Gain spectroscopy of excitonic molecules and its dynamics in a ZnSe single quantum well

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We demonstrate spectroscopically how optical gain is formed in an interacting system of excitons and biexcitons in a single ZnSe quantum well. The dynamics of gain formation are studied on a subpicosecond time scale in pump-probe experiments, revealing the influence of coherent effects and the impact of exciton-exciton and exciton-biexciton interactions. Spectrally resolved, polarization-dependent degenerate four-wave-mixing experiments further demonstrate how the excitonic many-body phenomena profoundly influence the nonlinear optical response in this II-VI semiconductor heterostructure. [S0163-1829(96)03043-3]

The development of wide band-gap II-VI heterostructures of high crystalline quality has led to progress in the fundamental understanding of their key electronic and optical properties, contributing directly to the evolution of the blue-green semiconductor diode lasers. A key issue of both fundamental and applied impact concerns those microscopic processes that are responsible for optical gain in the quantum well (QW) that forms the active region in a laser device, given the strong electron-hole Coulomb interaction (exciton) effects that are readily observed, e.g., in absorption. The Coulomb effects significantly enhance the interband optical cross section, both for absorption and radiative recombination, including a high-density electron-hole system in the regime of stimulated emission. There have been a number of reports of excitonically enhanced gain in II-VI heterostructures, mainly in the (Zn,Cd)Se QWs, ranging from low-temperature optically pumped systems[1–6] to room-temperature diode lasers.[7] Even at room temperature, the spectroscopic signature of excitonic correlations appears clearly in the experiment, while theoretical approaches based on the many-body semiconductor Bloch equations have discussed the problem in terms of excitonic enhancements gained by the Coulomb correlations.[8] The experimental fingerprints associated with the excitonic effects are strongly influenced by the system temperature and pair density; they are especially dramatic at low temperatures where scattering by optical phonons is weak and the e-h correlated bound states are clearly seen to dominate optical gain from direct spectroscopic evidence.

A particularly interesting aspect of the gain at cryogenic temperatures (roughly from $T=10$ to 100 K) is the recent discovery that excitonic molecules can play the central role in the formation of gain and stimulated emission.[9,10] The existence of molecular states in bulk II-VI materials[11] and in ZnSe QWs (Ref. 12) was discovered some time ago, but only now has the role of biexcitons in the formation of optical gain in a heterostructure been clearly identified.[9,10] The ideas of stimulated emission by excitonic molecules in semiconductors are not new per se, having been extensively studied, e.g., in bulk cuprite halides some time ago.[13] However, the manifestation of the molecular state in the blue-green II-VI laser material gives an unusually direct opportunity to examine these excitation and associated many-body interactions, including dynamical behavior, that has possible implications in the light-emitter device design.

In this work, we take advantage of a single binary ZnSe QW, in conjunction with sensitive spectroscopic measurement techniques, to study spectroscopically the exciton and biexciton dynamics in a high-density regime ($n_s \sim 10^{11}$ cm^{-2}) where very large optical gains, approaching 10^5 cm^{-1}, can be readily realized at low temperatures. Although strongly interacting, the e-h pair densities remain well below a ''Mott transition'' so that free-carrier screening effects are unimportant.

In our recent report,[10] the results of four-wave-mixing experiments and the observation of laser emission in a resonator structure under optical pumping were used to argue that the exciton molecules are the source of optical gain in a ZnSe QW at a low temperature. In this paper, we present results of actual gain spectroscopy that show unambiguously the dominant role of biexcitons and, more important, how the dynamics of the interacting exciton-biexciton system develops from the initial transient coherent regime on the subpicosecond time scale into the collision limited (incoherent) regime. These results provide a direct insight into the kinetics of formation of the exciton molecules under resonant excitation conditions. The choice of the ZnSe QW heterostructure offers us exceptional spectral clarity on a sub-electron-volts scale, so that the exciton and biexciton resonances are very well isolated spectrally.[10] Specifically, the absence of alloy potential fluctuations (such as in $Zn_xCd_{1-x}Se$) and the small degree of compositional and structural disorder in this binary QW gives us an opportunity to investigate a dense exciton-biexciton system in the absence of localization and/or disorder-induced scattering effects (see, e.g., Ref. 9).

