

STUDY OF RADIATIVE TRANSITIONS IN THE RANGE 1.5-2.1eV IN GaP

J.A. GARCIA

Departamento de Física Aplicada II, Facultad de Ciencias,  
Universidad del País Vasco, Lejona, Vizcaya (Spain)

A. REMON

Departamento de Física de la Materia Condensada, Facultad de  
Ciencias, Universidad del País Vasco, Lejona, Vizcaya (Spain)

F. DOMINGUEZ-ADAME and J. PIQUERAS

Departamento de Física de Materiales, Facultad de Ciencias  
Físicas, Universidad Complutense, Madrid (Spain)

Received January 8, 1991; accepted February 18, 1991

ABSTRACT

The spectral emission of GaP:S in the range 1.5- 2.1eV (800-600nm) has been studied by cathodoluminescence in the scanning electron microscope and by photoluminescence. In as-grown samples the spectra show two bands centered at about 700-730 and 800nm. Annealing the sample above 900K enhances the band of 700nm and causes the occurrence of a band centered at 610-620nm. The conditions under which each band is prominent in the luminescence spectrum are analyzed and discussed.

INTRODUCTION

The luminescence of GaP in the 1.5-2.1eV (825-590nm) spectral range shows a complex behaviour with the appearance of several bands whose wavelengths and intensities depend on the temperature of measurement, the previous thermal treatments of the sample and on the experimental procedure -photoluminescence (PL) or cathodoluminescence (CL)- used. In particular, a two component intense band observed at room temperature in n-type GaP has been previously studied by several authors [1-3]. Under certain experimental conditions, however, a band centered at about 610nm dominates in the luminescence spectra of the same material [1,4]. In the present work PL and CL techniques are used to study the emission bands at 710-730nm and at 610-620nm in crystals with different treatments. We analyze the conditions under which each band is prominent in the luminescence spectrum. The possible origin of the bands is then discussed.

## EXPERIMENTAL

The material used was S doped LEC GaP with a free carrier concentration  $n$  of  $3-4 \times 10^{17} \text{cm}^{-3}$ . Samples of about  $5 \times 5 \text{mm}^2$  were cut from a (100)-oriented wafer and some of them were annealed in argon atmosphere at temperatures up to 1300K. CL measurements were performed in a Cambridge S4-10 scanning electron microscope at temperatures between 90K and 300K. The CL attachment used has been previously described [5]. PL emission of the samples was measured between 90K and 300K by using a Jobin-Yvon JY3D spectrofluorometer with a R-928 photomultiplier. A He-Cd laser (441.6nm) had been adapted as PL excitation source.

## RESULTS

As-grown samples

According to previous results [3,6] the CL observations show the existence of a band at 732nm, at room temperature, that increases by defocusing the electron beam of the electron microscope. Due to the low intensity of this band when the electron beam is focused, CL-images of the sample could not be obtained. At temperatures below 180K the peak appears at 695nm [3]. The present observations show that the intensity of the 695nm peak follows the law  $I \sim \exp(E_a/KT)$  in the range 90-180K, with  $E_a \approx 33 \text{meV}$ . (Fig. 1).

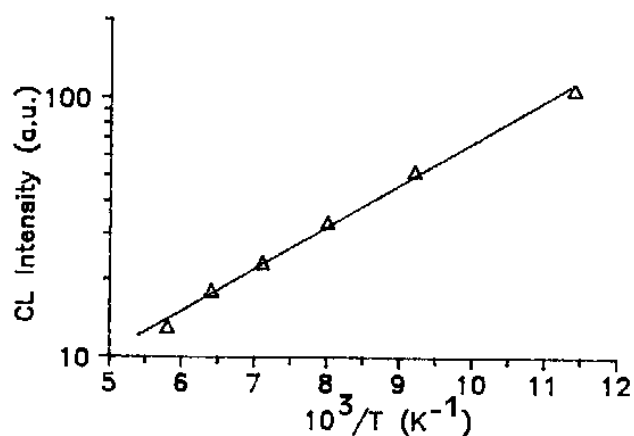


Fig. 1. Temperature dependence of the intensity of the red (695nm) CL band in the range 90-200K. The activation energy is about 33meV.

