Materials Science Forum Vol. 117-118 (1993) pp. 375-380

DONOR CONCENTRATION DEPENDENCE OF GaP LUMINESCENCE

T. Monteiro, E. Pereira (a), F. Domingues-Adame and J. Piqueras (b)
(a) Departamento de Física, Universidade de Aviero, P-3800 Aviero, Portugal
(b) Dpto. de Física de Materiales, Facultad de Ciências Físicas
Universidad Complutense, E-28040 Madrid, Spain

Keywords: GaP, donor, acceptor, excitons, complex defects

ABSTRACT

In n-type GaP:S samples the thermally populated excitonic luminescence bands envolving deep acceptors are studied, as function of donor concentration, Ga vacancies and defects trapped at dislocations.

1. INTRODUCTION

In lightly doped n-type GaP:S ($n_D \simeq 5 \times 10^{16} cm^{-3}$) samples besides the shallow green donor-acceptor (D-A) (S,C) band [1] a broad unstructured band peaked at 1.96 eV was found with an exciton-like behaviour [2]. In heavly doped GaP:S samples ($n_D \simeq 3 - 4 \times 10^{17} cm^{-3}$) besides the (S,C) pairs with the presence of nearest pairs, two main bands peaked at 1.79 eV and 1.5-1.55 eV at 11K are found. While the last one presents a typical D-A behaviour the 1.79 eV band is not dependent on the excitation intensity, does not shifts with increasing delay time and does not follow a power law decay [3].

Time resolved spectroscopy (TRS), ODMR and CL-SEM are powerfull techniques to study the broad unstructured bands that occur in n or p type GaP samples [4,5,6].

The broad red luminescence band in heavly doped n-type GaP:S samples is strongly dependent on temperature. For temperatures above 70K a new band peaked at 1.62 eV appears with a long exponential decay time $\tau \simeq 18\mu s$. The band maxima shifts to higher energies when the temperature is increased. CL-SEM analysis show that the red band emission occurs at dislocations.

In this work, the broad emission bands in heavly doped n-type GaP:S samples are studied as functions of time, temperature and CL-SEM images. The influence of Sulphur, Gallium vacanvies and dislocations on the defects are discussed. A comparison with bands that occur in the same spectral region in n-type GaP doped with transition metal ions, namely Mn [3] and Cu [6] is made.

2. EXPERIMENTAL RESULTS

The samples used in the present work are LEC grown and the experimental set up was described elswhere [4,8]. In Figure 1 the steady state luminescence spectra at 11K for above band gap excitation of n-type lightly and heavly doped GaP:S samples are shown.

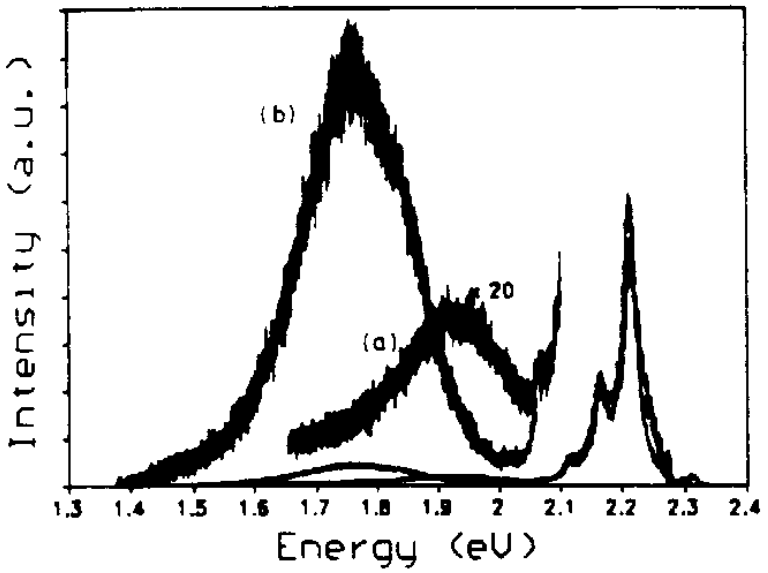

Figure 1 - Steady state luminescence at 11K: (a) lightly doped sample (b) heavly doped sample.

