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Recombination mechanisms and lasing in shallow $Zn_{0.9}Cd_{0.1}Se/ZnSe$ quantum-well structures

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Magnetoluminescence spectroscopy of the photopumped stimulated emission, together with systematic photoluminescence studies as a function of the photogeneration rate, were used to identify the main recombination mechanisms occurring in shallow $Zn_{0.10}Cd_{0.90}Se/ZnSe$ multiple quantum wells for blue-green laser applications. Although the main spontaneous recombination processes have excitonic character, we found that lasing originates from free-carrier transitions.

The physics and technology of blue-green lasers based on II-VI heterostructures have been the subject of increasing interest in the last few years. The most recent studies have been devoted to the implementation of electrically injected lasers[1-3] to be used in conjunction with blue-green modulators and detectors for the replacement of *conventional* infrared optoelectronics. A number of recent stimulating reports[4-8] have focused on $Zn_xCd_{1-x}Se/ZnSe$ multiple-quantum-well structures (MQWS's) as the materials of choice for these challenging applications. Besides other relevant fundamental and technological results, another mechanism of excitonic gain at the inhomogeneously broadened exciton density of states has been proposed to explain the lasing mechanism in these quantum wells.[7,8] This phenomenon has been interpreted as a consequence of the enhanced stability of the exciton, which is favored, in quantum wells of decreasing thickness, by (i) the increased exciton binding energy,[11] (ii) the reduction of the otherwise large exciton-phonon coupling,[12] and (iii) the exciton localization causing the inhomogeneous broadening.[7]

In this work we present a detailed study of the photo-pumped stimulated emission of narrow $Zn_{0.9}Cd_{0.1}Se/ZnSe$ MQWS's, to elucidate the excitonic or free-carrier nature of the recombination mechanism of shallow quantum wells where exciton confinement is small. High-excitation intensity photoluminescence in magnetic fields up to 8 T and optical gain spectra have been measured in $Zn_{0.9}Cd_{0.1}Se/ZnSe$ MQWS's grown by molecular-beam epitaxy (MBE). Ten-period $Zn_xCd_{1-x}Se$ MQWS were grown at 250 °C with growth interruption of 30 s at each interface on 1.5-μm-thick ZnSe buffer layers grown at 290 °C. The substrates were 0.5 μm thick, *n*-type ($n = 4\times10^{17}$ cm^{-3}) GaAs buffer layers grown at 580 °C on GaAs(001) wafers, following the methodology illustrated in Refs. 9 and 10.

High-excitation intensity photoluminescence measurements were performed by exciting the samples with a pulsed N_2 laser (337.1 nm), delivering 300-ps pulses with 300-kW peak power at a 5-Hz repetition rate. The samples were immersed in liquid helium in the cryostat of a superconducting magnet (Oxford T-4000 Spectromag), with the magnetic field perpendicular to the quantum-well basal plane. The optical gain spectra were measured by the variable-stripe-length method, normalizing at each wavelength the optical gain value to the intensity of the spontaneous emission just below the stimulated emission threshold.

Assessment of the structural quality of the MQWS and determination of the structural parameters were performed by means of high-resolution double-crystal x-ray-diffraction measurements, following the procedure described in Ref. 13. In Fig. 1 we show the (400) reflection of one of the MQWS investigated. Besides the GaAs substrate and ZnSe buffer peaks, distinct superlattice satellites up to the sixth order could be observed. From the fitting of the experimental diffraction curves we obtained the well and barrier widths of the MQWS and the Cd average content. For the two samples investigated here, we found $Zn_xCd_{1-x}Se$ wells widths $L_w = 2.8$ and 3.7 nm, and ZnSe barrier widths of 21.7 and 33.5 nm, respectively. For both samples the Cd content was close to the nominal 10% value. A detailed investigation of the correlation between growth conditions, x-ray-derived structural parameters, and optical properties is beyond the scope of the present Brief Report, and will be published elsewhere. Relevant to this paper is the excellent quality of the heterostructures investigated, which is also reflected in typical photoluminescence and absorption linewidths of less than 6 and 8 meV, respectively (at 10 K).

