Excitons and Electron-Hole plasma in ZnCdSe/ZnSe quantum wells

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Abstract

We report the results of pump and probe transmission and magneto-stimulated emission experiments performed in ZnCdSe/ZnSe multiple quantum wells of different well width and composition. The pumping conditions for the excitonic bleaching and the stimulated emission are directly correlated to the exciton stability in different samples. A transition from excitonic to free carrier lasing is observed by finely tuning the injection rate around the exciton ionization threshold.

1. Introduction

The enormous technological impact of wide band gap II-VI semiconductors for blue-green optoelectronic applications, and the clear manifestation of excitonic gain even at high temperature, have stimulated growing interest in the physics of radiative recombination processes of ZnSe-based heterostructures [1,2,3,4]. As far as lasing is concerned, the main point is the determination of the stimulated emission mechanism of ZnCdSe/ZnSe heterostructures whose exciton binding energy can be tuned, by a proper choice of composition and size, from the bulk value (about 20 meV) up to 60 meV or more [5]. Under these conditions the usual picture of many body interaction, exciton screening and electron-hole plasma dynamics, has to be revised, in order to account for the enhanced electrostatic and thermal stability of the excitonic quasi-particles. To contribute to the understanding of this issue, we have performed a number of optical experiments in $Zn_{(1-x)}Cd_xSe/ZnSe$ multiple quantum wells of different well width and composition. Non-linear pump and probe transmission spectroscopy has been used to evaluate the carrier density dependence of the excitonic bleaching induced by strong photopumping. Simultaneous stimulated emission measurements from the edge of the pumped samples allowed us to correlate the lasing with the actual presence of excitonic features in the non-linear transmission spectra. The exciton binding energy has been found to be the key-parameter for the interpretation of the optical spectra: heterostructures with moderate exciton confinement exhibit relatively low screening threshold, with the lasing line appearing at excitation powers around the bleaching intensity. Deeper quantum wells with stable excitons, exhibit stimulated emission at power densities below the typical bleaching intensity, indicating a dominant excitonic gain mechanism. Consistently, the shift of the stimulated emission in magnetic field has been found to be diamagnetic (excitonic-like) or Landau-like (free-carriers) in different samples, depending on whether the excitation intensity was below or above the bleaching threshold. The most important point is however, the coexistence of a dense exciton and free-carrier phase, analogous to the quasi equilibrium condition of an atomic and molecular gas phase, which has

been revealed by magneto-stimulated emission measurements, by finely tuning the exciton power just around the exciton bleaching threshold. These effects could be studied by virtue of the high quality of the investigated structures which allowed us to obtain stimulated emission at power densities of the order of 2.4 kWcm^{-2} at 10 K and about 10 kWcm^{-2} at room temperature ($L=20 \text{ nm}$ and $x=0.11$), which was comparable or sometimes smaller than the bleaching threshold of the exciton.

2.Experimental

The samples used in this study were grown by solid source Molecular Beam Epitaxy (MBE) on GaAs substrates. Details on the growth methodology can be found in ref.[6]. The well widths were comprised in the range $3\text{nm}<L<20 \text{ nm}$, whereas the Cd content was varied in the range $0.10<x<0.26$, thus changing the gap of the quantum well from about 2.72 eV to 2.5 eV (at cryogenic temperatures) and the total potential discontinuity from 0.1 to about 0.3 eV.

The substrates were chemically etched in order to measure the linear and non-linear transmission spectra. The pump and probe spectroscopy has been performed by using the output of a parametric oscillator laser (SPECTRA PHYSICS MOPO 710) as a probe, and the collinear pump beam of the 3rd harmonic Nd:Yag laser. The samples were placed in the cold finger of a closed cycle He cryostat and the stimulated emission induced by the pump beam was simultaneously collected from the edge and dispersed by a double monochromator (0.5 m focal length). This allowed us to correlate straightforwardly the degree of exciton ionization with the actual stimulated recombination spectrum of the samples. The magneto-optical stimulated emission spectra were measured under identical excitation conditions, by means of a superconducting optical magnet providing up to 9.5 Tesla at 2.2 K (Oxford Ltd). The spectral resolution in our experiments corresponds to 0.4 meV.

