Role of Biexcitons in the Stimulated Emission of Wide-Gap II-VI Quantum Wells

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(Received 7 February 1995)

On high-quality ZnCdSe/ZnSe quantum wells the occurrence of a new emission feature energetically below the exciton transition is demonstrated from which stimulated emission and gain emerge at elevated excitation levels (10 kW/cm^2). Application of a magnetic field allows us to distinguish this feature from bound excitons and evidence its biexciton nature. Subpicosecond excite-and-probe measurements reveal the scenario of exciton-exciton interaction in the presence of alloy disorder (localization). A model accounting for bound and antibound two-exciton states provides good agreement with the experimental data.

PACS numbers: 78.66.Hf, 78.45.+h

The laser action of semiconductors is normally described in terms of a degenerated electron-hole plasma. Indeed, that concept is very successful for GaAs and other III-V materials. On the other hand, it is well established that the exciton-exciton interaction plays an important part in the stimulated emission of wide-gap II-VI compounds [1]. The reason for that is the large exciton binding energy as result of which excitons are stable up to relatively high densities. The recent progress in the fabrication of II-VI quantum wells (QW's) and the related demonstration of blue-green light emitting devices gave rise to the question of how the laser processes are modified under two-dimensional confinement. In a pioneering study [2], the optical gain observed on ZnCdSe/ZnSe QW laser structures at low temperature was attributed to localized excitons. As a characteristic feature of those structures, the well is formed by a ternary compound, and the time-resolved and spectrally resolved photoluminescence (PL) clearly reveals localization of excitons on alloy fluctuations within a few 10 ps [3]. Indeed, if one assumes that only one exciton can be localized at a given site, stimulated emission necessarily occurs when a photon being resonant to a populated site is impinged on the structure. The conjecture behind that model, in the logical extreme, is an infinitely large repulsive exchange interaction between two localized excitons. However, excitons have a spin and, when oppositely aligned, the exchange interaction is even attractive under the right circumstances. In that case, a bound state (biexciton) is formed. In fact, biexcitons were observed in various II-VI bulk materials [1]. In the situation of two excitons on a localization site, the stability of the biexciton state depends crucially on the width and depth of the localization potential. Therefore, the question whether biexcitons exist in a disordered potential cannot be answered in a general way. In this Letter, we present direct experimental evidence that localized biexcitons occur in a ternary II-VI QW and that stimulated emission and gain at low temperature are related to those quasiparticles.

The samples are ZnCdSe/ZnSe multiple QW's grown on a (100) GaAs substrate by molecular beam epitaxy in a phase-locked epitaxy mode [4]. The structures are of excellent quality and exhibit pronounced and sharp exciton features. For absorption measurements, the substrate was removed by selective wet etching. We have studied a variety of structures differing by the width and Cd fraction of the QW's. Here we present typical data gained on a structure with five $Zn_{0.87}Cd_{0.13}Se$ QW's of 5 nm separated by 85 nm wide ZnSe barriers. For this design, magneto-optical studies [5] have yielded a binding energy of 33.6 meV for the heavy-hole (hh) exciton. The light-hole (lh) exciton is shifted by 35 meV to higher energies due to confinement and compressive in-plane strain. The high-excitation emission and the modal gain of the structure were studied in a steady-state regime. Dye laser pulses of 15 ns duration were used for resonant excitation of the 1h exciton state. The emission spectra were recorded in a backward geometry. The stripe-length-variation method [6] was used to measure the modal gain. Time-resolved excite-and-probe studies were performed with the amplified output of a hybrid-mode-locked dye laser (800 fs, 76 MHz) pumped by the third harmonic of a Nd-YLF laser. Pulse selection and amplification were achieved by a four stage excimer laser pumped dye amplifier. The amplifier output is used to excite the sample resonant to the 1h exciton and to generate a probe continuum in a D_2O cell. A spectrometer with a charge-coupled-device-matrix readout system is used to record simultaneously the transmitted probe light and a reference spectrum of the incident continuum. Only pump pulses with a fluctuation of less than 5% were accepted in the measurements. In addition, the unamplified pulse train output of the dye laser was utilized to measure the PL of the structure down to very low excitation levels in a time-integrated mode. Magnetic fields up to 12 T were applied in Faraday geometry by means of a split-coil magnetocryostat.

