Journal of Luminescence 45 (1990) 224–227
North-Holland

PHOTOLUMINESCENCE OF A ZnSe–ZnS STRAINED-LAYER SUPERLATTICE UNDER HIGH EXCITATIONS

Z.P. GUAN, X.W. FAN and G.H. FAN

Changchun Institute of Physics, Academia Sinica, Changchun, PR China

X.R. XU

Tianjing Institute of Technology, Tianjing, PR China

The luminescence spectra of high density excitons in a ZnSe–ZnS strained-layer superlattice (SLS) have been studied in the temperature range 77–250 K. The photoluminescence (PL) spectrum in the SLS usually has only one near edge emission band E_s. The E_s band is attributed to free exciton recombination following scattering from electrons in the conduction band. According to whether the binding energy of the free exciton increases as the well width of SLS decreases, it can be explained that why it is difficult to observe the separated P band in the ZnSe–ZnS SLS system.

1. Introduction

ZnSe is a II–VI compound semiconductor with a high exciton binding energy and a large nonlinear optical effect. Recently, attention has been paid to the superlattice using a ZnSe layer as the well material, which promises the possibility of being able to obtain excitonic emission and optical bistability using the two-dimensional exciton effect at room temperature. Saito et al. [1] have investigated the E and P bands in ZnSe single crystal over the temperature range 4.2–90 K under high excitation at 3371 Å and ascribed them to the exciton–electron (E_x–e) collision and exciton–exciton (E_x–E_x) collision, respectively. Catalano et al. [2] using dye laser ($h\nu = 2.88$ eV), and Colak et al. [3] with electron beam excitation, observed stimulated emission of the P band in ZnSe single crystals. Earlier we had studied the emission of free exciton [4] and E_x–E_x scattering [5]. Up to now, there has been no report on the origin of the E_s band in the SLS. In this paper, we explain the origin of the E_s band and discuss the tail in the low energy side of the E_s band.

2. Experiment

ZnSe–ZnS SLS structures were grown on (100) GaAs substrates by MOCVD at atmospheric pressure using dimethylzinc (DMZ), H_2Se, and H_2S as source materials for Zn, Se, and S, respectively. A Model QJD-9 nitrogen pulsed laser was used as the excitation source with $\lambda = 3371$ Å, $\tau = 10$ ns, $f = 10$ Hz, and $I_{max} = I_0 = 2$ MW/cm^2. The PL measurements were carried out with a Model 44W spectrometer and a RCA-C31034 photomultiplier.

3. Results and discussion

3.1. The origin of the E_s band

Fig. 1 shows the 77 K PL spectra of ZnSe–ZnS SLS under different excitation intensities. The E_s band is symmetrical under excitation intensities $I < 0.026\ I_0$, while with increasing excitation intensity it broadens and its peak position shifts to lower energy.

The peak energies for the E_s bands are shown as a function of temperature in fig. 2 for ZnSe film and ZnSe–ZnS SLSs. The curve labelled $E_x(T)$ in fig. 2 depicts the temperature dependence of the free exciton energy in ZnSe bulk single crystal. As can be seen in fig. 2, we found that the photon energies of the E_s bands for ZnSe(87 Å)–ZnS(11 Å) and ZnSe(57 Å)–ZnS(17 Å) SLSs are higher than that for bulk ZnSe film at the same temperature due to the quantum size effect in the SLSs. If the curve $E_x(T)$ is shifted vertically, making it overlap with the peak energies of E_s of two ZnSe–ZnS SLSs at 77 K, we obtain $E_x'(T)$ (not shown in the figure). It should be noticed from fig. 2 that the peak energies of E_s bands shift to the low energy side with temperature by amounts much more than the shift of the $E_x'(T)$. The inset of fig. 2 shows the variation with temperature of the energies separation $\Delta E(T) = E_x'(T) - E_s(T)$. It is found that the $\Delta E(T)$ depends linearly on temperature. This result is in good agreement with the E band obtained by Saito and Shionoya [1], who