All the samples were previously characterized by linear absorption spectroscopy in order to identify the main excitonic resonances and the exciton binding energies.

3.Results and discussion

In Fig.1 we display a summary of the main interband transition energies measured in the set of investigated samples by low temperature absorption measurements. The lines have been calculated within the usual envelope function formalism, including the strain and a conduction to valence band discontinuity equal to 80:20. The exciton binding energy for the various samples was determined by the line shape fitting of the absorption spectra (most of them showing sharp band edges) and compared with the outcome of a variational calculation. These data are summarized in Fig.2. Details on the linear characterization of these samples are reported elsewhere [7].

The results of Fig.2 provide a figure of merit for the exciton stability in these samples. Quantum wells with high Cd content ($x>0.2$) and relatively narrow width, exhibit an exciton binding energy larger than the LO phonon energy (31.6 meV in ZnSe), whereas shallow quantum wells thicker than 10 nm essentially show three-dimensional properties (binding

Fig.1 - Experimental (symbols) and calculated (curves) interband transition energies vs. the well width, for two sets of samples with Cd content equal to 0.11 and 0.23 . The heavy-hole and light-hole states are represented by full dots and continuous curves, and by empty dots and dashed lines, respectively. The temperature is 10 K.

Fig.2 Experimental (symbols) and calculated (curves) heavy-hole exciton binding energies (dots for $x=0.11$, triangles for $x=0.23$). The dashed lines were calculated by using the ZnSe dielectric constant ($\epsilon=9.2$). The continuous curves were obtained by linear interpolation of the dielectric constants of ZnSe and CdSe.

energy of about 20 meV). Assuming the simplest many body approach for the exciton bleaching induced by phase space filling [8], we can evaluate the carrier density for the absorption saturation according to :

$$N_c = \frac{1}{8\pi a_0} \quad (1)$$

where a_0 is the exciton Bohr radius. For the present set of samples we get $2 \cdot 10^{11} \text{ cm}^{-2} < N_c < 7.5 \cdot 10^{11} \text{ cm}^{-2}$, which has to be compared with the threshold density for the occurrence of stimulated emission.

In Figs.3a and 3b we plot the typical pump and probe transmission spectra measured in our samples. On the left hand side we report the experimental curves obtained under increasing pump power. In the right panel we display the calculated bleaching spectra obtained by modelling the exciton band with a Lorentzian line shape ($L[h\nu - (E_g - E_b), \Gamma]$), multiplied by the well known density dependent oscillator strength factor [9]. Actually a pump induced broadening (lifetime broadening) is phenomenologically included by assuming a density dependent broadening factor of the Lorentzian $\Gamma(N) = \Gamma_0 \cdot \left(1 + \frac{N}{N_c}\right)^2$ [9,10].

The continuum is modelled by the usual broadened step function ($\Theta[h\nu - E_g, \gamma]$). The resulting non-linear absorption line shape reads:

$$\alpha(h\nu, N) \approx \text{const} \cdot \left(1 - \frac{N}{N_c}\right) L[h\nu - (E_g - E_b), \Gamma(N)] \cdot \Theta(h\nu - E_g, \gamma) \quad (2)$$

Though rough the model reproduces the essential features of the pump and probe spectra without fitting parameters, the critical density being calculated by means of eq.(1) and using the experimentally determined exciton binding energy values. More accurate calculations following ref.[10] including a full many-body treatment of the non-linear absorption processes are underway and will be reported in the near future. The power density for the exciton ionization amounts to about 4 kWcm^{-2} for the shallow quantum well sample Fig.3a, and grows up to 30 kWcm^{-2} for the deep quantum well of Fig.3b.

In the former case, the stimulated emission is found to appear at pump intensities coincident with the exciton bleaching threshold. Therefore, for relatively shallow quantum wells like those investigated in Fig.3a, the transition from excitonic states to uncorrelated electron-hole pairs occurs concomitantly to the beginning of the stimulated emission. On the other hand, the stimulated emission measurements performed simultaneously to the pump and probe experiments in the deep ZnCdSe quantum wells ($x=0.26$), clearly show that the stimulated emission appears at power densities well below those necessary for the exciton bleaching, indicating the key role of the excitonic recombination in strongly confined ZnCdSe/ZnSe quantum wells [1].

