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Changchun Institute of Physics, Academia Sinica, Changchun¹⁾

Interaction between Excitons and Electrons in $\text{ZnSe}_{1-x}\text{S}_x$ Epilayers under High Excitation

By

Z. P. GUAN, Z. H. ZHENG, J. H. ZHANG, Y. M. LU, G. H. FAN, and X. W. FAN

Excitonic properties are investigated of $\text{ZnSe}_{1-x}\text{S}_x$ epilayer fabricated on GaAs substrate by a Ap-MOCVD. Luminescence, excitation, and time-resolved spectroscopy are employed to study the interaction between excitons and electrons at 77 and 300 K. Under pulsed N_2 laser excitation it is found that the peak shift of the near band edge emission are more large, especially at room temperature. This is due to the fact that the bottoms of the conduction bands are filled at the higher temperature, so the carriers from the exciton-exciton scattering must occupy higher energy levels. Therefore a shift of the peak towards lower energy is expected.

Es werden die Anregungseigenschaften von $\text{ZnSe}_{1-x}\text{S}_x$ -Epitaxieschichten untersucht, die mittels Ap-MOCVD auf GaAs-Substraten hergestellt werden. Lumineszenz, Anregung und zeitaufgelöste Spektroskopie werden benutzt, um die Wechselwirkung zwischen Exzitonen und Elektronen bei 77 und 300 K zu untersuchen. Unter N_2 -Impulslaseranregung wird gefunden, daß die Maximumverschiebung in der Nähe der Bandkantenemission größer ist, insbesondere bei Zimmertemperatur. Dies wird dadurch verursacht, daß die unteren Kanten der Leitungsbänder bei höherer Temperatur gefüllt sind; die Träger aus der Exziton-Exziton-Streuung müssen höhere Energieniveaus besetzen. Deshalb wird eine Verschiebung des Maximums zu niedrigen Energien erwartet.

1. Introduction

Much work has been performed on the behavior of high density carriers and excitons. It is found that when high concentrations of carriers and excitons are created, the interaction between these particles become essential. $\text{ZnSe}_{1-x}\text{S}_x$ is a ternary compound, in which the band gap energy changes continuously with the composition x . The increase in composition x causes a high emission rate of free excitons [1]. Therefore, in order to obtain blue and violet spontaneous and stimulated emission, it is important to study the free exciton emission of $\text{ZnSe}_{1-x}\text{S}_x$. In this paper we report the growth of $\text{ZnSe}_{1-x}\text{S}_x$ epilayer on GaAs substrate by MOCVD at atmospheric pressure and discuss the scattering properties between excitons and excitons (Ex-Ex) and excitons and electrons (Ex-e).

2. Experimental

The epilayer growth of $\text{ZnSe}_{1-x}\text{S}_x$ films on GaAs (100) substrate was carried out by Ap-MOCVD using dimethylzinc (DMZ), H_2Se , and H_2S as reactants. In designing the reactor we used the results of earlier studies [2 to 4]. The typical system parameters have been reported in [5]. The growth temperature was in the 300 to 450 °C range. The composition x of $\text{ZnSe}_{1-x}\text{S}_x$ epilayers was determined by double crystal X-ray diffraction measurements.

¹⁾ Changchun 130021, People's Republic of China.

Excitation spectra were recorded using a dye laser system with Coumarin 440 dyes pumped by a N_2 pulse laser. The 337.1 nm line of a Model UV-24 pulsed nitrogen laser with 10 ns duration was used as excitation source having a peak power $I_{\max} = I_0$ of 4 MW/cm^2 . The photoluminescence (PL) spectra and time-resolved spectra (TRS) under different excitation densities were detected using a SPEX 1404 double grating spectrometer with an RCA C-31034 cooled photomultiplier. TRS were measured by a Model 4400 boxcar.

3. Results and Discussion

The PL spectra at 10 K consist of three dominant peaks. The intensity as well as the peak energy of these peaks depend on temperature, excitation intensity, and composition. Typical results are shown in Fig. 1. These three peaks are located at $E_1 = 2.899 \text{ eV}$ (band A), $E_2 = 2.836 \text{ eV}$ (band B), and $E_3 = 2.789 \text{ eV}$ (band C), respectively. In this figure we also gave the PL spectra at 300 K of the same sample, it should be noticed that the band C was dissociated. Fig. 2 shows the time-resolved spectra of the sample at 77 K. At the early stage of the PL decay the peak intensity of band A is larger than that of band B. As the decay time increases the relative intensity of B becomes stronger and after 18 ns the intensities of bands A and B are almost the same. This is due to the fact that bands A and B have different decay times, as can be seen in Fig. 3. No appreciable peak shift was observed during decay for bands A and B excluding the possibility of a D-A pair process.