Besides the (S,C) pair in lightly doped samples a broad unstructured band peaked at 1.96 eV is observed [2] while in heavly doped samples the red 1.79 eV and a near infrared 1.5-1.55 eV band are detected. The 1.79 eV band presents a biexponential decay and is correlated with excitons bounded to complex defects. It is identical with the band found in GaP:S:Mn samples [3].

The 1.5-1.55 eV band shows a typical D-A behaviour, as indicated by the sligth shift towards lower energies with increasing delay time and temperature (Figure 2). The decay also follows a power law decay (inset Figure 2).

The intensity of the 1.79 eV band is quenched above 80K. However, for temperatures above 70K a new band peaked at 1.62 eV appears with a lifetime, $\tau = 18s$, at 70K. Time resolved spectra, due to the different decays of the 1.79 eV and 1.62 eV band separate the two emissions as shown also in Figure 2. A further increase on temperature favours the shift of the 1.62 eV band to higher energies. This shift is similar for any delay and window of observation, indicating that is due to thermalization between two excited levels in the same centre. This shift of the high temperature band was also observed from CL-SEM measurements [7].

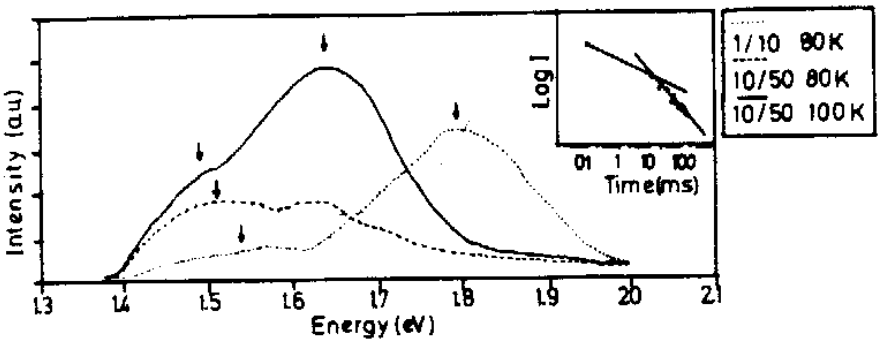

Figure 2 - Time resolved spectra for different times and temperature. Inset: decay time at of the 1.55 eV D-A pair.

From CL-SEM analysis the highly doped sample shows the characteristic dot and halo contrast which has been associated with the presence of dislocations [7]. While the emission from the halos with the electron beam focused is mainly green, corresponding to the (S,C) pairs, the red band is observed at the center of dislocations pits. The red band profile is similar to the profile of the vacancy concentration along the wafer diameter and is inverse of the green luminescence profile[9]. This indicates that the vacancies act as competitors of the (S,C) pairs. The observed profiles are consistent with a model of a vacancy-donor complex for the high temperature red 1.62 eV band.The CL spectra of a heavly doped GaP:S sample is shown in Figure 3a.

In lightly doped samples the CL-SEM spectra are in agreement with the photoluminescence results where no red band is observed with the beam focused or unfocused, the spectra corresponding to the 1.96 eV band. With the beam unfocused a sligtly broadning of the band is detected and can be explained by the presence of the shallow pairs (Figure 3b).

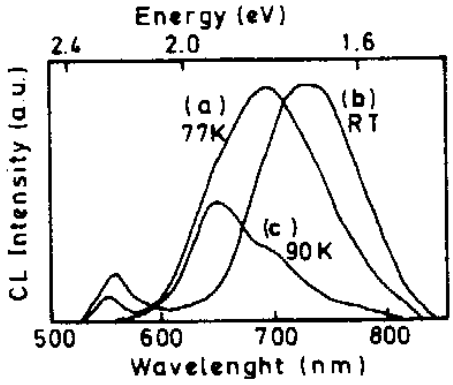

Figure 3 - CL spectra of: (a) heavly doped sample (77K) (b)heavly doped sample (RT), (c) lightly doped sample (90K).

In Figure 4 the intensity and decay time of the 1.62 eV band are plotted versus 1/kT.

