PHYSICAL REVIEW B VOLUME 50, NUMBER 8 15 AUGUST 1994-II

Role of Coulomb-correlated electron-hole pairs in ZnSe-based quantum-well diode lasers

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(Received 16 June 1994)

Gain and absorption spectra in ZnSe-based blue-green diode lasers have been measured to show the role of pairwise Coulomb correlation between electrons and holes in $Zn_{1-x}Cd_xSe/Zn_{1-x}S_xSe$ quantum wells (QW's) under lasing conditions at room temperature. In addition, the radiative decay rates of electron-hole pairs have been obtained from time-resolved photoluminescence measurements over a wide temperature range. These experiments also point out the importance of the Coulomb interactions on the QW optical properties near its fundamental absorption edge under device operating conditions.

Semiconductor diode lasers operating in the near infrared form the core of modern optoelectronics. Although the presence of many-body Coulomb interactions within the degenerate electron-hole plasma (EHP) that forms their optical gain has a long-standing theoretical origin,[1] it is rarely considered explicitly in experimental device physics. Rather, the one-electron, effective-mass analysis is empirically parametrized, and many electron effects are compacted, e.g., into a renormalized energy band gap. Recently, with the extension of the laser devices into the blue-green by wide-band-gap II-VI compound semiconductors, there are valid reasons to question this established practice. The progress in the new lasers has been rapid, culminating in the recent demonstration of brief room-temperature continuous-wave operation.[2,3] One important physical difference between the GaAs-based and ZnSe-based quantum wells (QW's) is a much stronger (Frohlich) coupling of carriers to the longitudinal-optical (LO) phonons for the latter due to increased polarity. Another feature, which is the focal point of this paper, is the importance of electron-hole (e-h) pairwise Coulomb interactions. For example, the exciton binding energy in a (Zn,Cd)Se QW [$E_x \approx 40$ meV (Ref. 4)] satisfies the condition $E_x > \hbar\omega_{LO}$ and $E_x > kT$ (at room temperature). This circumstance raises the question about the optical properties of a high-density e-h gas in a diode laser. At cryogenic temperatures (typically 10–100 K), we have earlier demonstrated under short pulse, resonant optical pumping experiments that stimulated emission is dominated by excitonic processes in the (Zn,Cd)Se QW's.[5] By employing very different methods, we perform here gain spectroscopy *at room temperature* in the new blue-green QW diode lasers. We show evidence for the presence of e-h pairwise Coulomb correlations for the diode laser under steady-state conditions. The accompanying enhancement in the interband matrix element is also directly observed in another experiment where the radiative lifetime of the excess electron-hole pairs is measured by time-resolved photoluminescence over a wide temperature domain.

The $Zn_{1-x}Cd_xSe/Zn_{1-x}Se_x/Zn_{1-x}Mg_xS_ySe_{1-y}$ separate confinement heterostructure (SCH) diode laser structures were grown by molecular-beam epitaxy on n-type GaAs buffer layers (homoepitaxially deposited on GaAs substrates). The active region was composed of three $Zn_{0.85}Cd_{0.15}Se$ QW's ($L_w = 75$ Å), separated by 100-Å-thick $ZnS_{0.07}Se_{0.93}$ barriers. To facilitate an Ohmic contact, a graded gap $ZnSe_{1-x}Te_x$ contact layer[6] was grown atop the p-type $Zn_{1-x}Mg_xS_ySe_{1-y}$. Details of the growth can be found in Ref. 7. Gain guided devices with 20-μm-wide stripes were fabricated with indium tin oxide top transparent electrodes. Spectroscopy was performed by recording the (unamplified) spontaneous emission through the top electrode and the stimulated (or amplified spontaneous) emission through the cleaved (uncoated) end facets, as shown schematically in the inset of Fig. 1. The room-temperature pulsed threshold current density for the laser devices was about $J_{th} \approx 1.4$ kA/cm^2, i.e., approximately 470 A/cm^2 per QW.