Key results from the work presented in this paper, where the many-exciton interactions dominate the optical response, include the formation dynamics of the excitonic molecular state and associated optical polarizations which have been tracked by time-resolved spectroscopy from the coherent to the incoherent regimes. In particular, we find a very strong carrier density dependence in the coherent regime, as illustrated below.

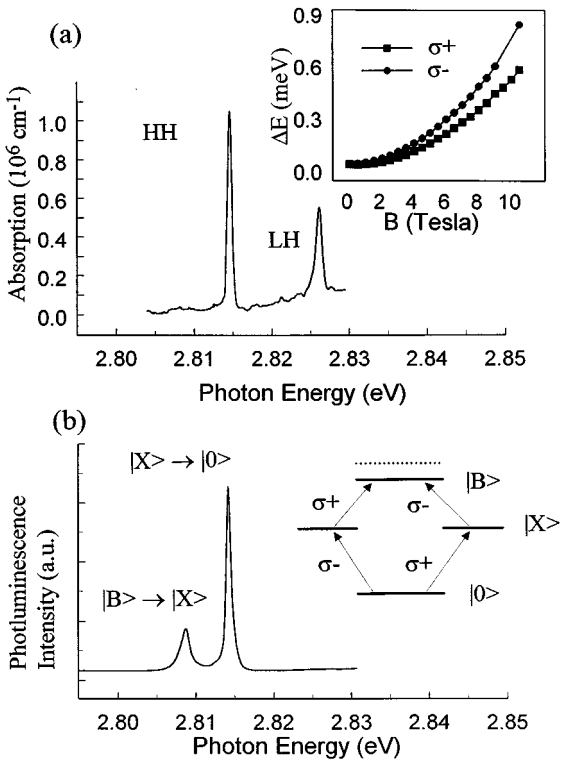

FIG. 1. (a) Absorption coefficient of and (b) photoluminescence from the single ZnSe QW sample at $T=10$ K near the $n=1$ QW exciton transition. Insets: (a) the diamagnetic shift of the heavy-hole exciton absorption for opposite circular polarizations; (b) the energy-level schematic for a system of excitons ($|X\rangle$) and biexcitons ($|B\rangle$); the dotted line above the $|B\rangle$ state denotes the antibound state of two excitons.

The samples for this study were grown by molecular-beam epitaxy on lattice-matched GaAs substrates and epitaxial buffer layers. The configuration for the pseudomorphic II-VI materials was a ZnSe/Zn(S,Se)/(Zn,Mg)(S,Se) separate confinement heterostructure (SCH). The active region was formed by a single 75-Å-thick QW, surrounded by 1000-Å-thick Zn(S,Se) barrier and optical waveguide layers, cladded by 0.5-μm-thick $Zn_xMg_{1-x}SSe$ optical confinement layers. The GaAs substrate and buffer layer were subsequently removed by wet chemical etching.

Figure 1 shows the absorption [Fig. 1(a)] and photoluminescence [PL, Fig. 1(b)] spectra at $T=10$ K near the $n=1$ QW exciton, displaying a linewidth of approximately $E=0.6$ meV for the heavy-hole (HH) resonance at $\hbar\omega=2.814$ eV. The peak value of the absorption coefficient for the HH transition is very large, $\alpha=1.1\times10^6$ cm^{-1}, corresponding to an oscillator strength $f_{ex}=2\times10^{13}$ cm^{-2}. The absence of a detectable Stokes shift between absorption and PL implies that excitons do not experience any significant localization and the peak in PL at $\hbar\omega=2.814$ eV is due to ''free'' exciton emission (labeled as the $|X\rangle\rightarrow|0\rangle$ transition). Under the low excitation conditions of Fig. 1 ($n_s=10^9$ cm^{-2}), the linewidth is nonetheless of inhomogeneous origin, as verified from transient four-wave-mixing data. The exciton binding energy 20–25 meV has been determined by measuring the shift of the excitonic absorption resonance in a magnetic field [inset in Fig. 1(a)].