In Fig. 2 we display representative spontaneous emission spectra from the 2.8-nm MQWS's collected from the sample surface (backscattering configuration) at different

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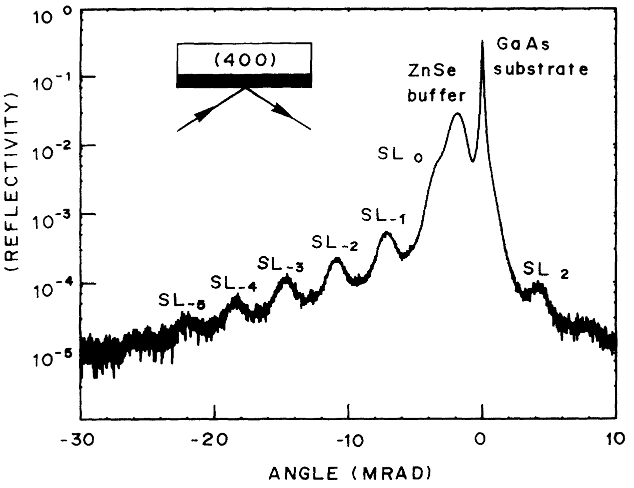

FIG. 1. Double-crystal x-ray-diffraction pattern of the $Zn_{0.9}Cd_{0.1}Se$(2.8 mm)/ZnSe(21.7 nm) multiple-quantum-well structure recorded in the vicinity of the (400) GaAs reflection by using Cu $K\alpha_1$ radiation.

photogeneration rates. As no differences are found between the two samples, in the following we concentrate on the 2.8-nm MQWS sample. At the lowest excitation intensity, a narrow excitonic spontaneous emission feature occurs around 457 nm (2.713 eV). With increasing carrier density the low-energy tail of the emission broadens, and a pronounced shoulder due to many-body interactions arises around 459 nm (2.702 eV). At excitation intensity of the order of few hundreds $kW\,cm^{-2}$, stimulated emission emerges on the low-energy wing of this shoulder (around 460.5 nm and 2.691 eV), and strongly redshifts with increasing excitation intensity.

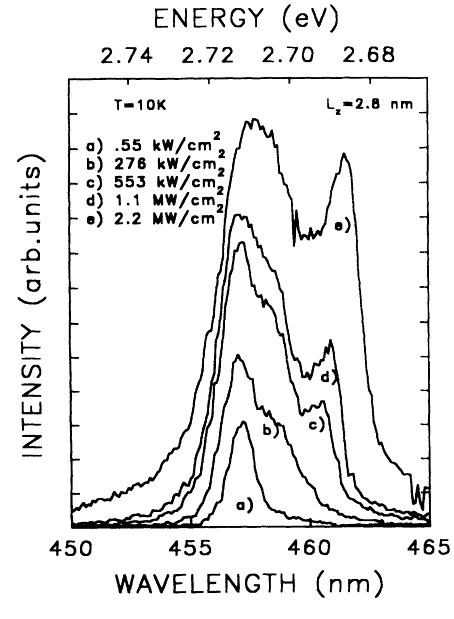

FIG. 2. Spontaneous photoluminescence spectra recorded in backscattering configuration under different excitation intensities. The temperature is 10 K.

Such stimulated emission (collected in the backscattering configuration) comes from surface imperfections which scatter the amplified luminescence traveling in the basal plane of the quantum well. Therefore it is not intense, and is overwhelmed by the dominant spontaneous emission. Conversely, collecting the photoluminescence from the sample edge (continuous lines in Fig. 3), the stimulated emission appears like a sharp line dominating the spectrum. Above the threshold, the stimulated emission grows superlinearly with the excitation intensity and exhibits a considerable redshift with increasing the excitation power, up to 8.5 meV in the intensity range investigated (see the inset of Fig. 3). On the contrary, the spontaneous emission exhibits no redshift and saturates, as a consequence of the dramatic decrease of the decay time,[14] under the same excitation conditions.