The correlation between spontaneous emission (top emission) and edge-stimulated emission spectra was employed by Henry, Logan, and Merritt to derive gain spectra for GaAs double heterostructure lasers.[8] It has been subsequently used

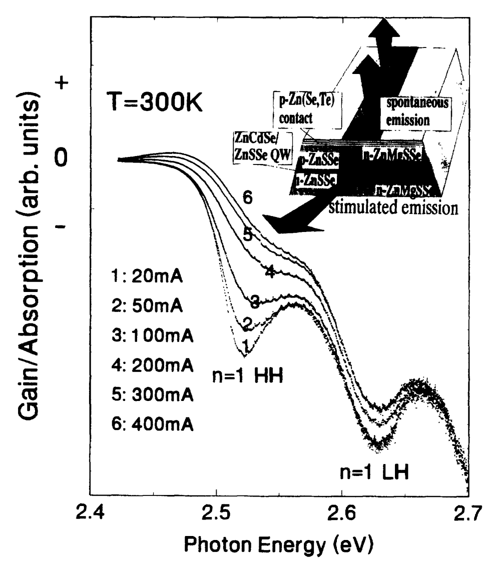

FIG. 1. Gain and/or absorption spectrum of a $Zn_{1-x}Cd_xSe/Zn_{1-x}S_xSe/Zn_{1-x}Mg_xS_ySe_{1-y}$ diode laser at $T = 300$ K, showing the effects of increasing current injection on the $n=1$ HH and LH QW exciton states. The inset shows the experimental geometry for recording the spontaneous and stimulated emission spectra.

to construct detailed gain spectra for GaAs QW diode lasers.[9–11] Given the present device geometries and fabrication restrictions, the technique is particularly attractive for the new blue-green lasers. A key aspect of the formulation, which is an extension of the relationship between Einstein's A and B coefficients, is its independence of the details of the gain mechanism or the nature of the electronic states that participate in the radiative process.[8,11,12] An explicit relationship exists between the gain spectrum $g(E)$ and experimentally obtained spontaneous emission spectrum $S(E)$:[8]

$$g(E,\Delta E_F)=C\,\frac{S(E)}{E^2}\{1-\exp[(E-\Delta E_F)/kT]\}, \quad (1)$$

where C includes fundamental constants and experimental amplitude calibration factors. The separation between the quasi-Fermi levels at threshold conditions, ΔE_F, is also experimentally obtained from the spontaneous emission spectrum and the known position of laser emission $E=\hbar\omega_L$.[13] (In principle, ΔE_F can be also obtained simply from the junction voltage[10] if there are no unknown voltage drops across the heterostructure.) By following this approach, Fig. 1 shows results from our experiments over a wide spectral range near the $n=1$ interband transition for the typical QW diode laser device at room temperature. Six curves are displayed, corresponding to different levels of current injection. The vertical axis is indicative of either absorption (<0) or gain (>0). The presence of the $n=1$ heavy-hole (HH) and light-hole (LH) exciton resonances is ambiguous, especially when the current is low, and the centers of these resonances occur at photon energies of $\hbar\omega=2.520$ and 2.625 eV, respectively. The identification of the LH state was confirmed by analyzing the polarization of the edge emission. With an increase in the injection current, the absorption at the HH exciton resonance becomes partially bleached, and for $I>200$ mA gain appears on its low-energy side. At laser threshold, the peak of the HH exciton can still be visually identified. The LH resonance is considerably less sensitive to the e-h pair injection.

A direct and useful comparison of our results with the III-V semiconductor lasers can be made, for example, through the work of Kesler and Harder,[9] who employed the same technique described here to derive gain and/or absorption spectra of a GaAs QW diode laser. In their case, while the $n=1$ HH QW absorptive exciton state is also distinct under low injection, this resonance is completely obliterated at carrier levels well before the appearance of gain. Furthermore, the gain spectrum shows an identifiable, broadened, two-dimensional (2D) density-of-states step that replaces the exciton resonance in a manner consistent with that of a degenerate electron-hole plasma. Given the exciton binding energy of $E_x\leq 10$ meV in a GaAs QW, such results are not unexpected. The data of Fig. 1 are at strong variance with this type of general behavior in III-V lasers, including the strained $In_xGa_{1-x}As$ system.[11]

Figure 2 shows details of the gain spectra at $T=77$ K and at room temperature over a narrower range of photon energies. From the dependence of the threshold current on cavity length, the peak modal gain coefficient at threshold condition for this particular device is determined to be 48 cm^{-1} which corresponds to volumetric QW gain of $g\approx 1200$ cm^{-1}. On