The low-energy peak in PL at $\hbar\omega=2.808$ eV is due to a radiative decay of a biexciton into an exciton and a photon, labeled as the $|B\rangle\rightarrow|X\rangle$ transition in Fig. 1(b). The biexcitonic origin of this emission has been revealed by degenerate four-wave-mixing (DFWM) experiments, as discussed in our recent report.[10] In particular, we have identified the contributions from both the $|X\rangle$ and $|B\rangle$ resonances in the spectrum of the DFWM signal (self-diffracted beam). However, the contribution from the $|B\rangle$ resonance is not observed in the DFWM spectra if circularly polarized beams are used in the experiment. It proves a biexcitonic origin of the resonance at $\hbar\omega=2.808$ eV, since a biexciton can be formed only by two excitons with opposite orientation of spins (different circular polarizations). The inset in Fig. 1(b) displays the energy-level diagram for an exciton-biexciton system, which has been initially introduced in Ref. 14. Strong polarization dependence of the DFWM spectra (which is a subject of a separate publication) implies the presence of many-body interactions in an exciton-biexciton system. Quantum beats between the $|X\rangle$ and $|B\rangle$ resonances have also been observed.[10]

A most interesting and attractive feature of a system of interacting excitons and biexcitons in the ZnSe-based heterostructures is the ability to form optical gain, leading to stimulated emission. As we reported recently the gain in a ZnSe SQW at cryogenic temperatures is large enough to attain laser action quite readily in structures with optical resonators.[10] For this purpose, our samples were cleaved into 300–500-μm long cavities and optically pumped by the fsec laser pulses perpendicular to the QW layer plane (and resonator axis). The stimulated emission was observed at the low-energy portion of the $|B\rangle$ resonance.

The observation of laser action from any device represents, of course, a clear manifestation for the presence of optical gain in the system, yet provides relatively little direct insight into the microscopic processes that determine and control the details of such gain. For example, since a laser operates with a careful internal balance between gain and losses, the spectral position of stimulated emission need not exactly coincide with the maximum in the optical gain. In order to elucidate the specific role of the excitonic molecules in the formation of gain in the ZnSe QW, we have performed a systematic set of transient pump-probe spectroscopic studies described next. The time-resolved techniques, with subpicosecond resolution, give important insight into the role of exciton-exciton interactions in a high-density regime under circumstances in which the bound states dominate the e-h pair energetics. Further, the time window which we examine here (from about 300 fsec to 10 psec) allows us to cover the range in which the excitonic gas makes a transition from an initially coherent regime of electromagnetic response into an incoherent one. We note that related gain spectroscopic experiments have been very recently carried out by Kreller *et al.* on $Zn_xCd_{1-x}Se$ MQW samples to show the key role of localized biexcitons on the optical gain in this weakly disordered quasi-two-dimensional system.[9]

For good experimental sensitivity and a signal-to-noise ratio, we have used the pump and probe method combined with a frequency down-conversion lock-in detection technique. With this type of electronic instrumentation, one can reach almost a shot-noise-limited detection of pump-induced changes in the case of a very weak probe beam.[15] In our

