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Photoluminescence Studies of Heat-Treated GaP:S Samples

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ABSTRACT

Time resolved photoluminescence (TRPL) of untreated and heat-treated n-type GaP:S samples has been investigated and compared with data from cathodoluminescence in a scanning electron microscope (CL-SEM). Special attention is given to broad emission bands in the region of 1.8 to 1.6 eV. TRPL shows that dependent on temperature different optical centers are responsible for the luminescence. While the low temperature emission presents a donor-acceptor (D-A) pair behavior above 70 K an excitonic emission dominates with an exponential decay (of the order of seconds at 70 K) in the whole temperature region where it is measured. The temperature behavior of the decay and intensity of these bands leads to the understanding of the processes involved in the luminescence. From the data the distribution of the defects and the levels involved in the emission are discussed. The influence of the annealing in the rearrangement of the defects is analyzed.

Although it is generally considered that broad emission bands in GaP are due to (D-A) pair recombination it is known that also broad emission bands due to complex defects in n and p type GaP samples present efficient luminescence. For instance, the Zn-O complex is responsible for the red electroluminescence.[1]

In n-type GaP material several broad emission bands have been detected in the red and near infrared region in sulfur doped samples,[2] and in samples codoped with transition metal ions.[3-5] These bands do not show the typical (D-A) behavior and are due to complex defects that bind an exciton. TRPL and CL-SEM have been used currently to characterize the complexes where the luminescence takes place.

In this work we study in detail the annealing effect on sulfur doped n-type GaP samples and the marked changes observed on the luminescence bands. For this purpose we use PL, TRPL, lifetime measurements (LT), and CL-SEM analysis.

The nature of the defects that originate broad emission bands before and after annealing are discussed and the influence of heat-treatment on the defect distribution is analyzed.

Experimental Details

Our samples are as-grown liquid-encapsulated Czochralski (LEC) single crystals oriented along <100> direction with $n_D \simeq 3 - 4 \times 10^{17}$ cm ^{3} and a dislocation density of $10^4 - 10^5$ cm^{-2}. The samples were observed in a Cambridge S4-10 scanning electron microscope at 30 kV at room temperature in the emissive and CL modes.

TRPL and LT measurements were performed using a SPEX 1934 C phosphorimeter with width of 3 μs and a tail that accounts for 1% of light after 10 μs. Steady state luminescence spectra were measured using an Ar-laser as excitation source. The samples were held in the cold tip of a closed cycle He cryostat (Air-Products) from 11 K to room temperature.

Experimental data were obtained in the same set of samples before and after annealing for 1 h at 1100 K in an Ar atmosphere.

Experimental Results

Before annealing.—In Fig. 1, the steady state luminescence spectrum at 11 K for above bandgap excitation is shown. Besides the green (S, C) (D-A) pair[6] and a weak deep (D-A) pair peaked at 1.5-1.55 eV [7] a broad emission band with maximum at 1.79 eV and a bi-exponential decay[5] is observed at 11 K.

When the temperature increases the luminescence quenching of the low temperature emission bands is observed while for $T > 70$ K a new broad emission band peaked at 1.62 eV is observed. This thermally populated band shows a single temperature dependent exponential decay with $\tau = 18$ s at 70 K.

In Fig. 2 the TRPL spectra for different times and temperatures allow for the separation of the overlapping emission bands showing the low temperature emission peaked at 1.79 eV for shorter observation times and the high temperature emission band with maximum at 1.62 eV for longer observation times. The shoulder on the low energy range corresponds to the 1.5-1.55 eV deep pair.[7]

Further increase on temperature favors the shift of the band maximum towards higher energies (from 1.62 to 1.72 eV) while a decrease in lifetime and intensity is observed. The presence of a common decay observed in the two band maxima and the fact that the band shape is independent of the time window indicate that thermalization occurs between two emission levels. The 1.62 eV band shows a behavior similar to the one found in the high temperature bands observed in n-type GaP samples doped with Cu [3] and Mn. [4]