Hereafter, only the properties of band A will be described in detail. The details about bands B and C will be published elsewhere.

With increasing excitation the shifts of band A toward the low-energy side widens. Fig. 4 shows the excitation density (I) dependence of the PL intensity (J) and energy position of band A at 77 K. In the relation of $J \sim I^\alpha$, α is about 1.1 in the region of excitation from $0.025I_0$ ($I_0 \approx 4 \text{ MW/cm}^2$) to I_0 . Under lower excitation ($I < 0.1I_0$) the peak energy increases slowly, while for $I > 0.1I_0$ the peak shift (ΔE) is almost linear. In above excitation region from $0.025I_0$ to I_0 , the red shift of the peak amounts to $\Delta E \approx 34 \text{ meV}$. This value is larger for only one emission process. In Fig. 4, it is noticed that the energy shift ΔE is slow and α value close to unity for low excitation ($I < 0.1I_0$). This feature is similar to our early work [6] in which it was attributed to the Ex-e scattering process. As excitation increases, the peak shifts to low energy so fast that it can not be the process of Ex-e

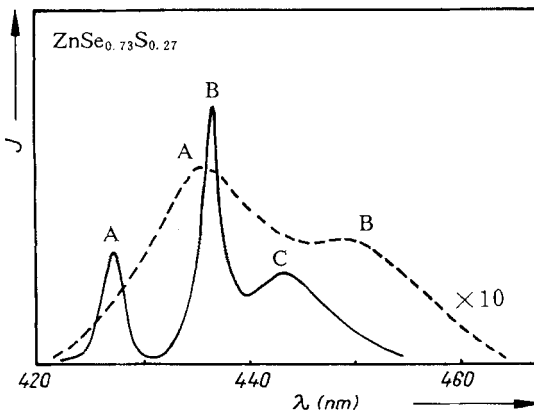


Fig. 1. PL spectra of $ZnSe_{0.73}S_{0.27}$ epilayer at 10 (solid line) and 300 K (dashed line)

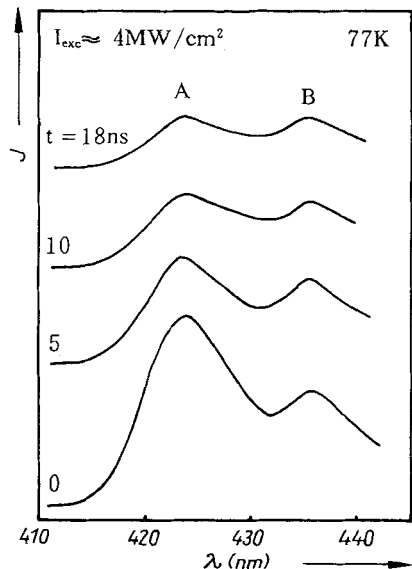


Fig. 2. Time-resolved spectra of bands A and B for ZnSe_{0.73}S_{0.27} sample at 77 K

scattering. As we know, the number of excitons increases greatly with increasing excitation and the exciton–exciton scattering process should be larger. In these cases, the dynamic equation of the above two processes can be written as

$$\frac{dn}{dt} = I - (A + A')np + K(C + C')n_x^2, \tag{1}$$

$$\frac{dn_x}{dt} = Anp - \frac{n_x}{\tau} - (B + B')nn_x - (C + C')n_x^2, \tag{2}$$

where I is the excitation electron–hole pair creation [7], Anp corresponds to the creation of excitons, $A'np$ describes the radiative or nonradiative direct recombination, B and B' are the radiative and the nonradiative terms of the (Ex–e) recombination process, C and C' are the radiative and the nonradiative terms for the Ex–Ex process, τ is the lifetime of free