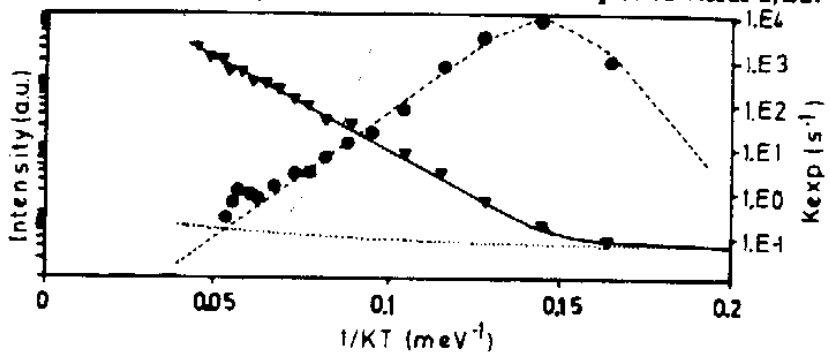

Figure 4 - Intensity and 1/r dependence on 1/kT.

3. DISCUSSION

From the experimental data we observe that the red low temperature 1.79 eV band and the high temperature 1.62 eV band are absent in lightly doped samples. For higher concentrations of the donor the red emission bands and a deep D-A pair are present.Also the red band profile across the diameter of the wafer is silmilar to the vacancy profile [9].

The analysis of the red band can be separated in two temperature regions. In the low temperature range the red 1.79 eV band presents an excitonic character in agreement with previous results in a GaP:S:Mn with similar S concentration [3]. The 1.62 eV observed for temperatures above 70K presents a behaviour similar to the one observed in n-type GaP samples doped with Cu[7] and Mn[4] where broad unstructured bands with lifetimes of a order of seconds appear for temperatures above 70K shifting towards higher energies on increasing temperature. They are correlated with the acceptors that give rise to levels located between 0.4 and 0.7 eV above the valence band.

To test if there is thermalization between the two excited levels we assume that the emissions have a gaussian line shape with strong vibronic coupling as expected from broad unstructured bands. The fit to two gaussians with maxima at 1.62 eV and 1.72 eV with halfwidths of 85 meV and 75 meV respectively was made for different temperatures and times of observation. The ratio of the two band intensities is shown in Figure 5. In inset the fit to the two gaussians is exemplified for 140K.

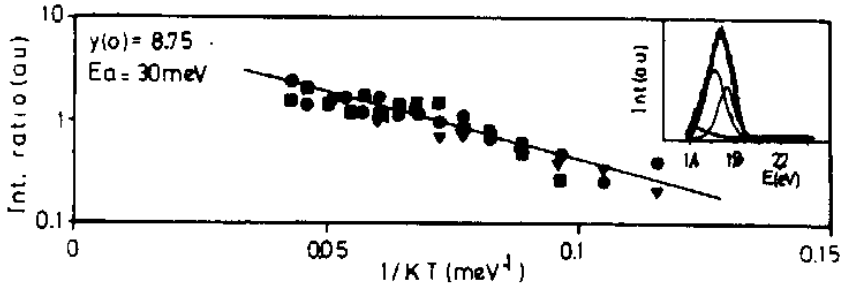

Figure 5 - Ratio of the two band intensities ($I_{1.72eV}/I_{1.62eV}$). Inset: fit to two gaussians.

From this plot, and assuming a simple thermal equilibrium law

$$\frac{I_{1.72eV}}{I_{1.62eV}} = g\frac{W_{1.72eV}}{W_{1.62eV}}\exp(-\Delta E/kT) \quad (1)$$

we obtain a value of 30 meV for the energy difference of the two levels (ΔE) and $gW_{1.72eV}/W_{1.62eV} = 8.75$. $W_{1.72eV}$ and $W_{1.62eV}$ are the transition probabilities from the levels where 1.72 eV band and 1.62 eV band originates and g is the degeneracy factor.

Taking into account that the band maxima separation is 100 meV the energy separation of 30 meV for the two levels is acceptable due to the different vibronic coupling in the two emissions, as shown by the different widthes of the gaussians.

Under the assumption of thermal equilibrium the common decay, τ, is given by:

$$\tau(T) = \tau_0\frac{1+g\exp(-\Delta E/kT)}{1+g(W_{1.72eV}/W_{1.62eV})\exp(-\Delta E/kT)} \quad (2)$$

with $\tau_0 = 18s$ (at 70K) the radiative decay of the lowest energy level.