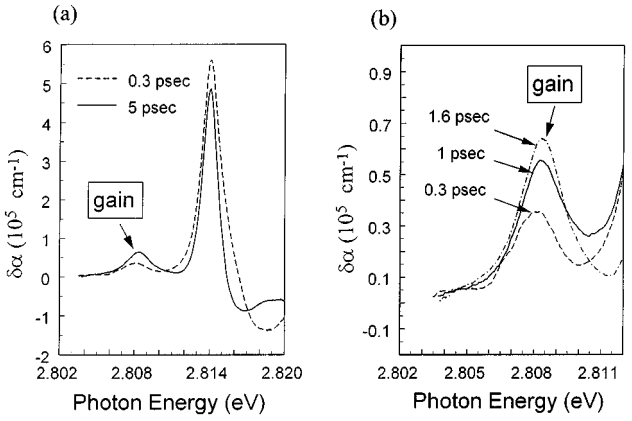

FIG. 2. (a) Differential probe spectra, expressed as a change in the absorption coefficient, in the vicinity of the exciton and biexciton resonances for two different pump-probe time delays, at a pump excitation corresponding to $n=4\times10^{11}$ cm^{-2}. Real net gain is measured at the $|B\rangle$ resonance as indicated; (b) shows the evolution of the gain in this high excitation regime ($T=10$ K).

experiments, the pump beam from the frequency doubled, mode-locked Ti: sapphire laser (whose spectrum overlapped both the exciton and biexciton resonances) was modulated by an acousto-optic modulator at a frequency $f=3.9$ MHz, where the Ti:sapphire laser noise is small. The transmitted probe beam (from the same Ti:sapphire laser) of relatively low intensity (about 10^{-2} of the pump) was directed into a monochromator and detected with a photodiode. Our detection system is capable of measuring differential transmission $\Delta T/T$ on the order of 10^{-6} for a low power probe (below 100 μW), as a result the signal-to-noise ratio in the spectra was excellent.

Measured differential transmission of the probe beam $\Delta T/T$ is directly related to pump-induced change in the absorption (gain) coefficient through the expression $\delta\alpha=\ln(1+dT/T)$. Figure 2(a) shows an example of a spectrum $\delta\alpha(\hbar\omega)$ of pump-induced changes at $T=10$ K for two time delays ($\tau=0.3$ psec and 5 psec, respectively), over a spectral range that covers both the HH exciton and biexciton transitions (parallel pump and probe polarization). The data were taken at an excitation level which from the linear absorption data for the HH exciton corresponds to an initial pair density of $n=4.0\times10^{11}$ cm^{-2}, approximately twice that required to reach the threshold for edge emitting laser action in the cleaved samples. In the following, we refer to this case as corresponding to the ''high excitation'' limit and compare it with two other levels of excitation, $n=2.0\times10^{11}$ cm^{-2} (''intermediate'') and $n=1.0\times10^{11}$ cm^{-2} (''low''). We will show how, within this rather small range of excitation levels, the pump-probe experiments display pronounced variation in the electromagnetic response by the interacting, dense exciton-biexciton system.

The important effects that can be distinguished in the spectrum of Fig. 2(a) are (a) enhanced transparency at the peak of the exciton transition ($|X\rangle$ resonance) at $\hbar\omega=2.814$ eV, where excitonic absorption is partly bleached by the pump; (b) pump-induced absorption on the high-energy side of $|X\rangle$ resonance, which is a combined consequence of a pump-induced broadening of excitonic absorption and the transient blueshift discussed below; (c) the pump-induced changes in the probe spectrum centered at the biexciton transition ($|B\rangle$ resonance) at $\hbar\omega=2.808$ eV. As mentioned above, there are no detectable features in the linear absorption spectrum for a ZnSe QW at this energy, hence positive changes in the probe correspond to *real optical gain* with a maximum coinciding with the $|B\rangle$ resonance, as determined from the PL and FWM experiments. The magnitude of optical gain can be also measured in this experiment; at the excitation level corresponding to Fig. 2, the optical gain coefficient reaches a maximum value of $g=0.7\times10^5$ cm^{-1}. Additional details of the time evolution of these spectral changes are illustrated in Fig. 2(b), which shows in detail the spectral range within the $|B\rangle$ resonance. In this ''high excitation'' case, we see that even for short-time delays comparable to the laser-pulse duration optical gain is already present in the system. The gain grows in real time, reaching its maximum at a pump-probe delay of $\tau=1.6$ psec.