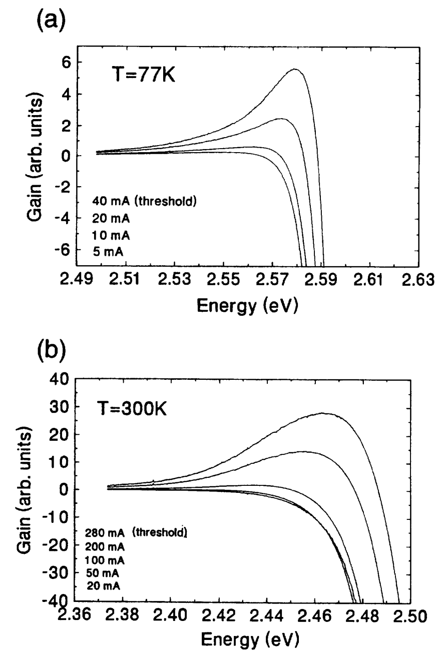

FIG. 2. Gain spectra obtained for the SCH QW diode laser at $T=77$ and 300 K for different levels of current injection.

the low-energy side (e.g., for $\hbar\omega<2.47$ eV at $T=300$ K), the spectral shape of the gain is mainly determined by carrier-carrier interaction and carrier–LO-phonon scattering, rendering the original inhomogeneous density of states invisible. Both processes increase in importance from $T=77$ to 300 K (including effects by an increased threshold current density). Given the focus of the present paper, we leave the discussion about the details of the gain spectral line shapes elsewhere but note that qualitatively similar, broadened line shapes are obtained in III-V diode lasers at room temperature. Hence, in examining the role of pairwise e-h correlations, spectroscopy of the entire $n=1$ resonance is necessary.

We now consider the interpretation of the evolution of the gain and/or absorption spectra of Fig. 1 with increasing pair density. To our knowledge, there are no published theoretical treatments for the optical spectra of a *high-density e-h system at room temperature* for the particular conditions encountered here, namely, that the 2D exciton remains rather stable against thermal phonon dissociation. Inclusion of Coulomb pairing effects at low temperatures (in GaAs QW's) has been theoretically shown to lead to singularities at the Fermi edge of a two-component plasma.[14] Elsewhere, many-body Coulomb interaction in GaAs diode lasers at room temperature has been explicitly included via the density-dependent bandgap renormalization into the gain model.[15] Furthermore, in ultrashort pulse optical pump-probe experiments on GaAs QW's, the observed saturation of the exciton absorption has been treated by phase-space filling (PSF) and screening models;[16] the experiment has not focused on the regime of inversion and gain in such work.

Phenomenologically, two opposite limits can be easily visualized in the usual context of interband transitions in semiconductors: a Coulomb-paired, e-h bound state (noninteracting exciton), and a degenerate EHP (a many-body Fermi liquid). In *room-temperature II-VI lasers*, the classification of the electron-hole Coulomb interactions is such as to lie somewhere between these two extremes, with strong damping (scattering) present. The puzzle is thus about the role of pairwise *e-h* correlations. The pair density implied for $I=470$ A/cm^2 is approximately 3.0×10^{12} cm^{-2} (assuming unity capture probability into the QW, and a carrier lifetime of $\tau_r\approx1\times10^{-9}$ sec as reported below). This density is still below that estimated from the elementary PSF argument (at $T=0$) for the stability of the 2D exciton phase, $n_{\rm PSF}\approx5.0\times10^{12}$ cm^{-2}. We give a plausibility argument below that Coulomb interaction processes also provide for a low-energy extension in the effective many-electron density of states and allow net gain to develop as seen in Figs. 1 and 2. Remarkably, the HH exciton resonance, even if partially bleached due to Pauli blocking and screening, remains clearly present when diode laser oscillations commence. The gradual evolution with increasing injection shows no clear evidence of band-gap renormalization phenomena, insofar as a "Mott" transition into an EHP is concerned.

