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# OPTICAL GAIN IN ZnS EPILAYERS

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The variable stripe length method is used to study optical gain in MOVPE-grown ZnS/GaAs epitaxial layers. Optical gain and spontaneous emission spectra are extracted from experimental results. A net optical gain of about 30 $cm^{-1}$ under excitation by a XeCl laser having a power density of 100 $kWcm^{-2}$ is observed at very low temperatures ($T < 20$ *K*) and it is rapidly quenched for higher temperatures. Gain is interpreted to be due to stimulated emission from the bound exciton state and from the biexciton ground state towards free exciton levels. The spectral shape of the gain spectrum is well fitted by the sum of these two contributions. Smaller gain at lower photon energies is obtained due to exciton-exciton collisions.

Keywords: A. semiconductors, B. epitaxy, D. excitons, E. nonlinear optics

## INTRODUCTION

These last years, zinc selenide has been thoroughly studied since it is considered as the most promising compound among II-VI semiconductors with large bandgap to obtain short wavelength light-emitting devices or lasers. Indeed, ZnSe light-emitting photodiodes first and then laser diodes have been developed (see references [1,2,3] reviewing this subject). On the contrary, little attention has been paid to another II-VI semiconductor, zinc sulphide (ZnS), which could have similar potentialities and has even a larger bandgap (3.8 *eV* compared to 2.7 *eV* for ZnSe at room temperature). Therefore, we have started (at the University of Montpellier) to prepare epitaxial layers of ZnS by Metal-Organic Vapour-Phase Epitaxy (MOVPE) on GaAs substrates [4,5]. The characteristics of ZnS electronic elementary excitations (free carriers and excitons) have been determined by transmission, reflection and photoluminescence spectroscopy (at the IPCMS-GONLO Strasbourg) [6]. We have also shown by studying the photoluminescence of ZnS under high excitation conditions that excitonic molecules or biexcitons are stable quasi-particles in that compound at low temperatures.

In this paper, we continue to study ZnS. We present results concerning the optical gain near the absorption edge of ZnS at different temperatures. The gain is measured by the well-known Variable Stripe Length

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(VSL) method [7], using the UV light of a XeCl excimer laser to excite the samples. The first section of this paper is devoted to the elaboration of zinc sulphide samples and to a summary of exciton and biexciton properties in this compound. In the second section, we recall the VSL method for gain measurements and its interest compared to other methods. In the third section, we present our experimental results and discuss them before giving conclusive remarks.

## ELABORATION OF ZnS SAMPLES AND THEIR SPECTROSCOPIC CHARACTERISATION

The ZnS layers studied in this work have been grown on crystalline GaAs (100) substrates by MOVPE at temperatures between 300 and 350 °C, using a «ASM France OMR 12» horizontal reactor. The precursors used were $H_2S$, 25% in $H_2$ and triethylamine dimethyl zinc adduct supplied by Epichem Ltd. ZnS epitaxial layers of a thickness between 1 and 2 $\mu m$ and a cubic structure ($T_d$ symmetry) have been obtained on GaAs substrates. More details about the sample preparation are given in [4].

The large lattice mismatch of 4.5% between ZnS layers and their GaAs substrates produces a biaxial compressive strain at the early elastic stage of growth. This strain relaxes rapidly through dislocations at a critical thickness of 10 *nm*. In the cooling stage after the growth of the epitaxial layers, an additional compressive strain is also induced by the difference of thermal expansion of ZnS and GaAs. This biaxial strain splits at the centre of the Brillouin zone the $\Gamma_8$ valence band into a heavy and a light hole subbands. This splitting ($\Delta_{hl} = 4meV$) as well as the transitions involving the exciton ground state and its excited states have been better seen in photoluminescence excitation spectra than in ordinary photoluminescence or in transmission spectra [6]. Furthermore, from the analysis of photoluminescence and photoluminescence excitation spectra, we could conclude on the existence of biexcitons in this compound and evaluate its binding energy to be of nearly 12 *meV* [6].

## EXPERIMENTAL SET-UP

To study the gain of the ZnS epilayers, we have used the VSL method [7]: the gain is determined from the dependence of the amplified photoluminescence intensity on the length of an excited stripe on the surface of the samples. The principle of the measurement is sketched in the inset of Fig.1.

