Exciton-related lasing mechanism in ZnSe-(Zn, Cd) Se multiple quantum wells

Y. Kawakami, I. Hauksson, H. Stewart, J. Simpson, I. Galbraith, K. Prior, B. Cavenett

► To cite this version:

Y. Kawakami, I. Hauksson, H. Stewart, J. Simpson, I. Galbraith, et al.. Exciton-related lasing mechanism in ZnSe-(Zn, Cd) Se multiple quantum wells. Journal de Physique IV Proceedings, 1993, 03 (C5), pp.C5-83-C5-90. 10.1051/jp4:1993515 . jpa-00251601

HAL Id: jpa-00251601

<https://hal.science/jpa-00251601>

Submitted on 1 Jan 1993

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Exciton-related lasing mechanism in ZnSe-(Zn, Cd)Se multiple quantum wells

Y. KAWAKAMI*, I. HAUSSON, H. STEWART, J. SIMPSON, I. GALBRAITH, K.A. PRIOR and B.C. CAVENETT

Department of Physics, Heriot-Watt University, Edinburgh EH14 4AS, U.K.

** Department of Electrical Engineering, Kyoto University, Kyoto 606, Japan*

Abstract: The processes involved in the stimulated emission by photo pumping in (Zn,Cd)Se-ZnSe multiple quantum wells (MQWs) have been investigated at 77K for a series of different well widths. It has been shown by means of photoluminescence excitation spectroscopy that the confined excitons in the well play an important role in determining the lasing mechanism. The optical gain just above the lasing threshold is attributed to the recombination of an exciton accompanied by emission of one LO phonon. Far above threshold inelastic exciton-exciton scattering processes contribute significantly to the gain.

1. Introduction

Progress in the growth technology of II-VI wide-gap semiconductors has opened the way to the first demonstration of blue-green laser diodes (LDs) based on strained (Zn,Cd)Se-Zn(S)Se quantum well structures.[1] More recently, the operation of blue LD has been reported in the lattice matched ZnSe-(Zn,Mg)(S,Se) system.[2]

A detailed understanding of the lasing mechanism in II-VI semiconductors is very important for the design of laser structures. In III-V semiconductors (like GaAs or InP), it has been shown that recombination from the electron-hole plasma(EHP) is the dominant process for the optical gain. Due to the large carrier densities present at the lasing threshold, the bound states of the excitons are screened out leaving only coulomb-correlated continuum transitions. Consequently, in III-V LDs, apart from few exceptions, for example,[3], only band-to-band transitions have been included in gain spectra calculations. However, the situation is different for II-VI semiconductors because the Mott density, above which excitons are screened out, is estimated to be much larger than that in III-V semiconductors ($7 \times 10^{16}/\text{cm}^3$ in GaAs compared with $6 \times 10^{18}/\text{cm}^3$ in ZnSe). This difference arises primarily from the much smaller dielectric constant in ZnSe and the larger electron effective mass.

In this paper, we discuss the recombination processes involved in the stimulated emission at 77K from a series of photo-pumped (Zn,Cd)Se-ZnSe MQW structures with different well widths by means of photo-luminescence excitation spectroscopy(PLE). Our intention is to optically probe the sample under lasing conditions. Specifically whether there remains a strong excitonic character to the absorption during lasing. We will do this by monitoring the PLE spectrum above threshold. We show that even above threshold there remains a strong excitonic character to the PLE spectrum so demonstrating that excitonic states play a central role in the lasing mechanism.

Historically, exciton-related lasing mechanisms have been studied for bulk II-VI crystals at low temperature. Guillaume et al.[4] attributed the optical gain in CdS excited by an electron beam at 10K to three exciton-related processes namely, (1) a low gain process owing to the annihilation of a free exciton with the emission of a photon and a LO phonon (E_x -LO phonon process), (2) a medium gain process of exciton-exciton inelastic scattering, (3) a high gain process involving exciton-electron scattering. More recently, Newbury et al.[5] concluded that the exciton-exciton inelastic collision is the dominant stimulated emission process at 6K in an optically pumped ZnSe epilayer. Exciton-related lasing processes have been investigated in multiple quantum well (MQW) structures such as (Zn,Cd)Se-ZnSe[6, 7, 8, 9], ZnSe-Zn(S,Se)[10], (Zn,Cd)Se-Zn(S,Se)[11] and (Zn,Cd)S-ZnS[12]. Since the exciton binding energy is enhanced and also the exciton-LO phonon coupling is reduced in the quasi-two dimensional confinement,[13], Ding et al.[8] have pointed out that excitons can play an important role even at room temperature.