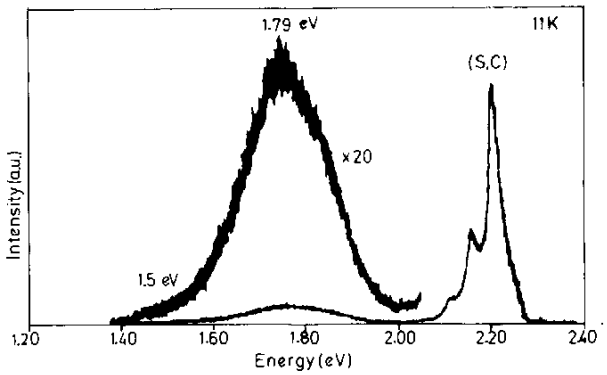

Fig. 1. Steady state luminescence at 11 K for above bandgap excitation of n-type GaP:S samples with $n_D = 3 - 4 \times 10^{17}$ cm^{-3}.

From CL-SEM analysis the dot and halo contrast associated with the presence of dislocations is observed.[3] In Fig. 3, we show the images of the as-grown samples in scanning electron microscope in the emissive mode and in cathodoluminescence mode after chemical etching. In Fig. 3 (a) large etch pits are observed on a background of smaller and shallow pits and in Fig. 3 (b) the total CL image of the area shown in the upper figure shows the dot and halo contrast only at the points where large pits appear in the emissive mode image. The CL dot and halo contrast appears also in unetched samples. On the other hand, previous CL work[8] has shown that the red band and the vacancy profiles along the wafer diameter are similar.

It should be noticed that in samples with lower sulfur concentration the 1.62 eV band is absent.[2]

After annealing.—After annealing at temperatures below 900 K no changes are observed on the luminescence spectra. After heat-treatment for 1 h at 1100 K the steady state luminescence spectra at 11 K for above bandgap excitation are shown in Fig. 4. Besides the (S, C) and (Si, S) (D-A) pair recombination[6] a new (D-A) emission not previously reported was observed. It has a maximum at 1.75 eV and the (D-A) character is revealed by the shift of the band maximum towards lower energies with increasing delay times and temperature and by the power law decay dependence (inset in Fig. 4).

This pair emission is thermally quenched and the temperature dependence of the luminescence intensity presents a multistage de-excitation process with activation energies of 7.8 meV in the low temperature region, 36 meV in intermediate temperature region, and 170 meV in the high temperature region. The band maximum shift towards higher energies is due to a new band with maximum at

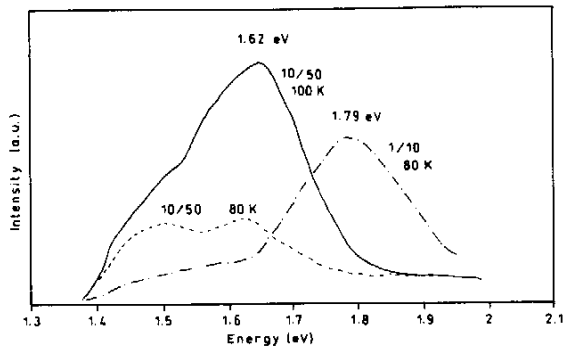

Fig. 2. Time resolved spectra for different times and temperatures of n-type GaP:S samples. Full line: luminescence viewed between 10 and 50 ms after the light pulse at 100 K; Broken line: luminescence viewed between 10 and 50 ms after the light pulse at 80 K; Chain line: luminescence viewed between 1 and 10 ms after the light pulse at 80 K.

