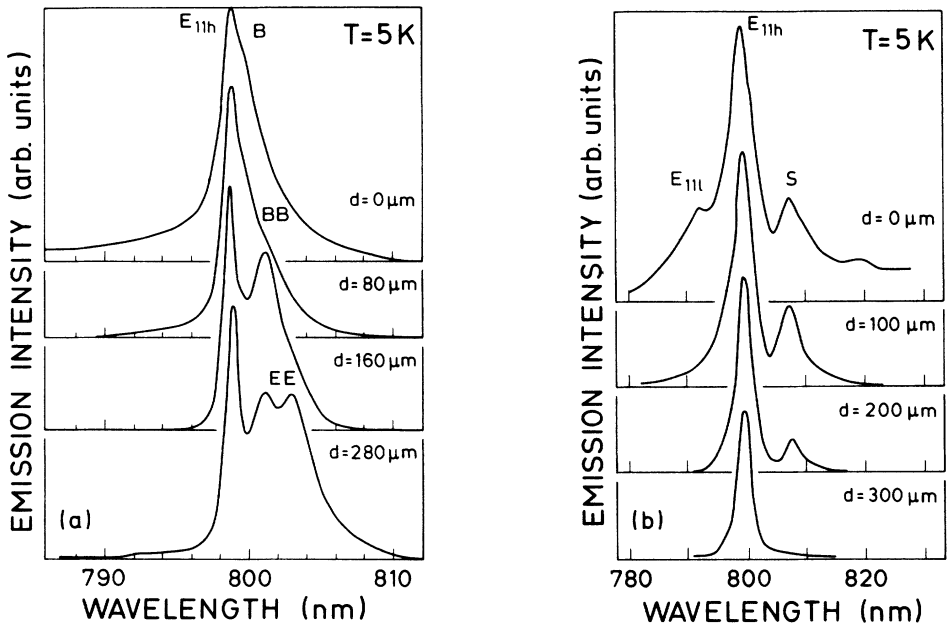

FIG. 1. Space-resolved luminescence spectra under (a) picosecond or (b) nanosecond excitation recorded at different distances d from the center of the excited spot. (BB represents inelastic biexciton-biexciton scattering, EE represents inelastic exciton-electron scattering.)

nounced changes are found in the PL spectra taken at different displacements d from the center of the excited spot. When the crystal is excited with picosecond pulses [Fig. 1(a)] the integrated PL spectrum at $d=0$ exhibits an excitonic peak corresponding to the $n=1$ heavy-hole exciton in the quantum well (E_{11h}) and a small shoulder (B band) about 2 meV on the low-energy side. When spatially resolving the luminescence far away from the spot center we observe an overall decrease of the emission intensity and the rising of new emission bands on the low-energy side of the E_{11h} emission. In particular, we detect a band (BB) peaked about 4 meV below the E_{11h} line at intermediate displacements ($80 < d < 180$ μm), and an additional line (EE) arising 7.5 meV below the E_{11h} line at $d > 160$ μm. It is worth noting that both the BB and the EE bands disappear when the excitation intensity is reduced (thus excluding the possibility that they can be due to any extrinsic or impurity-related emission) and that they can be selectively resolved by choosing the appropriate distance from the center of the excited spot, in allowance with the rapid expansion of the photogenerated carrier population[3,4] (a more detailed treatment of the quasiparticle density profile in space and time during the expansion will be the subject of a forthcoming paper).

A completely different behavior is observed under nanosecond excitation [Fig. 1(b)]. The luminescence spectrum taken from the center of the excited spot ($d=0$) exhibits broad emission lines and band filling of the higher-energy subbands (mainly the conduction-band to light-hole transition E_{11l}) and a sharp emission line (S) peaked about 12 meV below the exciton line. When increasing the displacement d, the S-band intensity decreases and the characteristic band-filling line shape is smoothed while the E_{11h} becomes sharper. About 300 μm away from the excitation spot center the emission spectrum recovers the excitonic character and closely resembles the usual luminescence curves measured at low excitation intensity.