To account for the intensity behaviour with temperature we have to consider both the processes of thermal population of the centre and nonradiative processes, shown by the departure of the decay behaviour given by equation 2 (dotted line in Figure 4). From the decay time dependence on temperature the parameters of the nonradiative process may be determined in a classical model from:

$$K_{exp} = K_{rad}(T) + K_0\exp(-E_a/kT) \quad (3)$$

The theoretical fit to equation 3 is shown by the solid line in Figure 4 with $K_{rad} = 1/\tau(T)$ given by equation 2 and $K_{arad} = K_0\exp(-E_a/kT)$, with $K_0 = 1.45 \times 10^6 s^{-1}$ and $E_a = 100meV$. As the deep D-A 1.55 eV pair shows a multistage nonradiative decay, the hypothesis that one of the ionization processes of the pair is responsible for the population of the 1.62 eV centre was tested. Under this assumption the intensity increase will be given by:

$$I(T) = I(T')\times\frac{K_{rad}}{K_{rad}+K_{arad}} \quad (4)$$

with

$$I(T') = \frac{W_{ti}\exp(-E_i/kT)}{\sum_i W_{ti}\exp(-E_i/kT)+W_{rad}} \quad (5)$$

where W_{ti} are the temperature independent frequency factors for the nonradiative decay of the deep pairs and W_{rad} stands for the competing deexcitation rate that we assume to be $10^8 s^{-1}$ in comparison with previous results for the same donor concentration of the (S,C) pairs. A fit to equation 4 assuming that it is

the decay path with E_1 = 160meV that populates the 1.62 eV centre is shown by the dashed line in Figure 4, giving good agreement with experiment.

It is interesting to note that taking into account the steady state photoluminescence intensity dependence on temperature the nonradiative quenching might be attributed to a process with activation energy of 33 meV in agreemment with previous results from CL [4]. It is only TRS that reveals the complexity of the luminescence processes.

4.CONCLUSIONS

The presence of a band of excitonic nature in heavly doped n-type GaP:S samples, that is thermally populated and shows an extremally large lifetime at intermediate temperatures (70 - 120K) is a common feature of these samples. Its peak position and decay parameters are strongly dependent on the presence of acceptor levels in the mid gap as happens in n-type GaP doped with Mn [3] and Cu [6]. The data from the lightly and heavly doped GaP:S samples allows us to assume that in some way the donor and vacancies must be involved on the defect that is responsible for the high temperature red band. The enhancement of the emission around the dislocations provides the hypothesis that the defect must be captured by them. From a comparison with transition metal ions doped n-type GaP samples we can attribute that the intrinsic defect originates a level close to .5 eV above the valence band.

ACKNOWLEDGEMENTS

Financial support from JNICT and DGICYT (Project PB 90-1017) is gratefully acknowledged. One of us (T. M.) thanks to JNICT for a maintenance grant (BD - 88/90 rm). This work was partially supported by the Portuguese-Spanish joint programm. Also, the support of C.M.Aveiro is acknowledged. The authors want to thank Criolab for technical assistance with vacuum and cryogenic equipment, and Decada with Lasers and Spectrometers. Mr. J. Januário helped in the experiments.

REFERENCES

[1] - Dean, P.J.: Prog. Sol. St. Chem., 1973, 1, 1.

[2] - Pereira, E., Monteiro, T.: J. of Lum., 1992, 53, 395.

[3] - Monteiro, T.,Pereira, E.: J. of Lum., 1992, 53, 375.

[4] - Monteiro, T., Pereira, E.: J. of Lum., 1991, 48 & 49, 671.

[5] - Garcia, J.A., Remon, A., Domingues-Adame, F., Piqueras, J.: Mat. Chem. Phys., 1991, 28, 267.

[6] - Godlewski, M., Monemar, B.: J. Appl. Phys., 1988, 64, 200.

[7] - Buynova, I.A., Ostapenko, S.S., Sheinkman, M.K.: Sov. Phys. Sem., 1986, 20, 1123.

[8] - Domingues-Adame, F., Piqueras, J.: Mat. Chem. Phys., 1989, 21, 539.

[9] - Domingues-Adame, F., Piqueras, J., deDiego, N., Llopis, J.: J. Appl. Phys., 1988, 63, 2583.