2. Experimental procedure

The (Zn,Cd)Se-ZnSe MQW layers were grown in a VG Semicon molecular beam epitaxy system using conventional Knudsen cell sources of zinc, cadmium and selenium on semi-insulating (Cr-doped) (100) GaAs substrates at a temperature of 280 °C. Details of the growth techniques have been published previously.[14]

The MQW structures consist of a ZnSe buffer layer (1.0 μ m), 15 cycles of Zn_{0.80}Cd_{0.20}Se wells and ZnSe barriers and a ZnSe cap layer (0.20 μ m) and in these experiments, a series of samples with different well widths 15Å, 30Å and 120Å and a constant barrier width of 80Å were investigated. Given an exciton Bohr radius (a_B) of 35Å in bulk Zn_{0.80}Cd_{0.20}Se, these well widths cover the range from 0.43 a_B to 3.4 a_B . Thus we span the transition from quasi-two-dimensional to bulk excitonic character.

The samples were cleaved to approximately 500 μ m and mounted on a copper cryostat holder. An Xe-Cl excimer laser (LAMBDA PHYSIK LPX-100) pumped tunable dye laser (LAMBDA PHYSIK FL2001) with dyes of Coumarin 120 and Coumarin 47 was used for the photopumping to cover the spectral range from 440 to 476nm. The pulse duration of the pump laser is 5 ns which is much longer than the recombination time in the materials, so that the excitation was quasi-cw. The pump intensity was controlled using neutral density filters and was focused onto the sample surface using a cylindrical lens. The pulsed emission signal with a repetition rate of 15 Hz from the cleaved edge of the sample was focused into a Spex 0.6m single grating monochromator using collection optics and was averaged using a boxcar integrator. The temperature was held constant at 77K.

3. Results and discussion

Figure 1, curve (a) shows the cw photoluminescence (PL) spectrum from top face of the sample with a well width of 15Å under low power excitation (10mW/cm²). Since the light hole valence band in the well is lowered in energy with respect to the heavy hole band due to the compressive strain and confinement, the emission peak at 2.7411eV originates from the radiative recombination of the confined n=1 heavy hole excitons (designated as E_{x1hh}). Reflectivity and cw-absorption measurements show that the Stokes shift of this peak is 3.0meV. Figure 1, curves (b)-(d) are the emission spectra from the cleaved facet as a function of increasing excitation intensity. The excitation photon energy is 2.8171eV in this case. At an excitation intensity of 0.079kW/cm², the spectrum has a single peak whose position is same as that in the cw PL. An emission band designated as L appears in the low energy side of the main peak at about 1.0kW/cm² and grows superlinearly with increasing excitation intensity. The superlinear increase and spectral narrowing of the L band, indicates the initiation of stimulated emission, and occurs at an excitation intensity of 10kW/cm². We note that the emission peak of the lower band (E_{x1hh}) does not shift with the increase of the excitation intensity and is still be observable above the lasing threshold so that the lasing line is at a substantially lower energy than the cw PL peak. The energy separation between the cw PL and the lasing peak at the threshold is 24meV.

Figure 1

Emission spectra taken from the $\text{Zn}_{0.80}\text{Cd}_{0.20}\text{Se}$ - ZnSe MQW whose well width is $15\text{\AA}$.

(a) PL from the top surface under the cw excitation of 10 mW/cm^2 .

(b)~(d) Emission from the cleaved edge under pulsed photo(2.8171 eV) excitation of : (b) 0.079 kW/cm^2 , (c) 6.3 kW/cm^2 and (d) 12.5 kW/cm^2 .

Figure 2

Lasing peak intensity taken from the MQW ($L_w=15\text{\AA}$) as a function of excitation wavelength under excitation intensity of (a) $1.0I_{th}$, (b) $2.0I_{th}$, (c) $4.0I_{th}$ and (d) $16.0I_{th}$, respectively. In this case, I_{th} is the threshold intensity under the resonant excitation condition to the E_{x1hh} line.