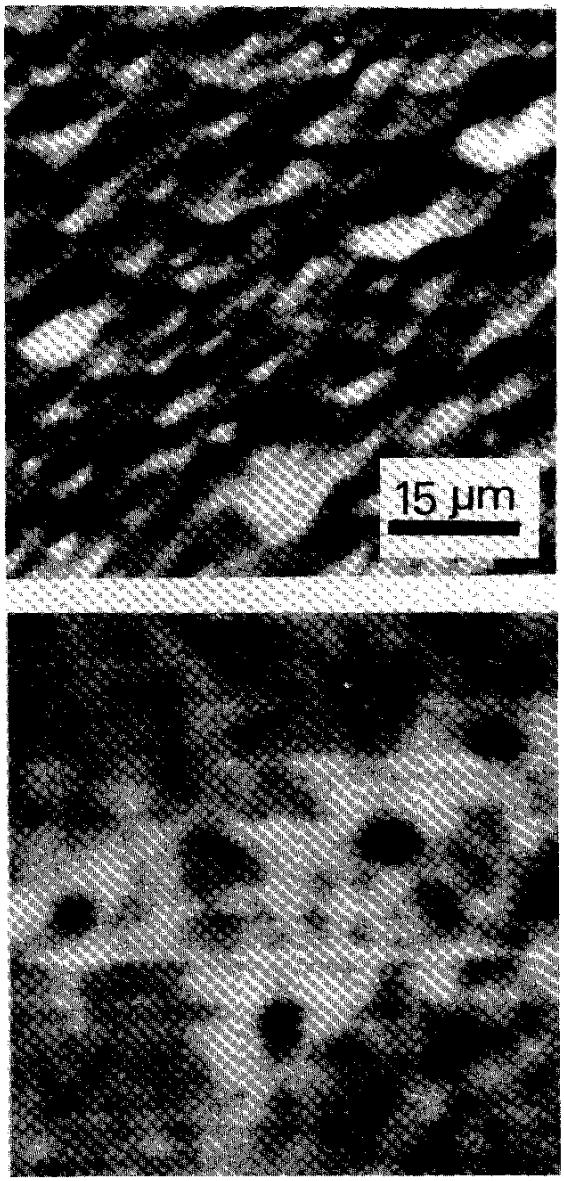

Fig. 3. Images of n-type GaP:S samples in the scanning electron microscope: (a) emissive mode, (b) cathodoluminescence mode.

1.78 eV. In Fig. 5 a comparison of the steady state luminescence spectra for different temperatures is shown. The 1.78 eV band presents a temperature dependent single exponential decay with a lifetime of $\tau = 1.12$ s at 90 K. The temperature dependence of lifetime and intensity of this band is shown in Fig. 6.

From CL-SEM analysis the dot and halo contrast is observed. The emission from the haloes is mainly green (Fig. 7a). Some of the dark spots in the near band-edge image, associated with the presence of dislocations, appear as bright spots in the red CL images (Fig. 7b).

Discussion

Before annealing.—The analysis of the red band can be separated in two temperature regions. In the low temperature region the red 1.79 eV band presents an excitonic character in agreement with previous results in n-type GaP:S, Mn samples with similar sulfur concentration.[5] The presence of the transition metal (TM) ion does not affect the 1.79 eV luminescence indicating that this band is not correlated with the TM ion.

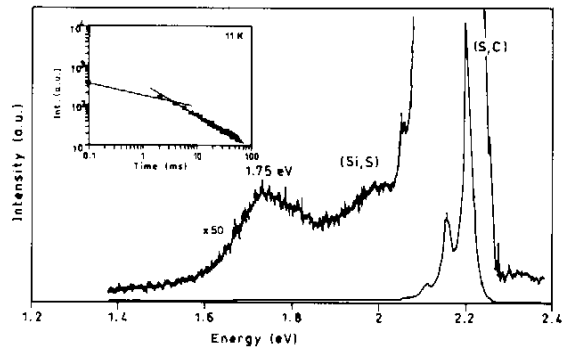

Fig. 4. Steady state luminescence at 11 K for above bandgap excitation of GaP:S annealed samples 1 h at 1100 K. Inset: power law decay dependence of the 1.75 eV D-A pair.

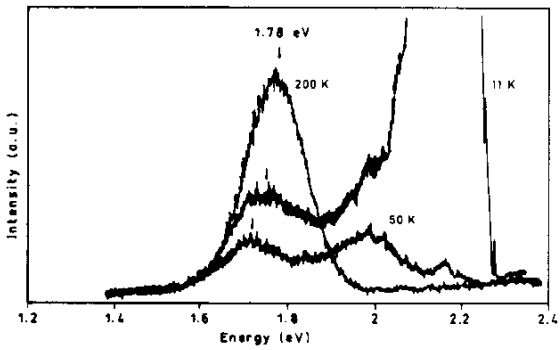

Fig. 5. Comparison of steady state luminescence spectra of the annealed samples for different temperatures.

