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EXCITONS AND BIEXCITONS IN MOVPE-GROWN ZnS EPITAXIAL LAYERS

D. Guennani, J. Valenta*, A. Manar** and J.B. Grun

Institut de Physique et Chimie des Matériaux de Strasbourg (UM 380046, CNRS-ULP-EHICS) Groupe d'Optique Nonlinéaire et d'Optoélectronique
23, rue du Loess, 67037 Strasbourg Cédex 02, France

* on leave from Charles University, Faculty of Mathematics and Physics, Department of Chemical Physics, Prague, Czech Republic

** on leave from Ibnou Zohr University, Faculty of Science, Department of Physics, Agadir, Morocco

T. Cloitre, O. Briot and R.L. Aulombard

Groupe d'Etude des Semiconducteurs (URA 357) - Université de Montpellier II
34095 Montpellier Cédex 05, France

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High quality MOVPE-grown ZnS/GaAs epilayers are characterized by reflection, transmission and linear photoluminescence (PL) spectroscopy at 2 K. The GaAs substrate of a part of each ZnS layer is removed and the optical properties of as-grown and etched surfaces are compared. The splitting (caused by the thermally induced strain) of the topmost Γ_8 valence band into the heavy and light-hole subbands (Δ_{hl}=4 *meV*) and the transitions involving exciton ground and excited states are better seen in PL excitation spectra than in ordinary PL spectra. From the analysis of the nonlinear PL and PL excitation spectra, we can conclude the existence of biexcitons with a binding energy of about 10 to 12 *meV* under an intermediate intensity of excitation (a density of about 2.5×10^{16} to 2.5×10^{17} e-h excited pairs per cm^3).

Keywords: A. semiconductors, B. epitaxy, D. optical properties, E. luminescence, E. nonlinear optics

INTRODUCTION

II-VI direct band-gap semiconductors have attracted an increasing attention these last years. Indeed, they are interesting as potential materials for optoelectronic devices (e.g. light-emitting diodes (LED) and semiconductor injection lasers) working in the blue-green spectral region. During the years, the interest remarkably shifted to larger gap materials, from CdTe to CdSe, CdS and ZnSe. Continuing this tendency, zinc sulphide (ZnS), with the largest band-gap (3.7 *eV* at room temperature (RT)) of all II-VI compounds, is now also starting to be studied. The optical properties of pure cubic-ZnS have been barely investigated [1-3] in contrast to doped-ZnS, which has for

a long time been used for electroluminescent devices. One reason is the difficulty to excite and to detect UV optical signals near 4 *eV*. Another reason is the difficulty of growing single-crystals of cubic-ZnS, since ZnS is naturally a polytypic material with cubic (sfalerit) and hexagonal (wurtzite) phases.

The aim of this work is to investigate in details the basic optical properties of high quality thin layers of ZnS in the near-band-gap region, especially excitonic phenomena, by means of photoluminescence (PL) excitation spectroscopy.

SAMPLES

The ZnS layers have been grown on GaAs (100) substrates by Metal Organic Vapour-Phase Epitaxy (MOVPE) at temperature of 300°C and 350 °C using an ASM France OMR 12 horizontal reactor. The precursors used were H_2S, 25% in H_2 and triethylamine dimethylzinc adduct supplied by Epichem Ltd.. The layers of a thickness of about 1 μm have a cubic structure (T_d -symmetry). The details concerning the growth have been published elsewhere [4]. The free surface of each sample has been glued on a quartz plate and the substrate has then been first mechanically polished and finally removed by a chemical etching technique as described in [5].

Let us mention here the effect of the GaAs substrate on the growth of ZnS epitaxial layers. The large lattice mismatch (about 4.5%) between ZnS and GaAs produces a biaxial compressive strain at the early (elastic) stage of growth. This strain is afterwards relaxed through (plastic) dislocations. The critical thickness at which the layer is completely relaxed is smaller than 10 *nm* [3]. Furthermore, during the decrease of temperature of the ZnS/GaAs epitaxial layer after its growth, an additional compressive strain is introduced through the difference of the thermal expansion coefficients of ZnS and GaAs ($6.7 \times 10^{-6}\ K^{-1}$ and $5.7 \times 10^{-6}\ K^{-1}$, respectively [6]). This biaxial strain diminishes the T_d -symmetry of ZnS and, at the center of the Brillouin zone, splits the Γ_8 valence band into heavy-hole (hh) and light-hole (lh) subbands.