The samples studied are excited in their band-to-band absorption (Eg ~3.84 *eV* for ZnS at low temperatures) by ultraviolet (308 *nm*, 4.02 *eV*) light pulses of 18 *ns* duration (FWHM) emitted by a XeCl excimer laser (EMG 101 from Lambda Physik), at a repetition rate of 10 *Hz*. The laser beam is first focused by a cylindrical lens to form a rectangular light spot on a slit with a fixed and a moving jaw. A reduced image of the slit is then projected by a spherical lens onto the surface of the sample. The fixed jaw is adjusted to coincide with the edge of the sample. Its moving jaw allows us to control the length l of the stripe of UV light which is incident on the surface of the sample. The dimensions of the stripe were typically 50 $\mu m$ for its width and between 10 and 1200 $\mu m$ for its length. We limit the power density of the UV excitation to a few $MW/cm^2$, which is the damage threshold of the samples studied.

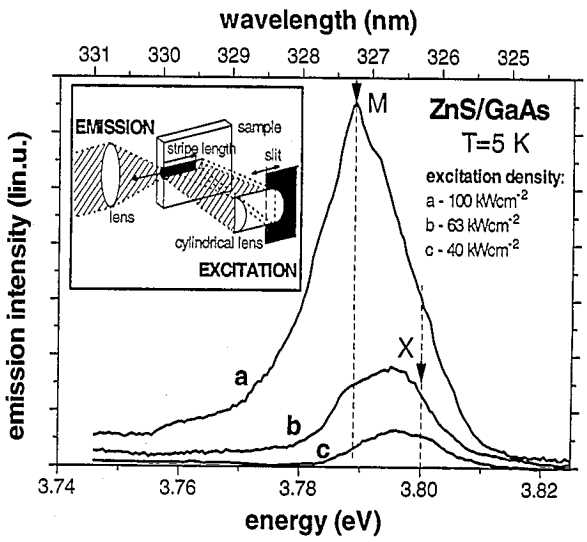


**Fig.1** Emission spectra at 5 *K* for fixed excited stripe length of 1.2 mm and for three different power densities: a - 100 $kWcm^{-2}$, b - 63 $kWcm^{-2}$ and c - 40 $kWcm^{-2}$. The inset shows the principle of the VSL method. Positions of the free-exciton (X) and the biexciton (M) emission are indicated.

The samples were mounted inside a continuous flow cryostat CF 1204 of Oxford Instruments which allows for spectroscopic measurements from 4 to 300 *K*. For lower temperatures (2 *K*), the samples were cooled in superfluid helium in a helium-bath cryostat made of quartz glass.

The light emitted on the direction of the excitation stripe from the edge of the sample is focused onto the entrance slit of a ¾ *m* Spex monochromator. Its intensity is detected as a function of the photon energy by an UVP photomultiplier of RTC-Philips. The signal of the photomultiplier is time integrated through a boxcar.

At low excitation intensities, we detect the intensity of the luminescence spontaneously emitted in the direction x of the excitation stripe. Let us call $I_{sp}(\lambda)$ this luminescence intensity, emitted per unit volume of the excited region of the sample, at the wavelength $\lambda$. When the excitation is intense enough to create a gain g (includes both absorption and emission) at the wavelength $\lambda$, which overcomes the losses K due to sample imperfections, the light which propagates along the stripe is amplified. The effective gain $G=(g(\lambda)-K)$ can be defined as the relative change per unit length of the light intensity I(x) travelling in the direction x of the exciting stripe :

$$G = g(\lambda)-K = [dI(x,\lambda) / dx] / I(x,\lambda)) \qquad (1)$$

The total increase of the light intensity in a region dx of the exciting stripe is given by the sum of spontaneous emission from this region and the amplification of the light intensity travelling through this region:

$$d\, I_T(x,\lambda) = [g(\lambda) - K\,]\, I(x,\lambda)\, dx + I_{sp}(\lambda)\, dx \qquad (2)$$

If $g(\lambda)$ and $I_{sp}$ $(\lambda)$ are independent of x, i.e. if no saturation is taking place, the total light intensity $I_T(\ell,\lambda)$ measured at the end of the stripe of length $\ell$ is the following [8] :

$$I_T(\ell,\lambda) = I_{sp}(\lambda)\, \{\, \exp[(g(\lambda)-K)\ell] - 1\} \,/\, (g(\lambda)-K) \qquad (3)$$

From the measurement of $I_T(\ell,\lambda)$ as a function of $\ell$, we can determine the spontaneous emission $I_{sp}$ $(\lambda)$ as well as the effective gain coefficient $G = g(\lambda)-K$ . The value of K can be obtained separately at long wavelengths where the gain $g(\lambda)$ tends to zero.