In the high temperature range a new band peaked at 1.62 eV appears. It is thermally populated from the deep 1.5-1.55 eV (D-A) pairs. The band shows a longer single exponential lifetime (τ = 18 s at 70 K) and the shift of the band maximum towards higher energies with further increase on temperature can be explained by a thermalization between two excited levels that are 30 meV apart.[2]

From CL-SEM data and from the fact that this band appears only in moderately doped samples the donor and vacancies must be involved on the defect that originates the 1.62 eV band.

After annealing.—At low temperatures the heat-treatment has favored a new (D-A) pair peaked at 1.75 eV while the excitonic emission found in the unannealed samples is no longer present. To our knowledge it was the first time that this pair emission was observed. The hypothesis that Si is one of the species of the pair cannot be excluded as Si

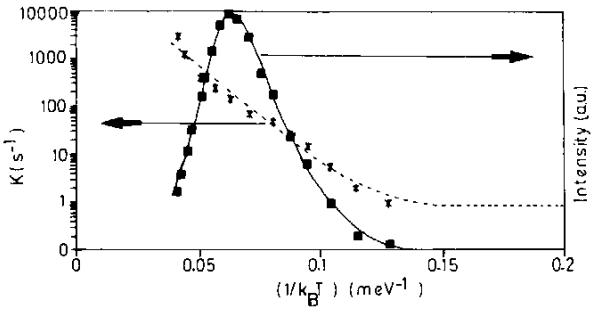

Fig. 6. Experimental data: Intensity (■) and $1/\tau$ (*) dependence on $1/k_BT$ of the 1.78 eV band in the annealed sample. Broken line: theoretical fit in accordance with Eq. 1. Full line: theoretical fit in agreement with Eq. 2.

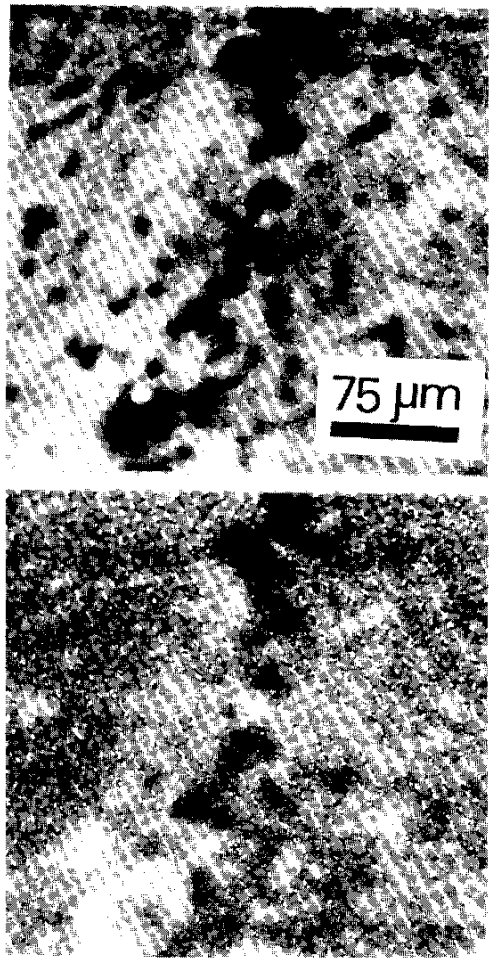

Fig. 7. Images of the annealed samples in SEM: (a) green and (b) red CL images.

contamination was detected after annealing by the presence of the (Si, S) (D-A) pair.[6]

When the temperature is increased a new band with maximum at 1.78 eV appears. The intensity and $1/\tau$ dependence on temperature is shown in Fig. 6.

To account for the intensity behavior we have to consider both the processes of thermal population of the center and the nonradiative processes of the center.

The decrease in intensity and decay indicates that some nonradiative processes originating in the emitting levels compete with luminescence. Thus the measured decay rate is given by

$$K_{exp} = K_{rad} + K_o \exp(-E_a/k_BT) \quad [1]$$

with $K_{rad} = 1/\tau_o$ the radiative decay at 90 K (τ_o = 1.12 s). The best fit of the data according Eq. 1 was obtained for E_a = 95 meV, $K_o = 9.4 \times 10^4\ s^{-1}$ and the theoretical curve is shown by the broken line on Fig. 6.