Figure 1(a) displays the PL spectrum for an optically injected 2D exciton density (n_{ex}) on the order of 10^8 cm^{-2}. The hh exciton emission feature (X_{hh}, FWHM = 5 meV) has an asymmetric line shape with a tail to lower energies. When the excitation power is increased, a second emission feature denoted by G emerges on the low-energy shoulder of the X_{hh} line shown in

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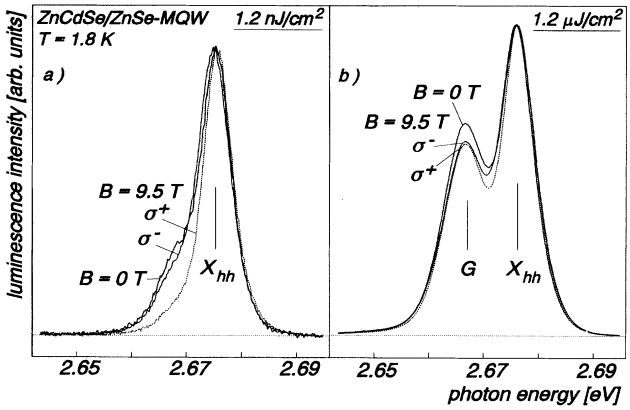

FIG. 1. PL spectra of a 5 × ($Zn_{0.87}Cd_{0.13}Se$/ZnSe, 5 nm, 85 nm) MQW at low and moderate excitation of the 1h continuum without and with external magnetic field (B).

Fig. 1(b) for $n_{ex} \approx 10^{11}$ cm^{-2}. No indication of G is found in the absorption or PL excitation spectrum. The nature of the G line turns out when a magnetic field is applied perpendicular to the QW's. The central X_{hh} structure exhibits the behavior expected for a single exciton state. Besides a diamagnetic shift (3.8 μeV/T^2), it shows a small Zeeman splitting of 0.2 meV and becomes weakly σ^- polarized (less than 20%). Since electron and hole spin are oppositely oriented in an optically allowed exciton, the Zeeman splittings compensate each other to a large extent. There is no significant effect of the excitation power upon the magnetic field behavior of X_{hh}. In contrast, the magnetic field data uncover a striking change of the mechanism responsible for the emission on the low-energy side of X_{hh} as a function of the exciton density. At low densities [Fig. 1(a)], the shoulder is strongly σ^- polarized. That behavior is characteristic for a bound exciton involving three spins, two of them oppositely aligned. Therefore, the Zeeman splitting is determined by the g factor of the third particle and, already at moderate magnetic fields, large enough that almost complete thermalization occurs at 1.8 K. We emphasize that the slight bound-exciton contribution identified in Fig. 1(a) substantiates the high sample quality and, together with the small exciton width, it is of key importance for the observations presented here. Increasing the excitation power, the bound-exciton emission saturates and, at fluxes of about 30 nJ/cm^2, the G line begins to develop. It occurs roughly in the same range where the bound-exciton transition was formerly observed, but its magnetic field behavior is entirely different. There is no measurable polarization of this lineup to the highest fields applied. That is the characteristic indication of a biexciton state with antiparallel spins of both the electrons and holes and, thus, a Zeeman splitting being exactly zero. Note that the G line is very sensitive on the excitation power and fluctuations of the pump laser are the cause of the slight changes seen for G in Fig. 1(b). A thorough evaluation of the data reveals a splitting of G similar to X_{hh} being the final state of the biexciton recombination. In previous PL studies on ZnCdSe/ZnSe [7] and ZnCdSe/ZnSSe [8] QW structures, respectively, low-energy bands located a similar distance from the X_{hh} peak were also attributed to bound excitons and biexcitons. But those features were sample dependent [7], and no direct evidence for their assignment could be given.