The lasing peak intensity of this sample as a function of excitation wavelength is shown in Fig. 2 for various pump intensities. The photo-luminescence excitation spectrum, curve (a), is very similar to the low power cw-absorption, and consists of energy levels of the ZnSe barriers (and/or ZnSe cladding layer) and confined levels in the $\text{Zn}_{0.80}\text{Cd}_{0.20}\text{Se}$ wells. The peak at 2.7450eV is assigned E_{x1hh} and the peak at 2.7618eV originates from the $n=1$ light hole exciton (E_{x1lh}). With increasing excitation intensity, the excitonic peaks become less distinct, and there is a small shift to higher energy and a decrease in the exciton transition strengths. The net shift of the peak is the result of several effects, namely, the exciton-band filling (a blue-shift), a reduction of the exciton binding energy due to the exciton-self screening (a blue-shift) and the renormalization of the bandgap (a red-shift). Similar, small blue-shifts has been seen in GaAs/(Al,Ga)AS MQWs under short pulse excitation which creates a population of excitons[15, 16] and are attributed to exciton-exciton interactions. The blue shift is observed only for the E_{x1hh} , the shift for E_{x1lh} is essentially zero. A complete theoretical analysis of the many-body interactions is needed for a quantitative understanding of the peak shifts and bleaching.

It is important to clarify the energy shifts observed. To be consistent with the notation in III-V semiconductors we define the Stokes shift as the difference between the absorption (or PLE) and the emission energies. We also define ΔE_{laser} to be the energy difference between the E_{x1hh} peak in the PLE and the lasing line. Thus ΔE_{laser} changes with excitation intensity.

The ΔE_{laser} value at the lasing threshold (denoted ΔE_{laser}^{th}) of this sample is much larger ($\Delta E_{laser}^{th} = 27.1\text{meV}$) than the Stokes shift (3meV). This value is close to both the LO-phonon energy of 31meV and the exciton binding energy of $\approx 35\text{meV}$. Two possible processes can be responsible for the lasing. One is the LO-phonon assisted recombination of excitons and the other is the exciton-exciton scattering process. The phonon assisted process is

and the energy balance for the process is given by $\hbar\omega_L = E_g - E_{ex} - E_{LO} + E_{kin}^{ex}$ where E_g is the band gap, E_{ex} is the exciton binding energy, E_{LO} is the LO-phonon energy and E_{kin}^{ex} is the kinetic energy of the exciton. In this case, $\Delta E_{laser}^{th} = E_{LO}$ assuming that E_{kin}^{ex} is negligibly small.

Recent investigations of Raman spectra of $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ mixed crystal have shown that LO-phonon spectrum versus solid composition (x) is a single mode type, and the E_{LO} of the $\text{Zn}_{0.80}\text{Cd}_{0.20}\text{Se}$ alloy is estimated to be about 30meV.[17]

If this process is the mechanism of the stimulated emission then first the ΔE_{laser}^{th} value should be equal to E_{LO} and should not depend on the well width (L_W). Secondly no red shift of the lasing line could be observed with increasing the photo pump intensity.

The exciton-exciton scattering process can be described as follows:

The energy conservation condition can be written as $\hbar\omega_P = E_g - 2E_x - \delta E_{kin} + E_{kin}^{ex(A)} + E_{kin}^{ex(B)}$ where δE_{kin} is the kinetic energy of the free electron and hole resulting from this process. If the lowest conduction and the highest valence bands are unfilled and the kinetic energy of the excitons are small enough at the lasing threshold, the δE_{kin} value is expected to be zero. Therefore, $\Delta E_{laser}^{th} = E_{ex}$. With increasing excitation intensity, the conduction and valence bands begin to be filled with free carriers. In the three dimensional case, we can show that [5]

$$\Delta E = \delta E_{kin} + E_{kin}^{ex(A)} + E_{kin}^{ex(B)} \quad (1)$$

$$\simeq \delta E_{kin} \propto I_e^{1/3} \quad (2)$$

where ΔE represents the red shift of the lasing line. In the two-dimensional case, we obtain similarly $\Delta E \propto I_e^{1/2}$. If the exciton-exciton scattering is the process for the lasing in the MQW structures at the threshold, the ΔE_{laser}^{th} value corresponds to the binding energy of quasi-two dimensional excitons which varies with the L_W . Figure 3 shows the exciton binding energy of $n=1$ heavy-hole exciton

(E_{ex}) in the ZnSe-Zn_{0.80}Cd_{0.20}Se-ZnSe quantum well as a function of L_W calculated using a two parameter variational approach. In this analysis, the conduction and heavy hole band discontinuity ($\Delta E_c, \Delta E_{v-hh}$) is assumed to be $\Delta E_c=168\text{meV}$ and $\Delta E_{v-hh}=66\text{meV}$, respectively and the calculation has been done for the two different in-plane masses of heavy hole ((a) $m_{hh\parallel} = 1.46m_0$, (b) $m_{hh\parallel} = 0.50m_0$). As far as we are aware there exists to date no comprehensive measurements of the valence subband dispersion in these materials. However, the actual in-plane mass would be between the two. The E_{ex} value at $L_W=15\text{\AA}$ is estimated to be in the range between 37meV and 45meV which is substantially larger than the observed ΔE_{laser}^{th} value (27.1meV). If exciton-exciton scattering is responsible for the lasing action $\Delta E_{laser}^{th} = E_{ex}$, and should follow the well width dependence of the binding energy. Furthermore with increasing photo-pump intensity there should be a square-root dependency on the photo-pump intensity.

