Excitonic Gain and Laser Emission in ZnSe-Based Quantum Wells

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We show spectroscopically that the origin of optical gain and laser emission in (Zn,Cd)Se/ZnSe quantum wells at blue-green wavelengths is of excitonic nature. This circumstance derives from the large enhancement in the exciton binding and its oscillator strength which occurs in the quasi-2D case, so that an exciton gas is stable against ionization by optical phonons up to room temperature and that gain in the context of partial phase-space filling can develop at pair densities below the onset to an electron-hole plasma.

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Major recent developments in wide-band-gap II-VI semiconductor heterostructures have culminated in the demonstration of blue-green [1,2] and blue [3] diode lasers in ZnSe-based quantum wells (QW's). A key issue in optimizing such diode lasers for eventual applications (e.g., high-density optical memories) concerns the microscopic mechanism responsible for gain and stimulated emission. That is, are there departures from the standard degenerate electron-hole (e-h) pair picture which is deeply rooted in population-inversion models, e.g., for the III-V semiconductor lasers? Closer examination is appropriate given the strong excitonic effects which have been recently observed in the optical properties of ZnSe-based QW's. In particular, we have demonstrated for the type-I (Zn,Cd)Se/ZnSe QW system that the quasi-two-dimensional confinement of electron-hole pairs leads to enhancement of the exciton oscillator strength (measured typically to be about a factor of 6 over the bulk value) and its binding energy E_x (to ≈ 40 meV), so that the latter exceeds the longitudinal optical (LO) phonon energy $\hbar\omega_{LO}=31$ meV [4]. Given the very large Fröhlich interaction in these relatively ionic materials, inelastic scattering of excitons by LO phonons into the free pair continuum is a primary reason for the lack of exciton features in absorption in bulk ZnSe above cryogenic temperatures. In striking contrast to bulk ZnSe, strong, distinct exciton absorption features can be seen in the QW's beyond room temperature [4].

Here we present experimental evidence that excitons also play a central role in the formation of gain in the (Zn,Cd)Se/ZnSe QW's which have emerged as the prime candidates for diode lasers in the blue-green portion of the spectrum. In particular, we argue that the pair density at which laser emission commences remains sufficiently low so that the system remains predominantly excitonic and has not evolved into a degenerate electron-hole plasma (EHP), over a wide range of temperatures. Three types of experiments underscore this argument: (i) laser action under resonant optical pumping into the lowest exciton resonance, (ii) the near spectral constancy of emission over several decades of excitation, starting with spontaneous emission well below laser threshold, and (iii) pump-probe experiments to show that the exciton resonance remains present under excitation density equivalent to that in a laser device.

We concentrate below on a multiple-quantum-well structure composed of six $Zn_{0.76}Cd_{0.24}Se$ well layers of $L_w=90$ Å, separated by 500-Å-thick ZnSe barrier layers. The same type-I heterostructure also defines the active region in the recent diode lasers, and its electronic structure is discussed elsewhere [4,5]. For reference, the exciton diameter in bulk ZnSe is about 90 Å. Optically pumped laser action was studied in cleaved structures of various lengths, with pump excitation directed along the z direction, perpendicular to the QW layer plane (and the optical axis of the resonator).

Figure 1 shows an example of laser performance in such an edge emission geometry for a 150-μm-long device, where the pump photon energy is varied near the $n=1$ heavy-hole (HH) exciton ground state. For spectral reference, the absorption spectrum of an unexcited sample is included in the top trace. (Recall that the free e-h pair continuum is approximately 40 meV higher in energy.) The data were taken under short pulsed excitation ($\tau_p \approx 5$ psec) of constant intensity so that the initially absorbed photon density could be accurately translated to determine the maximum exciton density deposited directly into the QW's. At near threshold excitation level (a form of excitation spectroscopy for *stimulated* emission), Fig. 1 demonstrates vividly that laser emission, occurring in the low-energy tail of the absorption resonance, is optimized when the incident photon energy is set at the peak of the HH exciton absorption (where $\alpha_p=1.1\times10^5$ cm^{-1}). At the temperature of $T=10$ K, we have $kT \ll E_x, \hbar\omega_{LO}$ so that the photoexcited electron-hole system remains unambiguously cold, including allowances for carrier-carrier and carrier-phonon inelastic scattering events. Furthermore, we find that the electron-hole pair density at threshold for laser emission is at most $n_T \approx 7.3\times10^{11}$ cm^{-2} in the QW's. This value is nearly an order of magnitude below the density at which the exciton phase becomes unstable with respect to an EHP,