Figure 2 shows the PL spectra at 300K and 90K respectively of an as-grown sample. At room temperature the 802nm band, not observed in the CL spectra, dominates and the red band appears at 779nm instead of 732nm. At least, part of this shift should be due to the presence of the intense 802nm band. At 90K a peak at 708nm is observed.

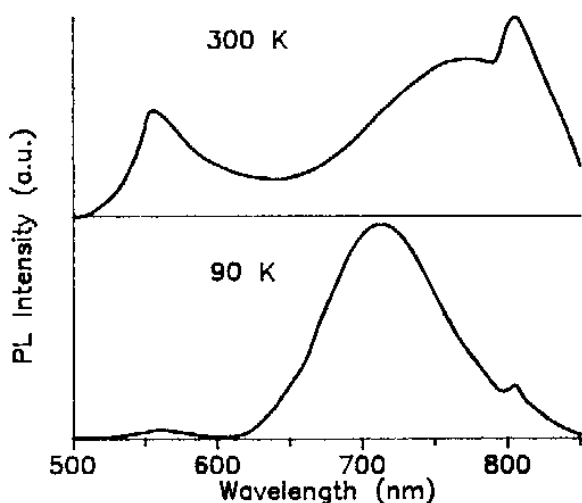


Fig. 2. PL spectra of an as-grown sample at room temperature and 90K.

#### Annealed samples

Annealings at temperatures below 900K do not cause spectral shifts or intensity changes of the red band. After one hour annealing at 900K the CL band appears at about 705nm at room temperature [3]. In the PL spectra at room temperature of samples that have received the same treatment a band centered at 710nm dominates (Fig. 3) while the 802nm emission shows a decrease of the relative intensity.

The observed spectral change is due to an increase of the 705-710nm emission rather than to the intensity decrease of other bands. On the other side, it has been observed that after 1000K annealing the high emission enables to record CL images corresponding to the red spectral region (Fig. 4).

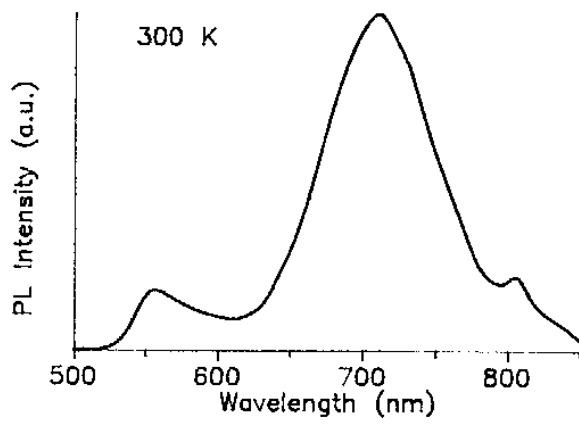


Fig. 3. PL spectra at room temperature of a sample annealed one hour at 900K.

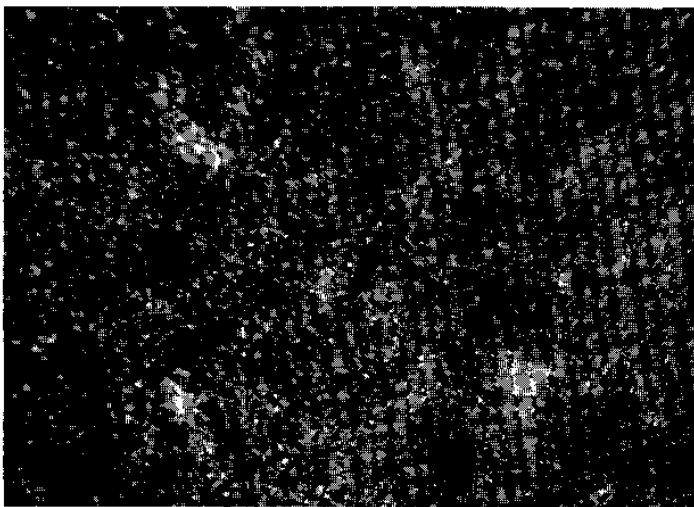
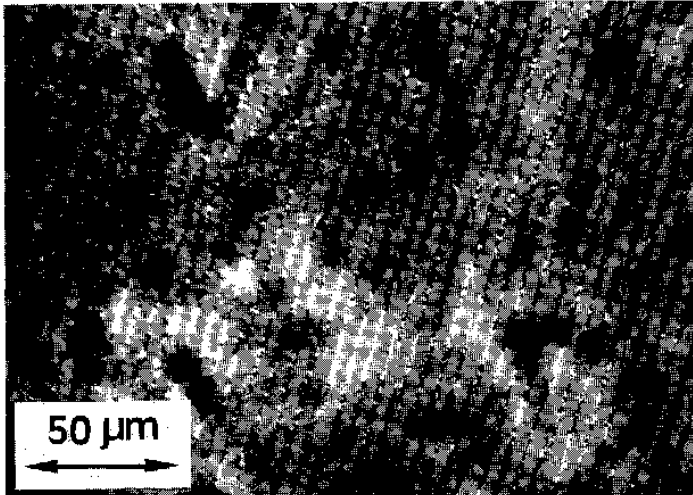