The origin of this remarkable change in the spatially resolved PL spectra lies in the different relaxation processes underlying the quasiparticle photogeneration under different excitation conditions. During the pulse transient the picosecond excitation results in the photogeneration of a dense electron-hole plasma which relaxes to the bottom of the subband and forms excitons on a time scale of the order of 0.4 ns.[5] This leads to the establishment of a dense exciton gas in the time interval between two following pump pulses which gives rise to different excitonic radiative decay processes detectable in a time-integrated luminescence spectrum. Conversely, the nanosecond excitation leads to the generation of a dense electron-hole plasma under stationary conditions thus preventing the formation of excitons due to screening effects. In both cases the spatially resolved PL measurements allow us to study different species of photogenerated quasiparticles undergoing a fast expansion due to scattering and diffusion processes.

The attribution of the luminescence bands observed under ps excitation can be made on the basis of simple energetic arguments and according to the temperature and intensity dependence of the emission spectra shown in Fig. 2. The B band arising about 2 meV on the low-energy side of the E_{11h} line is found to grow superlinearly with the excitation intensity. Its energy position well accounts for the radiative recombination of biexcitons in 10-nm GaAs quantum wells.[6,7] This attribution is supported by the decay time of the B band which is found to be about one half of the exciton decay time measured at the same

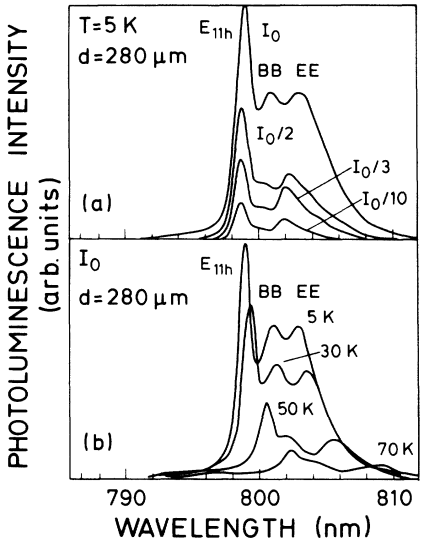

FIG. 2. (a) Intensity dependence and (b) temperature dependence of the space-resolved luminescence spectrum recorded 280 μm away from the center of the excited spot. The spectra of (b) have been measured at the maximum excitation intensity $I_0 = 0.5$ MW cm^{-2}.

excitation intensity, in agreement with previous biexciton studies in other MQW heterostructures.[8] The *BB* band lies one biexciton binding energy below the *B* band, showing a superlinear intensity dependence [Fig. 2(a)] and a temperature dependence very similar to the GaAs band gap [Fig. 2(b)]. In analogy to the case of II-VI semiconductors,[9] conservation of energy and momentum in the inelastic biexciton-biexciton scattering resulting in the creation of free excitons and a photon must lead to the observed emission spectrum peaked around $E = E_{11h} - 2E_b$ (where E_b is the biexciton binding energy). In addition, as discussed in the following, the time decay of this radiative recombination process is shorter than the biexciton decay time but longer than any excitonic scattering process, in accordance with the formation time of the biexciton itself. As far as the *EE* band is concerned [Fig. 2(b)], it lies well below the fundamental E_{11h} line and shifts to the red faster than the gap when the temperature is increased. The deviation from the expected temperature dependence of the gap is almost linear in the range 20–120 K and closely resembles the spectral behavior of the luminescence emitted by inelastic exciton-electron scattering process resulting in the ionization of one exciton and in the diffusion of a hot electron.[10–12]