Equation (3) is only valid if there is no feedback from the surface opposite to the observed one, i. e. if no amplified light is reflected or scattered back by the opposite surface into the excited region of the sample. Therefore, we must choose samples with non-parallel surfaces. We must also excite the samples along a stripe of very short transverse width and of a length smaller than the length of the sample. We are in good experimental conditions when no appreciable light is emitted from the opposite surface.

The VSL method is equivalent to the pump and probe experiment [9], the spontaneous emission playing then the role of the probe. It allows to test large optical paths and therefore to detect weak gain and small absorption changes. However, the measurements are only possible in the spectral region where some spontaneous emission is present [8].

## EXPERIMENTAL RESULTS

We detect the luminescence emitted from the edge of epitaxial layers of ZnS cooled down to low temperatures. The emission intensity is drawn in Fig.1 as a function of the photon energy for a given stripe length of

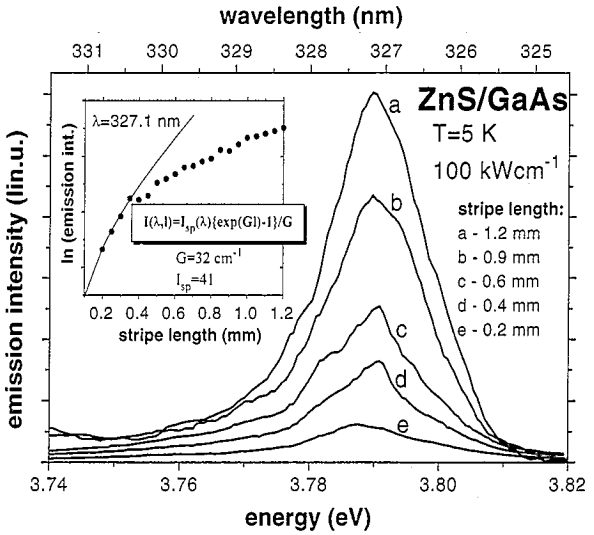


**Fig.2** Emission spectra at 5 *K* detected for the excited stripe lengths between 0.2 and 1.2 *mm* (power density 100 $kWcm^{-2}$). The increase of emission intensity at 327.1 *nm* with expanding stripe length is shown in the inset (full circles). The solid line is calculated according to Eq.3.

1200 $\mu m$ but for different power densities of the UV light, at 5 *K*. We observe, at lower power densities (Fig.1 curves b and c), a broad luminescence band at spectral positions close to the exciton resonance (3.800 *eV*). At the highest power density (Fig.1 curve a), an intense band appears on the low energy side of the preceding band (3.788 *eV*), in a spectral region corresponding to biexciton-exciton transitions. In Fig.2 , we have drawn the spectra obtained for a given power density of 100 $kW/cm^2$ and different stripe lengths (between 200 and 1200 $\mu m$), at the same temperature. We observe an increase of the low energy emission band with stripe length. It is important to notice that this band remains at nearly the same spectral position independently of the stripe length.

We have plotted, in a semilogarithmic scale, the intensity of the luminescence at different wavelengths as a function of the stripe length. The inset in Fig.2 represents for instance the experimental points deduced from the spectra (a,...,e) drawn in Fig.2 . We have then fitted these experimental points by a curve representing the variation of the amplified spontaneous emission as a function of the stripe length as given by equation (3). An exponential increase of the luminescence intensity followed by a saturation (for l>0.4 *mm*) is observed. We could determine by these fittings the values of the spontaneous emission intensity and of the effective gain for the different wavelengths. They are represented in Fig. 3 a and b, respectively. One can see that the main features of these spontaneous and stimulated emission spectra are observed in the spectral region of the exciton-biexciton transitions.