EXPERIMENTAL DETAILS

The experimental methods used in this study include linear transmission and reflection, photoluminescence (PL) and PL-excitation spectroscopy. All the experiments were done at low temperatures, the samples beeing directly immersed in superfluid liquid helium (T≈2 *K*) in a quartz cryostat. Transmission and reflection spectra have been measured using the white emission radiation of a Xe-lamp. The linear photoluminescence was excited by the 100 W high-pressure mercury lamp (HBO 100) filtered by an 243 nm interference filter. The nonlinear PL was excited either directly by band to band transitions by means of XeCl-excimer laser (Lambda Physik EMG 101) delivering

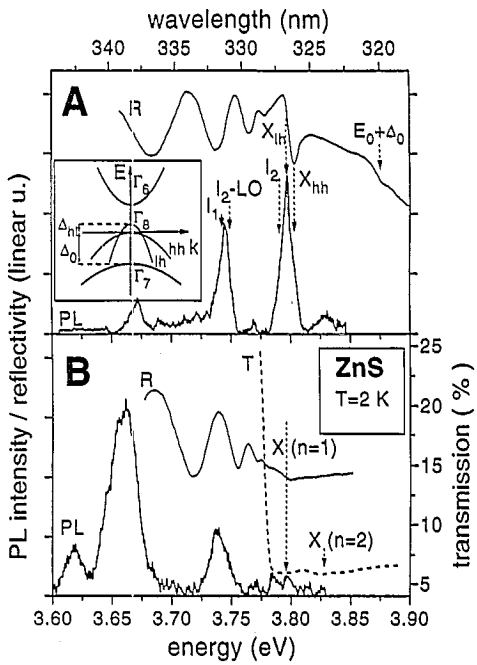

Fig.1 Linear optical characterization of a ZnS/GaAs epilayer at T=2 K: Hg-lamp excited luminescence spectra (area graph), reflection (solid line) and transmission (dashed line) spectra for an as-grown suface (A) and an etched surface (B). The inset shows the schematic band structure of ZnS/GaAs epilayer. For the different labels see text.

pulses of 20 *ns* duration (FWHM), at the wavelength of 308.5 *nm* (4.019 *eV*) or by using a KDP frequency-doubled light of a dye-laser working with a solution of DCM in methanol. This laser had a grating working at grazing incidence and was pumped transversally by an excimer laser [7]. Its emission could be turned from 612 (2.03 *eV*) to 680 *nm* (1.82 *eV*). The spectral width of the dye-laser emission is better than 0.2 meV (FWHM). Before having its frequency doubled, the red laser radiation was two times amplified into two dye cells filled by the same dye excited by parts of the XeCl-excimer laser radiation. Excitation intensities as high as several megawatts per cm^2 (it is the damage limit of the thin ZnS layer studied) could be reached when we focused, onto the sample surface, pulses of typical 1.5 μJ energy and 2 *ns* duration. Excitation wavelengths cover the whole near-band-gap region of ZnS from 306 (4.05 *eV*) to 340 *nm* (3.65 *eV*). The photoluminescence was detected in a backward configuration at an angle of about 45° from the excitation beam. This PL was dispersed in a single grating 3/4 *m* monochromator (Spex), detected by a S-20 photocathode photomultiplier tube and processed by a box-car integrator connected to a computer.

RESULTS

1. Linear Optical Characterization

We present first (Fig.1) the linear spectra of reflection and photoluminescence of the as-grown surface of a ZnS sample (A) and of the surface left once the GaAs substrate has been etched away (B). The reflection spectra show interference fringes in the region of low absorption ($\leq$ 3.78 *eV*). In addition, two typical reflection features corresponding to the two excitonic resonances are observed on the as-grown surface (A). The stronger one is centered at 3.800 *eV* and can be attributed to the ground state of the free-exciton (FX) made of a Γ_6 conduction band and the Γ_8 (lh) valence band. The second one at 3.872 *eV* corresponds to the Γ_6-Γ_7 exciton resonance with a spin-orbit splitting Δ_0 =72 *meV* [3]. Surface (B), in contrast with the preceding one, does not show such excitonic structures. This is probably a consequence of the bad crystalline structure (high density of strain-relaxing dislocations and impurities (such as GaAs diffusion)) in this near-substrate surface of the layer. For the same reason the transmission spectrum (the dashed curve in Fig.1 B) show only a wide and weak free-exciton absorption.