Figure 2 depicts the further development of the emission spectrum under excitation with more intensive pulses in a quasi-steady-state regime. For comparison, the PL excitation spectrum taken at the maximum of the X_{hh} PL structure is presented. The Stokes shift of 4 meV between emission and absorption demonstrates again the localization of the QW excitons on alloy fluctuations [3]. Specifically for II-VI materials, the localization is related to the excitonic center-of-mass motion as a result of the large binding energy. Similar to Fig. 1, the growth of G with increasing pulse intensity is seen, but, in addition, the appearance of stimulated emission on the position of G is manifested for excitation levels in the 10 kW/cm^2 range. From the 100 ps exciton lifetime observed in time-resolved PL measurements [3] and the absorption at the pump wavelength, one readily estimates $n_{ex} \approx 10^{11}$ cm^{-2}, which is definitively below the Mott density [9] (3 × 10^{12} cm^{-2}) of the present structure. Figure 3 displays emission spectra recorded from the sample edge for various lengths of the excitation stripe and the constructed gain curve. The correlation with the G feature is evident. For stripes longer than 250 μm gain saturation sets on.

Unlike studies on bulk materials [6], a more elaborate analysis of the stripe-length-variation data requires for the present sample design consideration of a fairly involved waveguide problem. More direct access to the gain and its dynamics is given by time-resolved excite-and-probe measurements. In addition, the use of pump pulses much shorter than the quasiparticle lifetime allows a better control of the exciton density, the precise knowledge of which is paramount for the interpretation of the experimental

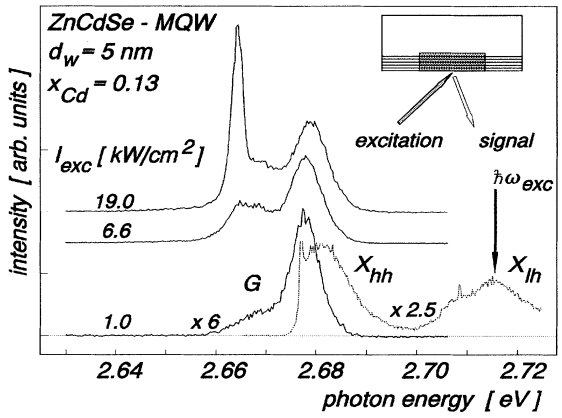

FIG. 2. High density emission spectra in backward geometry (see inset). Dotted curve: PL excitation spectrum.

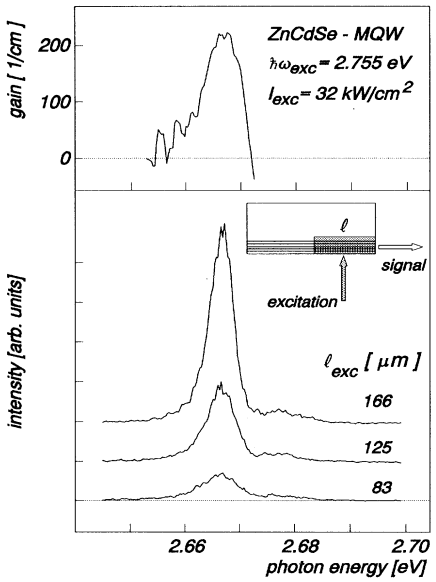

FIG. 3. Lower part: Emission spectra observed from the sample edges. l_{exc} is the length of the excitation stripe (see inset). Upper part: Modal gain deduced from the data.

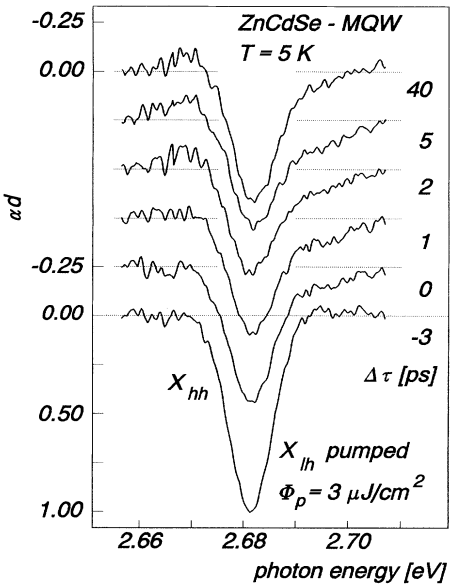

FIG. 4. Absorption of the excited structure as a function of the pump-probe delay. Excitation is resonant to the light-hole exciton resonance.