Fig. 1. The P

ascribed the E ban collision. From th think that the E_s SLSs is produced l comparison of the of ZnSe(48 Å)–Zn the theoretical cur the theory of Ber $I = 0.16 I_0$ and the 110 K. The fact th

PHOTON ENERGY (eV)

Fig. 2. Temperature Å)–ZnS(11 Å), a

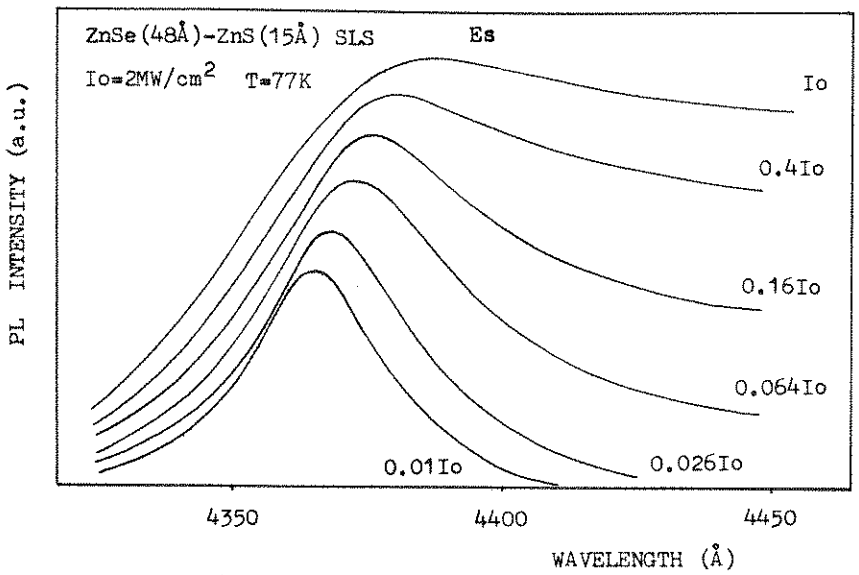

Fig. 1. The PL spectra of ZnSe(48 Å)–ZnS(15 Å) SLS under different excitation intensities at 77 K, $I_0 = 2$ MW/cm^2.

ascribed the E band in CdS, CdSe, and ZnSe to E_x–e collision. From this consideration, it is reasonable to think that the E_s band obtained from the ZnSe–ZnS SLSs is produced by the E_x–e collision. Fig. 3 shows a comparison of the shape of the Es (for $I = 0.16 I_0$) band of ZnSe(48 Å)–ZnS(15 Å) SLS measured at 77 K with the theoretical curve (broken) calculated according to the theory of Benoit a la Guillaume et al. [7] with $I = 0.16 I_0$ and the effective electron temperature $T_e =$ 110 K. The fact that the theoretical curve of the E_x–e collision is also in good agreement with the experimental result, presents further support for the above conclusion. The dependence of PL intensities J on excitation intensities I in ZnSe film and ZnSe–ZnS SLS with the different well widths has also been measured. The J–I curves have the forms of $J \sim I^n$, where $n = 1.3$–1.5 for all samples. This indicates that the origin of the E_s band in SLS is the same as that of the film. It follows that the E_s band of ZnSe–ZnS SLS originates from the E_x–e collision.