The present data differ dramatically from those of Refs. 7 and 8, in which the stimulated emission line occurred at the peak of a broad exciton-related spontaneous emission band. In Refs. 7 and 8 no intensity-dependent spectral shift of the stimulated emission could be observed by varying the power densities over four decades. This suggests that the stimulated recombination mechanism is not excitonic in our samples, and that lasing occurs through free-carrier recombination. We should point out that other stimulated recombination mechanisms like inelastic exciton-exciton or exciton-phonon scattering can be ruled out based on the energy position of the emission lines, which does not satisfy energy-

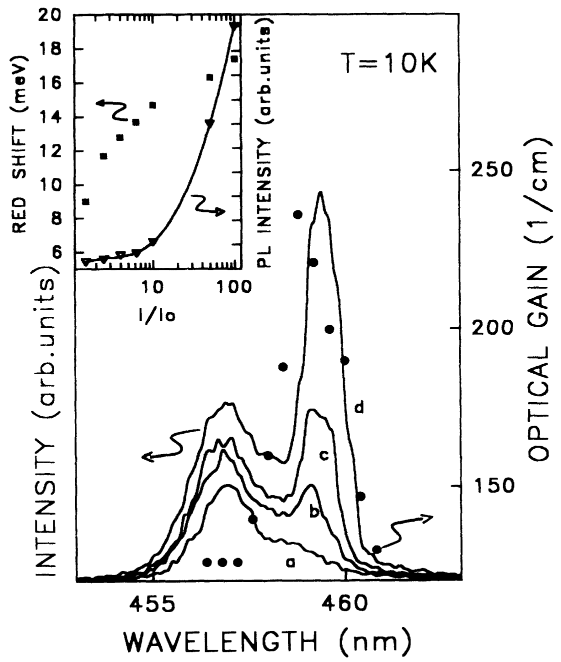

FIG. 3. Stimulated emission spectra collected from the sample edge under different excitation intensities: (a) 68.6, (b) 114.3, (c) 182.8, and (d) 288.6 KW/cm^2. The circles superimposed on the photoluminescence curves represent the optical gain spectrum (right axis). In the inset, the redshift (squares) and integrated intensity (triangles) of the stimulated emission line vs the excitation intensity. All data were obtained at 10 K.

conservation requirements.

Further information can be obtained from the low-temperature optical gain spectrum displayed in Fig. 3 (solid circles and right-hand axis). The gain curve peaks at the threshold energy of the stimulated emission (around 459 nm, 2.702 eV), with a peak value of about 240 cm^{-1} and a spectral width of some 20 meV. This lower value of the peak gain, as compared with III-V materials, is consistent with theoretical predictions for the electron-hole plasma optical gain in $\mathrm{Zn}_x\mathrm{Cd}_{1-x}\mathrm{Se/ZnSe}$ MQWS's.[15] Assuming a simple thermodynamic description of the electron-hole plasma based on a quasiequilibrium Fermi-Dirac distribution function, the linewidth of the optical gain can be correlated to the zero-temperature chemical potential of the electron-hole plasma. Our experimental value of 20 meV would be consistent with a carrier density of the order of 9×10^{11} cm^{-2}, that is in reasonable agreement with the predictions of Ref. 15. In particular, an optical gain of the order of 250 cm^{-1} is expected at carrier densities of 2×10^{18} cm^{-3}, corresponding to about 6×10^{11} cm^{-2} in the 3-nm quantum wells considered here.[15]

The above results indicate that the excitonic gain picture may be inadequate to explain the radiative lasing mechanism in shallow $\mathrm{Zn}_{0.9}\mathrm{Cd}_{0.1}\mathrm{Se}$ quantum wells, where the total band-gap discontinuity is of the order of 120 meV, and the enhancement of the exciton confinement is not very strong. In fact, absorption measurements performed at low temperature in the same samples (not shown here) clearly show an exciton binding energy of about 20 meV which is comparable to the bulk value. Furthermore, the linewidth of the excitonic resonances amounts to about 8 meV, indicating that compositional disorder causing inhomogeneous broadening of the excitonic states is not dominant in our samples.

To unambiguously identify the actual recombination process occurring in our samples, we have thus measured the spectral shift of the spontaneous and stimulated emission lines in magnetic fields up to 8 T. The basic idea, which was already successfully applied to GaAs quantum wells,[16] relies on the different magnetoluminescence shift exhibited by excitonic and free-carrier-related features in the optical spectra. The excitonic recombination in the magnetic field (B) exhibits a diamagnetic shift quadratic in the field:

$$\Delta E \simeq \frac{\hbar^4 \epsilon^2}{e^2 \mu^3} B^2 \, , \tag{1}$$

where μ is the reduced exciton mass. By using the correct in-plane heavy-hole mass, a very small diamagnetic shift, of the order of 1.95 $\mu\mathrm{eV/T}^2$, is expected for $\mathrm{Zn}_{0.9}\mathrm{Cd}_{0.1}\mathrm{Se}$. Conversely, the free-carrier recombination is characterized by the well-known Landau shift, linear in the magnetic field

$$\Delta E \simeq \frac{1}{2} \left[\frac{\hbar e}{m_e} + \frac{\hbar e}{m_h} \right] B \, . \tag{2}$$