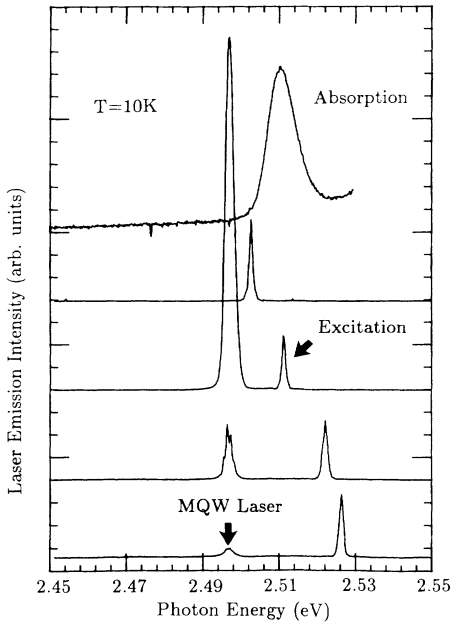

FIG. 1. Resonant pumping of the (Zn,Cd)Se/ZnSe MQW laser at $T=10$ K, with the top trace showing the $n=1$ HH exciton absorption resonance of the unexcited sample for reference. The pump photon energy is measured by simultaneously scattering some of this source into the spectrometer.

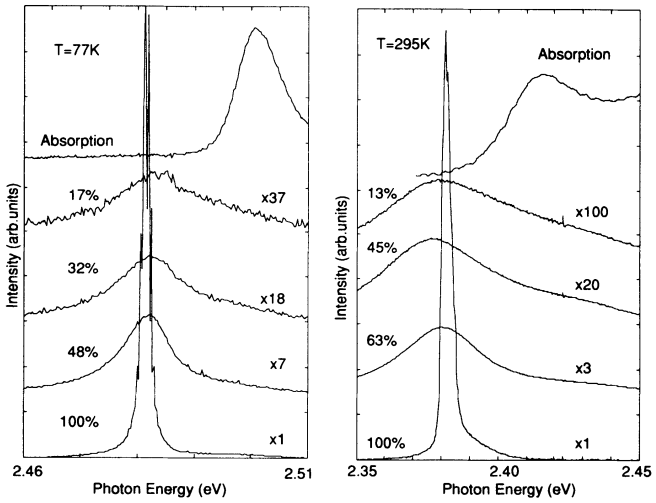

FIG. 2. Evolution of laser emission from the spontaneous emission spectrum at $T=77$ and 295 K. The $n=1$ HH exciton absorption resonance is shown for reference. The excitation level is indicated as percentage of the maximum used in the experiment, slightly above the laser threshold.

when using the commonly accepted criteria [6] of $n_c \approx (\pi a_B^2)^{-1} \approx 5.7\times10^{12}$ cm^{-2} for parameters in ZnSe.

The criterion for n_c takes into account many-electron-hole interactions in the following well-known way. With increasing pair density, the exciton (i.e., bound pair state) energy remains remarkably constant due to a near cancellation of attractive (van der Waal-like) and repulsive (core-potential-like) contributions [7]. The free-particle band gap, on the other hand, is subject to renormalization effects which eventually lower its value below the exciton state; hence the latter becomes unstable. In terms of such a "phase diagram," while the III-V semiconductor lasers commonly operate at densities well into the EHP regime, the experimentally determined pair density in the present case strongly suggests that the many-electron-hole system has remained excitonic under laser operating conditions. We have performed the resonant pumping experiments up to $T=240$ K while injecting a pair density which is below n_c at the onset of lasing (the upper temperature determined by limitations in our pump dye laser tuning range and power).

Figure 2 demonstrates how the stimulated emission emerges directly from spontaneous emission spectra in the $n=1$ HH exciton region without spectral shifts which might be indicators on an exciton-EHP transition. The data are shown at $T=77$ and 295 K for 150- and 780-μm-long devices, respectively, pumped under steady-state conditions in the edge emission geometry. (In order to maintain a comparable intensity of excitation in both cases, the lower gain at room temperature required the use of a longer resonator.) We have studied the emission at excitation levels as low as 4 orders of magnitude below the laser threshold to demonstrate the lack of any substantial spectral shifts. Note also that the condition $E_x > \hbar\omega_{LO}$ ensures that quasi-2D excitons are expected to dominate the spontaneous emission. (In edge geometry, the spontaneous emission is subject to finite self-absorption and hence a spectral redshift due to the long optical path length; however, we have verified by simultaneous measurement of the surface emission in the z direction that the spontaneous emission very nearly coincides with the $n=1$ HH absorption peak to room temperature.) Details of the temperature dependence of these measurements will be given elsewhere; both the laser (and spontaneous) emission smoothly track the exciton resonance, on its low-energy tail, from $T=10$ K to room temperature.