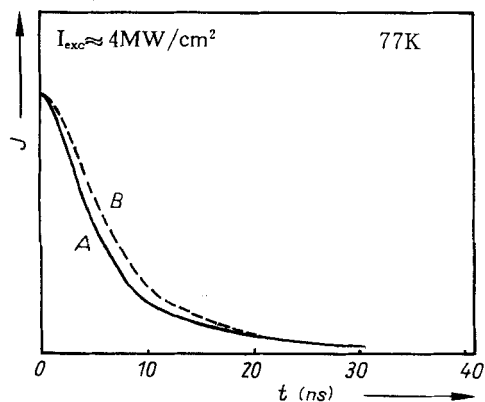


Fig. 3. PL intensity vs. time after removal of excitation

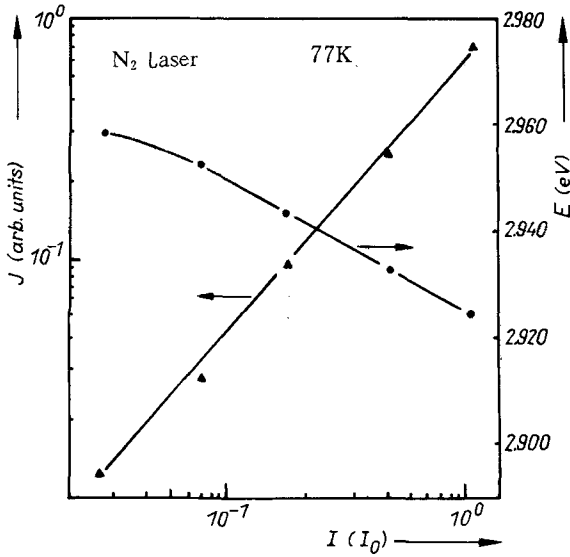


Fig. 4. Excitation dependence of the PL intensity and peak shift for $\text{ZnSe}_{1-x}\text{S}_x$ epilayer at 77 K

excitons, K a constant, and n , p , and n_x are the number of electrons, holes, and free excitons, respectively. Under dynamic equilibrium $dn/dt = dp/dt = 0$, and $n \sim p$, therefore

$$I = (A + A')n^2 - K(C + C')n_x^2, \quad (3)$$

$$An^2 = \frac{n_x}{\tau} + (B + B')nn_x + (C + C')n_x^2; \quad (4)$$

for weak excitation the $(B + B')nn_x$ and $(C + C')n_x^2$ processes are negligible, therefore,

$$J_1 \sim \frac{n_x}{\tau} \approx An^2 = \frac{A}{A + A'}I, \quad (5)$$

i.e., the number of free excitons and that of electron-hole pairs are proportional to the excitation I , respectively. So, at medium excitation the scattering processes Ex-e and Ex-Ex exist simultaneously. From (3) and (4) the Ex-e scattering intensity is as follows:

$$J_2 \sim nn_x \approx \frac{I + [(K - 1)A - A']n^2 - Kn_x/\tau}{K(B + B')} \sim I. \quad (6)$$

In this case n_x has a $I^{1/2}$ variation and the exciton number is proportional to the number of electrons.

For high excitation $(C + C')n_x^2$ is dominant, and it is clear from (3) that

$$J_3 \sim n_x^2 \approx \frac{(A + A')n^2 - I}{K(C + C')} \sim I. \quad (7)$$

In all above three cases ((5), (6), and (7)) the excitation density is proportional to the PL intensity. It is reasonable to think that the PL process in Fig. 4 should include the Ex-e and Ex-Ex scattering process.

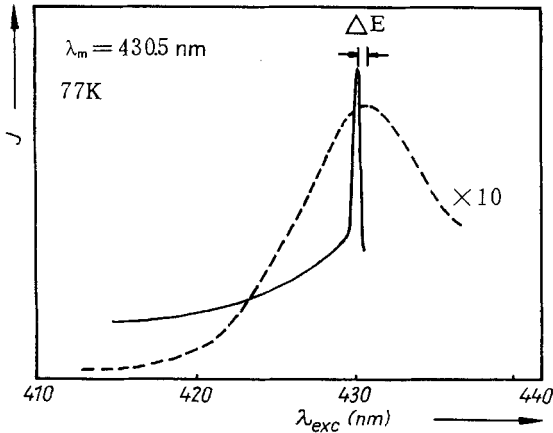


Fig. 5. Excitation spectra of band A at 77 K. λ_m represents the peak wavelength of band A at which the excitation spectrum was measured. The dashed line is the PL spectrum for the same sample