Let us consider the mechanism for optical gain formation in this high excitation regime, where the overall spectral shape of $\delta\alpha(\hbar\omega)$ at the biexciton resonance is relatively time independent (apart from a small blueshift). Following the initial coherent transient regime, the probe beam measures gain which can be thought of in a conventional sense as requiring population inversion for the biexciton-exciton transition. In our experimental circumstances we thus look for efficient means of generating a high-density biexciton gas, by two different pathways. In process No. 1 an excitonic molecule is formed in a (coherent) two-photon absorption process:

$$\hbar\omega_1+\hbar\omega_2=\text{biexciton},$$

where photons of two different energies are provided by the broadband ultrashort excitation laser pulses. In process No. 2, an excitonic molecule is formed, as in a chemical reaction, by the merging of two excitons in an inelastic (incoherent) event, with emission of an acoustical phonon to satisfy the energy conservation:

$$\text{exciton}+\text{exciton}=\text{biexciton}+\text{phonon}.$$

Alternatively, another exciton could participate in a three-body scattering process to consume the excess energy of approximately 5 meV, or if one takes into account that polariton effects a biexciton formation process with no ''side products'' is also possible.

The observed time evolution of optical gain at the excitation level corresponding to Fig. 2(b) shows how both processes Nos. 1 and 2 make a finite contribution to the creation of excitonic molecules and gain from this four-particle excitation. The ''instantaneous'' appearance of a finite amount of gain is dominated by the direct two-photon absorption process, contributing to the gain through a coherent polarization state created in the ZnSe QW. The FWM data for this excitation density shows a phase decay of approximately 600 fsec, i.e., considerably longer than the duration of the pump/probe pulses. On the other hand, since the maximum in the gain is reached only after a delay time of 1.6 psec, and decays subsequently on a much slower time scale (50 psec), it is clear that process No. 2 must also contribute to the gain. The formation of a population (and population inversion) of excitonic molecules from excitons through inelastic events

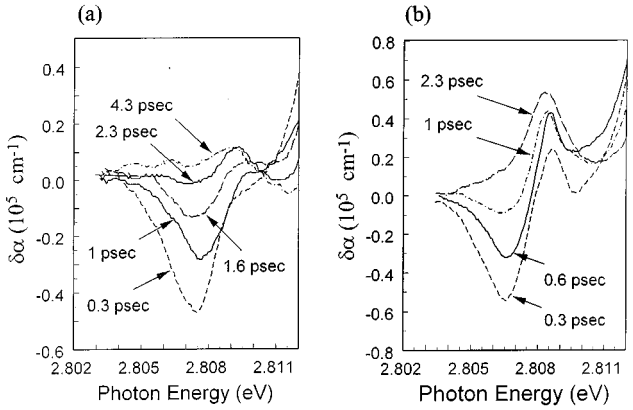

FIG. 3. Time evolution of the differential probe spectra at the biexcitonic resonance. The excitation level corresponds to an initial pair density of (a) $n=10^{11}$ cm^{-2} and (b) $n=2\times10^{11}$ cm^{-2}.

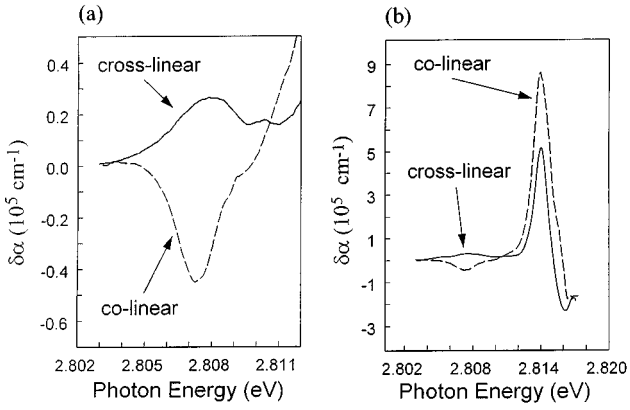

FIG. 4. Comparison of the differential probe spectra for collinearly and cross linearly polarized pump and probe pulses at (a) the $|B\rangle$ resonance, and (b) including the $|X\rangle$ resonance.