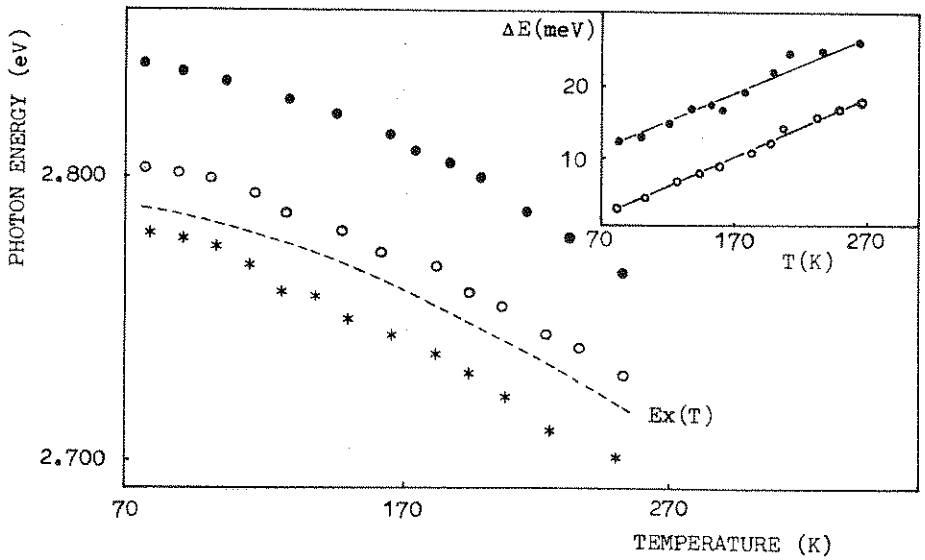

Fig. 2. Temperature dependence of photon energies of the PL emission peak for various samples: (*) ZnSe film; (○) ZnSe(87 Å)–ZnS(11 Å), and (●) ZnSe(57 Å)–ZnS(17 Å). The inset shows the variation with temperature of $\Delta E(T) = E_x'(T) - E_s(T)$.

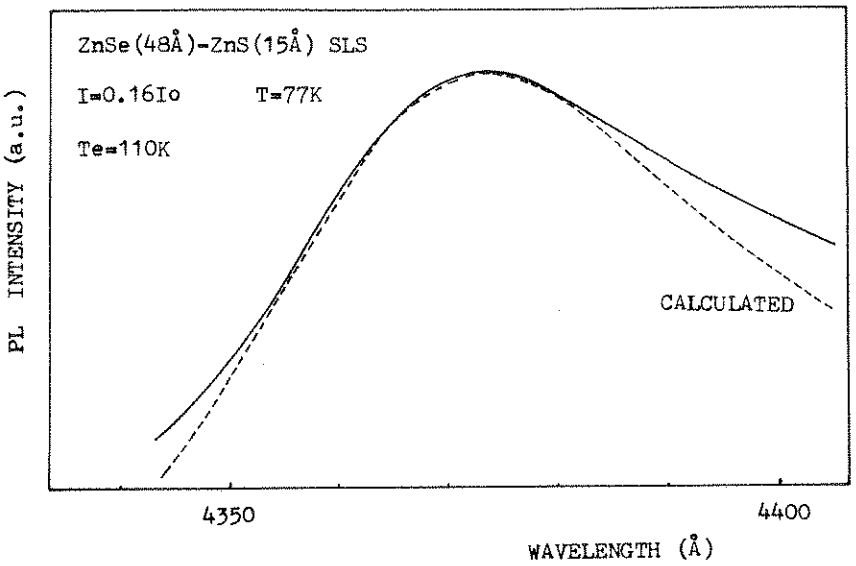

Fig. 3. Comparison of the theoretical curve (broken) with the experimental curve (solid).