In this case a stronger shift of about 0.65 meV/T is expected for the investigated MQWS. The experimental magnetic-field-induced shifts of the different emission features are shown in Fig. 4 (symbols) together with the expected theoretical dependence that more closely matches the experimental behavior [solid and dashed lines from Eqs. (1) and (2), respectively]. The measurements were carried out either in backscattering or in edge emission configurations, tuning the power density in such a way that the three different emission lines—namely the main excitonic recombination at 2.713 eV (solid circles), the high-density spontaneous emission band around 2.702 (open circles), and its sharp stimulated emission around 2.696 (triangles)—could be spectrally resolved. The position of the high-density spontaneous emission band around 2.702 eV was extracted by using a least-square fitting procedure of the overall spectrum in terms of Lorentzian line shapes. The experimental shifts provide clear evidence of the different nature of the recombination mechanisms involved. The highest-energy spontaneous emission exhibits a clear excitonic nature, in agreement with the negligible shift predicted by Eq. (1) (continuous line). Conversely, the broad spontaneous emission band at 2.7 eV and its sharp stimulated emission exhibit a much larger shift with increasing magnetic field, in fair agreement with the prediction of Eq. (2) (dashed lines) for the free-carrier transitions. The observed deviation from the expected free-carrier shift probably indicates that carrier mass renormalization should be included in the calculation, especially at higher fields. Other excitonic-related processes like inelastic exciton-electron or exciton-phonon scattering can be ruled out, as they should exhibit the same diamagnetic shift as the free exciton (inelastic exciton-exciton scattering should even exhibit a blueshift at low fields[16]).

In conclusion, our experiments indicate that free-carrier recombination plays an important role in the

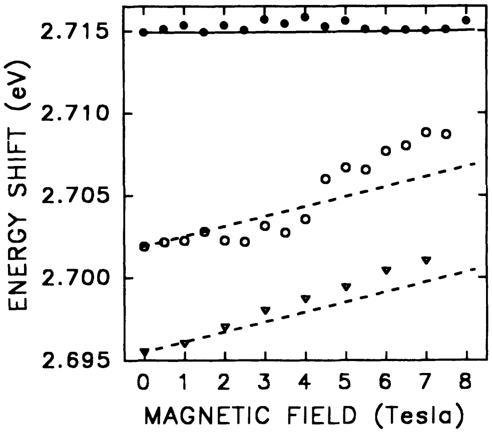

FIG. 4. Experimental (symbols) and theoretical (lines) magnetic shifts of the main spontaneous and stimulated luminescence bands measured at 3.5 K. The exciton luminescence (solid circles) does not exhibit a strong shift, in agreement with the predictions of Eq. (1) (continuous line). The spontaneous emission arising around 2.702 eV in Fig. 1 (open circles) and its sharp stimulated emission (triangles) exhibit a free-carrier magnetic shift, consistent with the predictions of Eq. (2) (dashed lines). The peak position of the spontaneous emission at 2.702 eV has been extracted by a line-shape fitting, with an uncertainty of about ±1.5 meV.

stimulated emission of shallow $Zn_{0.9}Cd_{0.1}Se/ZnSe$ quantum wells. The mechanism of excitonic gain recently proposed to explain lasing in this type of MQWS's (Refs. 7 and 8) does not apply to the actual MQWS examined here, in which lasing originates from free-carrier transitions although the main spontaneous emission has excitonic character. Excitonic gain, as opposed to electron-hole plasma gain, is likely to be dominant when the exciton stability is enhanced by the confinement (i.e., the exciton binding energy is larger than the longitudinal-optical-phonon energy) and in the presence of sufficient exciton localization at defects. This causes a dominant inhomogeneous broadening of the density of states which in turn allows the population inversion of the thermally stable excitons at the low-energy tail of the exciton absorption band. Conversely, in shallow quantum wells the weaker confinement and the small compositional disorder do not favor the exciton stability and localization, thus causing the lasing to be mainly of free-carrier origin. Additional experiments are presently underway in quantum wells with higher Cd content, to determine the critical composition for the transition from free-carrier lasing to excitonic lasing.

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