Consequently, as far as the energy value is considered, the exciton-LO phonon scattering process is more probable for the stimulated emission at the threshold pumping intensity. In order to test this assignment further, the well width dependence of the lasing transition has been studied.

Figure 4 shows the ΔE_{laser}^{th} and the Stokes shifts of the cw PL as a function of well width. The ΔE_{laser}^{th} data lie between 27.1meV and 31.5meV , and do not show any distinct dependence on the well width. This is consistent with the lasing mechanism at threshold being LO-phonon mediated rather than due to exciton-exciton scattering. The Stokes shifts are in the range between 3.0 and 7.7meV , which is substantially smaller than the ΔE_{laser}^{th} . Therefore, it is expected that the localization of excitons to the alloy disorder and/or the fluctuation of the well width is not directly related to the lasing mechanism in the series of samples investigated here.

This is in contrast to some recent work [7, 8, 9] in which it was convincingly argued that the lasing mechanism arose from an inhomogeneously broadened band-edge. This was demonstrated by showing the emergence of the stimulated emission from the peak of the luminescence. In our samples the stimulated emission does *not* emerge from the peak of the cw-luminescence but at some 30meV lower energy. The difference is due to the presence of a large apparent Stokes shift in their samples which they attribute to re-absorption. As the cw-PL from the top surface and the low intensity pulsed PL from the cleaved facet show peaks at the same energy (see Fig. 1) we are confident that re-absorption is not shifting the peaks in our sample.

Thus we believe the LO-phonon mechanism is responsible for the lasing at threshold in our samples but not necessarily in theirs.

The dependence of the E_{x1hh} excitation peak, the lasing energy and the ΔE_{laser} on the excitation intensity for the MQW sample ($L_W=30\text{\AA}$) are shown in Fig. 5. In this sample, the excitonic peak can be observed up to about $I = 50 \times I_{th}$ which is the largest among the three MQWs. The lasing energy drops rapidly by about 3meV if the excitation power is increased from $1.0 \times I_{th}$ to $1.5 \times I_{th}$, remains constant in the range between $1.5 \times I_{th}$ and $8.0 \times I_{th}$ and tends to decrease again above $I = 8.0 \times I_{th}$.

In order to analyse the red shift of the lasing peak (designated as ΔE), the detailed data of ΔE are plotted as a function of $(I - I_{th})$ in a log-log scale (Fig. 6 (b)). The data obtained in the ZnSe epitaxial layer at 10K are also plotted (Fig. 6 (a)) for comparison.[5] ΔE of the ZnSe epitaxial layer is proportional to the $(I - I_{th})^{1/3}$ in the range from $I - I_{th} = 2.0 \times I_{th}$ to $10 \times I_{th}$. This has been interpreted as the lasing occurs as a result of the annihilation of an exciton via exciton-exciton inelastic scattering. In the case of the MQW sample, we expect, as above, $\Delta E \propto (I - I_{th})^{1/2}$. As can be seen from Figure 6(b) this is found if $I - I_{th}$ is above about $7 \times I_{th}$. Thus we believe that the dominant lasing mechanism above about $7 \times I_{th}$ is inelastic exciton-exciton scattering. This is further supported by the fact that above about $7 \times I_{th}$ the PLE spectrum begins to blue-shift in accord with the exciton-exciton scattering mechanism[15, 16].

4. Conclusions

PLE spectra of the stimulated emission in the ZnSe-Zn_{0.80}Cd_{0.20}Se MQWs have been investigated at 77K with the series of different well widths. It has been shown that the ΔE_{laser}^{th} value is substan-

Figure 3
Calculated binding energy of excitons confined in the $\text{Zn}_{0.80}\text{Cd}_{0.20}\text{Se}$ QW as a function of well width, assuming that the in-plane effective mass of the heavy-hole in $\text{Zn}_{0.80}\text{Cd}_{0.20}\text{Se}$ is (a) $1.46m_0$ and (b) $0.50m_0$, respectively.