Simple energetic arguments[10] allow us to account for this anomalous temperature dependence: Momentum and energy conservation in the exciton-electron scattering process results in a characteristic emission peaked at $E = E_{11h} - (M/m_e)\hbar^2K^2/2M$ [where $m_{e(h)}$ is the electron (hole) mass and $M = m_e + m_h$ is the total exciton mass]. By assuming a Boltzmann distribution of the excitons involved in the scattering processes the exciton-electron emission peaks at $E = E_{11h} - 1/2(M/m_e)k_BT$, which linearly deviates from the expected band-gap temperature dependence (in particular, for the case of GaAs quantum wells, it results in $E \cong E_{11h} - 3k_BT$). Inspection of our experimental spectra shows that the *EE* band shifts according to $E \cong E_{11h} - 2k_BT$ in the temperature range 20–120 K, in reasonable agreement with the theoretical prediction. It is worth noting that the exciton-exciton scattering process can hardly be invoked in order to explain the *EE* emission. Momentum and energy conservation for this collision process would lead to a characteristic emission peaked at $E = E_{11h} - \mathcal{R}_y + \hbar^2K^2/2M$ (Ref. 11) (where $\mathcal{R}_y$ is the exciton binding energy equal to 9.5 meV in a 10-nm GaAs quantum well[13]) which does not fit with our experimental findings.

The interpretation of the spectra taken under stationary conditions is more straightforward. The sharp superlinear peak observed at $d = 0$ is related to the electron-hole plasma emission (probably some scattered stimulated emission) also showing very high optical gain[14] and weak excitonic emission. At large displacements ($d > 100$ μm) the spatial expansion of the electron-hole plasma (EHP) results in the formation of excitons in the region of the crystal where the EHP density is reduced [it has been recently shown that the actual density of the EHP reduces by a factor of 5 in 10 μm after about 500 ps (Ref. 4)], thus resulting in the exciton luminescence at large d values.

Further insight into the above-discussed many-particle dynamics is obtained from the results of the time-resolved PL measurements. In Fig. 3 we show the time evolution of the E_{11h}, *BB*, and *EE* bands recorded by measuring the decay time of the PL collected 280 μm away from the center of the excited spot [spectrum $d = 280$ μm in Fig. 1(a)]. At the power density involved in our experiment we find an exciton decay time of about 2 ns and a biexci-

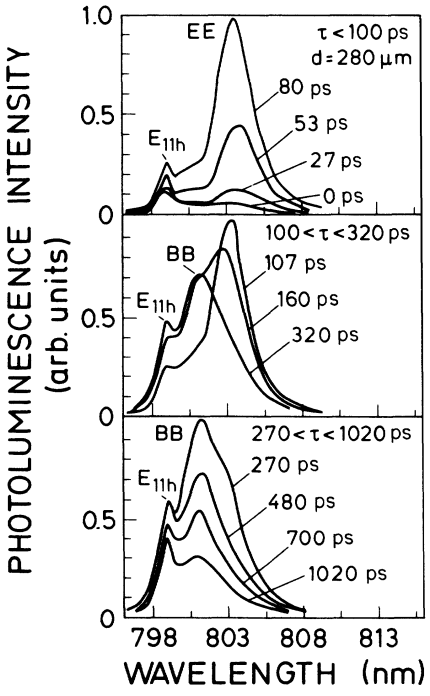

FIG. 3. Time evolution of the space-resolved luminescence spectrum recorded at $d = 280$ μm. The time τ is the time delay in the measurement. The temperature is 5 K.

ton lifetime of about 1 ns. The *BB* and *EE* bands exhibit much shorter decay times, about 600 and 250 ps, respectively, thus supporting our interpretation in terms of scattering processes in a dense exciton gas. In particular, in the early times [Fig. 3(a)] the *EE* band is found to arise with the pump pulse while a weaker emission can be observed at the E_{11h} energy position. Within the first 300 ps the *EE* band disappears [Fig. 3(b)] while the *BB* emission band grows and becomes dominant. At longer delays the *BB* reduces in intensity and, after about 1 ns [Fig. 3(c)], the E_{11h} is the main emission channel with a broad low-energy shoulder in the *BB*-band spectral region.