also means that a concomitant depletion of excitons must take place at the $|X\rangle$ state. This depletion can, in fact, be seen in the decrease in the pump-induced transparency at the $|X\rangle$ resonance [Fig. 2(a)] as more phase space opens up for absorption from the ground state (radiative decay of excitons is not significant on this time scale).

In the coherent regime of excitonic response (short pump-probe delays), where the quantum mechanical phase relationships between the excitonic states and their polarizations as well as the coupling to the external optical fields are important, we expect the experiment to be especially sensitive to the initial excitation conditions (overall density of the excitonic gas and its partitioning into the biexciton and exciton components). The excitonic polarizations include contributions from exciton-exciton interactions, such as the so-called ''induced interaction fields'' that act as source terms, e.g., for the DFWM signals at the exciton and the biexciton transition for negative time delays.[10] The impact of this anticipated sensitivity to excitation conditions on the observed transient probe spectra is dramatic, as we now illustrate by presenting data for the ''low'' and ''intermediate'' excitation levels (corresponding to an initial pair density of $n=1.0\times10^{11}$ cm^{-2} and $n=2.0\times10^{11}$ cm^{-2}, respectively). In the low excitation case, coherence is maintained in the ZnSe QW for nearly 2 psec, as observed from the FWM experiments.[10] In this case, the time evolution of pump-induced changes in the probe spectrum is strongly affected by the coherent polarization interference effects which intermediate the pump-probe interaction.

The gain spectra shown in Fig. 3(a) for five different time delays correspond to the ''low excitation'' case and, when compared with Fig. 2(b), show strikingly different dynamics in the vicinity of the biexciton resonance. In early times ($\tau<1$ psec), where the coherent aspect of the QW response is important, a large negative value for $\delta\alpha(\hbar\omega,\tau)$ is observed at the excitonic molecular resonance, appearing as ''pump-induced absorption.''

Such pump-induced absorption at a biexcitonic resonance was observed in the incoherent regime in CuCl,[16] where it was interpreted in a rate equation model as being due to the population dynamics that caused an increase in the exciton-biexciton transition rate. Such a process, called ''*two-step-induced absorption*''[17] can be visualized as following: an excitonic molecule is formed by the absorption of a photon $\hbar\omega_1$ from the pump pulse (creating an exciton), followed by a subsequent absorption of a photon from the probe pulse $\hbar\omega_2$ to complete the transition, the latter probability being proportional to the population of the $|X\rangle$ state.

However, the coherent polarization created by the pump pulse can also interact with photons from the probe and a biexciton can be formed in a *two-photon absorptionlike* process:

$$\text{coherent exciton}+\hbar\omega_2=\text{biexciton}.$$

In order to complete such a process, two optical fields contributing to biexciton formation [$\hbar\omega_1$ (or a coherent exciton) and $\hbar\omega_2$] should have the same polarization, while for a two-step absorption process the polarization of the pump and probe beams is not important. We found that in our case the pump-induced absorption in the probe spectrum is mainly due to coherent two-photon-like process. The polarization dependence of our gain spectra (discussed below) leads to such a conclusion.