It is also useful to compare the present conditions for the measurements of the QW diode laser gain spectra with those in the earlier optical pumping studies on the same $Zn_{1-x}Cd_xSe$ system at cryogenic temperatures.[5] At low temperatures, a phenomenological model based on partial phase-space filling of an inhomogenously broadened $n=1$ HH exciton resonance predicted the experimentally observed gain from this resonance.[5] In the near-resonant pump-probe measurements at cryogenic lattice temperatures the nonequilibrium exciton population remained "cold" while in the room-temperature diode laser the (higher density) electron-hole pairs in steady state are much "warmer." Consequently, profound differences in the role of intraband scattering are encountered.

A normal assumption used in a semiconductor laser at steady state is that both electrons and holes are in quasiequilibrium, respectively. Other time-dependent perturbations (carrier-carrier and carrier-phonon scattering) are treated through a broadening function $\Gamma(E,E',kT)$. The standard convolution integral for the gain can thus be written as

$$g(E)=\int D(E')[f_c(E',E_{Fc})-f_v(E',E_{Fv})]\Gamma(E,E',kT)dE', \qquad (2)$$

where $D(E')$ is the joint density of conduction-band–valence-band states and $f_c(E',E_{Fc})$, $f_v(E',E_{Fv})$ are the Fermi distribution functions. The linewidth implied by the broadening function corresponds to the typical scattering rate ($\sim h/\tau_c$) of the carriers. There is discussion in recent literature about the proper incorporation of intraband scattering to calculate the gain line shape in III-V lasers: while a Lorentzian line shape is evoked when $\Delta E\tau_c\gg h$ (where ΔE is the energy width of the carrier distributions),[17] the case $\Delta E\tau_c<h$ implies that non-Markovian processes dominate. Gaussian line shapes have been adapted to approximate this case.[18] Especially in this instance, a rigorous model for the gain spectrum seems yet to be established.

In the room-temperature II-VI lasers, there appears to be a severe problem to such a treatment of the carrier scattering processes (i.e., interactions). As noted, the *e-h* Coulomb interaction and the carrier–LO-phonon interaction in the ZnSe-based materials are much stronger than in III-V semiconductors. Given the initial inhomogeneous exciton linewidth of 7 meV (from low-temperature absorption) and the room-temperature gain linewidth of 40–60 meV (depending on the injection level), the simple model of Eq. (2) predicts that the peak gain should appear near the peak of the exciton absorption. This is clearly contradictory to the observation that the observed peak gain appears about *60 meV below* the peak of the exciton absorption. We suggest here that the *e-h* pair states are renormalized by the many-particle Coulomb interaction, including possibly the interaction with optical phonons. In terms of the idea of line-shape broadening function, we now write

$$g(E)=[f_c(E,E_{Fc})-f_v(E,E_{Fv})]\left\{\int D(E')\Gamma(E,E')dE\right\}. \qquad (3)$$

Effectively, the broadening function $\Gamma(E,E')$, being physically quite different from that in Eq. (2), is contributing to the gain and/or absorption in the same way that an inhomogeneous broadening does in the conventional description of the problem.

The impact of such pairwise correlations that exist at densities typical in the diode laser at room temperature can be experimentally accessed by another route, namely, by measuring the radiative recombination rate (in the absence of stimulated emission). This rate is, of course, directly related to the strength of the interband matrix element and is accessible in a properly configured experiment. We performed transient photoluminescence (PL) experiments in the same SCH diode laser structure in which current injection was

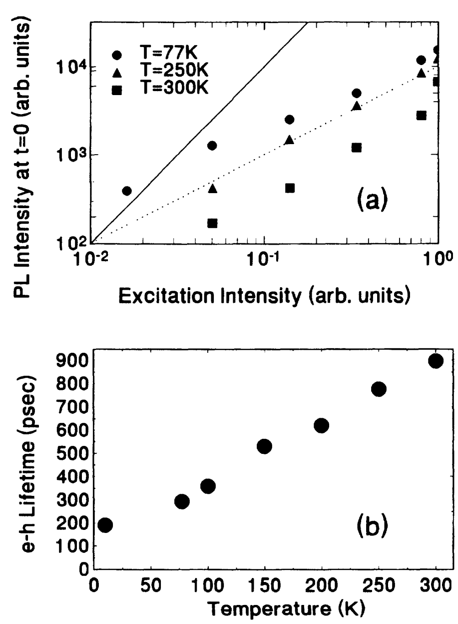

FIG. 3. (a) Spectrally integrated photoluminescence intensity at the $n=1$ HH exciton resonance at $t=0$ in a transient PL experiment as a function of excitation. The solid and dashed lines depict quadratic and linear dependences, respectively. (b) *e-h* pair lifetime from $T=10$ K to room temperature at a carrier density corresponding to diode laser threshold.