The observed time evolution supports the previous interpretation: Exciton-electron scattering processes are quite fast and follow the time evolution of the pulse. This indicates that the radiative recombination process underlying the *EE* emission involves excitons and electrons photogenerated in the transient of the pump pulse and quickly expanding along the crystal surface. In the 300 ps following the pump pulse [Fig. 3(b)] the *EE* scattering process disappears and a mixed exciton-biexciton gas is formed. The emission spectra in Fig. 3(b) are very similar to the ones obtained at lower pump intensities, when the photogenerated particle density is not high enough to generate exciton-electron scattering and only the E_{11h} and the *BB* emission are present. In this transient phase the biexciton-biexciton scattering seems to be the most efficient radiative recombination process. For longer times [Fig. 3(c)] these interacting excitonic processes lose importance and the excitonic character of the spontaneous emission is recovered. It is worth noting that the *EE* and *BB* bands can easily be observed only by means of spatially resolved luminescence measurements, which allows us to probe points of the crystal surface where the actual density of the quasiparticle is changing in time owing to the particle expansion.[3,4]

In conclusion, we have reported the first experimental evidence of exciton-electron and biexciton-biexciton inelastic scattering in GaAs MQW's by means of time- and space-resolved luminescence measurements. The observation of the exciton-electron scattering in GaAs MQW's indicates that this process is the most efficient radiative recombination mechanism also in two-dimensional GaAs at high exciton density, thus confirming previous studies on bulk GaAs.[15] In addition, the observation of biexciton-biexciton scattering can be considered a consequence of the biexciton wave-function confinement which strongly enhances the quantum properties of these excitonic molecules as compared to the bulk case.[6] It is worth noting that the investigated class of processes in quantum wells exhibits spectral features which are common to all semiconductors under intense optical excitation,[3,10–12,15] apparently independent of the dimensionality.

We are pleased to thank L. Tapfer for many stimulating discussions and for the structural study of the investigated samples. This work has been partly supported by the Bundesministerium für Forschung und Technologie of the Federal Republic of Germany.

[1]For a recent review, see S. Schmitt-Rink, D. S. Chemla, and D. A. B. Miller, Adv. Phys. **38**, 89 (1989).

[2]H. Q. Le, B. Lax, B. A. Vojak, and A. R. Calawa, Phys. Rev. B **32**, 1419 (1985).

[3]K. M. Romanek, H. Nather, J. Fischer, and E. O. Göbel, J. Lumin. **24/25**, 585 (1981).

[4]K. T. Tsen, O. F. Sankey, G. Halama, S. C. Y. Tsen, and H. Morkoc, Phys. Rev. B **39**, 6276 (1989); H. Hillmer, S. Hansmann, A. Forchel, M. Morohashi, E. Lopez, H. P. Meyer, and K. Ploog, Appl. Phys. Lett. **53**, 1937 (1988).

[5]Similar results on the exciton formation time have been recently reported by J. Kusano, Y. Segawa, Y. Aoyagi, S. Namba, and H. Okamoto, Phys. Rev. B **40**, 1685 (1989).

[6]D. A. Kleinman, Phys. Rev. B **28**, 871 (1983).

[7]R. Cingolani, Y. Chen, and K. Ploog, Phys. Rev. B **38**, 13487 (1988).

[8]S. Charbonneau, T. Steiner, M. L. W. Thewalt, E. S. Koteles, J. Y. Chi, and B. Elman, Phys. Rev. B **38**, 3583 (1988).

[9]H. Saito, S. Shionoya, and E. Hanamura, Solid State Commun. **12**, 227 (1973); H. Kuroda and S. Shionoya, J. Phys. Soc. Jpn. **36**, 476 (1974).

[10]C. I. Yu, T. Goto, and M. Ueta, J. Phys. Soc. Jpn. **34**, 693 (1973).

[11]T. Fisher and J. Bille, J. Appl. Phys. **45**, 3937 (1974).

[12]C. Klingshirn, Phys. Status Solidi (b) **71**, 547 (1975).

[13]See, e.g., E. J. Koteles and J. Y. Chi, Phys. Rev. B **37**, 6332 (1988).

[14]R. Cingolani, A. Cingolani, M. Ferrara, C. Moro, and K. Ploog (unpublished).

[15]E. Gobel, K. L. Shaklee, and R. Epworth, Solid State Commun. **17**, 1185 (1975).