Whereas in the experiments described above both pump and probe beams have the same linear polarization (collinearly polarized), Fig. 4 compares this geometry with the arrangement where the pump and probe beams are cross-linearly polarized. The spectra are displayed at zero time delay and for the low excitation level, showing an overview of the exciton and biexciton resonances in Fig. 4(b), and the details at the biexciton transition in Fig. 4(a). While the spectrum for the collinearly polarized probe is dominated by large negative values of $\delta\alpha(\hbar\omega,\tau)$ (''pump-induced absorption''), finite optical gain is observed in the cross-polarized pump/probe configuration. In the experiments represented by Fig. 4, the probe spectra for both the cross linearly and collinearly polarized probe converged to the same line shape for time delays longer than about 1.5 psec, and the maximum in the (small) optical gain at the $|B\rangle$ resonance was reached at a time delay $\tau=2.3$ psec after the pump. We note that for excitation levels corresponding to e-h pair densities $n<5\times10^{10}$ cm^{-2} no optical gain could be detected in the QW in the experiments. The magnitude of induced transparency at the $|X\rangle$ resonance is also polarization dependent.

A most intriguing time evolution of gain spectra is shown in Fig. 3(b). In this case, the excitation level corresponds to $n=2\times10^{11}$ cm^{-2} (''intermediate'' excitation level). The gain spectra at time delays from 0.3 to 1 psec show a very interesting physical phenomenon: while optical gain is observed on the high-energy side of the $|B\rangle$ resonance, pump-induced absorption is observed on the low-energy side. In the regime of an incoherent response such a situation would normally require the presence of an inhomogeneously broadened resonance.[2] However, as we clearly showed in our DFWM experiments,[10] the excitonic resonance becomes homogeneously broadened at carrier densities above $n=10^{11}$ cm^{-2}, therefore it is not possible and, indeed, incorrect to attempt at the description of the simultaneous presence of gain and absorption in terms of populations of the $|B\rangle$ and $|X\rangle$ states.

Similar to the ''low'' excitation level, the spectra at the ''intermediate'' excitation level show strong polarization dependence: no pump-induced absorption is detected if pump and probe beams are cross linearly polarized. It proves a coherent nature of observed pump-induced absorption, while optical gain on the high-energy side of the $|B\rangle$ resonance is entirely due to incoherent populations of the $|B\rangle$ and $|X\rangle$ states (since it is not sensitive to polarization of the probe beam).

While the microscopic theoretical modeling of the observed effects is beyond the scope of present work (and of available theoretical models[18]), one can make a conclusion, based on experimental data, that both incoherent, population related optical gain, and coherent polarization-induced absorption influence the pump-induced changes in the probe spectrum at the ''intermediate'' excitation level. The interplay between coherent and incoherent effects leads to an observation of optical gain and absorption across the $|B\rangle$ resonance.

To further verify the biexcitonic nature of observed optical gain, we also performed an experiment with circularly polarized pump and probe beams. At the excitation level, corresponding to an initial pair density of $n=2\times10^{11}$ cm^{-2} (the ''intermediate'' excitation level for a linearly polarized pump), neither gain nor induced absorption was detected in the vicinity of $|B\rangle$ resonance on the time scale of pump-probe delays discussed above. The absence of a response is expected from the selection rules that can also be inferred from the schematic inset of Fig. 1(b). Very small optical gain was eventually observed to emerge in the probe spectra in the circular polarization experiments under high excitation for time delays longer than 5 psec, presumably due to exciton spin-reversing scattering processes. We also note that in our study of optically pumped stimulated emission (samples equipped with optical resonators prepared by facet cleaving), excitation spectroscopy of the lasing with a *monochromatic* laser showed a pronounced and sharp maximum at the $n=1$ HH excitonic absorption resonance.[10] No two-photon absorption processes are possible in this case for reaching the biexciton state, so that process No. 2 defined above provides the only means of forming optical gain in this circumstance.

The oscillatory structure in the probe spectra at both exciton and biexciton transitions was found for negative pump/probe time delays (probe pulse precedes the pump). Such effects have been observed in GaAs quantum wells[19,20] and attributed to the perturbed free (coherent) polarization decay. These observations provide further means of studying the excitonic interactions but will not be detailed further in this paper.

