Exciton scattering processes in $\text{ZnSe}/\text{ZnS}_x\text{Se}_{1-x}$ MQW structures

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Abstract: Inelastic excitonic scattering processes have been investigated in $\text{ZnSe}/\text{ZnS}_x\text{Se}_{1-x}$ multiple-quantum-well structures of different well width and strain content. The free-exciton energies have been determined by photoluminescence excitation spectroscopy and compared with those calculated accounting for the actual strain contribution. All the samples show strong luminescence related to bound or localized excitons. In strain relaxed samples, the interaction of these states with free-electrons gives rise to optical gain at low temperature. In addition, a stronger stimulated emission is observable up to room temperature. The temperature and pumping intensity dependences of this latter amplification process suggest that two different lasing mechanisms may be invoked, namely free-exciton—bound-exciton or free-exciton—longitudinal-optical-phonon inelastic scattering.

II-VI semiconductors have been extensively studied to investigate the physical properties of the dense excitonic systems¹, and for the possible optoelectronic applications. However, despite laser operation of ZnSe multiple-quantum-wells (MQWs) has been recently documented², the underlying physical process has not yet been clarified^{3,4}. In a recent paper some of us presented experimental data indicating that inelastic excitonic scattering can be a possible lasing channel⁵, as already demonstrated for ZnSe epilayers⁶. In this communication we address the problem of the excitonic scattering in $\text{ZnSe}/\text{ZnS}_x\text{Se}_{1-x}$ MQWs presenting new results on a larger set of samples of different layer width and strain in order to elucidate the role of bound excitons or LO-phonons in the inelastic scattering processes.

The $\text{ZnSe}/\text{ZnS}_x\text{Se}_{1-x}$ samples of this study were grown by MOCVD at atmospheric pressure with 18% of sulphur content in the barrier layers. The nominal well and barrier thicknesses were equal and determined by the calibration of the flux rates. The third harmonics of a Nd:YAG laser (10Hz, 10ns) were used directly as pumping source in photoluminescence (PL) measurements and to excite the dye solution (0.2nm resolution) in PLE. The samples were mounted in a temperature controlled (10–300K) closed cycle He cryostat. The luminescence emission were dispersed in a 0.6m single pass (0.13nm resolution) or in a 0.25m double pass (0.25nm resolution) monochromator, in PL and PLE

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measurements, respectively. The strain in the ZnSe layers were estimated following the same procedure discussed in Ref. [7].

In Fig.1 we report the PLE spectra of sample S83 ($L_z=8.3nm$) taken at 10K. Two main peaks and two weaker shoulders are observable below the continuum edge. These structures have been attributed³ on the basis of a simple envelope function model, accounting for the effective strain in the ZnSe layer (-2.4×10^{-3}). The band alignment has been assumed of type-I and the conduction band offset has been arbitrarily chosen equal to 10meV ($\sim 6\%$) for all the samples. All the other relevant parameters needed for the calculation have been taken from Ref. [9]. The exciton binding energy has been fixed at 20meV, irrespective to the well width. The inset of Fig.1 shows the experimental and theoretical fundamental exciton energies in the investigated samples. The overall agreement (within few meV) observed over the large range of well thicknesses, supports the assumption of a nearly constant exciton binding energy close to the bulk value¹⁰.

Fig.2 shows two PL spectra of sample S62 ($L_z=6.2nm$) taken at 10K from the surface (SE) and from the edge (EE) of the sample cleaved to submillimeter dimensions. The cw PL (excitation by a Xe lamp) is also reported for comparison. The weak emission at 2.824eV in the cw spectrum coincides with the heavy-hole FE resonance in PLE. From their spectral position, the dominant emissions around 2.81eV should be related to localized and/or extrinsic energy states, even if their emission intensity do not saturate up to a photon density of $10^{23}cm^{-2}s^{-1}$. This attribution, based on time resolved PL measurements, has been discussed in Ref. [11]. The lower energy doublets at 2.789/2.782 and 2.758/2.751eV are LO phonon replicas and will be discussed elsewhere [12]. Two main points should be mentioned: *i*) the main emission around 2.81eV in the SE and EE spectra (I_b) is observable in the same spectral range of the localized states in cw PL spectrum; *ii*) the EE spectrum shows an additional stronger emission (SC) $\sim 15meV$ below the I_b band. These features are common to most of the investigated samples. As mentioned before, the intensity of the I_b band increases linearly up to a power density of $10^5W/cm^2$, while the SC emission shows optical amplification above a threshold (I_{tr}) of about $18kW/cm^2$. The carrier density at laser threshold can be roughly estimated by:

$$n_c = I_{tr} \alpha \tau \eta \ll 4 \times 10^{17} cm^{-3}$$

where τ has taken around 250ps according to Ref. [11] and η is usually much less than unity. These results allowed us to rule out the phase transition to an electron-hole plasma, because the Mott density in ZnSe should be at least of the order of $10^{18}cm^{-3}$. The spectral position of the emission band labelled I_b shifts proportionally to $1/2kT$ to lower energy, with respect the ZnSe band-gap thermal shrinkage¹³, as expected for a bound state. On the other hand, the SC peak energy shifts toward the red, with respect the I_b peak, with a thermal energy coefficient around 1.1-1.2kT (see inset of Fig.2). These experimental findings lead us to the following considerations: *i*) inelastic exciton-electron scattering (X) can be excluded in this case because its thermal coefficient should be about 2.2kT, (also, at low temperature, its peak is expected to rise close to the exciton emission); *ii*) the observed thermal shift can be accounted for either by the interaction between a free-exciton and a bound-exciton or by the exciton-LO scattering process. Both

processes are consistent with the observed spectral peak energies. For the former, the energy splitting between the FE and the SC band amounts to about one binding energy of the I_b excitons ($E_{FE} - E_{SC} \sim E_g - E_{I_b}$), whereas for the latter, the splitting between the FE and the SC transitions ($E_{FE} - E_{SC} \sim \hbar\omega_{LO}$), amounts to about one LO-energy (31 meV in bulk ZnSe). A further insight into this problem can be gained from the investigation of the stimulated emission behavior in magnetic fields and from the estimate of the electron-phonon coupling, which are now in progress in our laboratories.

Finally we want to address the different behavior shown by the samples for which no strain has been measured in the ZnSe layers. In this case the strain energy should be relaxed by a strong intermixing and/or misfit dislocation: in either cases the samples quality should be poorer and the density of defect-related energy states greater. The gain spectrum of one of these sample (S150b) is reported in Fig.3. In addition to the SC stimulated emission, a new feature (X) is observable only 4 meV below the I_b band. The temperature shift of its peak position (reported in the inset) is about $2kT$, close to the theoretical $2.2kT$ expected for the exciton-electron recombination. This additional feature has been observed only in strain-relaxed samples where a strong red-shift of the I_b band with the excitation intensity has also been observed. The optical gain of this emission is about half that of the SC transition and is easily saturated. A model considering the relative population of free electrons and free-excitons as a function of the defect density, suggests that the scattering between free-electrons and bound-excitons should be favoured in this case.

Conclusions and acknowledgments

Radiative transitions related to excitonic scattering processes have been observed in $ZnSe/ZnS_xSe_{1-x}$ MQWs. Strong stimulated emission is observable up to room temperature in all the samples. The reported data indicate that the amplification process can be due to free-exciton—bound-exciton or free-exciton—LO-phonon inelastic scattering processes. This work has been partially supported by C.N.R. under the special project *Tecnologie Elettroottiche*.

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Fig.1 PLE spectrum of sample S83: the line is only a guide to the eye. Inset: experimental and calculated fundamental excitonic transitions in the investigated samples.

Fig. 2 PL spectra of sample S62. Inset: energy splitting between I and SC transitions.

Fig.3 Gain spectrum of sample S150b. Inset: X and I peak energy positions.