Figure 4
Stokes shift of the cw PL (open square) and the ΔE_{laser} value (closed circle) as a function of well width.
Data obtained at $\text{Zn}_{0.85}\text{Cd}_{0.15}\text{Se}-\text{ZnS}_{0.08}\text{Se}_{0.92}$ MQW ($L_W=50\text{Å}$) are also shown with triangular mark[11].

Figure 5

The dependence of the E_{x1hh} excitation peak (open circle), the lasing peak (open square) and the ΔE_{laser} value (closed circle) on the excitation intensity observed in the MQW ($L_W=30\text{\AA}$).

Figure 6

Red shifts of the lasing line (ΔE) observed in the MQW ($L_W=30\text{\AA}$) as a function of $I - I_{th}$. Data obtained in the ZnSe epilayer (ref.[5]) are also shown for the comparison.

tially larger than the Stokes shift of the cw PL and equal to the LO-phonon energy. Furthermore it is independent of the well width. Even under lasing conditions, excitonic peaks are clearly seen in the PLE spectra confirming the importance of excitonic transitions in the lasing process. We conclude that exciton-LO phonon scattering is the dominant process for the optical gain in the range from $I = I_{th}$ to $7 \times I_{th}$.

At higher excitation levels, exciton-exciton inelastic scattering comes to dominate to the gain .

The authors are grateful to SERC, The Royal Society and VG Semicon Ltd. for support of this research. YK would like to express his sincere thanks to Prof. S. Fujita for valuable discussions.

References

- [1] M. A. Haase, J. Qiu, J. M. DePuydt, and H. Cheng. *Appl. Phys. Lett.* **59**, 1272 (1991).
- [2] H. Okuyama, T. Miyajima, Y. Morinaga, F. Hiei, O. Ozawa, and K. Akimoto. *Electron. Lett.* **28**, 1798 (1992).
- [3] H. Haug and S. W. Koch. *Phys. Rev. B* **39**, 1887 (1989).
- [4] C. B. Guillaume, J. M. Deveber, and F. Salvan. *Phys. Rev.* **177**, 567 (1969).
- [5] P. R. Newbury, K. Shazard, and D. A. Cammack. *Appl. Phys. Lett.* **58**, 1065 (1991).
- [6] H. Jeon, J. Ding, A. V. Nurmikko, H. Luo, N. Samarth, and J. K. Furdyna. *Appl. Phys. Lett.* **59**, 1293 (1991).
- [7] J. Ding, H. Jeon, T. Ishihara, A. V. Nurmikko, H. Luo, N. Samarth, and J. Furdyna. *Surf. Sci.* **267**, 616 (1992).
- [8] J. Ding, H. Jeon, T. Ishihara, M. Hagerott, A. V. Nurmikko, H. Luo, N. Samarth, and J. Furdyna. *Phys. Rev. Lett.* **69**, 1707 (1992).
- [9] J. Ding, M. Hagerott, T. Ishihara, H. Jeon, and A. V. Nurmikko. *Phys. Rev. B* **47**, 10528 (1993).
- [10] Y. Kuroda, I. Suemune, Y. Fujii, and M. Fujimoto. *Appl. Phys. Lett.* **61**, 1182 (1992).
- [11] Y. Kawakami, B. C. Cavenett, K. Ichino, S. Fujita, and S. Fujita. *Jpn. J. Appl. Phys.* **32**, L730 (1993).
- [12] Y. Yamada, Y. Masumoto, J. T. Mullins, and T. Taguchi. *Appl. Phys. Lett.* **61**, 2190 (1992).
- [13] N. T. Pelekanos, J. Ding, M. Hagerrot, A. V. Nurmikko, H. Luo, N. Samarth, and J. K. Furdyna. *Phys. Rev. B* **45**, 6037 (1992).
- [14] K. A. Prior, J. M. Wallace, J. T. Hunter, S. J. Adams, M. S. Haines, M. Saoudi, and B. C. Cavenett. *J. Cryst. Growth* **101**, 176 (1990).
- [15] N. Peyghambarian, H. M. Gibbs, J. L. Jewell, A. M. A. Antonetti, D. Hulin, and A. Mysyrowicz. *Phys. Rev. Lett* **53**, 2433 (1984).
- [16] D. Hulin, A. Mysyrowicz, A. Antonetti, A. Migus, W. T. Masselink, H. Morkoc, H. M. Gibbs, and N. Peyghambarian. *Phys. Rev. B* **33**, 4389 (1986).
- [17] H. J. Lozykowski and V. K. Shastri. *J. Appl. Phys.* **59**, 3235 (1991).