The linear photoluminescence spectra were excited by the 243 *nm* (5.1 *eV*) line of the mercury lamp, which is highly absorbed in ZnS. Therefore, the superficial part of the ZnS layer contributes predominantly to the PL spectra. In the case of the as-grown surface, the PL spectra consist of two structured bands. The high-energetic one can be interpreted as the contribution of three radiative recombinations of the heavy-hole exciton (X_{hh}) at 3.802 *eV*, the light-hole exciton (X_{lh}) at 3.798 *eV* and the exciton bound to a neutral donor (I_2) at 3.792 *eV* [1]. The band between 3.73 *eV* and 3.76 *eV* is probably composed of the I_2-LO phonon replica (the LO-phonon energy in ZnS is 43 *meV* [6]) and of I_1 peaks corresponding to radiative recombinations of neutral-acceptor bound excitons (BX) [8]. The PL spectra of the near substrate surface of the samples have almost no free-exciton emission structure at these low excitation intensities but new emission bands appear deeper in the energy gap (at 3.62 *eV* and 3.66 *eV*). They could be attributed to intrinsic defects of the crystal.

2. Nonlinear Photoluminescence

Fig.2 represents the variation of the ZnS emission spectra with the excitation intensity of the excimer laser which increases from 2 kW/cm^2 to 1 MW/cm^2. First, one observes a saturation of the BX-peak centered at 331 *nm* and a broadening of the high-energy peak. Under intermediate excitation intensities (from 30 to 300 kW/cm^2), a rapidly expanding peak appears at 3.788 *eV* (327.3 *nm*) (labeled M-band) which we will discuss later on. Above an excitation intensity of about 300 kW/cm^2, one observes a red-shift of the M-band due to a renormalisation of the gap and an extension of the low-energy tail of emission spectra.

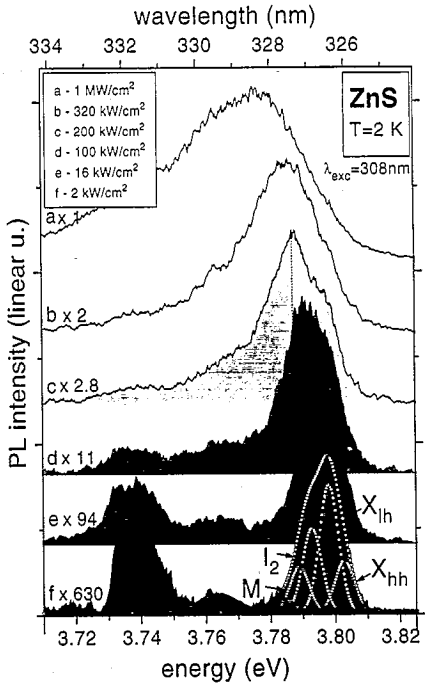

Fig.2 (XeCl) excimer laser excited PL spectra at T=2 K. The excitation intensity increases from 2 *kW/cm²* (bottom) to 2 *MW/cm²* (top). The deconvolution of the spectrum (a) into the six gaussian bands is represented by open circles. For details see text.

If we assume a homogeneous excitation of the sample in a spot of 250 μm radius, an exciton binding energy of $E_B^{ex} \cong 40$ *meV* and an exciton lifetime of $\tau \cong 1$ *ns* (a typical value for large direct band-gap semiconductors [9]), we can approximatively estimate that the carrier density ($n \cong I_{exc}.\tau / h\nu_{exc}.d$, [9]) is of 2.4×10^{18} cm^{-3} at the highest intensity of excitation (I_{exc} = 1 *MW/cm²*) and therefore that the density should be 4.8×10^{15} cm^{-3} for 2 *kW/cm²*. This value corresponds to the excitation intensity at which high-excitation phenomena generally start to appear in this material [9]. According to [10], the Mott density for ZnS can be estimated (taking $E_B^{ex} \cong 40$ *meV*)

$$n_{Mott}(cm^{-3}) \cong 9.4\times10^{16}(\sqrt{(1+9.8\times10^{-5}.T_e^2)}+1)$$

The value of n_{Mott} is (only slightly temperature dependent): 1.9×10^{17} cm^{-3} for an effective carrier temperature of $T_e \approx 2$ *K* and 2.0×10^{17} cm^{-3} for $T_e \approx 50$ *K*. So, one can assume that up to an excitation of about 100 *kW/cm²* , the exciton gas does not reach the Mott density.