Fig. 4. (a) Near-band edge image and (b) red CL image of a sample annealed one hour at 1000K.

As stated above it is not possible to obtain such images in the as-grown samples with our experimental arrangement. Some of the dark spots in the near edge band image, associated with the presence of dislocations [6], appear as bright spots in the red band image.

In Fig. 5a the CL spectrum shows a weak 610nm emission that appears only after annealing for five hours at 1100K. Fig. 5b shows the PL spectra at 90K of samples annealed for one hour at 900K and 1300K, with a strong 610nm band. The 610nm PL band is stable up to an annealing temperature of about 1300K.

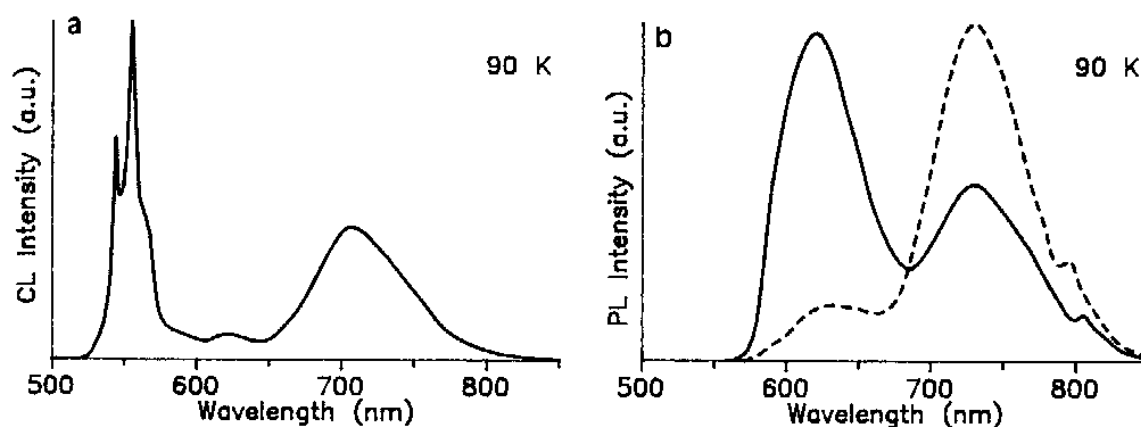


Fig. 5. (a) CL spectrum at 90K of a sample annealed five hours at 1100K and (b) PL spectra at 90K of samples annealed one hour at 900K (full curve) and 1300K (broken curve).

#### DISCUSSION

In a previous work [3] it has been described that the red CL emission has two components with wavelengths of 732nm and 705nm observed in as-grown and annealed samples respectively. Transitions related to this emission can be represented by an energy diagram similar to that proposed by Dishman *et al.* [1]. Figure 6 shows the transitions observed in the present work and in [3].

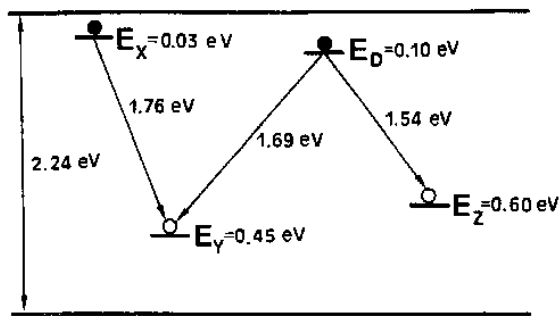


Fig. 6 Energy level diagram for the different radiative transitions.