Fig.3a Left panel: pump and probe absorption spectra of a MQW sample with 3 nm well width and Cd content $x=0.11$, recorded at different pump intensities. Right panel: calculated non-linear absorption spectra at different injected carrier densities. The parameters of the spectra are: a) 1 Wcm^{-2} and $N=0 \text{ cm}^{-2}$, b) 60 Wcm^{-2} and $N=4 \cdot 10^{10} \text{ cm}^{-2}$, c) 200 Wcm^{-2} and $N=1.6 \cdot 10^{11} \text{ cm}^{-2}$, d) 1100 Wcm^{-2} and $N=2.2 \cdot 10^{11} \text{ cm}^{-2}$, e) 10000 Wcm^{-2} and $N=3 \cdot 10^{11} \text{ cm}^{-2}$, for the experimental and calculated curves, respectively.

Fig. 3b. The same as in Fig. 3a, but for the $x=0.23$ MQW sample. The parameters of the spectra are: a) 70 Wcm^{-2} and $N=0 \text{ cm}^{-2}$, b) 700 Wcm^{-2} and $N=7 \cdot 10^{10} \text{ cm}^{-2}$, c) 50000 Wcm^{-2} and $N=1 \cdot 10^{11} \text{ cm}^{-2}$, d) 65000 Wcm^{-2} and $N=4 \cdot 10^{11} \text{ cm}^{-2}$, e) 100000 Wcm^{-2} and $N=6 \cdot 10^{11} \text{ cm}^{-2}$, for the experimental and calculated curves, respectively.

An unambiguous discrimination of the basic recombination mechanism is obtained by measuring the shift of the stimulated emission in magnetic field. In this case, we exploit the different dependence of the exciton and free-carrier eigenstates on the magnetic field, namely a quadratic dependence for the exciton and a linear dependence for the electrons. For the specific case of ZnSe based heterostructures we expect typical diamagnetic shifts of the order of $2 \mu\text{eV} / T^2$ for the excitons, and about 0.5 meV/T for the Landau shift. We should mention that, due to the large effective masses, the change of the quasi-Fermi level induced by the magnetic field is negligible, so that any spectral shift of the stimulated emission can be ascribed to the nature of the recombination process.

Consistent with the pump and probe data, the shift of the stimulated emission of deep quantum wells samples (strongly bound excitons) results to be diamagnetic at any reasonable excitation intensity above threshold. Further increase of the power density to observe the change into free-carrier recombination, is prevented in these samples by the surface damage induced by the strong pumping. The situation is more interesting in shallow quantum wells. In Fig.4 we plot the results obtained on the 20 nm wide wells with $x=0.11$. The magneto-stimulated emission measurements have been performed at threshold (corresponding to the spectrum labelled (b) in the inset) and above threshold (spectrum (c) of the inset). Under these conditions we were able to monitor the change from excitonic recombination to free-carrier recombination, witnessed by the increased magnetic shift of the stimulated emission.

Fig.4 - Energy shift of the stimulated emission of a MQW sample with $L=7 \text{ nm}$ and $x=0.11$ in magnetic field. In the inset: stimulated emission spectra around the stimulation threshold. The dots are measured under the conditions of spectrum (c), above the lasing threshold. The triangles are measured under the excitation conditions of spectrum (b), at threshold. Above threshold the shift is Landau-like.

Obviously further increase in the pump power results in a well defined Landau shift, as already reported in our previous work [4]. It is interesting to note that even at threshold the observed shift is slightly larger than that expected for pure excitonic recombination. This suggests the occurrence of a mixed exciton-electron-hole plasma phase near equilibrium, which is established at power densities close to the bleaching threshold. These results are consistent with the observation of lasing threshold comparable to the bleaching threshold in the pump and probe spectra. A quantitative treatment of this effect requires a self-consistent description of the exciton and plasma phase taking into account the density dependent stability of the exciton gas. Further experimental and theoretical work is in progress in our laboratories in order to understand this interesting phenomenon.

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