Fig. 5 shows the excitation spectrum of band A at 77 K under $I \approx 0.05I_0$ excitation. The PL spectrum (dashed line) is also shown in the same figure for comparison. The shape of the excitation spectrum was found to be asymmetrical and very narrow. The peak energy difference (ΔE) between band A and the excitation spectrum is of the order of 4 meV. It is obvious that the peak energy in the excitation spectrum corresponds to the exciton energy levels, and the band A cannot be related to the impurity. This value of ΔE is in good agreement with the calculated one using (21) for Ex-e scattering in [7]. For high excitation the scattering process between excitons and electrons is dominant. The energy balance in this process can be expressed as follows:

free exciton + free exciton ... electron-hole pair + photon ,

so

$$hv = E_g - 2E^x - E_{ch} , \quad (8)$$

where hv is the energy of the emitted photon, E_g the width of the band gap, E^x , E_{ch} are the binding energy of the free exciton and the kinetic energy of the unbound electron-hole pair created during the collision, respectively. As the electron is a Fermi particle, the kinetic energy E_{ch} will increase for a high density of free carriers created at increasing excitation because of the bottoms of the conduction bands are filled. When the Ex-Ex scattering process takes place, the unbound pairs created in the process must occupy higher energy levels. Their kinetic energy E_{ch} will enhance, therefore, a shift of the Ex-Ex line towards lower energy is expected.

Fig. 6 shows the peak position and its FWHM variation as a function of excitation for the above sample at 77 and 300 K. It is obvious that the shift of the peak energy and the FWHM for band A at 300 K are much larger than at 77 K. The results show that the processes exclusively depend on the excitation density. For the Ex-Ex scattering process the greatest distance of the red shift relative to the free exciton energy E_0 is $(E_0 - E^x)$ [8]. In Fig. 6 the energy variation ΔE is larger than $E_0 - E^x$ (for ZnSe_{0.73}S_{0.27}, $E^x \approx 25$ meV). As the temperature increases the density of hot electrons in the conduction band is very large, so the unbound e-h pair created in the Ex-Ex scattering process must occupy higher energy levels. The broadening of the high energy tail (in Fig. 1) may be considered to come from the kinetic energy of free carriers.

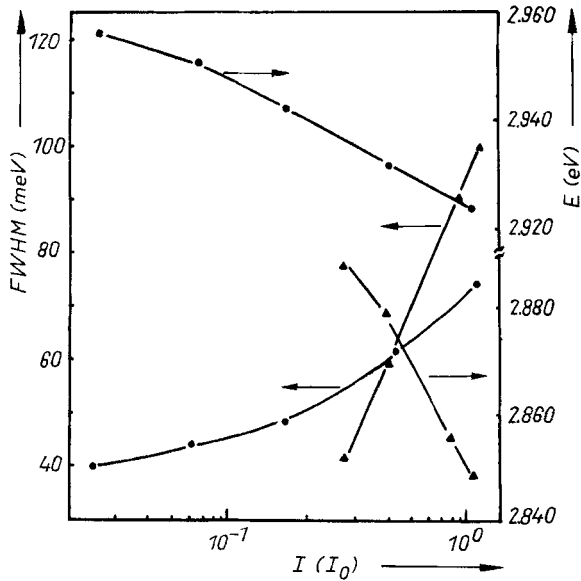


Fig. 6. Excitation dependence of the FWHM of band A and peak shift at 77 (●) and 300 K (▲)

4. Conclusion

The photoluminescence of $\text{ZnSe}_{1-x}\text{S}_x$ ($x \approx 0.27$) epitaxial layers grown on GaAs (100) has been studied at 10, 77, and 300 K. It is found that the peak energy of the near band edge emission (band A) shifts to the high-energy side with lowering the temperature. A noticeable narrowing with decreasing temperature and excitation intensity was observed. Its peak energy and intensity were closely dependent on the excitation density. Analysing the FWHM and the lineshape of the high-energy tail, this near band edge emission was attributed to the process of free exciton-free electron (Ex-e) scattering for low excitation and free exciton-free exciton (Ex-Ex) scattering for high excitation, respectively.

Acknowledgement

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