We also performed time-resolved pump-probe experiments at $T=10$ K on uncleaved samples where the opaque GaAs substrate was chemically removed. The experiments were carried out under resonant excitation conditions at excitation levels which were sufficient to initiate the laser emission in corresponding cleaved laser structures (e.g., Fig. 1 where the laser threshold corresponds to an incident energy density of 0.9 μJ/cm^2). In these experiments, changes in the probe beam transmission $\delta T/T \approx -\delta\alpha L$ (through the QW section of thickness L) in the z direction were measured as a function of time, following initial excitation at time $t=0$ at various pump photon energies.

The uppermost trace of Fig. 3 shows the photon energies of the pump and probe beams relative to $n=1$ HH exciton absorption in one such experiment. The bottom three panels display the transient differential probe

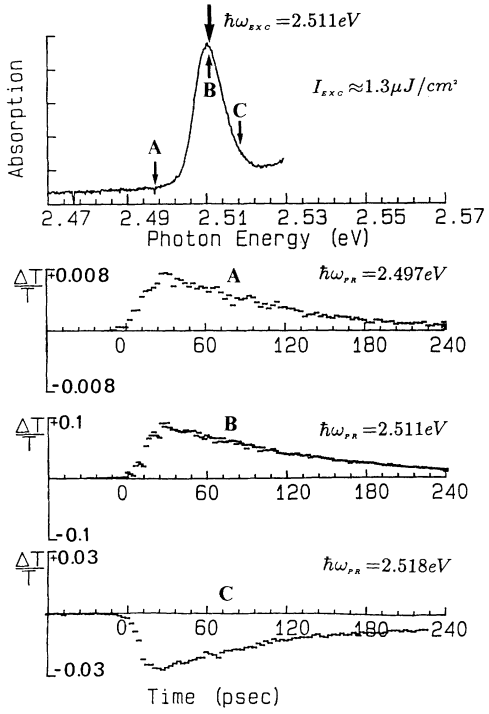

FIG. 3. Transient differential probe transmission $\delta T(t)/T$ for three different probe energies, following excitation at $t=0$ by a psec pulse at 2.511 eV. The top trace indicates the photon energies relative to the $n=1$ HH exciton resonance.

transmission. The excitation level for all the traces corresponds to 1.3 μJ/cm^2 in the 5-psec-long pump pulses. For the probe position at $\hbar\omega_{pr}=2.497$ eV, where $\alpha L=6.4\times10^{-3}$ without excitation, the peak value of $\delta T/T=8\times10^{-3}$ *unambiguously indicates the presence of real gain* (measured in the z direction), whereas at $\hbar\omega_{pr}=2.511$ eV the measured value of $\delta T/T=0.1$ shows the presence of diminished absorption (note the initial absorption $\alpha L=0.56$ at the latter probe position). At $\hbar\omega_{pr}=2.518$ eV, $\delta T/T=-3\times10^{-2}$, where the sign reversal indicates the presence of *induced absorption.* The typical decay time associated with the traces in Fig. 3 is approximately 200 psec, a characteristic quasi-2D exciton recombination time obtained from transient photoluminescence experiments. A fuller description of extensive pump-probe experiments will be given elsewhere. The key point in Fig. 3 is that while the peak absorption strength is reduced (indicated by the partial absorption saturation) and its width is broadened by exciton-exciton scattering (induced absorption on the high-energy side), the exciton resonance is maintained while supplying gain to the low-energy side of the resonance.

The possibility of excitonic stimulated emission in wide gap II-VI semiconductors was first suggested by Hvam in experiments on bulk CdS and ZnO [8], followed by comparable work in other bulk II-VI materials [9], recently revisited in bulk ZnSe [10]. These experiments were limited to liquid-helium temperature, lacked clear definition of the exciton absorption resonance, and argued that exciton-exciton or exciton-optical phonon scattering processes would lead to gain at photon energies well below the excitonic absorption edge. Our measured stimulated emission wavelengths (typically about 12–15 meV below the exciton absorption peak) show directly that neither of these processes is energetically feasible in the present QW system.

We now outline a phenomenological model for excitonic gain in the (Zn,Cd)Se/ZnSe QW's beginning with the inhomogeneous, isolated $n=1$ HH exciton resonance. Excitons are subject to localization (at low temperature) and scattering (at higher temperatures) due to the alloy composition fluctuations and the random well thickness variations which lead to an inhomogeneously broadened absorption profile with a Gaussian line shape [11]. If a given localization site or a volume defined by the mean free path can only be occupied by one exciton, that is, that the exchange interaction between the electrons and holes of different excitons is considered to be infinitely large, the population inversion condition for such excitons is $f-(1-f)=2f-1>0$, where f is the probability of the state being occupied. (The validity of this assumption will be examined below for a high-temperature situation where homogeneous broadening dominates.) The gain or absorption at a particular energy is the sum of the contributions of the exciton states which originate from different localized sites because of finite homogeneous broadening. The contribution is positive (gain) if the "localization site" is occupied and negative (absorption) if unoccupied. The argument is a variation of the phase-space-filling argument, now applied to an *inhomogeneous* system [6].