simulated by a pulsed laser ($\tau_p \approx 5$ psec), tuned to the bandgap energy of the $Zn_{1-x}S_xSe$ barrier layer. The detection system was composed of a spectrometer, streak camera, and a two-dimensional charge-coupled device array. We studied systematically the intensity and temperature dependences of both the transient and time-integrated luminescence to ensure that under excitation levels (typically $\Delta n = \Delta p \approx 2\times10^{12}$ cm^{-2}) closely corresponding to those in the actual diode lasers, radiative recombination dominated over possible nonradiative paths. Figure 3(a) shows the PL intensity, immediately following the excitation at $t=0$ (spectrally integrated over the $n=1$ HH exciton resonance), as a function of the excitation intensity for three different temperatures. The dashed and solid lines represent linear and quadratic dependences, respectively. The linear dependence observed experimentally suggests that the recombination mechanism is much closer to that of excitons (or correlated pairs), as opposed to that of totally uncorrelated pairs for which bimolecular recombination statistics would apply.

The lower panel of Fig. 3 summarizes the measured radiative decay as a function of temperature from $T=10$ K to room temperature. The room-temperature value of approximately 900 psec can be used to compare with a theoretical estimate obtained from a one-electron effective-mass model.[19,20] The following effective-mass parameters for ZnSe were used for the uppermost strain-split valence band: $m_\| = 0.147m_0$, $m_\perp = 0.23m_0$. For a concentration of $\Delta n = \Delta p = 2\times10^{12}$ cm^{-2}, we obtain a radiative recombination (bimolecular) rate of $\approx 10^8$ sec^{-1}, hence implying a much longer lifetime than actually measured. This distinct enhancement in the radiative recombination rate is consistent with the argument that the electron-hole pairwise correlations in our ZnSe-based QW's increase the electron-hole wave-function overlap and hence the oscillator strength. In addition, the approximately linear increase in the radiative lifetime with increasing temperature and the clear single exponential decays in the transient PL intensity over the carrier density range of interest are also in support of an excitonlike radiative recombination kinetics, as argued in work on GaAs and $In_xGa_{1-x}As$ QW's at low densities, although these experiments were limited to a narrower temperature range than examined here.[21,20] From a theoretical standpoint, Hangleiter has considered very recently how the Coulomb correlation between electrons and holes results in an enhancement in radiative recombination rate at room temperature in an $In_xGa_{1-x}As/InP$ QW system,[22] including its density dependence. The two-particle correlation function was employed in a calculation that includes screening of the Coulomb potential and Pauli blocking. Even at room temperature and for densities such that $\pi a_0^2 n_s \approx 1$, with a_0 the exciton Bohr radius, the two-particle correlation effects were found to be significant in their impact on the radiative lifetime.

This research was supported by the ARPA, NSF, and AFOSR.

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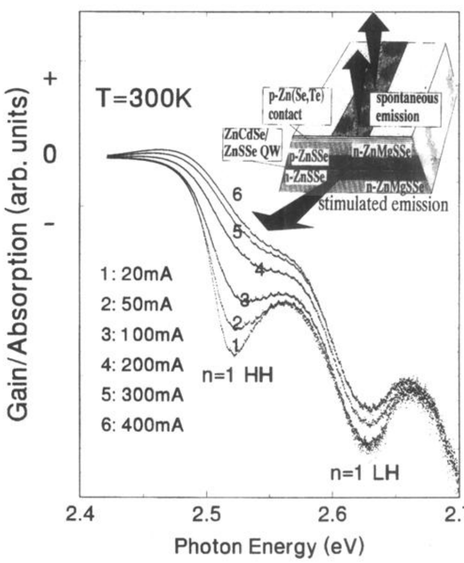

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