data. In a single-beam configuration, we have first measured the absorption of the pump flux for various incident levels. From the absorbed flux, the exciton density follows in a straightforward way, automatically accounting for nonlinear absorption changes for the pump photons. In Fig. 4, the adjusted exciton density is 5×10^{11} cm^{-2}, which guarantees that the absorption changes are caused by exciton-exciton interaction rather than an electron-hole plasma. Indeed, the absorption of the excited structure is still dominated by the X_{hh} exciton peak that is, however, quite different from the linear absorption feature. On the low-energy side, at the location of the G band seen in emission, gain develops a few ps after excitation. The total width of the QW layers is $d = 25$ nm. Thus the weak but clearly present amplification of the probe light corresponds to gain of some 10^4 cm^{-1}. The recovery (not displayed in Fig. 4) of the absorption changes takes place on a 100 ps time scale consistent with the lifetime seen in PL [3].

Currently, the lasing mechanism in II-VI QW's is under extensive discussion [2,10–13]. Doubtless, electron-hole plasma gain will occur at high excitation levels as observed by Cingolani *et al.* [11] for pump intensities of some 100 kW/cm^2. Here, we focus on a density range being at least 1 order of magnitude lower. In some aspects (excitation level, magnitude, and location of gain) our findings agree fairly well with those of Ding *et al.* [2]. The principal discrepancy is, however, that the gain develops in our structures from a separate transition being distinctly different from the inhomogeneous X_{hh} band. The magnetic field behavior as well as the excitation kinetics and its absence in absorption prove the biexcitonic nature of this transition. The model intimated by our data for the exciton-exciton interaction in the presence of localization is illustrated in Fig. 5 (inset). A similar model has been used to explain diffusive four wave mixing data of GaAs QW's [14], but it might be even more appropriate to the present situation. Since the quasiparticles are confined in one space dimension by the QW and in the two others by the localization potential one is, in analogy to a quantum dot [15], faced with a system of discrete energy levels. The two optically allowed single exciton states of angular momentum $J_x = \pm 1$ are radiatively coupled to four two-exciton states with $J_m = 0, \pm 2$, where one of the $J_m = 0$ states is a bound state (attraction $E_b < 2E_x$), while the other three have a positive interaction energy (repulsion $E_a > 2E_x$). Inclusion of the antibound states, omitted in Ref. [14], gives a correct description of what is termed phase space filling and exchange in extended systems [9]. A straightforward treatment of the density matrix yields for the contribution from a single site to the susceptibility (linear photon polarization)

$$\chi_0(\omega) = \chi_x(\omega) \quad \text{(no exciton excited)},$$

$$\chi_1(\omega) = -\tfrac{1}{2}\chi_x(\omega) + \tfrac{1}{4}G_b^2\chi_b(\omega) + \tfrac{5}{4}G_a^2\chi_a(\omega) \quad \text{(one exciton excited)},$$

$$\chi_2(\omega) = -\tfrac{1}{4}G_b^2\chi_b(\omega) \quad \text{(biexciton excited)},$$

with

$$\chi_x(\omega) = d^2\delta_{\gamma_x}(E_x - \hbar\omega),$$
$$\chi_{a/b}(\omega) = d^2\delta_{\gamma_{a/b}}(E_{a/b} - E_x - \hbar\omega).$$

d is the excitonic dipole moment, $G_{(a/b)}$ defines the modification for the two-exciton transition, and δ_γ denotes