In order to analyse the evolution of the spectra with increasing excitation intensity, a deconvolution of the experimental spectra has first been done. We assume that a Gaussian line (inhomogeneous broadening) at a fixed spectral position and constant width but a variable amplitude may be introduced for the six emission peaks: the free-exciton one at 3.802 *eV* and 3.798 *eV* (hh-exciton and lh-exciton, respectively), the I_2 peak at 3.792 *eV*, two M-peaks at 3.789 *eV* and a 3.782 *eV* peak (see Discussion). The positions of the X_{hh}, X_{lh} and I_2 peaks were determined from linear PL spectrum (Fig.1A). The last peak at 3.765 *eV* had to be introduced to take into account the increasing low-energy tail of the emission band. The best fit is represented in Fig.2 by open circles for the different Gaussian bands, and by open squares for the sum. The variation of the integrated intensities of the

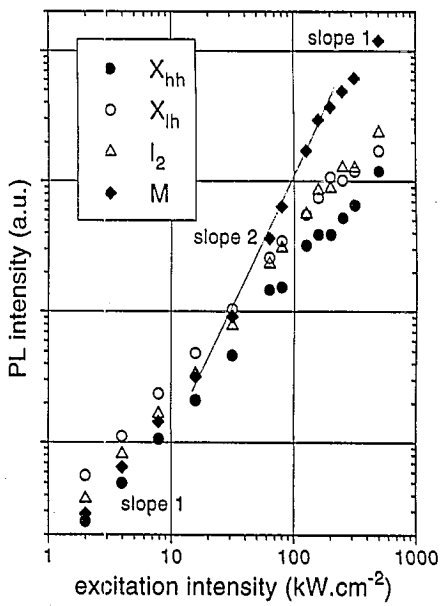

Fig.3 Excitation intensity dependence of the integrated intensity of the different emission bands (in a log-log plot). The quadratic and the linear slopes are represented by a solid line and a dotted one, respectively.

different emission bands with the increasing excitation intensity is then plotted in Fig.3. One can see that they increase approximatively linearly with the excitation intensity except the M-band, which increases superlinearly (with a slope between 1 and 2). Between 16 kW/cm^2 and 160 kW/cm^2, the M-band shows a clear quadratic increase while the X and I_2 bands increase slightly nonlinearly (slope about 1.3).

3. PL Excitation Spectroscopy

The PL excitation spectra have been derived from the measurement of the whole PL spectra under the excitation of the frequency-doubled dye laser emission described above. A constant excitation intensity of 50 kW/cm^2 was taken (i.e. it is an intermediate excitation intensity at which the M-band is already more intense than the other emission lines). The excitation photon energy was tuned in the range of 3.787 eV to 3.901eV by steps of about 3 meV. Every luminescence spectrum measured was deconvoluted as described in the previous paragraph. The PL excitation spectrum was thus obtained for each emission band and drawn in Fig.4. Above the band-gap energy, three maxima could be distinguished: from their spectral positions, one can assume that they correspond to the creation of one FX and one LO phonon, one FX and 2LO as well as to the Γ_6 -Γ_7 transition (if we compare with the E_0 +Δ_0 transition in the reflection spectra, as can be seen in Fig.1 A). Below the band gap energy, resonances corresponding to the FX ground state (n=1) and to the n=2 excited states are observed. The M-band shows an additional maximum at 3.792 eV. A detailed discussion of these results will be the subject of the next paragraph. The band-gap energy 3.84 eV and the corresponding band to band absorption is given in the lower part of the Fig.4 for comparison.

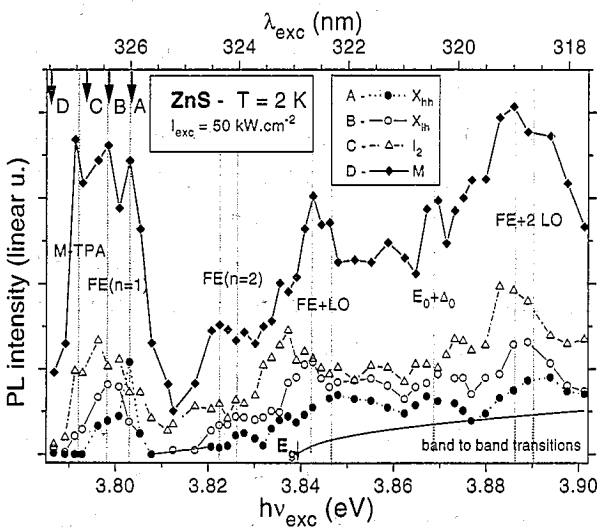

Fig.4 PL excitation spectra of the X_{hh}, X_{lh}, I_2 and M bands. The spectral positions of these bands are indicated by arrows. The free-exciton (FX) ground (n=1) and excited (n=2) state resonances, the phonon assisted transitions (FX+LO, FX+2 LO) and the two-photon absorption to the biexciton ground state (M-TPA) are shown. The gray area represents the rise of the band-to-band (parabolic bands) transitions.