In terms of a highly simplified three-energy-level scheme, electron-hole-pair or exciton energy relaxation occurs from initially excited states $|X\rangle$ to $n=1$ HH exciton states $|X'\rangle$ where gain is possible in terms of induced emission to the ground state $|0\rangle$. The relaxation of the e-h pair or the exciton population to such states is quite rapid in the (Zn,Cd)Se/ZnSe system and beyond the resolution of the approximately 20-psec cross-correlation temporal jitter of the dye lasers in our transient experiments (e.g., rise times in Fig. 3). In broad analogy with the case of conventional degenerate free electron-hole plasma system, one needs here also sufficient excitation to drive the initially absorptive material through the transparency condition into the gain regime. The gain/absorption coefficient then can be written as the following, if the chemical potential μ is introduced:

$$g(E)=\int_{-\infty}^{\infty} D_i(E')D_h(E-E')\left[\frac{2}{e^{(E'-\mu)/kT}}-1\right]dE', \tag{1}$$

where $D_i(E)$ is the inhomogeneous and $D_h(E)$ the homogeneous line shape function. The normalized total density of excitons n is given by

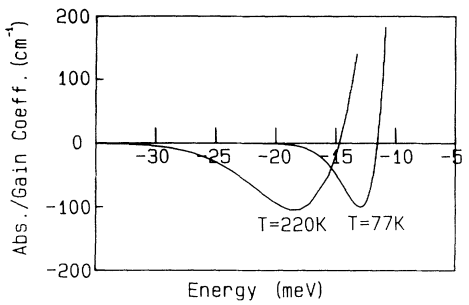

FIG. 4. Relevant portion of the calculated absorption/gain spectrum at $T=77$ and 220 K according to the phenomenological model described in the text. The horizontal axis indicates the photon energy measured from the center of the $n=1$ HH inhomogeneously broadened exciton resonance.

$$n=\int_{-\infty}^{\infty} D_i(E)\frac{1}{e^{(E-\mu)/kT}+1}dE\,. \tag{2}$$

The energies in both equations are defined with respect to the center of the exciton resonance. The quantity $g(E)$ is normalized to the peak value of the absorption coefficient in unexcited material while the exciton density n is normalized to the maximum density of excitons $N_{\max}$, a good estimate of which is given by the phase-space-filling criterion for the entire inhomogeneous line, $N_{\max}=n_c \approx (\pi a_B^2)^{-1}$. An example of our calculations is shown in Fig. 4 where exciton gain is displayed at $T=77$ and 220 K (the value for the gain reflects our typical circumstances in either optically of electrically pumped lasers, including the optical waveguide confinement factor). The latter temperature is an approximate limit for our model with an inhomogeneous line. The e-h pair densities per QW correspond to $n_s=0.9\times10^{12}$ and 2.5×10^{12} cm^{-2} for the two temperatures, respectively. Note that in this highly simplified approach, exciton-exciton interaction effects are completely ignored. To first order, such interaction leads to finite spectral shifts in the position of the gain maxima. Note that the densities are both below the estimated EHP phase transition.

If all the exciton states are empty, Eq. (1) yields absorption profiles at different temperatures. The linewidth can be written as $(\Delta_i^2+\Delta_h^2)^{1/2}$ if the homogeneous line shape is also taken as a Gaussian to simplify the algebra. The measured inhomogeneous linewidth in our QW samples was ≈ 9 meV. It is illustrative to consider two limits of linewidth broadening. In the limit of extreme inhomogeneous broadening, Eq. (1) evolves to

$$g(E)=D_i(E)\{2[\exp((E-\mu)/kT)]^{-1}-1\}\,.$$

For an exciton resonance with a large oscillator strength it is difficult to achieve gain near the peak of the absorption line; on the other hand, the necessary threshold gain for laser operation is readily available on the low-energy side. In the opposite limit of homogeneous broadening dominating, we obtain $g(E)=D_h(E)(2n-1)$. In this case gain is only possible under extreme conditions ($n>0.5$) where the excitonic gas is beginning to lose its stability with respect to the phase transition to an EHP.

Based on our phenomenological model we have obtained good agreement with our experimental observations for the temperature dependence of the threshold exciton density. Beyond the temperature of approximately 220 K, however, homogeneous broadening due to the exciton-LO-phonon interaction in our system (obtained from measured absorption linewidths [4]) becomes an increasingly important factor and the required e-h pair density implies that the system is beginning to adapt an EHP-like aspect as well. Further work at and above room temperature, the range important for practical diode lasers, is in progress. An attractive feature of the exciton gain mechanism is a lower e-h pair density at threshold for laser action when compared with the degenerate EHP case; hence our results should also be useful in the further development of the new blue-green diode lasers.

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