As the 1.75 eV low temperature pair shows a multistage nonradiative decay, the hypothesis that one of the ionization processes of the pair is responsible for the population of the 1.78 eV center was tested. The intensity decrease of the 1.75 eV band pairs occurs in the same temperatures region where the intensity of the 1.78 eV band increases.

Under this assumption the intensity increase will be given by

$$I(T) = I'(T) \times \frac{K_{rad}}{K_{rad} + K_{nrad}} \quad [2]$$

Table I. High temperature emission bands.

Sample:	GaP:S [2]	GaP:S annealed	GaP:S, Mn[5]	GaP:S, Cu[3]
T of appearance:	$T > 70$ K	$T > 90$ K	$T > 70$ K	$T > 77$ K
Band maximum:	1.62 eV	1.78 eV	1.64 eV	1.61 eV
Lifetime:	$\tau = 18$ s	$\tau = 1.12$ s	$\tau = 3.8$ s	$\tau > 10^2$ s
Populated from:	1.5-1.55 eV pairs	1.75 eV pairs	Mn^{*2}	(NN_1) pair
Activation	$W_t = 10^{13}$ s^{-1}	$W_t = 10^{8}$ s^{-1}	$W_t = 4 \times 10^{9}$ s^{-1}	.....
Energies:	$E = 160$ meV	$E = 170$ meV	$E = 130$ meV	$E = 95$ meV
Higher T	shifts to	remains constant	shifts to	shifts to
behavior:	1.72 eV	1.78 eV	1.72 eV	1.64 eV
	common τ	....	common τ	common τ
Excited	$\Delta E = 30$ meV	....	$\Delta E = 78$ meV	$\Delta E = 30$ meV
Levels:	$g\frac{W_{1.72\,eV}}{W_{1.82\,eV}} = 8.75$	....	$g\frac{W_{1.72\,eV}}{W_{1.64\,eV}} = 2300$	....
Deactivation	$E_a = 100$ meV	$E_a = 95$ meV	$E_a = 110$ meV	$E_a = 120$ meV
Processes	$K_o = 1.45 \times 10^5$ s^{-1}	$K_o = 9.4 \times 10^5$ s^{-1}	$K_o = 3 \times 10^4$ s^{-1}	....

with

$$I'(T) = \frac{W_{ij} \times \exp(-E_i/k_B T)}{\sum_j W_{ij} \times \exp(-E_j/k_B T) + W_{rad}} \quad [3]$$

where $I'(T)$ account for the thermal population. W_{ij} are the temperature independent frequency factors for the nonradiative decay of the 1.75 eV pairs and W_{rad} stands for the competing radiative deexcitation rate of 10^2 s^{-1}.

The best fit to Eq. 2 was obtained assuming that it is the decay path with $E_1 = 170$ meV that populates the 1.78 eV center and is shown by the full line in Fig. 6.

A comparison of thermally populated bands occurring in n-type GaP samples is presented in Table I.

It is interesting to note that E_a is very close to the donor ionization energy and the frequency factor of the same order of magnitude.

CL-SEM analysis.—At temperatures at which the high temperature bands dominate, the CL images show besides the dot and halo contrast that the red 1.62 eV emission of the unannealed samples presents a homogeneous distribution. After annealing the 1.78 eV red band shows an intensity increase with rearrangement of the luminescence centers in the proximity of dislocations.

Conclusions

From a comparison with the excitons bounded to complex defects in n-type GaP doped with Cu and Mn we may conclude that the 1.62 eV band must be due to an exciton bounded to a complex defect. The correlation between the emission and the vacancy profile suggests that the complex must involve vacancies and sulfur. The intrinsic defect must give rise to a deep acceptor level close to 0.5 eV above the valence band. The defect is homogeneously distributed around dislocations.

After heat-treatment and from the enhancement of the red 1.78 eV band at dislocations due to the rearrangement of luminescence centers we can conclude that the 1.78 eV band is due to an exciton bounded to a complex defect, the complex being captured by the dislocations.

The similarity between the bands, namely, the similarity in the deactivation parameters indicates that the exciton must involve sulfur and another species most probably vacancies that originate an acceptor level between 400 meV and 500 meV in accordance with the bands that appear in TM doped n-type GaP.[3,4]

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