DISCUSSION

If the samples are not yet good enough for directly observing by transmission the whole exciton spectrum, by PL excitation spectroscopy one can clearly see the n=1 and n=2 exciton states as well as some LO phonon-assisted transitions. Furthermore, the thermally induced strain in ZnS/GaAs samples induces a splitting of about 4 meV between the hh and lh valence subbands. This splitting is observed in the PL spectra (Fig.1A) in the doublet structure of the free-exciton emission line (X) but even more clearly in the PL excitation spectra in the shift of 4 meV between all maxima corresponding to X_{hh} (Fig.4, spectrum A) and the X_{lh} (Fig.4, spectrum B).

One of the most interesting features of the luminescence spectra is the band labeled M-band. As observed above, its intensity increases quadratically with the excitation intensity from about 16 kW/cm^2 to 160 kW/cm^2. A strong maximum in the PL excitation spectrum of this band is seen in the mean photon energy between the M-band and the X_{lh} line (3.792 eV). Such a behaviour is typical of biexcitons (excitonic molecules) which can be directly excited by strong two-photon absorption (TPA)

[11, 12]. The radiative recombination of the biexciton towards the exciton level creates a photon with an energy smaller than the energy of the exciton. The difference corresponds to the binding energy E_B^{bi} of the biexciton. It is equal to the spectral energy difference between the exciton and the biexciton emission bands. The TPA maximum lies at half the biexciton binding energy ($E_B^{bi}/2$) below the free-exciton.

From our experiments, one can deduce the value of the biexciton binding energy (10 to 12 *meV*). From the effective masses $m^*_e = 0.184m_0$, $m^*_{lh} = 0.23m_0$ and $m^*_{hh} = 1.76\ m_0$ for electron, light hole and heavy hole, respectively, calculated in [13], we have $\sigma = m^*_e/m^*_h$ values $\sigma_l = 0.79$ and $\sigma_h = 0.11$. According to the different available theoretical models [9, 11, 14] we have deduced a lower and an upper limit for the biexciton binding energy of the hh-exciton (4 to 9 *meV*) and (1.5 to 5 *meV*) for the lh-exciton. Our experimental values are slightly higher. But for several other materials (e.g. ZnO [15]), the theoretical values of E_B^{bi} obtained are also lower than the experimental ones. This is due to the fact that the real situation is more complicated than the one described by theoretical models. For example, the carrier-phonon interaction seems to further stabilize biexcitons [9].

The effect on PL excitation spectra of the thin and partially disordered layer can be manyfold. The photons with energies, which do not correspond to any specific energy level in the perfect ZnS crystal, are poorly absorbed and penetrate deeper in the sample till they are absorbed in the disordered part of the layer. Therefore we observe a PL signal also out of the intrinsic resonances and PL excitation spectra are subsequently smoothed. Another effect could be the confinement of the excitonic gas in a thin part of the layer and further on a resulting faster thermalisation of the gas due to a reduced diffusion.

One question which remains open is the appearance of a low-energy tail in the emission spectra (around 3.77 *eV*) which rises also almost quadratically with the increasing excitation. However if the excitation intensity is not homogeneous in the whole spot, the coexistence of an electron-hole plasma (in the highest excited regions) with an exciton and a biexciton gas (in the lowest excited regions) could be possible. An explanation of these effects by an exciton condensation [2] is not very plausible due to the short lifetime of excitons in direct-gap semiconductors, which prevents the creation of a phase boundary [15].

Concerning the type of UV-light source used to photoluminescence characteristic of ZnS, one can notice that the He-Cd laser predominantly used (e.g. [16]) is not very convenient for low-temperature PL. Indeed, the He-Cd laser radiation (325 *nm*, 3.81 *eV*) lies exactly in the gap of the PL-excitation spectrum (Fig.4). According to our experiments, the high-pressure mercury lamp (filtered at 240 or 280 *nm*) seems to be a much better choice.

CONCLUSIONS

By the study of the transmission, reflection and photoluminescence (PL) spectra of MOVPE grown epitaxial layers of ZnS, as well by the analysis of the PL excitation spectra new data on excitons and biexcitons (such as their binding energies) are presented for the first time. ZnS being a material with promising possibilities for optoelectronics, we shall complement this study by the measurement of its nonlinear optical properties. The one photon, two photon transitions are observed here as well as phonon assisted transitions.

For a better understanding of the different aspects of the nonlinear optical properties of ZnS epilayers complementary studies will be necessary: laser induced variation of absorption by pump and probe technique, the variation with temperature of the PL and the measurement of gain by the study of the nonlinear absorption and stimulated emission.

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