When exciton-biexciton transitions are involved, two reverse processes are taking place : the radiative recombination of the biexciton (energy $E_B$ (**K**) and wave vector **K**) which emits a photon (energy hν and wave vector **q**) and generates simultaneously an exciton (energy $E_X$ (**k**) and wave vector **k**); the formation of a biexciton by the simultaneous annihilation of an exciton and a photon.

$$\text{biexciton} \longleftrightarrow \text{exciton} + \text{photon}$$

Energy and momentum have to be conserved during the two reverse processes

$$E_B(\mathbf{K}) \longleftrightarrow E_X(\mathbf{k}) + h\nu \qquad (5a)$$

$$\mathbf{K} \longleftrightarrow \mathbf{k} + \mathbf{q} \quad (\sim \mathbf{k}) \qquad (5b)$$

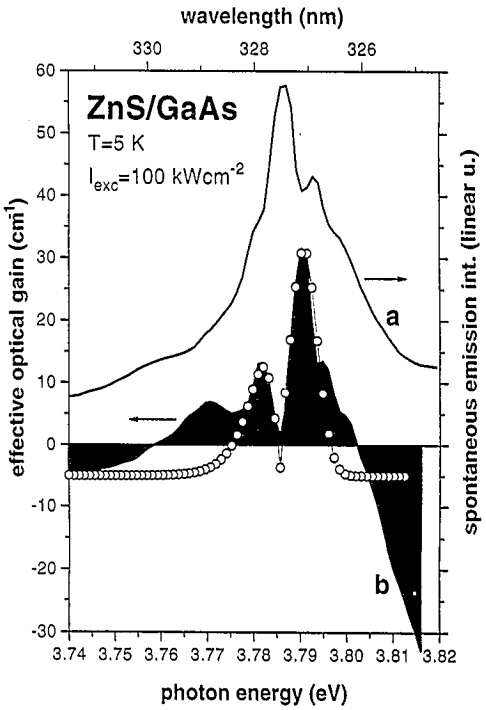


**Fig.3** Spontaneous emission (a) and net optical gain (b) spectra extracted from experiments employing Eq.3. The gain spectrum is modelled as a sum of bound exciton and biexciton recombination (open circles), for details see text.

Emission and absorption are both taking place. The resulting spectral profile has been calculated neglecting polariton effects [10,11]. It presents the following form :

$$g(E) = C N_B \beta^{3/2} [1 - \eta \exp.(-\beta E)] E^{1/2} \exp.(-\beta E) \qquad (6)$$

The different letters and expressions are defined as follows :

$$E = E_B - E_X - h\nu \qquad (7)$$

$E_B$ , $E_X$ being the biexciton and the exciton ground state energies at the centre of the Brillouin zone.

$$\beta = 1 / k_B T_X \qquad (8)$$

$T_X$ being the effective temperature of the exciton and the biexciton populations.

$$\eta = 2^{3/2} N_X / N_B \qquad (9)$$

$N_X$ and $N_B$ being the density of excitons and of biexcitons, respectively.

The experimental gain spectrum is drawn in Fig. 3b in continuous line. It presents a profile with an intense double-structured band. We interpret this structure in

accord with our previous paper [6] as follows: The highest maximum of gain (3.791 *eV*) coincides with the $I_2$ (exciton bound to neutral donor) line which is inhomogeneously broadened in our epilayers and can be fitted with a gaussian line-shape:

$$g(E) = g_{max} \exp(-0.5[(E-E_{max})/w]^2) \qquad (10)$$

where the parameters of the fit are: the gain maximum $g_{max}$=36.5 $cm^{-1}$, the position of maximum $E_{max}$=3.7909 *eV* and the line width w=0.0029. The second maximum at 3.782 *eV* is considered to be due to biexciton recombination and induced absorption and is fitted by equation (6). We have obtained the following values for the parameters :

$(E_B - E_X)_1$ = 3.786 *eV* (if the exciton energy is 3.798 *eV* [6], the biexciton binding energy will be 12 *meV*)

$N_X / N_B$ =0.48 and

$T_X$=36 *K* for the exciton and biexciton temperature.

The photogenerated carriers are supposed to relax very rapidly through LO phonon scattering into exciton and biexciton ground states. They are then thermally distributed on their dispersion curve with a temperature $T_X$. As observed here a unique temperature may characterize the two populations of excitons and biexcitons, since they are strongly mixed through the absorption and emission processes introduced above. Furthermore, this temperature is higher than that of lattice since the cooling down of elementary-excitons which involves acoustical phonons is rather slow.