The  $E_Y$  level corresponds to an isoelectronic center called Y in [1], that has been suggested to be a  $V_{Ga}3Sp$  complex. It is assumed that both components are related to the  $E_Y$  level. The 732nm component has been represented, according to [1], as the transition from the S donor level to  $E_Y$ . This provides the value of 0.45eV for  $E_Y$  in GaP:S and consequently the 705nm emission would be due to the transition from a level at 0.03eV below the conduction band to  $E_Y$ . The value of 0.03eV is close to the  $E_a$  obtained by temperature dependence measurements. **Figure 6 also shows the 802nm transition between the donor level of S,  $E_D$ , and a deep acceptor center Z.** A similar transition (820nm) is described in [1] in GaP:Te and is attributed to the existence of the acceptor level of the complex  $V_{Ga}2Tep$ . Godlewski and Monemar [7] have observed the 800nm emission in undoped and donor doped (S, Te, Se, Ge) crystals and have shown that is due to a donor-acceptor pair recombination. Their results are consistent with the suggestion of an acceptor complex formed by a gallium vacancy and two adjacent donors. In the present work the 800nm emission is readily observed in the PL spectra but does not appear in CL. This result can be due to a saturation effect if the concentration of Z centers is lower than that of Y centers, and if the excitation density is higher in CL than in PL. A similar effect has been observed in the CL spectra of GaP:S [6] which show the 732nm red band only by low excitation density (defocused electron beam). The Z centers would be then less numerous and/or less efficient than the Y centers.

The temperature dependence of CL and PL spectra shows a similar behaviour of both, 732nm and 802nm, bands related to the S donor level. The intensity decreases by decreasing temperature while the emission related to the 30meV level is enhanced. The parallel behaviour of the 732nm (CL) and 800nm (PL) bands is also observed in samples annealed above 900K. Both bands disappear or at least strongly decrease giving rise to a prominent band at 705-710nm. Due to the increase of the 705nm band it becomes possible to record the CL images shown in Fig. 4. A possible explanation of this observation is the increase of Y center concentration by an aggregation process during annealing.

Finally we discuss the presence of a band at 610nm at low temperatures in annealed samples. This emission appears much more intense in the PL than in the CL spectra (Fig. 5). The differences in both kinds of spectra can be due to the different excitation density in both cases if the 610nm band saturates before that of the 710nm band. A band at 600nm is attributed in [1] to an isoelectronic center involving group VI donors and Ga vacancies. The results of [1] show that the 600nm band at 1.8K is weak compared with the 730nm band and its intensity rapidly decreases on increasing the temperature. On the contrary the 610nm PL band of this work is prominent at 90K and at 120K is still about half as intense as the 710nm peak. The relative intensity of the 610nm emission depends on the annealing temperature with a formation threshold of about 900K and a stability up to about 1300K. These temperatures should correspond to the formation and annealing respectively of the donor-vacancy complex responsible for the emission. The fact that in the present work the relative intensity of the 610nm emission is higher than previously described can be due to different details of the thermal treatments causing the band as well as a different initial defect structure in the sample. The last possibility is supported by the fact [3] that electron irradiation previous to the annealing strongly favors the appearance of an intense band at 610nm.

#### ACKNOWLEDGEMENTS

We thank Wacker-Chemitronic (Dr. K. Löhnert) for providing the samples. This work was partially supported by CICYT (Project MAT 90-0047), by Volkswagen Stiftung and by DGICYT-DAAD.

## REFERENCES

- 1 J.M. Dishman, D.F. Daly and W.P. Knox, J. Appl. Phys., 43 (1972) 4693.
- 2 A.N. Barchuk, V.V. Cerasimenko, A.I. Ivashchenko, F.Ya. Kopanskaya, A.I. Solomonov and V.P. Tarchenko, Sov. Phys. Semicond., 21 (1987) 794.
- 3 F. Domínguez-Adame and J. Piqueras, Mater. Chem. Phys., 21 (1989) 539.
- 4 F. Domínguez-Adame, J. Piqueras, N. de Diego and P. Moser, Solid State Commun., 67 (1988) 665.
- 5 B. Méndez and J. Piqueras, J. Appl. Phys. (in press)
- 6 F. Domínguez-Adame, J. Piqueras, N. de Diego and J. Llopis, J. Appl. Phys., 63 (1988) 2583.
- 7 M. Godkewski and B. Monemar, J. Appl. Phys., 64 (1988) 200.