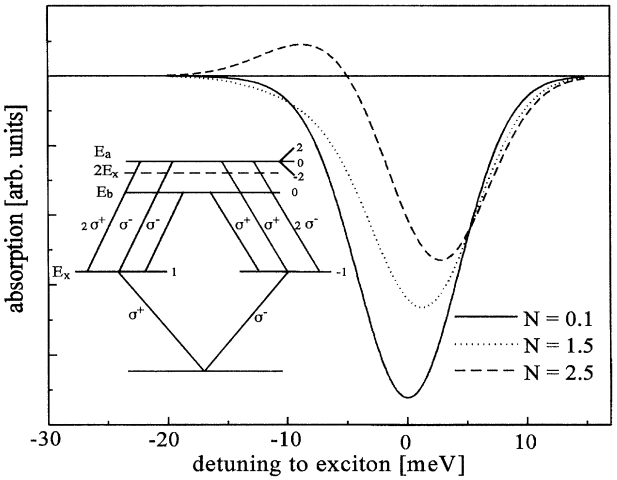

FIG. 5. Calculated absorption and gain spectrum (see text). N is the average number of excitons per site. $G_a = 0.5$, $G_b = 0.8$, $2E_x - E_a = -2$ meV, $2E_x - E_b = 8$ meV, $\gamma_x = \gamma_a = \gamma_b = 6$ meV. Inset: transition schematics.

energy conservation with broadening γ. Dropping off the two-pair contributions ($G_{a/b} = 0$ or $E_{a/b} = \infty$), one obtains gain $\chi_1 = -\frac{1}{2}\chi_x$ due to localized excitons [2]. On the other hand, neglecting the exciton-exciton interaction ($G_{a/b} = 1$ and $E_{a/b} = 2E_x$) [16] yields $\chi_1 = \chi_0$, which recovers the boson character of independent excitons. The true situation is intermediate between those limits and the relative contributions from the above susceptibilities to the total absorption are controlled by the occupation statistics of the localization sites. A plot assuming Poisson statistics, a Gaussian line shape, and parameters appropriate to the experiment is presented in Fig. 5. Following Wilkinson *et al.* [17], we estimate a density of 3×10^{11} cm^{-2} for the localization sites in the structure being very close to the density of photoexcited excitons of the pump-probe study. This explains why only excited state absorption is seen in Fig. 4 at early delays. Once created, the excitons move in the potential landscape to local minima where they meet and form biexcitons. That explains the formation time of the gain which, in fact, is consistent with the time scale of the exciton localization deduced from PL [3]. A detailed description of the excited state absorption and gain requires the treatment of the localization kinetics and a correct account of the inhomogeneous line shape, both being beyond the scope of this Letter. Nonetheless, the simple qualitative model reproduces the main features of the experimental findings—first absorption with an asymmetry to higher energies due to antibound two-exciton states and subsequent formation of biexcitonic gain—in a satisfactory way.

The average biexciton binding energy deduced from the PL data in Fig. 1 is about 10 meV, which is larger than both the value known for ZnSe bulk material (3.2 meV [1]) and the one theoretically expected for a QW [18] reflecting the anticipated increase of the two-exciton correlation energy in the situation of 3D confinement [15]. Zero-dimensional biexcitons localized on well width fluctuations recently observed on GaAs/GaAlAs QW's [19] exhibit a binding energy increase even by a factor of 20 relative to bulk GaAs (0.2 meV). The markedly smaller enhancement seen in ZnCdSe QW's is obviously a consequence of the much different localization potential provided by the alloy fluctuations. We note that on ZnSe/ZnMnSe structures with a binary well, no hint at localized biexciton emission was found and the observed gain is well explained in terms of an electron-hole plasma [13]. In a given structure, various laser mechanisms (localized excitons [2] and biexcitons, exciton phonon [10], inelastic exciton exciton [12], plasma [11], etc.) complete with each other, the threshold of which is also design and geometry dependent. The present QW samples are characterized by a radiatively dominated exciton lifetime at low temperature and a homogeneous width of 0.1 meV [3].

In conclusion, we have demonstrated the existence of localized biexcitons in ternary ZnCdSe QW's and their important role in the lasing properties at low temperatures. In view of the relatively large binding energy, biexcitons might be even present at elevated temperatures.

We want to thank J. Griesche, N. Hoffmann, and M. Rabe for growth of the samples and acknowledge helpful discussions with H. J. Wünsche.

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