K = 5 $cm^{-1}$ for the losses due to sample imperfections

The value of K is obtained at high wavelengths. It corresponds to diffusion losses of the transmitted light on the surface rugorosity of the sample.

G =32 $cm^{-1}$ for the maximum value of the effective optical gain

The gain at its peak value is quite large. At higher excitation intensities, its saturation appears at lower wavelengths, corresponding to an exciton to biexciton absorption which becomes more efficient than the biexciton to exciton stimulated emission. We can also notice that no drastic red shift of the gain bands is observed This agrees quite well with bound exciton and biexciton processes and excludes the creation of a plasma under the present conditions of excitation.

We made similar gain studies at higher temperatures. We observed the same process involving biexcitons up to 80 *K*. In Fig.4, the maximum of gain is plotted versus inverse temperature 1/T (full circles). We can fit the experimental points by the simple function

$$G= G_0 / [1+ c \exp(-E_a / k_B T)] \qquad (11)$$

representing thermally activated quenching of emission. The parameters of the fit (solid line in Fig.4) are $G_0$=31 $cm^{-1}$, c=36 and $E_a$=7.8 *meV*. The activation energy $E_a$ is in a good agreement with a exciton localization energy of about 7 *meV* (taking 3.798 *eV* as the free exciton ground state).

Finally, another gain structure is observed at lower photon energies; indeed if we subtract from the total gain the biexciton one, another broad band is obtained with a maximum at 3.77 *eV* and a wide spectral extension to lower photon energies.It can be explained by the following well-known exciton-exciton collision process [12] ($P_n$ lines):

exciton - exciton ⟶ photon + exciton, n = 2,3,.....∞

The binding energy of the exciton being of 40 *meV*, such a band should be observed from 3.77 (n = 2) to 3.76

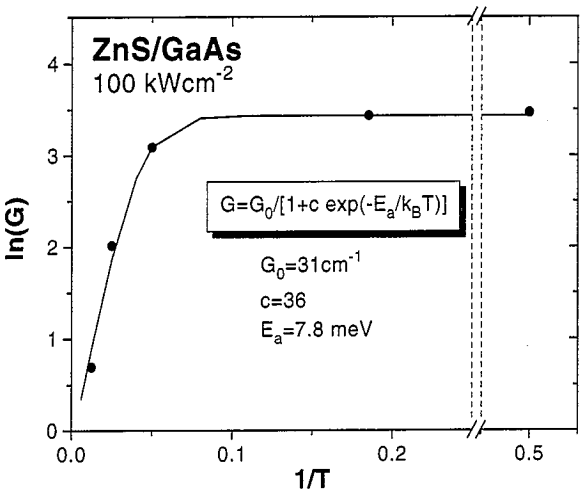


**Fig.4** Semilogarithmic plot of the maximum of optical gain versus inverse temperature 1/T (full circles). The solid line is a fit by a simple thermal quenching function (Eq.10), parameters corresponding to the fit are indicated.

$eV$ (n = ∞ ). This spectral extension fits well with the observed gain structure.

## CONCLUSIONS

We observed the effective gain of about 30 $cm^{-1}$ in MOVPE-grown ZnS epitaxial layers for moderate (band-to-band) excitation density of 100 $kWcm^{-2}$ at low temperatures T < 20 $K$. The spectral shape of gain as well as its rapid thermal quenching can be explained as bound exciton and biexciton recombination. These results confirm our previous measurements of non-linear photoluminescence and photoluminescence excitation spectra showing the stability of biexcitons in thin ZnS epitaxial layers at low temperatures. Excitation spectroscopy of gain would be useful for understanding of different biexciton-exciton processes in ZnS epilayers.

The value of optical gain deduced from our experiments is relatively high. As the biexciton binding energy is known to increase strongly with confinement in low-dimensional structures (for example in ZnSe-based quantum wells [13,14]), it will be interesting to study exciton-biexciton phenomena in quantum wells of ZnS (We suggest $Zn_XMg_{1-X}S$ or MgS as barrier layers - these materials should have its lattice constant better matched to the GaAs substrate than ZnS and the energy band gap is higher than ZnS ($E_g$(MgS)=4.4 eV at RT [2,15])

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