

SHORT COMMUNICATION

COMPOSITE CHARACTER OF THE RED BAND EMISSION IN LEC GaP:S

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ABSTRACT

Red cathodoluminescence (CL) from S doped LEC GaP has been investigated. Observations at different temperatures indicate that the emission has two components of wavelengths 732 and 705 nm, respectively. The results are discussed in terms of existing models involving donor-vacancy complexes.

INTRODUCTION

Due to the use of GaP in the field of light emitting diodes, its red luminescence emission, in the range 700–720 nm, has been often investigated. Dishman *et al.* [1] have studied n-type LEC GaP and concluded that an isoelectronic hole trap, 0.4 eV above the valence band edge, produces red emission (720 nm) with two components due to bound exciton and pair recombination respectively. Barchuk *et al.* [2] have also proposed that the photoluminescence band at about 725 nm that they observe in Si doped GaP is due to two different radiative recombination channels. In [1] the two components of the red band were not observed while in [2] the existence of two components was deduced from the small shift (0.05 eV) of the red band observed in LPE samples cooled at different rates. In the present work cathodoluminescence (CL) in the scanning electron microscope (SEM) has been used to study the red emission in S doped LEC GaP crystals and in particular to investigate the composite character of the band.

EXPERIMENTAL

The material used in this study was a $\langle 100 \rangle$ oriented S-doped LEC-GaP wafer with 50 mm diameter and a free carrier concentration of $3 - 4 \times 10^{17} \text{ cm}^{-3}$. Samples of about $5 \times 5 \text{ mm}^2$ were cut from the wafer with a diamond saw and some of them were annealed in argon atmosphere at temperatures between 620 and 820 °C during one or five hours. The samples were observed in a Cambridge S4-10 scanning electron microscope at 30 kV in the emissive and CL modes. The attachment for the CL measurements has been previously described [3]. The CL spectra were recorded at temperatures between 300 K and 77 K.

RESULTS AND DISCUSSION

In the CL image of the wafer the dot and halo contrast which has been often associated to the presence of dislocations is observed. Previous observations [4] have shown that the emission from the haloes is mainly green. CL spectra obtained with the electron beam focused on the sample show only a green band centered at about 563 nm. With a defocused beam the spectrum of Fig. 1 (curve a) with a red band at about 732 nm is obtained.

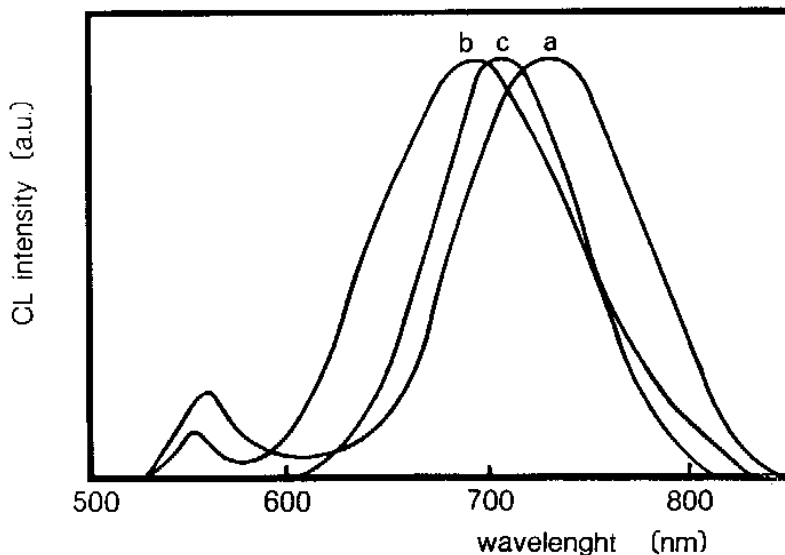


Fig. 1. CL spectra at room temperature (curve a) and at 77 K (curve b) from an untreated sample. The room temperature CL spectrum after annealing five hours at 820 °C shows the narrowing and the shift of the red band (curve c).

No CL image could be obtained with the red luminescence. Decreasing the sample temperature causes a continuous shift of the red band peak toward shorter wavelengths and the increase of the emission intensity. At liquid nitrogen

temperature the peak appears at about 693 nm (Fig. 1, curve b). The room temperature CL spectrum of a sample annealed one hour at 620 °C and slowly cooled shows a peak at 705 nm. Annealing at lower temperature or shorter times has not been found to produce the shift of the peak from 732 to 704 nm. Annealing at higher temperatures causes the enhancement of the red emission and a narrowing of the band (the halfwidth decreases from 102 nm to 82 nm) but not further spectral shifts. Figure 1 (curve c) shows the spectrum after annealing for 5 hours at 820 °C. The fact that the red band is readily observed only when the beam is defocused can be explained by a low concentration of the centers responsible for the emission as discussed in [5].

The present results indicate that the red band is composite. Under different experimental conditions, or after different treatments, two bands, centered respectively at 705 nm and 732 nm are observed. The shift of the red band peak toward shorter wavelengths, which is observed by decreasing temperature, is too large to be explained only by a variation of the band gap. It rather indicates that lowering the temperature causes the increase of a higher energy component, relative to the 732 nm emission which is dominant at room temperature. Dishman *et al.* [1] deduced from time decay measurements the existence of two components of the red band in GaP although they were not able to observe the two component spectral output. In both components the isoelectronic center, called Y, would be involved. One component is due to pair recombination between holes trapped on Y centers and electrons of Te donors. A second component is due to the recombination of bound excitons formed at Y sites after the capture of an electron into a shallow level. Both components would appear in the case of the doped samples, at about 705 nm and 720 nm respectively.

The wavelengths of the peaks observed in this work agree in principle with the model of Dishman *et al.* The wavelengths which correspond to the two transitions in the S-doped crystals used here cannot be directly obtained by comparison with the case of Te doped samples. Although the ionization energies of the donors Te and S are known, the level Y changes slightly with the kind of dopant. Dishman *et al.* explain their result that the two components are not resolved in their spectra by the high level of doping (10^{18}cm^{-3}) in the samples they use. According to Montgomery [6] the activation energy of the donors varies as the cube root of the donor concentration. At $2 \times 10^{18} \text{ cm}^{-3}$ he obtains an energy of about 50 meV. The closeness of this value to the shallow level involved in the transition would explain the absence of discrete high and low energy components. A higher ionization energy and a lower concentration of the donors in our samples have probably made easier the observation of two bands in the spectra recorded at different temperatures.

In the present work it has been found that annealing causes the increase of the red emission and in particular favours the 705 nm component. Since the emission has been attributed to donor-vacancy complexes [1,7,8] we suggest that during annealing the concentration and possibly the nature of the complexes changes, which can cause the observed luminescence changes.

The present results seem to agree reasonably with the model presented in [1] and cannot be directly compared with the results reported in [2]. In our case the two components can be observed in a single sample while in [2] the spectral shift is detected when different samples (cooled at high or low rate) are compared. On the other hand the temperature dependent position of the maximum, reported here, was not observed in [2].

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