3.2. *The low energy tail of the E_s band*

As can be seen in fig. 1 the low energy tail of the E_s band rapidly increases with increasing excitation intensity and its peak position in SLS shifts more rapidly than that of the band calculated according to the E_x–e scattering formula [7]. The shape of the E_s band in ZnSe–ZnS SLS was calculated according to E_x–E_x formulas [6] and the E_x–e formula [7]. The above theoretical results are in good agreement with the experimental results, as shown in fig. 4. Curve 1 is experimental, and the curves 2–5 represent the E_x–E_x interaction (i.e. the P band) of the following types: (2) (E_K^{1S}, $E_{K'}^{1S} \rightarrow h\nu$, e–h); (3) ($E_K^{1S}$, $E_{K'}^{2S,2P} \rightarrow h\nu$, e–h); (4) ($E_K^{1S}$, $E_{K'}^{1S} \rightarrow h\nu$, $E_{K''}^{1S}$); (5) (E_K^{12}, $E_{K'}^{1S} \rightarrow h\nu$, $E_{K''}^{2S,2P}$). Curve 6 represents the E_x–e interaction. The resultant spectrum due to superposition of the foregoing spectra is shown by curve 7. Considering that the concentration of electrons in the 2S and 2P states is less than that in the 1S state at 77 K in ZnSe single crystal, the P band can only be observed

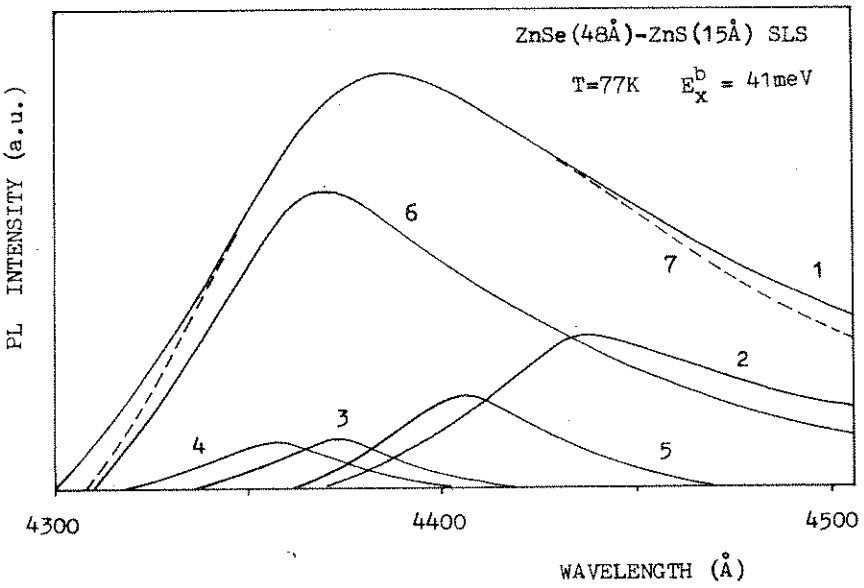

Fig. 4. Comparison of the theoretical resultant curve (7) with the experimental spectrum (curve 1). Curves (2) to (6) represent theoretical results calculated by various interactions of E_x–E_x or E_x–e (see text).

[6] under high excitation. It is well known that with decreasing well width in SLS the binding energy of the free exciton increases. This result in ZnSe–ZnS SLS will be reported in a separate paper in the near future. As an example, the binding energy of 41 meV is obtained in ZnSe (48 Å)–ZnS(15 Å) SLS. In this case, the emission related to processes (3) and (5) in fig. 4 should be taken into account. It follows that it is difficult to observe the separated P band in ZnSe–ZnS SLS.

Acknowledgement

This work was supported by the National Natural Science Foundation of China.

References

[1] H. Saito and S. Shionoya, J. Phys. Soc. Jpn. 37 (1974) 423.
[2] I.M. Catalano, A. Cingolani, M. Ferrara and M. Lugata, Solid State Commun. 43 (1982) 371.
[3] S. Colak, B.J. Fitzpatrick and R.N. Bhargava, J. Cryst. Growth 72 (1985) 504.
[4] X.W. Fan and J. Woods, IEEE Trans-ED, ED-28 (1981) 428.
[5] D.Z. Shen and X.W. Fan, Chinese J. Lumin. 9 (1988) 26.
[6] T. Muriya and T. Kushida, J. Phys. Soc. Jpn. 40 (1976) 1668.
[7] C.B. a la Guillaume, J.M. Debever and F. Salvan, Phys. Rev. 177 (1969) 567.