The blueshift of the $|X\rangle$ resonance at high carrier densities, observed in spectra such as Fig. 2(a), is well known from work in GaAs/Al$_x$Ga$_{1-x}$As MQW's.[21] It is a result of the exchange interaction between excitons (Pauli repulsion) exceeding the van der Waals–like Coulomb attraction. Theoretical prediction[22] in the 2D exciton limit yields the following magnitude for the shift:

$$\Delta E=8\pi n a_0^2\left(1-\frac{315\pi^2}{4096}\right)E_0,$$

where n is the exciton (sheet) density, a_0 the exciton Bohr radius, and E_0 the exciton binding energy. Substituting the parameters for ZnSe in the 2D limit, one finds that $\Delta E=6$ meV. In our experiment ΔE reaches a maximum value of only about 1–1.5 meV, a result not altogether unsurprising considering the relatively weak conduction-band confinement (reflected also in the relatively modest enhancement of the exciton binding energy over the bulk value[10]). In the fully 3D case, the exciton energy remains nearly independent of the e-h pair density, as the blueshift due to exchange interactions is compensated for by a redshift related to screening.[22]

An intriguing aspect in our data concerns the evolution of the blueshift at the $|X\rangle$ resonance. The experimentally measured time dependence of the blueshift can be approximated by the following simple function:

$$E=A\ \exp(-t/\tau_1)+B\ \exp(-t/\tau_2),$$

where A and B are constants, $\tau_1=2$ psec and $\tau_2=200$ psec. The appearance of the initial maximum value for the blueshift is considered to be instantaneous within experimental resolution. The two different time constants contributing to the process are interpreted as follows: The longer decay can be associated with a radiative recombination of excitons (consistent with time-resolved PL studies[10]). The shorter decay ($\tau_1=2$ psec) is viewed to reflect the biexciton formation process in inelastic-scattering events from pairs of excitons. A rough estimate for the biexciton formation time as 1.5–2 psec can be made from our gain dynamics study Fig. 2, which is close to the time constant for the transient blueshift. In this interpretation, it follows that, given the time dependence of the blueshift as related to biexciton formation, creation of excitonic molecules (at fixed initial pair density) decreases the exchange energy in the system.

In summary, we have shown how a gas of interacting excitons and biexcitons dominate the optical response of a single ZnSe QW at low temperatures. The narrow (sub-meV) linewidth at the $n=1$ HH exciton resonance allows us to access both the linear and nonlinear optical response of a dense exciton gas with high spectral resolution. As a consequence, the role of excitonic molecules in providing the dominant electronic excitation for optical gain has been clearly demonstrated. A very large value for biexcitonic optical gain up to 7×10^4 cm^{-1} at $T=10$ K was measured. The presence of such a gain leads to laser action in an edge emitting device geometry, on a time scale ($\tau\gg1$ psec) long

enough to have scattering processes placed the biexciton/exciton system into the incoherent regime of a polarization response.

With experimental access to the excitonic optical response by pump-probe and four-wave-mixing techniques on a subpicosecond time scale, we have also reached the regime of coherent excitations in the density regime where stimulated emission is achieved. The coherent effects lead to pump-induced absorption at the biexciton state and show a highly nonlinear dependence on the incident excitation. Within the coherent regime we have isolated two pathways along which optical gain emerges: (i) a direct two-photon process in the creation of biexciton polarization and (ii) the formation of excitonic molecules from excitons by inelastic collisions. The interplay between coherent and incoherent effects leads to the simultaneous observation of pump-induced absorption and optical gain in the vicinity of the biexcitonic resonance. The dependence of the pump-probe spectra on the polarization geometry allows these contributions to be identified so as to provide input for a possible microscopic model to treat the interacting exciton gas in the ZnSe QW. While such a model presents substantial theoretical challenges, e.g., in terms of describing the interaction of the exciton and biexciton states, the experimental system described in this paper should provide a wealth of spectroscopically explicit input into such analysis, not available in the better studied GaAs QW case.

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